

440182007

United States
Environmental Protection
Agency

Guidelines Division
WH-552
Washington DC 20460

Water and Waste Management



Development Document for Effluent Limitations Guidelines and Standards for the

Final

Inorganic Chemicals Manufacturing

Point Source Category





DEVELOPMENT DOCUMENT
for
EFFLUENT LIMITATIONS GUIDELINES
NEW SOURCE PERFORMANCE STANDARDS
and
PRETREATMENT STANDARDS
for the
INORGANIC CHEMICALS MANUFACTURING
POINT SOURCE CATEGORY

Anne M. Gorsuch
Administrator

Steven Schatzow
Director
Office of Water Regulations and Standards



Jeffery Denit, Acting Director
Effluent Guidelines Division

G. Edward Stigall
Chief, Inorganic Chemicals Branch

Dr. Thomas Fielding
Dwight Hlustick
Elwood E. Martin

June 1982

Effluent Guidelines Division
Office of Water Regulations and Standards
U.S. Environmental Protection Agency
Washington, D.C. 20460

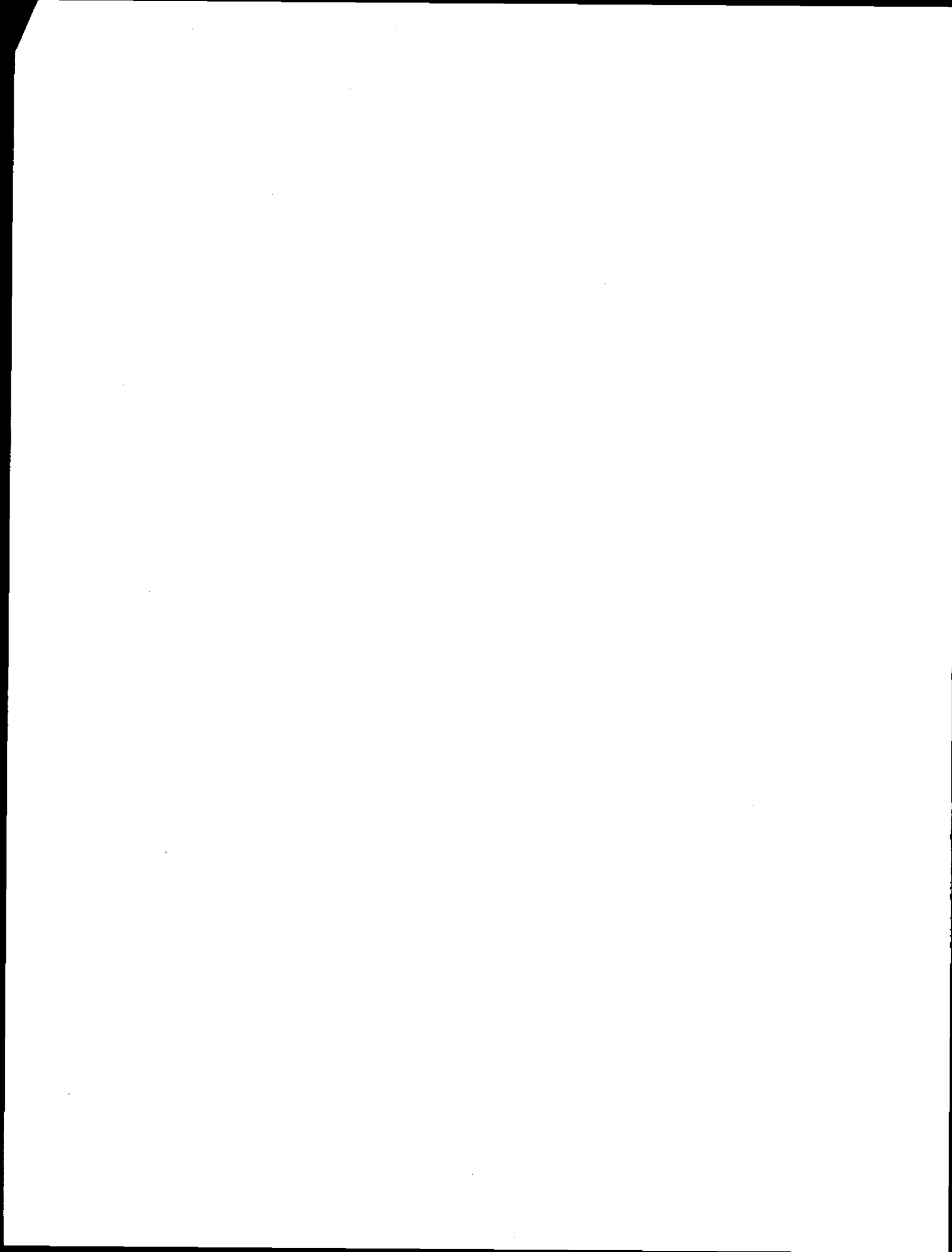


TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	xx
LIST OF TABLES	xxviii
ACKNOWLEDGEMENTS	xliv
1. CONCLUSIONS AND SUMMARY	1
TOXIC POLLUTANTS	1
CONTROL AND TREATMENT TECHNOLOGY	2
COSTS OF ADDITIONAL IN-PLANT TREATMENT	2
SUBCATEGORIZATION	2
RESTDY OF REMANDED REGULATIONS	3
2. RECOMMENDATIONS	5
3. INTRODUCTION	17
AUTHORITY	17
The Federal Water Pollution	17
Control Act Amendments	
Court Remand of Regulations	19
The Settlement Agreement	21
GENERAL APPROACH AND METHODOLOGY	25
Industry Data Base Development	26
and Subcategorization Review	
The Screening and Verification	26
Sampling Programs	
Engineering Evaluations	26
Treatment System Cost Estimates	26
Treatability Study	27
GENERAL CRITERIA FOR EFFLUENT LIMITATIONS	27
BPT Effluent Limitations	27
BAT Effluent Limitations	28
BCT Effluent Limitations	28
New Source Performance	30
Standards	
Pretreatment Standards for	30
Existing Sources	
Pretreatment Standards for	31
New Sources	

TABLE OF CONTENTS - Continued

	<u>Page</u>
4. SUBCATEGORIZATION REVIEW	33
BASIS FOR SUBCATEGORIZATION	33
Factors Considered	33
General Conclusions	36
SECONDARY SUBCATEGORIZATION	36
Chlor-Alkali	36
Titanium Dioxide	37
Hydrogen Cyanide	38
REVIEW OF POSSIBLE INTEGRATION OF SUBCATEGORIES	38
Hydrofluoric Acid and Aluminum Fluoride	38
SUMMARY	39
5. SCREENING AND VERIFICATION SAMPLING PROGRAMS	41
SCOPE AND METHODOLOGY	41
Selecting Plants and Making Preliminary Contacts	41
Screening and Verification Sampling	42
Analytical Methodology for Toxic Pollutants	45
Quality Assurance Provisions	50
SUMMARY OF ANALYTICAL RESULTS	53
6. PROCESS AND WASTE TREATMENT INFORMATION DEVELOPMENT AND EVALUATION	59
INDUSTRY DATA BASE DESCRIPTION	59
Literature Review	59
Plant Visits	59
Telephone and Direct Contact	59
308-Questionnaire Responses	59
PROCESS WASTE SOURCES AND CURRENT TREATMENT PRACTICES	60
Data Acquisition	60
Evaluation of Data	60
Model Plant and BPT Treatment System Specification	62
Dissolved Solids in Wastewater Effluents	63

TABLE OF CONTENTS - Continued

		<u>Page</u>
7.	ASSESSMENT OF TECHNOLOGY FOR ADVANCED TREATMENT AND CONTROL	65
	INTRODUCTION	65
	HYDROXIDE PRECIPITATION	66
	FERRITE COPRECIPITATION	70
	SULFIDE PRECIPITATION	71
	THE XANTHATE PROCESS	74
	ION EXCHANGE	76
	REDUCTION PROCESSES	78
	OXIDATION PROCESSES	79
	MEMBRANE PROCESSES	82
	ADSORPTION	83
	FLUORIDE REMOVAL	87
	CHLORINE REMOVAL	88
8.	TREATABILITY ESTIMATES AND LONG-TERM DATA ANALYSIS	91
	THE DEVELOPMENT OF TREATABILITY ESTIMATES	91
	Preliminary Analysis	91
	Final Analysis	101
	SELECTION OF TOXIC METAL CONTROL PARAMETERS	109
	Control Parameters for Hydroxide Precipitation	109
	Control Parameters for Sulfide Precipitation	109
	THE USE OF HISTORICAL POLLUTANT DATA	111
	Determination of Limitation Guidelines Based Upon Historical Performance	111
	Assumptions Concerning Daily Pollutant Level Measurements	112
	Assumptions Concerning 30-Day Average Pollutant Level Observation	117
9.	TREATMENT TECHNOLOGY APPLICATIONS FOR TOXIC POLLUTANT REMOVAL	125
	SELECTION OF POLLUTANTS TO BE CONTROLLED	125
	APPLICATION OF ADVANCE LEVEL TREATMENT AND CONTROL ALTERNATIVES	125
	General Design Objectives	125
	Pretreatment Technology	128

TABLE OF CONTENTS - Continued

	<u>Page</u>
New Source Performance Standards	128
ESTIMATED ACHIEVABLE PERFORMANCE CHARACTERISTICS FOR ADVANCED LEVEL APPLICATIONS	128
Advanced Level Removal of BPT Pollutants	128
Advanced Level Removal of Toxic Pollutants	129
POLLUTION CONTROL PARAMETERS TO BE REGULATED	129
Conventional Pollutants	129
Nonconventional Pollutants	130
Toxic Pollutants	130
10. COST OF TREATMENT AND CONTROL SYSTEMS	133
INTRODUCTION	133
Purpose of Cost Data	133
General Approach	134
Cost References and Rationale	134
Definition of Levels of Treatment and Control Cost Development	134
Treatment and Disposal Rationale Applied to Cost Development	135
Expression of Costs	135
COST ESTIMATES FOR EACH SUBCATEGORY	142
11. CHLOR-ALKALI INDUSTRY	145
INDUSTRY PROFILE	145
General Description	145
Subcategorization	145
MERCURY CELL PROCESS INDUSTRY PROFILE	146
General Description	146
General Process Description	146
WATER USE AND WASTEWATER SOURCE CHARACTERISTICS	149
Water Use	149
Waste Sources	151
DESCRIPTION OF SPECIFIC PLANTS	153
Screening Program	153
Verification	153

TABLE OF CONTENTS - Continued

	<u>Page</u>
Descriptions of Plants Not Sampled	158
Summary of the Toxic Pollutant Data	163
POLLUTION ABATEMENT OPTIONS	165
Toxic Pollutants of Concern	165
Prevailing Control and Treatment Practices	166
Process Modifications and Technology Transfer Options	166
Best Management Practices	170
Advanced Treatment Technologies	170
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	170
Technologies for Different Treatment Levels	170
Equipment for Different Treatment Levels	171
TREATMENT COST ESTIMATES	172
General Discussion	172
Chlorine Bearing Wastes	172
Model Plant Treatment Costs	175
BASIS FOR REGULATIONS	175
Basis for BPT Limitations	175
Basis for Final BAT Effluent Limitations	176
Basis for BCT Effluent Limitations	192
Basis for New Source Performance Standards	192
Basis for Pretreatment Standards	192
DIAPHRAGM CELL PROCESS INDUSTRY PROFILE	192
General Description	193
General Process Description	193
WATER USE AND WASTE WATER SOURCES	196
Water Use	196
Waste Sources	196
DESCRIPTIONS OF SPECIFIC PLANTS	199
Screening	199
Verification	200
Descriptions of Plants Not Sampled	200
Toxic Pollutant Concentrations	202
POLLUTION ABATEMENT OPTIONS	218
Toxic Pollutants of Concern	218

TABLE OF CONTENTS - Continued

	<u>Page</u>
Prevailing Control and Treatment Practices	218
Process Modifications and Technology Transfer Options	223
Best Management Practices	224
Advanced Treatment Technologies	224
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	225
Technologies for Different Treatment Levels	225
Equipment for Different Treatment Levels	226
TREATMENT COST ESTIMATES	227
General Discussion	227
Model Plant Treatment Costs	233
BASIS FOR REGULATIONS	233
Basis for BPT Limitations	233
Basis for BAT Effluent Limitations	249
BCT Limitations	254
Basis for New Source Performance Standards	255
Basis for Pretreatment Standards	256
12. HYDROFLUORIC ACID INDUSTRY	261
INDUSTRY PROFILE	
General Description	261
Subcategorization	261
General Process Description and Raw Materials	264
WATER USE AND WASTE SOURCE CHARACTERISTICS	267
Water Use	267
Waste Sources	267
DESCRIPTION OF PLANTS VISITED AND SAMPLED	272
Screening	272
Verification	272
Summary of the Toxic Pollutant Data	278
POLLUTION ABATEMENT OPTIONS	282
Toxic Pollutants of Concern	282
Process Modifications and Technology Transfer Options	282
Best Management Practices	285

TABLE OF CONTENTS - Continued

		<u>Page</u>
	Prevailing Control and Treatment Practices	286
	Advanced Treatment Technologies	286
	SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	287
	Technologies for Different Treatment Levels	287
	Equipment for Different Treatment Levels	288
	TREATMENT COST ESTIMATES	293
	General Discussion	293
	Model Plant Control Costs for Existing Sources	295
	BASIS FOR REGULATIONS	295
	Evaluation of BPT Treatment Practices	295
	Basis for BPT Effluent Limitations	303
	Basis for BCT Effluent Limitations	316
	Basis for BAT Effluent Limitations	316
	Basis for the New Source Performance Standards	323
	Basis for the Pretreatment Standards	323
13.	HYDROGEN PEROXIDE INDUSTRY	327
	SUMMARY OF DETERMINATIONS	327
	ASSESSMENT OF THE WATER POLLUTION POTENTIAL	327
	Production Processes and Effluents	327
	Plants	327
	Toxic Pollutants	329
	STATUS OF REGULATIONS	329
14.	TITANIUM DIOXIDE INDUSTRY	331
	TITANIUM DIOXIDE, CHLORIDE PROCESS	331
	INDUSTRY PROFILE	
	General Description	331
	Subcategorization	331
	General Process Description and Raw Materials	331

TABLE OF CONTENTS - Continued

	<u>Page</u>
WATER USE AND WASTE SOURCE	335
CHARACTERISTICS	
Water Use	335
Waste Sources	335
DESCRIPTION OF PLANTS VISITED AND SAMPLED	338
Screening	338
Verification	338
Toxic Pollutant Concentrations	340
POLLUTION ABATEMENT OPTIONS	345
Toxic Pollutants of Concern	345
Process Modification and	345
Technology Transfer Options	
Best Management Practices	345
Prevailing Control and	347
Treatment Practices	
Advanced Treatment Technologies	348
SELECTION OF APPROPRIATE TECHNOLOGY AND	348
EQUIPMENT	
Technologies for Different	348
Treatment Levels	
Equipment for Different	349
Treatment Levels	
TREATMENT COST ESTIMATES	349
General Discussion	349
Model Plant Control and	354
Treatment Costs	
BASIS FOR REGULATIONS	354
Evaluations of BPT Treatment	354
Practices	
Basis for BPT Effluent	361
Limitations	
Basis for BCT Effluent	370
Limitations	
Basis for BAT Effluent	371
Limitations	
Basis for New Source	374
Performance Standards	
Basis for Pretreatment	377
Standards	
TITANIUM DIOXIDE - SULFATE PROCESS	377
INDUSTRY PROFILE	
General Description	377
General Process Description and	381
Raw Materials	
WATER USE AND WASTE SOURCE	384
CHARACTERISTICS	
Water Use	384
Waste Sources	384

TABLE OF CONTENTS - Continued

	<u>Page</u>
DESCRIPTION OF PLANTS	385
Screening	385
Verification	387
Other Plant Descriptions	387
Toxic Pollutant Concentrations	390
POI - VISION ABATEMENT OPTIONS	395
Toxic Pollutants of Concern	395
Process Modifications and Technology Transfer Options	396
Best Management Practices	396
Prevailing Control and Treatment Practices	396
Advanced Treatment Technologies	396
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	396
Technologies for Different Treatment Levels	396
Equipment for Different Treatment Levels	400
TREATMENT COST ESTIMATES	402
General Discussion	402
Model Plant Control and Treatment Costs	403
BASIS FOR REGULATIONS	404
Evaluation of BPT Practices	404
Basis for BPT Effluent. Limitations	404
Basis for BCT Effluent Limitations	417
Basis for BAT Effluent Limitations	417
Basis for New Source Performance Standards	417
Basis for Pretreatment Standards	424
TITANIUM DIOXIDE - CHLORIDE ILMENITE	427
PROCESS INDUSTRY PROFILE	
General Description	427
General Process Description and Raw Materials	427
WATER USE AND WASTE SOURCE	430
CHARACTERISTICS	
Water Use	430
Waste Sources	430
DESCRIPTION OF PLANTS VISTED AND SAMPLED	431
Screening	431
Verification Program	431
Toxic Pollutant Concentration	431

TABLE OF CONTENTS - Continued

	<u>Page</u>
POLLUTION ABATEMENT OPTIONS	435
Toxic Pollutants of Concern	435
Process Modifications and Technology Transfer Options	436
Best Management Practices	436
Prevailing Control and Treatment Practices	436
Advanced Treatment Technology	436
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	437
Technologies for Different Treatment Levels	437
Equipment for Different Treatment Levels	440
TREATMENT COST ESTIMATES	441
General Discussion	441
Model Plant Control and Treatment Costs	442
BASIS FOR REGULATIONS	452
Evaluation of BPT Treatment Practices	452
Basis for BPT Effluent Limitation	452
Basis for BCT Effluent Limitations	456
Basis for BAT Effluent Limitations	456
Basis for the New Source Performance Standards	456
Basis for Pretreatment Standards	460
 15. ALUMINUM FLUORIDE INDUSTRY	 461
INDUSTRY PROFILE	461
General Description	461
General Process Description and Raw Materials	461
WATER USE AND WASTE SOURCE CHARACTERISTICS	461
Water Use	461
Waste Sources	461
DESCRIPTION OF PLANTS VISITED AND SAMPLED	465
Screening	465
Verification	467
Summary of the Toxic Pollutant Data	467

TABLE OF CONTENTS - Continued

	<u>Page</u>
POLLUTION ABATEMENT OPTIONS	476
Toxic Pollutants of Concern	476
Process Modifications and Technology Transfer Options	476
Best Management Practices	477
Prevailing Control and Treatment Practices	477
Advanced Treatment Technologies	477
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	478
Technologies for Different Treatment Levels	478
Equipment for Different Treatment Levels	482
TREATMENT COST ESTIMATES	484
General Discussion	484
BASIS FOR REGULATIONS	485
Evaluation of BPT Treatment Practices	485
BPT Effluent Limitations	485
Basis for the BCT Effluent Limitations	495
Basis for BAT Effluent Limitations	495
Basis for New Source Performance Standards	496
Basis for Pretreatment Standards	498
 16. CHROME PIGMENTS INDUSTRY	 499
INDUSTRY PROFILE	499
General Description	499
Subcategorization	499
General Process Description and Raw Materials	499
WATER USE AND WASTE SOURCE CHARACTERISTICS	508
Water Use	508
Waste Sources	508
DESCRIPTION OF PLANTS	513
Screening	513
Verification	513
Toxic Pollutant Concentrations	515

TABLE OF CONTENTS - Continued

	<u>Page</u>
POLLUTION ABATEMENT OPTIONS	525
Toxic Pollutants of Concern	525
Process Modifications and Technology Transfer Options	526
Best Management Practices	526
Prevailing Control and Treatment Practices	527
Advanced Treatment Technologies	528
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	528
Technologies for Different Treatment Levels	528
Equipment for Treatment	530
TREATMENT COST ESTIMATES	532
General Discussion	532
Model Plant Costs	533
BASIS FOR REGULATIONS	533
Evaluation of BPT Treatment Practices	533
Basis for BPT Effluent Limitations	540
Basis for BCT Limitations	548
Basis for BAT Effluent Limitations	548
Basis for New Source Performance Standards	549
Basis for Pretreatment Standards	550
17. HYDROGEN CYANIDE INDUSTRY	551
INDUSTRY PROFILE	551
General Description	551
Subcategorization	551
General Process Description and Raw Materials	551
WATER USE AND WASTE SOURCE	554
CHARACTERISTICS	
Water Use	554
Waste Sources	554
DESCRIPTION OF PLANTS VISITED AND SAMPLED	557
Screening	557
Verification	559
Toxic Pollutant Concentrations	562

TABLE OF CONTENTS - Continued

	<u>Page</u>
POLLUTION ABATEMENT OPTIONS	568
Toxic Pollutants of Concern	568
Process Modifications and Technology Transfer Options	568
Best Management Practices	568
Prevailing Control and Treatment Practices	568
Advanced Treatment Technologies	570
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	571
Technologies for Different Treatment Levels	571
Equipment for Different Treatment Levels	571
TREATMENT COST ESTIMATES	573
General Discussion	573
BASIS FOR REGULATIONS	575
Evaluation of BPT Treatment Practices	575
Basis for BPT Limitations	576
Basis for BCT Limitations	586
Basis for BAT Limitations	586
Basis for New Source Performance Standards	588
Basis for Pretreatment Standards	590
 18. SODIUM DICHROMATE INDUSTRY	 593
INDUSTRY PROFILE	593
General Description	593
Subcategorization	593
General Process Description and Raw Materials	593
WATER USE AND WASTE SOURCE	596
CHARACTERISTICS	
Water Use	596
Waste Sources	596
DESCRIPTION OF PLANTS VISITED AND SAMPLED	599
Screening	599
Verification	599
Toxic Pollutant Concentrations and Loadings	602

TABLE OF CONTENTS - Continued

	<u>Page</u>
POLLUTION ABATEMENT OPTIONS	606
Toxic Pollutants of Concern	606
Process Modifications and Technology Transfer Options	606
<i>Best Management Practices</i>	609
Prevailing Control and Treatment Practices	609
Advanced Treatment Technologies	609
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	610
Technology for Different Treatment Levels	610
TREATMENT COST ESTIMATES	614
General Discussion	614
Model Plant Control Costs	615
BASIS FOR REGULATIONS	615
BPT Effluent Limitations	615
BCT Effluent Limitations	625
BAT Effluent Limitations	625
NSPS Effluent Limitations	625
Pretreatment Standards	626
19. CARBON DIOXIDE INDUSTRY	627
SUMMARY OF DETERMINATIONS	627
ASSESSMENT OF THE WATER POLLUTION POTENTIAL	627
Production Processes and Effluents	627
STATUS OF REGULATIONS	627
20. CARBON MONOXIDE AND BY-PRODUCT HYDROGEN INDUSTRY	629
SUMMARY OF DETERMINATIONS	629
ASSESSMENT OF THE WATER POLLUTION POTENTIAL	629
Production Processes and Effluents	629
STATUS OF REGULATIONS	629
21. COPPER SULFATE INDUSTRY	631
INDUSTRIAL PROFILE	631
General Description	631
Subcategorization	631
General Process Description and Raw Materials	631

TABLE OF CONTENTS - Continued

	<u>Page</u>
WATER USE AND WASTE SOURCE CHARACTERISTICS	634
Water Use	634
Waste Sources	634
DESCRIPTION OF PLANTS VISITED AND SAMPLED	637
Screening	637
Verification	639
Toxic Pollutant Concentrations	639
POLLUTION ABATEMENT OPTIONS	643
Toxic Pollutants of Concern	643
Process Modifications and Technology Transfer Options	645
Best Management Practices	645
Prevailing Control and Treatment Practices	645
Advanced Treatment Technologies	646
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	646
Technologies for Different Treatment Levels	646
Equipment for Different Treatment Levels	647
TREATMENT COST ESTIMATES	649
General Discussion	649
Model Plant Cost Estimates	651
BASIS FOR REGULATIONS	651
Evaluation of BPT Treatment Practices	651
Basis for BPT Effluent Limitations	652
Basis for BCT Effluent Limitations	663
Basis for BAT Effluent Limitations	663
Basis for New Source Performance Standards	664
Basis for Pretreatment Standards	664
Basis for Level 1 Treatment Performance	664
 22. NICKEL SULFATE INDUSTRY	 673
INDUSTRIAL PROFILE	673
General Description	673
Subcategorization	673
General Process Description and Raw Materials	673

TABLE OF CONTENTS - Continued

	<u>Page</u>
WATER USE AND WASTE SOURCE CHARACTERISTICS	676
Water Use	676
Waste Sources	676
DESCRIPTION OF PLANTS VISITED AND SAMPLED	676
Screening	676
Verification	679
Summary of Toxic Pollutant Data	679
POLLUTION ABATEMENT OPTIONS	685
Toxic Pollutants of Concern	685
Process Modifications and Technology Transfer Options	687
Best Management Practices	687
Prevailing Control and Treatment Practices	687
Advanced Treatment Technologies	688
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	688
Technologies for Different Treatment Levels	688
Equipment for Different Treatment Levels	689
TREATMENT COST ESTIMATES	694
General Discussion	694
Model Plant Control Costs	694
BASIS FOR REGULATIONS	695
Evaluation of BPT Treatment Practices	695
Basis for BPT Effluent Limitations	695
Basis for BCT Effluent Limitations	700
Basis for BAT Effluent Limitations	700
New Source Performance Standards	708
Basis for Pretreatment Standards	708
23. SILVER NITRATE INDUSTRY	709
SUMMARY OF DETERMINATIONS	709
ASSESSMENT OF THE WATER POLLUTION POTENTIAL	709
Production Processes and Effluents	709
STATUS OF REGULATIONS	709

TABLE OF CONTENTS - Continued

	<u>Page</u>
24. SODIUM BISULFITE INDUSTRY	711
INDUSTRY PROFILE	711
General Description	711
Subcategorization	711
General Process Description and Raw Materials	711
WATER USE AND WASTE SOURCE CHARACTERISTICS	711
Water Use	711
Waste Sources	714
DESCRIPTION OF PLANTS VISITED AND SAMPLED	714
Screening	714
Verification	714
Toxic Pollutant Analytical Results	714
POLLUTION ABATEMENT OPTIONS	724
Toxic Pollutants of Concern	724
Prevailing Control and Treatment Practices	728
Advanced Treatment Technologies	728
SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	728
Technologies for Different Treatment Levels	728
Equipment for Different Treatment Levels	729
TREATMENT COST ESTIMATES	733
General Discussion	733
Cost Estimates	734
BASIS FOR REGULATIONS	734
Evaluation of BPT Treatment Practices	734
Basis for BPT Effluent Limitations	734
Basis for BCT Effluent Limitations	746
Basis for BAT Effluent Limitations	746
Basis for New Source Performance Standards	747
Basis for Pretreatment Standards	747

TABLE OF CONTENTS - Continued

		<u>Page</u>
25.	SODIUM HYDROSULFITE (FORMATE PROCESS) Industry (Excluded)	749
	SUMMARY OF DETERMINATIONS	749
	INDUSTRY PROFILE	749
	General Description	749
	Subcategorization	749
	General Process Description and Raw Materials	749
	WATER USE AND WASTE SOURCE	752
	CHARACTERISTICS	
	Water Use	752
	Waste Sources	754
	DESCRIPTION OF PLANTS VISITED AND SAMPLED	754
	Screening and Verification	754
	Toxic Pollutant Concentrations	757
	POLLUTION ABATEMENT OPTIONS	762
	Toxic Pollutants of Concern	762
	Prevailing Control and Treatment Practices	762
	Advanced Treatment Technologies	763
	SELECTION OF APPROPRIATE TECHNOLOGY AND EQUIPMENT	763
	Technologies for Different Treatment Levels	763
	Equipment for Different Treatment Levels	764
	TREATMENT COST ESTIMATES	767
	General Discussion	767
	Cost Estimates	767
	BASIS FOR GUIDANCE	767
	Evaluation of Level 1 Treatment Practices	767
	Basis for Level 1 Treatment Performance	773
	Basis for Level 2 Treatment Performance	777
26.	EXCLUDED SUBCATEGORIES	781
	ALUMINUM SULFATE	781
	AMMONIUM CHLORIDE	782
	AMMONIUM HYDROXIDE	784
	BARIUM CARBONATE	784
	BORAX	786
	BORIC ACID	788
	BROMINE	789
	CALCIUM CARBIDE	791
	CALCIUM CARBONATE	791

TABLE OF CONTENTS - Continued

	<i>new</i>	<i>carbon dioxide carbon monoxide hydrogen</i>	<i>P. 35</i>	Page
CALCIUM CHLORIDE				793
CALCIUM HYDROXIDE				795
CHROMIC ACID				795
CUPROUS OXIDE				796
FERRIC CHLORIDE				796
FERROUS SULFATE				797
FLUORINE				798
HYDROCHLORIC ACID				799
HYDROGEN				800
IODINE		<i>Hydrogen Peroxide?</i>		802
LEAD MONOXIDE				802
LITHIUM CARBONATE				803
MANGANESE SULFATE				804
NITRIC ACID				805
OXYGEN AND NITROGEN				806
POTASSIUM CHLORIDE				808
POTASSIUM DICHROMATE				810
POTASSIUM IODIDE		<i>Same as IODIDE?</i>		811
POTASSIUM METAL				812
POTASSIUM PERMANGANATE				813
POTASSIUM SULFATE		<i>new</i>		815
SODIUM BICARBONATE				815
SODIUM CARBONATE				816
SODIUM CHLORIDE		<i>new</i>		817
SODIUM FLUORIDE				818
SODIUM HYDROSULFIDE				818
SODIUM METAL				820
SODIUM SILICATE				821
SODIUM SULICOFLUORIDE		<i>new</i>		822
SODIUM SULFITE				824
SODIUM THIOSULFATE				824
STANNIC OXIDE				826
STRONG NITRIC ACID				826
SULFUR DIOXIDE				828
SULFURIC ACID INDUSTRY				830
ZINC OXIDE				832
ZINC SULFATE				834
REFERENCES				841
BIBLIOGRAPHY				847
APPENDIX A	Analysis of Long-Term Effluent Monitoring Data for the Inorganic Chemicals Industry			A-1

LIST OF FIGURES

	<u>Page</u>
5-1 Sample flow sheet for metal analysis	47
7-1 Theoretical solubilities of toxic metal hydroxides/oxides as a function of pH	68
7-2 Theoretical solubilities of toxic metal sulfides as a function of pH	73
7-3 Electrodialysis process	85
8-1 Cumulative distribution of daily concentrations of mercury in treated effluent from Plant #251	115
8-2 Cumulative distribution of daily concentrations of cyanide in treated effluent from Plant #765	116
8-3 Statistical distribution for daily pollution measurements	119
8-4 Cumulative distribution of 30-day averages of total cyanide in treated effluent from Plant #782	121
8-5 Cumulative distribution of 30-day averages of ammonia in treated effluent from Plant #782	122
8-6 Statistical distributions for 30-day average pollution measurements	123
11-1 General process diagram for production of chlorine/caustic by mercury cells	150
11-2 General process flow diagram at Plant #299 showing the sampling points. Chlorine/caustic (mercury cell) manufacture	155
11-3 General process flow diagram at Plant #747. showing the sampling points. Chlorine/caustic (mercury cell) manufacture	159

LIST OF FIGURES - Continued

	<u>Page</u>
11-4 General process flow diagram at plant #167 showing the sampling points. Chlorine/caustic (mercury cell) manufacture	160
11-5 General process flow diagram at Plant #317 showing the sampling points. Chlorine/caustic (mercury cell) manufacture	161
11-6 Level 1 waste water treatment for chlorine-mercury cell subcategory	173
11-7 Level 2 waste water treatment for chlorine-mercury cell subcategory	174
11-8 General process flow diagram for production of chlorine/caustic by diaphragm cells	198
11-9 General process flow diagram at Plant #014 showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture	203
11-10 General process flow diagram at Plant #261 showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture	206
11-11 General process flowsheet at Plant #738-A showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture	207
11-12 General process flow diagram at Plant #738-B showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture	208
11-13 General process flow diagram at Plant #736 showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture	209
11-14 General process flow diagram at Plant #967 showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture	210
11-15 Level 1 waste water treatment for chlorine-diaphragm cell subcategory	228
11-16 Level 2 waste water treatment for chlorine-diaphragm cell subcategory	229
11-17 Level 3 waste water treatment for chlorine-diaphragm cell subcategory	230

LIST OF FIGURES - Continued

	<u>Page</u>
12-1 General process flow diagram for production of hydrofluoric acid	266
12-2 Production vs. waste flow data for HF plants	270
12-3 General process flow diagram at Plant #705 showing the sampling points. Hydrofluoric acid manufacture	276
12-4 General process flow diagram at Plant #251 showing the sampling points. Hydrofluoric acid manufacture	280
12-5 Level 1 waste water treatment for hydrofluoric acid subcategory	289
12-6 Level 2 waste water treatment for hydrofluoric acid subcategory	290
12-7 Level 3 waste water treatment for hydrofluoric acid subcategory	291
12-8 Level 4 waste water treatment for hydrofluoric acid subcategory	292
12-9 Level 5 waste water treatment for hydrofluoric acid subcategory	294
12-10 Fluoride loads and concentrations discharged at selected hydrofluoric acid plants	308
14-1 General process diagram for production of titanium dioxide (chloride process) from high grade ores	336
14-2 General flow diagram at Plant #559 showing the sampling points. (Titanium dioxide -chloride process manufacture)	341
14-3 General flow diagram at Plant #172 showing the sampling points. Titanium dioxide (chloride process) manufacture	343
14-4 Level 1 (BPT/BAT) waste water treatment for titanium dioxide - chloride process	350
14-5 Level 2 (NSPS) waste water treatment for titanium dioxide - chloride process	351

LIST OF FIGURES - Continued

	<u>Page</u>
14-6 Level 3 waste water treatment for titanium dioxide - chloride process	352
14-7 General process flow diagram for production of titanium dioxide by sulfate process	382
14-8 General flow diagram at Plant #559 showing the sampling points. (Titanium dioxide - sulfate process)	388
14-9a Level 1 waste water treatment for titanium dioxide - sulfate process	398
14-9b Level 2 waste water treatment for titanium dioxide - sulfate process	399
14-10 Level 3 waste water treatment for titanium dioxide - sulfate process	401
14-11 General process flow diagram of the titanium tetrachloride portion of a titanium dioxide plant using the chloride-ilmenite process.	426
14-12 Level 1 waste water treatment for titanium dioxide - chloride (ilmenite ore) process	438
14-13 Level 2 waste water treatment for titanium dioxide - chloride (ilmenite ore) process	439
15-1 General process flow diagram for production of aluminum fluoride	463
15-2 General process flow diagram at Plant #705 showing the sampling points. (Aluminum fluoride manufacture)	468
15-3 General process flow diagram at Plant #251 showing the sampling points. (Aluminum fluoride manufacture)	470
15-4 Level 1 waste water treatment for aluminum fluoride subcategory	479
15-5 Level 2 waste water treatment for aluminum fluoride subcategory	480
15-6 Level 3 waste water treatment for aluminum fluoride subcategory	481

LIST OF FIGURES - Continued

	<u>Page</u>
15-7 Level 4 waste water treatment for aluminum fluoride subcategory	483
16-1 General process diagram for production of anhydrous chrome oxide	503
16-2 General process diagram for production of hydrated chromic oxide	504
16-3 General process diagram for production of chrome yellow	506
16-4 General process diagram for production of molybdenum orange	507
16-5 General process diagram for production of chrome green	509
16-6 General process diagram for production of zinc yellow	510
16-7 General process diagram for production of chrome pigment complexes	512
16-8 General waste water treatment process flow diagram at Plant #002 showing the sampling points. (Chrome pigment manufacture)	516
16-9 General waste water treatment process flow diagram at Plant #894 showing the sampling points. (Chrome pigment manufacture)	518
16-10 Level 1 waste water treatment for chrome pigments	529
16-11 Level 2 waste water treatment for chrome pigments	531
17-1 General process flow diagram for production of hydrogen cyanide by the Andrussow Process	555
17-2 General waste water treatment process flow diagram at Plant #765 showing the sampling points. (Hydrogen cyanide manufacture)	560
17-3 General waste water treatment process flow diagram at Plant #782 showing sampling points. (Hydrogen cyanide manufacture)	564

LIST OF FIGURES - Continued

		<u>Page</u>
17-4	Level 1 waste water treatment for hydrogen cyanide subcategory	572
17-5	Level 2 waste water treatment for hydrogen cyanide subcategory	574
18-1	General process diagram for production of sodium dichromate	597
18-2	General waste water treatment process flow diagram at Plant #493 showing the sampling points. (Sodium dichromate manufacture)	600
18-3	General waste water treatment process flow diagram at Plant #376 showing the sampling points. (Sodium dichromate manufacture)	603
18-4	Level 1 waste water treatment for sodium dichromate subcategory	612
18-5	Level 2 waste water treatment for sodium dichromate subcategory	613
21-1	General process flow diagram of the manufacture of copper sulfate	635
21-2	General process flow diagram at Plant #034 showing the sampling points. (Copper sulfate manufacture)	640
21-3	Level 1 waste water treatment for copper sulfate subcategory - batch process	648
21-4	Level 2 waste water treatment for copper sulfate subcategory - batch process	650
22-1	General process flow diagram for nickel sulfate manufacture	677
22-2	General waste water treatment process flow diagram showing sampling points at Plant #369. (Nickel sulfate subcategory.)	680
22-3	General process flow diagram at Plant #572 showing the sampling points. (Nickel sulfate manufacture.)	682

LIST OF FIGURES - Continued

		<u>Page</u>
22-4	General waste water treatment process flow diagram at Plant #120 showing the sampling points. (Nickel sulfate manufacture)	683
22-5	Level 1 waste water treatment for nickel sulfate subcategory - high production model - batch process	690
22-6	Level 1 waste water treatment for nickel sulfate subcategory - low and medium production models - batch process	691
22-7	Level 2 waste water treatment for nickel sulfate subcategory - high production model - batch process	692
22-8	Level 2 waste water treatment for nickel sulfate - low and medium production models - batch process	693
24-1	General process flow diagram at Plant #282 showing the sampling points. Sodium bisulfite manufacture	718
24-2	General flow diagram at Plant #586 showing the sampling points. Sodium bisulfite manufacture	719
24-3	General process flow diagram at Plant #987 showing the sampling points. Sodium bisulfite manufacture	722
24-4	Level 1 waste water treatment for sodium bisulfite subcategory - batch process	730
24-5	Level 2 waste water treatment for sodium bisulfite subcategory - batch process	731
24-6	Level 3 waste water treatment for sodium bisulfite subcategory - batch process	732
25-1	General process flow diagram at Plant #672. (Sodium hydrosulfite manufacture)	753
25-2	General process flow diagram at Plant #672 showing the sampling points. (Sodium hydrosulfite manufacture)	756

LIST OF FIGURES - Continued

	<u>Page</u>
25-3 Level 1 waste water treatment for sodium hydrosulfite subcategory	765
25-4 Level 2 waste water treatment for sodium hydrosulfite subcategory	766

LIST OF TABLES

		<u>Page</u>
2-1	Summary of Regulations - Best Practicable Control Technology Currently Available (BPT)	6
2-2	Summary of Regulations - Best Available Technology (BAT)	8
2-3	Summary of Regulations -Pretreatment Standards for Existing Sources (PSES)	10
2-4	Summary of Regulations - New Source Performance Standards (NSPS)	12
2-5	Summary of Regulations -Pretreatment Standards for New Sources (PSNS)	15
3-1	Recommended List of Toxic Pollutants	23
3-2	Scope of Industry Coverage within the Inorganic Chemicals Manufacturing Point Source Category	24
5-1	Analytical Detection Limits for Metals	51
5-2	Pollutant Frequency Based on Sampling Program Results Including Raw Waste	55
5-3	Distribution of Pollutants According to Subcategory	56
6-1	308-Questionnaire Response Data	61
7-1	Solubility Products of Toxic Metals	69
7-2	Comparison of Reverse Osmosis Concepts	86
8-1	Waste Water Treatment Options and Performance Data Summary - Antimony and Arsenic Removal	92

LIST OF TABLES - Continued

		<u>Page</u>
8-2	Waste Water Treatment Options and Performance Data Summary - Beryllium and Cadmium Removal	93
8-3	Waste Water Treatment Options and Performance Data Summary - Copper Removal	94
8-4	Waste Water Treatment Options and Performance Data Summary - Chromium III and Chromium VI Removal	95
8-5	Waste Water Treatment Options and Performance Data Summary - Lead Removal	96
8-6	Waste Water Treatment Options and Performance Data Summary - Mercury II Removal	97
8-7	Waste Water Treatment Options and Performance Data Summary - Nickel Removal	98
8-8	Waste Water Treatment Options and Performance Data Summary - Silver Removal	98
8-9	Waste Water Treatment Options and Performance Data Summary - Selenium and Thallium Removal	99
8-10	Waste Water Treatment Options and Performance Data Summary - Zinc Removal	100
8-11	Estimated Achievable Maximum 30-Day Averages for the Applied Technologies	102
8-12	Industrial Waste Water Treatment System Performance -- Summary of Effluent Concentration Data on Toxic Metals	105
8-13	Estimated Achievable Long-Term Average Concentrations for Toxic Metals with BPT or BAT Treatment Options	108
8-14	Theoretical Solubilities of Toxic Metal Hydroxides/Oxides at Various pH Values	110
9-1	Prioritization of Toxic Pollutants Found in Each Subcategory	126
11-1	Subcategory Profile Data Summary	147

LIST OF TABLES - Continued

		<u>Page</u>
11-2	Status of Regulations - Effluent Limitation Guidelines	148
11-3	Summary of Waste Water Flow Data for Chlorine Mercury Cell Plants	154
11-4	Pollutant Concentrations and Loads at Plant #299	156
11-5	Pollutant Concentrations and Loads at Verification Plants	157
11-6	Average Toxic Pollutant Raw Waste Concentrations and Loads at Verification Plants	167
11-7	Summary of Raw Waste Loadings at Verification Plants	168
11-8	Model Plant Treatment Costs	178
11-9	Model Plant Treatment Costs	179
11-10	Model Plant Treatment Costs	180
11-11	Model Plant Unit Treatment Costs	181
11-12	Mercury Discharges from Selected Chlor-Alkali Mercury Cell Plants	182
11-13	Residual Chlorine Discharges at Selected Chlor-Alkali Plants	184
11-14	Comparison of Raw Waste Concentrations of Toxic Pollutants with Treatability	185
11-15	Effluent Limitations, BAT	187
11-16	Effluent Concentrations of Toxic Pollutants from Verification Sampling	189
11-17	Subcategory Profile Data Summary	194
11-18	Status of Regulations - Effluent Limitation Guidelines	195
11-19	Waste Water Flows at Diaphragm Cell Chlorine Plants	201

LIST OF TABLES - Continued

		<u>Page</u>
11-20	Pollutant Concentrations and Loads at Screening and Verification Plants	204
11-21	Results of Asbestos Sampling at Diaphragm Cell Plants	213
11-22	Maximum Raw Waste Concentrations of Toxic Metals Observed at Diaphragm Cell Chlorine Plants (mg/l)	214
11-23	Toxic Metal Concentrations and Loads at Screening and Verification Plants	216
11-24	Summary of Raw Waste Loadings at Screening and Verification Metal Anode Plants	217
11-25	Toxic Metal Concentrations and Loads in Cell Room Waste Waters at Screening and Verification Plants	219
11-26	Raw Waste Toxic Metals Concentration and Loads in Process Streams Other Than Cell Room Wastes from Screening and Verification Plants	220
11-27	Raw Waste Toxic Organics at a Graphite Anode Plant	221
11-28	Raw Waste Toxic Organics by Waste Water Source at a Graphite Anode Plant	222
11-29	Model Plant Treatment Costs	235
11-30	Model Plant Treatment Costs	236
11-31	Model Plant Treatment Costs	237
11-32	Model Plant Unit Treatment Costs	238
11-33	Summary of Unit Flows at Diaphragm Cell Plants	240
11-34	Comparison of Raw Waste Concentrations of Toxic Pollutants with Treatability	241
11-35	Effluent Limitations, BPCTCA	243

LIST OF TABLES - Continued

		<u>Page</u>
11-36	Lead and TSS Discharges from Selected Diaphragm Cell Chlorine Plants	246
11-37	Comparison of Toxic Pollutants in Diaphragm Cell Plant Effluents with Treatability	247
11-38	Effluent Limitations, BAT	252
11-39	Comparison of Raw Waste Characteristics at a New Metal Anode Plant with Treatability of Toxic Metals	257
11-40	Effluent Limitations, NSPS	259
12-1	Subcategory Profile Data Summary	262
12-2	Status of Regulations - Effluent Limitation Guidelines	263
12-3	Water Usage in the Hydrofluoric Acid Subcategory	268
12-4	Waste Water Flow and Reuse Data for the Hydrofluoric Acid Subcategory	269
12-5	Waste Flow from Hydrofluoric Acid Manufacturing Plants	273
12-6	Flow and Pollution Concentration Data of Spar Drying and Total Process Waste Water for Plants #251 and #837 Producing Hydrofluoric Acid	274
12-7	Solid Waste Generated at the Hydrofluoric Acid Plants Sampled	274
12-8	Gypsum Solids Production in the Hydrofluoric Acid Subcategory	275
12-9	Flow and Pollutant Concentration Data of the Sampled Waste Streams of Plant #705 Producing Hydrofluoric Acid	277
12-10	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plants #705, #251, and #167 Producing Hydrofluoric Acid	279
12-11	Toxic Pollutant Raw Waste Data	283

LIST OF TABLES - Continued

	<u>Page</u>
12-12 Summary of Raw Waste Loadings Found in Screening and Verification Sampling	284
12-13 Model Plant Treatment Costs	297
12-14 Model Plant Treatment Costs	298
12-15 Model Plant Treatment Costs	299
12-16 Model Plant Unit Treatment Costs	300
12-17 Summary of Waste Water Control and Treatment Technology Employed at Hydrofluoric Acid Plants	302
12-18 Summary of Long-Term Monitoring Data from Four Hydrofluoric Acid Plants	304
12-19 Toxic Pollutant Treated Effluent Data	305
12-20 Development of TSS and Fluoride Limitations	311
12-21 Effluent Limitations, BPCTCA	312
12-22 Summary of Concentrations and Filter Removal Efficiencies of Pollutants Selected for Study in the Hydrofluoric Acid Subcategory	319
12-23 Effluent Limitations, BAT	321
12-24 Effluent Limitations, NSPS	325
13-1 Subcategory Profile Data Summary	328
14-1 Subcategory Profile Data Summary (Chloride Process)	332
14-2 Status of Regulations - Effluent Limitation Guidelines	333
14-3 Water Usage in Titanium Dioxide-Chloride Process/High Grade Ores Subcategory	337
14-4 Waste Water Flow for Titanium Dioxide-Chloride Process Subcategory	339

LIST OF TABLES - Continued

		<u>Page</u>
14-5	Flow and Pollutant Concentration Data of the Sampled Waste Streams of Plant #559 Producing Titanium Dioxide by Chloride-Rutile Process	342
14-6	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plant #172 Producing Titanium Dioxide (Chloride Process)	344
14-7	Raw Waste Pollutant Data Summary of the Sampled Streams	346
14-8	Model Plant Treatment Costs	355
14-9	Model Plant Treatment Costs	356
14-10	Model Plant Treatment Costs	357
14-11	Model Plant Treatment Costs	358
14-12	Model Plant Treatment Costs	359
14-13	Model Plant Treatment Costs	360
14-14	Model Plant Unit Treatment Costs	362
14-15	Historical Effluent Monitoring Data Summary with Variability Factor -- Daily Measurements, Plant #559	363
14-16	Historical Effluent Monitoring Data Summary with Variability Factors -- Daily Measurements, Plant #172	364
14-17	Treatment Performance Data of Sampled Plants #599 and #172	365
14-18	Effluent Limitations, BPCTCA	371
14-19	Effluent Limitations, BAT	373
14-20	Effluent Limitations, NSPS	378
14-21	Subcategory Profile Data Summary (Sulfate Process)	379
14-22	Analysis of Ilmenite Ores	380

LIST OF TABLES - Continued

		<u>Page</u>
14-23	Water Usage in Titanium Dioxide - Sulfate Process Subcategory	383
14-24	Raw Waste Characteristics (Industry Data) for Plant #555 (Production of TiO_2 by Sulfate Process)	386
14-25	Flows and Pollutant Concentrations for the Waste Streams Sampled for Plant #559 Producing Titanium Dioxide	389
14-26	Process Waste Water Flow at Plants #555, #694 and #559 Titanium Dioxide (Sulfate Process)	391
14-27	Summary of Raw Waste Loadings Found in Screening and Verification Sampling	393
14-28	Toxic Pollutants: Average Raw Waste Loads and Concentrations	394
14-29	Model Plant Treatment Costs	405
14-30	Model Plant Treatment Costs	406
14-31	Model Plant Treatment Costs	407
14-32	Model Plant Unit Treatment Costs	408
14-33a	Historical Effluent Monitoring Data Summary-- Treatment Without Iron Removal	410
14-33b	Historical Effluent Monitoring Data Summary-- Treatment With Iron Removal	411
14-34	Verification Results from - Sulfate Process Titanium Dioxide Plant #559	412
14-35	Effluent Limitations, BPCTCA	415
14-36	Effluent Limitations, BAT	418
14-37	Effluent Limitations, NSPS	420
14-38	Subcategory Profile Data Summary (Chloride-Ilmenite)	425
14-39	Average Water Usage for TiO_2 Production by the Chloride - Ilmenite Process	428

LIST OF TABLES - Continued

		<u>Page</u>
14-40	Average Raw Waste Loads for TiO_2 Production by the Chloride - Ilmenite Process	429
14-41	Summary of Raw Waste Loadings Found in Screening and Verification Sampling	433
14-42	Toxic Pollutant Average Raw Waste Loads and Concentrations	434
14-43	Model Plant Treatment Costs	443
14-44	Model Plant Treatment Costs	444
14-45	Model Plant Treatment Costs	445
14-46	Model Plant Treatment Costs	446
14-47	Model Plant Treatment Costs	447
14-48	Model Plant Treatment Costs	448
14-49	Model Plant Treatment Costs	449
14-50	Model Plant Treatment Costs	450
14-51	Model Plant Unit Treatment Costs	451
14-52	Effluent Limitations, BPCTCA	454
14-53	Effluent Limitations, NSPS	458
15-1	Subcategory Profile Data Summary	462
15-2	Status of Regulations - Effluent Limitation Guidelines	464
15-3	Water Usage in the Aluminum Fluoride Subcategory	464
15-4	Waste Water Flow at Plants #837, #705 and #251 for Aluminum Fluoride Subcategory	466
15-5	Solids Generated at Plant #705 and #251 Producing Aluminum Fluoride	466
15-6	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plant #705 Producing Aluminum Fluoride	469

LIST OF TABLES - Continued

		<u>Page</u>
15-7	Flow and Pollutant Concentration Data of the Sampled Streams for Plant #251 Producing Aluminum Fluoride	471
15-8	Toxic Pollutant Average Raw Waste Loads and Concentrations	473
15-9	Toxic Pollutant Effluent Concentrations During Sampling	474
15-10	Summary of Raw Waste Loadings Found in Screening and Verification Sampling	475
15-11	Model Plant Treatment Costs	486
15-12	Model Plant Treatment Costs	487
15-13	Model Plant Treatment Costs	488
15-14	Model Plant Unit Treatment Costs	489
15-15	Effluent Limitations, BPCTCA	497
16-1	Subcategory Profile Data Summary	500
16-2	Status of Regulations - Effluent Limitation Guidelines	501
16-3	Water Usage in the Chrome Pigments Subcategory	511
16-4	Summary of Waste Water Flow	514
16-5	Flow, Pollutant Concentration and Load Data of the Sampled Waste Streams for Plant #002	517
16-6	Flow, Pollutant Concentration and Load Data for the Sampled Streams at Plant #894	519
16-7	Toxic Pollutant Raw Waste Data	522
16-8	Summary of Raw Waste Loadings Found in Screening and Verification Sampling	523
16-9	Toxic Pollutant Treated Waste Data	524
16-10	Model Plant Treatment Costs	534
16-11	Model Plant Treatment Costs	535

LIST OF TABLES - Continued

		<u>Page</u>
16-12	Model Plant Treatment Costs	536
16-13	Model Plant Treatment Costs	537
16-14	Model Plant Unit Treatment Costs	539
16-15	Summary of Long Term and Verification Effluent Sampling Results at Plant #894	541
16-16	Effluent Limitations, BPCTCA	545
17-1	Subcategory Profile Data Summary	552
17-2	Status of Regulations - Effluent Limitation Guidelines	553
17-3	Water Usage in Hydrogen Cyanide - Andrussow Process Subcategory	556
17-4	Waste Flow Data for HCN Production by the Andrussow Process	558
17-5	Flow and Pollutant Data of the Raw and Treated Waste Streams of Plant #765 Producing Hydrogen Cyanide by Andrussow Process	561
17-6	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plant #765 Producing Hydrogen Cyanide	563
17-7	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plant #782 Producing Hydrogen Cyanide	565
17-8	Unit Flow and Unit Pollutant Loading for Raw and Treated Waste Effluents at Plant #782	566
17-9	Summary of Pollutant Raw Waste Loading Found in Screening and Verification Sampling	569
17-10	Model Plant Treatment Costs	577
17-11	Model Plant Treatment Costs	578
17-12	Model Plant Treatment Costs	579
17-13	Model Plant Unit Treatment Costs	580

LIST OF TABLES - Continued

		<u>Page</u>
17-14	Statistical Analysis of Historical Effluent Monitoring Data on Free Cyanide and Ammonia from Plant #765	582
17-15	Statistical Analysis of the 28-Day Effluent Sampling Results on Total Cyanide from Plant #765	585
17-16	Effluent Limitations, BPCTCA	587
17-17	Effluent Limitations, BAT	589
17-18	Effluent Limitations, NSPS	591
18-1	Subcategory Profile Data Summary	594
18-2	Status of Regulations - Effluent Limitation Guidelines	595
18-3	Water Usage in Sodium Dichromate Subcategory	598
18-4	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plant #493 Producing Sodium Dichromate	601
18-5	Flow and Pollutant Loading Data of the Sampled Waste Streams for Plant #376 Producing Sodium Dichromate	604
18-6	Flow and Pollutant Loading Data of the Sampled Waste Streams for Plant #398 Producing Sodium Dichromate	605
18-7	Toxic Pollutant Raw Waste Data	607
18-8	Summary of Raw Waste Loadings Found in Screening and Verification Sampling	608
18-9	Model Plant Treatment Costs	616
18-10	Model Plant Treatment Costs	617
18-11	Model Plant Treatment Costs	618
18-12	Model Plant Unit Treatment Costs	619
18-13	Effluent Sampling Data from Sodium Dichromate Plants	622
18-14	Effluent Limitations, BPCTCA	624

LIST OF TABLES - Continued

		<u>Page</u>
19-1	Subcategory Profile Data Summary	628
20-1	Subcategory Profile Data Summary	630
21-1	Subcategory Profile Data Summary	632
21-2	Status of Regulations - Effluent Limitation Guidelines	633
21-3	Water Usage in Copper Sulfate Subcategory	636
21-4	Waste Water Flow for the Copper Sulfate Subcategory	638
21-5	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plant #034 Producing Copper Sulfate	641
21-6	Raw Waste Data	644
21-7	Model Plant Treatment Costs	653
21-8	Model Plant Unit Treatment Costs	654
21-9	Summary of Long-Term Monitoring Data from Plant #034	655
21-10	Treated Effluent Data	657
21-11	Average Pollutant Levels and Removal Efficiency for Plant #034	658
21-12	Effluent Limitations, BPCTCA	662
21-13	Effluent Limitations, BAT	665
21-14	Guidance for Effluent Control	668
22-1	Subcategory Profile Data Summary	674
22-2	Status of Regulations - Effluent Limitation Guidelines	675
22-3	Water Use in the Nickel Sulfate Subcategory	678
22-4	Flow and Pollutant Concentration Data of the Sampled Waste Streams for Plants Producing Nickel Sulfate	681
22-5	Toxic Pollutant Raw Waste Data	686

LIST OF TABLES - Continued

	<u>Page</u>
22-6	Model Plant Treatment Costs 696
22-7	Model Plant Treatment Costs 697
22-8	Model Plant Treatment Costs 698
22-9	Model Plant Unit Treatment Costs 699
22-10	Toxic Pollutant Treated Effluent Data 701
22-11	Effluent Limitations, BAT 705
23-1	Subcategory Profile Data Summary 710
24-1	Subcategory Profile Data Summary 712
24-2	Status of Regulations - Effluent Limitation Guidelines 713
24-3	Water Usage in the Sodium Bisulfite Subcategory 715
24-4	Waste Water Flow at Plants #987 and #282 for Sodium Bisulfite Subcategory 716
24-5	Flow and Pollutant Load Data of the Sampled Waste Streams for Plant #282 Producing Sodium Bisulfite 717
24-6	Flow and Pollutant Load Data of the Sampled Waste Streams for Plant #586 720
24-7	Flow and Pollutant Load Data of the Sampled Waste Streams for Plant #987 721
24-8	Toxic Pollutant Raw Waste Loads 725
24-9	Summary of Raw Waste Loadings Found in Screening and Verification Sampling 726
24-10	Toxic Pollutant Concentrations Observed in Treated Effluent During Verification Sampling 727
24-11	Model Plant Treatment Costs 735
24-12	Model Plant Treatment Costs 736
24-13	Model Plant Treatment Costs 737
24-14	Model Plant Unit Treatment Costs 738

LIST OF TABLES - Continued

		<u>Page</u>
24-15	Comparison of Maximum Raw Waste Concentrations with Treatability	739
24-16	Effluent Limitations, BPCTCA	742
25-1	Subcategory Profile Data Summary	750
25-2	Status of Regulations - Effluent Limitation Guidelines	751
25-3	Waste Source Data at Plant #672	755
25-4	Flow, Pollutant Concentration, and Load Data of the Sampled Waste Streams for Plant #672 Producing Sodium Hydrosulfite	758
25-5	Sampling Results and Treatment System Performance for Toxic Pollutants -- Plant #672	760
25-6	Summary of Raw Waste Loadings and Concentrations Found at a Sodium Hydrosulfite Plant (Formate Process)	761
25-7	Model Plant Treatment Costs	768
25-8	Model Plant Unit Treatment Costs	769
25-9	Subcategory Performance Evaluation Summary at Plant #672 for Conventional and Nonconventional Pollutants in the Effluents	772
25-10	Guidance for Effluent Control - Level 1	776
25-11	Guidance for Effluent Control - Level 2	779
26.2-1	Subcategory Profile Data Summary	783
26.3-1	Subcategory Profile Data Summary	785
26.4-1	Subcategory Profile Data Summary	787
26.6-1	Subcategory Profile Data Summary	790
26.9-1	Subcategory Profile Data Summary	794
26.17-1	Subcategory Profile Data Summary	801

LIST OF TABLES - Continued

	<u>Page</u>
26.23-1 Subcategory Profile Data Summary	807
26.24-1 Subcategory Profile Data Summary	809
26.27-1 Subcategory Profile Data Summary	814
26.32-1 Subcategory Profile Data Summary	819
26.35-1 Subcategory Profile Data Summary	823
26.36-1 Subcategory Profile Data Summary	825
26.37-1 Subcategory Profile Data Summary	827
26.38-1 Subcategory Profile Data Summary	829
26.40-1 Subcategory Profile Data Summary	831
26.42-1 Subcategory Profile Data Summary	833
26.43-1 Subcategory Profile Data Summary	836
26.44-1 Subcategory Profile Data Summary	837

ACKNOWLEDGEMENTS

The technical study supporting the proposed regulation was conducted by Jacobs Environmental Division of Jacobs Engineering Group Inc. of Pasadena, California under the direction of Mr. Henry Cruse, Vice President, and Mr. Michael Warner, Project Manager. Major contributors were Ms. Bonnie J. Parrott, Mr. Chester Kaminski, Mr. Mahendra L. Shah, Mr. Dale Newkirk, Mr. Carl B. Johnston, Mr. Dennis Merklin, Mr. William E. Rorie, Dr. David Ben Hur, Dr. Ashley Levy, Mr. Milford Walker, Jr., Ms. Garnett Gray, Mr. Dale Rushneck, Dr. Ben C. Edmondson and Dr. Martin D. Schwartz.

Cooperation and assistance of the Chemical Manufacturers Association and the Chlorine Institute and numerous individual corporations is appreciated for their review and comment on the draft development document. The numerous company and plant personnel who submitted information, opened their plants to the program staff, and otherwise cooperated are acknowledged and thanked for their patience and help.

Mr. Steve Schatzow, Director, Office of Water Regulations and Standards, is gratefully acknowledged for his contributions to the project.

Ms. Susan Lepow, Mr. Joseph Freedman, and Staff of the Office of General Counsel are specially acknowledged for their extensive contribution to the drafting of the regulations and this development document.

Ms. Debra Maness and Mr. Richard Cotz of the Office of Analysis and Evaluation, Ms. Alexandra Tarnay, Monitoring and Data Support Division, and Mr. Fred Talcott, Office of Planning and Evaluation are acknowledged for their assistance.

SECTION 1

CONCLUSIONS AND SUMMARY

Toxic Pollutants

The following 35 inorganic chemical product subcategories were screened for the purpose of establishing wastewater effluent limitations guidelines for existing sources, standards of performance for new sources, and pretreatment standards for new and existing sources in this study:

- | | |
|-------------------------|--|
| 1. Chlor-Alkali | 19. Carbon Dioxide |
| 2. Hydrofluoric Acid | 20. Carbon Monoxide and
by-product Hydrogen |
| 3. Titanium Dioxide | 21. Silver Nitrate |
| 4. Aluminum Fluoride | 22. Ammonium Chloride |
| 5. Chrome Pigments | 23. Ammonium Hydroxide |
| 6. Hydrogen Cyanide | 24. Barium Carbonate |
| 7. Sodium Dichromate | 25. Boric Acid |
| 8. Copper Sulfate | 26. Calcium Carbonate |
| 9. Nickel Sulfate | 27. Cuprous Oxide |
| 10. Sodium Bisulfite | 28. Manganese Sulfate |
| 11. Sodium Hydrosulfite | 29. Strong Nitric Acid |
| 12. Hydrogen Peroxide | 30. Oxygen and Nitrogen |
| 13. Hydrochloric Acid | 31. Potassium Iodide |
| 14. Nitric Acid | 32. Sodium Hydrosulfide |
| 15. Sodium Carbonate | 33. Sodium Silicofluoride |
| 16. Sodium Metal | 34. Sodium Thiosulfate |
| 17. Sodium Silicate | 35. Sulfur Dioxide |
| 18. Sulfuric Acid | |

The screening studies showed that only the plant process wastewaters from subcategories 1 through 11 contain treatable amounts of toxic metals (see Table 3-1), cyanide and asbestos. Very few of the organic toxic pollutants were found in process waste streams and those that were identified were present at low level concentrations.

The screening results which indicated the presence of toxic pollutants in significant amounts were largely confirmed by the results of the verification program. Verification sampling accounted for 50 to 75 percent of the current inorganic chemical production rate in the subcategories covered.

The sources of most of the toxic pollutants found in the raw wastes and treated effluents were traced to specific process-related raw materials and chemicals used in the manufacturing operations. In the case of certain pollutants found in widely varying amounts or with erratic frequencies of occurrence, the precise identities of the

sources remain unknown at this time, but are suspected to be process-related.

Control and Treatment Technology

A considerable amount of toxic pollutant removal is presently achieved in the industry by the existing control and treatment practices. Additional removal can be accomplished by the application of available and demonstrated technologies which would add to or modify existing treatment systems. Recovery of toxic metals for value or reuse in a process does not appear to be an attractive alternative in those industries where the product recovery practices now in effect do not already accomplish this.

The treatment of toxic metal-bearing waste streams results in the production of sludges or residues which are potentially hazardous and may require special means for handling and disposal under the Resource Conservation and Recovery Act (RCRA) regulations.

Costs of Additional In-Plant Treatment

The estimated incremental costs of applying the candidate BAT treatment options represent a relatively small proportion of the investment and operating and maintenance costs already committed to the existing BPT level treatment systems. These costs, however, vary widely from industry to industry and are highly dependent on site-specific factors.

Subcategorization

A review of the product/process basis for subcategorization of the inorganic chemical product subcategories designated for study revealed that certain modifications may be appropriate in the interest of developing effective regulations. The toxic pollutant problem per se impacts sub-categorization directly only in the Chlor-Alkali Industry where the use of graphite anodes contributes to the generation of chlorinated hydrocarbons. In the Titanium Dioxide Industry, major process and raw material differences justify the creation of a separate segment for the sulfate process, the chloride process, and for the chloride process using ilmenite ore. Consideration was given to creating a subcategory for the combined production of hydrofluoric acid and aluminum fluoride in view of their similar waste characteristics and the current practice of combined treatment at several plants. However, combining these products into a single subcategory does not appear to offer any regulatory advantages.

Hydrogen cyanide is produced by the Andrussov process and as a by-product in the manufacture of acrylonitrile. By-product hydrogen cyanide will be covered under its primary product, acrylonitrile, in the Organic Chemicals Manufacturing Category. The hydrogen cyanide subcategory includes only manufacture by the Andrussov process.

Restudy of Remanded Regulations

The Fourth Circuit, U.S. Court of Appeals remanded effluent limitations guidelines promulgated for 11 major inorganic chemical products. *E.I. du Pont de Nemours versus Train*, 541 F. 2d 1018 (4th. Cir. 1976) reversed in part, 430 U.S. 112 (1977). The factors affecting the control and treatment of pollutant discharges in those industries have been studied in response to the remanded issues. It has been concluded that alternative control and treatment technologies to those originally considered for BAT and NSPS may be appropriate.

SECTION 2

RECOMMENDATIONS

On the basis of the toxic pollutant screening and verification results and the evaluation of applicable technologies for discharge control and treatment, it is recommended that effluent limitation guidelines, new source performance standards and pretreatment standards for new and existing sources be promulgated for the following 10 inorganic chemicals manufacturing subcategories:

Chlor-Alkali	Hydrogen Cyanide
Hydrofluoric Acid	Sodium Dichromate
Titanium Dioxide	Copper Sulfate
Aluminum Fluoride	Nickel Sulfate
Chrome Pigments	Sodium Bisulfite

Table 2-1 summarizes the regulations for Best Practicable Control Technology Currently Available (BPT). Summaries of regulations for Best Available Technology (BAT), Pretreatment Standards, and New Source Performance Standards are given in Tables 2-2, 2-3, 2-4, and 2-5. These tables indicate that Chlor-Alkali has been divided into two segments and Titanium Dioxide in three segments before listing the numerical effluent limitations.

The Agency proposed BPT, BCT, and BAT limitations and NSPS, PSES, and PSNS for the Sodium Hydrosulfite (Formate Process) subcategory. The proposed regulation basically added control of selected toxic metal pollutants to existing treatment practiced in the industry. The Agency reviewed the basis for the proposed regulation and concluded that the total current treated discharge load of only 0.42 pounds per day total toxic metals from all plants in the subcategory is too insignificant to justify developing a national regulation. Accordingly, this subcategory has been excluded from national regulation development under Paragraph 8(a)(iv) of the Settlement Agreement.

TABLE 2-1. SUMMARY OF REGULATIONS -
BEST PRACTICABLE CONTROL TECHNOLOGY
CURRENTLY AVAILABLE (BPT)

Subcategory	Parameter	Effluent Limitations		pH Range
		Max	24-hr	
		30-day Avg kg/kg (or lb/1000 lb) of product	Max	
Chlor-alkali, Mercury Cells	TSS	0.32	0.64	6.0 to 9.0
	Mercury	0.00014	0.00028	
	pH			
Chlor-alkali, Diaphragm Cells	TSS	0.51	1.1	6.0 to 9.0
	Copper (T)	0.0070	0.018	
	Lead (T)	0.010	0.026	
	Nickel (T)	0.0056	0.014	
	pH			
Hydrofluoric Acid	TSS	5.3	11.0	6.0 to 9.0
	Fluoride (T)	2.9	6.1	
	Nickel (T)	0.011	0.036	
	Zinc (T)	0.036	0.12	
	pH			
Sodium Dichromate	TSS	0.22	0.44	6.0 to 9.0
	Hexavalent Chromium	0.00050	0.00090	
	Chromium (T)	0.0044	0.0088	
	Nickel (T)	0.0034	0.0068	
	pH			
Titanium Dioxide (sulfate process)	TSS	38	140	6.0 to 9.0
	Chromium (T)	0.21	0.48	
	Nickel (T)	0.14	0.29	
	pH			
Titanium Dioxide (chloride process)	TSS	6.4	23	6.0 to 9.0
	Chromium (T)	0.030	0.057	
	pH			
Titanium Dioxide (chlor- ide ilmenite process)	TSS	9.6	35	6.0 to 9.0
	Chromium (T)	0.053	0.12	
	Nickel (T)	0.035	0.072	
	pH			

(continued)

Table 2-1. Continued

Subcategory	Parameter	Effluent Limitations		pH Range
		Max	24-hr	
		30-day Avg kg/kg (or lb/1000 lb) of product	Max of product	
Aluminum Fluoride	TSS	1.2	2.4	6.0 to 9.0
	Fluoride (T)	0.63	1.3	
	Chromium (T)	0.0045	0.015	
	Nickel (T)	0.0024	0.0079	
	pH			
Copper Sulfate	TSS	0.023	0.069	6.0 to 9.0
	Copper (T)	0.0010	0.0030	
	Nickel (T)	0.0020	0.0060	
	Selenium (T)	0.00050	0.0015	
	pH			
Hydrogen Cyanide	TSS	3.2	8.6	6.0 to 10.5
	Cyanide A	0.021	0.10	
	Cyanide (T)	0.23	0.65	
	pH			
Nickel Sulfate	TSS	0.032	0.096	6.0 to 9.0
	Nickel (T)	0.0020	0.0060	
	pH			
Chrome Pigments	TSS	3.8	9.1	6.0 to 9.0
	Chromium (T)	0.13	0.31	
	Lead (T)	0.15	0.36	
	Zinc (T)	0.13	0.31	
	pH			
Sodium Bisulfite	TSS	0.080	0.32	6.0 to 9.0
	COD	0.95	3.8	
	Chromium (T)	0.00063	0.0020	
	Zinc (T)	0.0015	0.0051	
	pH			

TABLE 2-2. SUMMARY OF REGULATIONS -
BEST AVAILABLE TECHNOLOGY (BAT)

Subcategory	Parameter	Effluent Limitations	
		Max	24-hr
		30-day Avg	Max
		kg/kg (or lb/1000 lb) of product	
Chlor-alkali	Mercury (T)	0.00010	0.00023
Mercury Cells	Total Residual Chlorine	0.0019	0.0032
Chlor-alkali	Copper (T)	0.0049	0.012
Diaphragm Cells	Lead (T)	0.0024	0.0059
	Nickel (T)	0.0037	0.0097
	Total Residual Chlorine	0.0079	0.013
Hydrofluoric Acid	Fluoride (T)	1.6	3.4
	Nickel (T)	0.0060	0.020
	Zinc (T)	0.022	0.072
Sodium Dichromate	Chromium (T)	0.0044	0.0088
	Hexavalent Chromium	0.00050	0.00090
	Nickel (T)	0.0034	0.0068
Titanium Dioxide (sulfate process)	Chromium (T)	0.21	0.48
	Nickel (T)	0.14	0.29
Titanium Dioxide (chloride process)	Chromium (T)	0.030	0.057
Titanium Dioxide (chloride-ilmenite process)	Chromium (T)	0.053	0.12
	Nickel (T)	0.035	0.072
Aluminum Fluoride	Fluoride (T)	0.63	1.3
	Chromium (T)	0.0045	0.013
	Nickel (T)	0.0024	0.0079

(continued)

Table 2-2. Continued

Subcategory	Parameter	Effluent Limitations	
		Max	24-hr
		30-day Avg kg/kg (or lb/1000 lb) of product	Max
Chrome Pigments	Chromium	0.13	0.31
	Lead (T)	0.15	0.36
	Zinc (T)	0.13	0.31
Copper Sulfate	Copper (T)	0.0010	0.0030
	Nickel (T)	0.0020	0.0060
	Selenium (T)	0.00050	0.0015
Hydrogen Cyanide	Cyanide A	0.021	0.10
	Cyanide (T)	0.23	0.65
	Total Residual Chlorine	0.051	0.086
Nickel Sulfate	Copper (T)	0.00024	0.00074
	Nickel (T)	0.00024	0.00074
Sodium Bisulfite	COD	0.95	3.8
	Chromium (T)	0.00063	0.0020
	Zinc (T)	0.0015	0.0051

TABLE 2-3. SUMMARY OF REGULATIONS -
PRETREATMENT STANDARDS FOR EXISTING
SOURCES (PSES)

Subcategory	Parameter	Effluent Limitations			
		Max 30-day Avg (mg/l) or (kg/kkg)		24-hr Max (mg/l) or (kg/kkg)	
Chlor-alkali Mercury Cells	Mercury (T)	0.048	0.00010	0.11	0.00023
Chlor-alkali Diaphragm Cells	Copper (T)	0.80	0.0070	2.1	0.018
	Lead (T)	1.1	0.010	2.9	0.026
	Nickel (T)	0.64	0.0056	1.6	0.014
Hydrofluoric Acid	Fluoride (T)	50	1.6	100	3.4
	Nickel (T)	0.20	0.0060	0.66	0.020
	Zinc (T)	0.66	0.022	2.2	0.072
Sodium Dichromate	Chromium (T)	0.50	0.0044	1.0	0.0088
	Hexavalent Chromium	0.060	0.00050	0.11	0.00090
	Nickel (T)	0.40	0.0034	0.80	0.0068
Titanium Dioxide (sulfate process)	Chromium (T)	0.44	0.21	1.0	0.48
	Nickel (T)	0.29	0.14	0.60	0.29
Titanium Dioxide (chloride process)	Chromium (T)	0.30	0.030	0.57	0.057
Titanium Dioxide (chloride- ilmenite process)	Chromium (T)	0.44	0.053	1.0	0.12
	Nickel (T)	0.29	0.035	0.60	0.072
Chrome Pigments	Chromium (T)	1.2	0.13	2.9	0.31
	Lead (T)	1.4	0.15	3.4	0.36
	Zinc	1.2	0.13	2.9	0.31

(continued)

TABLE 2-3. Continued

Subcategory	Parameter	Effluent Limitations			
		Max 30-day Avg (mg/l) or (kg/kg)		24-hr Max (mg/l) or (kg/kg)	
Copper Sulfate	Copper (T)	1.1	0.0010	3.2	0.0030
	Nickel (T)	2.1	0.0020	6.4	0.0060
	Selenium (T)	0.53	0.00050	1.6	0.0015
Hydrogen Cyanide	Cyanide A	0.36	0.021	1.7	0.10
	Cyanide (T)	4.0	0.23	11	0.65
Nickel Sulfate	Copper (T)	0.36	0.00024	1.1	0.00074
	Nickel (T)	0.36	0.00024	1.1	0.00074
Sodium Bisulfate	COD	630	0.95	2500	3.8
	Chromium (T)	0.42	0.00063	1.3	0.0020
	Zinc (T)	1.0	0.0015	3.4	0.0051

TABLE 2-4. SUMMARY OF REGULATIONS -
NEW SOURCE PERFORMANCE STANDARDS (NSPS)

Subcategory	Parameter	Effluent Limitations		pH Range
		Max	24-hr	
		30-day Avg kg/kg (or lb/1000 lb) of product	Max of product	
Chlor-alkali Mercury Cells	TSS	0.32	0.64	6.0 to 9.0
	Mercury (T)	0.00010	0.00023	
	Total Residual Chlorine	0.0019	0.0032	
	pH			
Chlor-alkali Diaphragm Cells	TSS	0.32	1.0	6.0 to 9.0
	Lead (T)	0.0018	0.0047	
	Total Residual Chlorine	0.0079	0.013	
	pH			
Hydrofluoric Acid	TSS	3.0	6.0	6.0 to 9.0
	Fluoride (T)	1.6	3.4	
	Nickel (T)	0.0060	0.020	
	Zinc (T)	0.022	0.072	
	pH			
Sodium Dichromate	TSS	0.22	0.44	6.0 to 9.0
	Chromium (T)	0.0044	0.0088	
	Hexavalent Chromium	0.00050	0.00090	
	Nickel (T)	0.0034	0.0068	
	pH			
Titanium Dioxide (sulfate process)	TSS	30	110	6.0 to 9.0
	Iron (T)	1.2	4.0	
	Chromium (T)	0.14	0.27	
	Nickel (T)	0.095	0.18	
	pH			
Titanium Dioxide (chloride process)	TSS	4.0	14	6.0 to 9.0
	Iron (T)	0.16	0.52	
	Chromium (T)	0.012	0.023	
	pH			

(continued)

TABLE 2-4. Continued

Subcategory	Parameter	Effluent Limitations		pH Range
		Max	24-hr	
		30-day Avg kg/kg (or lb/1000 lb) of product	Max	
Titanium Dioxide (chloride-ilmenite process)	TSS	2.4	8.4	6.0 to 9.0
	Iron (T)	0.096	0.32	
	Chromium (T)	0.0072	0.014	
	Nickel (T)	0.010	0.020	
	pH			
Aluminum Fluoride	TSS	1.2	2.4	6.0 to 9.0
	Fluoride (T)	0.63	1.3	
	Chromium (T)	0.0045	0.015	
	Nickel (T)	0.0024	0.0079	
	pH			
Chrome Pigments	TSS	3.8	9.1	6.0 to 9.0
	Chromium (T)	0.13	0.31	
	Lead (T)	0.15	0.36	
	Zinc (T)	0.13	0.31	
	pH			
Copper Sulfate	TSS	0.023	0.069	6.0 to 9.0
	Copper (T)	0.0010	0.0030	
	Nickel (T)	0.0020	0.0060	
	Selenium (T)	0.00050	0.0015	
	pH			
Hydrogen Cyanide	TSS	3.2	8.6	6.0 to 10.5
	Cyanide A	0.021	0.10	
	Cyanide (T)	0.23	0.65	
	Total Residual Chlorine	0.051	0.086	
	pH			
Nickel Sulfate	TSS	0.032	0.096	6.0 to 9.0
	Copper (T)	0.00024	0.00074	
	Nickel (T)	0.00024	0.00074	
	pH			

(continued)

TABLE 2-4. Continued

Subcategory	Parameter	Effluent Limitations		pH Range
		Max	24-hr	
		30-day Avg	Max	
		kg/kg (or lb/1000 lb) of product		
Sodium Bisulfite	TSS	0.080	0.32	6.0 to 9.0
	COD	0.95	3.8	
	Chromium (T)	0.00063	0.0020	
	Zinc (T)	0.0015	0.0051	
	pH			

TABLE 2-5. SUMMARY OF REGULATIONS -
PRETREATMENT STANDARDS FOR NEW SOURCES (PSNS)

Subcategory	Parameter	Effluent Limitations			
		Max 30-day Avg (mg/l) or (kg/kg)		24-hr Max (mg/l) or (kg/kg)	
Chlor-alkali Mercury Cells	Mercury	0.048	0.00010	0.11	0.00023
Chlor-alkali Diaphragm Cells	Lead (T)	0.21	0.0018	0.53	0.0047
Hydrofluoric Acid	Fluoride (T)	50	1.6	100	3.4
	Nickel (T)	0.20	0.0060	0.66	0.20
	Zinc (T)	0.66	0.022	2.2	0.072
Sodium Dichromate	Chromium (T)	0.50	0.0044	1.0	0.0088
	Hexavalent Chromium	0.060	0.00050	0.11	0.00090
	Nickel (T)	0.40	0.0034	0.80	0.0068
Titanium Dioxide (sulfate process)	Iron (T)	2.5	1.2	8.5	4.0
	Chromium (T)	0.30	0.14	0.57	0.27
	Nickel (T)	0.20	0.095	0.38	0.18
Titanium Dioxide (chloride process)	Iron (T)	1.6	0.16	5.3	0.52
	Chromium (T)	0.12	0.012	0.23	0.023
Titanium Dioxide (chloride- ilmenite process)	Iron (T)	1.6	0.096	5.3	0.32
	Chromium (T)	0.12	0.0072	0.23	0.014
	Nickel (T)	0.17	0.010	0.33	0.020
Chrome Pigments	Chromium (T)	1.2	0.13	2.9	0.31
	Lead (T)	1.4	0.15	3.4	0.36
	Zinc (T)	1.2	0.13	2.9	0.31

(continued)

TABLE 2-5. Continued

Subcategory	Parameter	Effluent Limitations			
		Max 30-day Avg		24-hr Max	
		(mg/l) or (kg/kg)		(mg/l) or (kg/kg)	
Copper Sulfate	Copper (T)	1.1	0.0010	3.2	0.0030
	Nickel (T)	2.1	0.0020	6.4	0.0060
	Selenium (T)	0.53	0.00050	1.6	0.0015
Hydrogen Cyanide	Cyanide A	0.36	0.021	1.7	0.10
	Cyanide (T)	4.0	0.23	11	0.65
Nickel Sulfate	Copper (T)	0.36	0.00024	1.1	0.00074
	Nickel (T)	0.36	0.00024	1.1	0.00074
Sodium Bisulfite	COD	630	0.95	2500	3.8
	Chromium (T)	0.42	0.00063	1.3	0.0020
	Zinc (T)	1.0	0.0015	3.4	0.0051

SECTION 3
INTRODUCTION

AUTHORITY

The Federal Water Pollution Control Act Amendments

The Federal Water Pollution Control Act (the Act) Amendments of 1972, 33 USC 1251 et seq., stated the national goal of attaining by July 1, 1983, a water quality which provides for the protection and propagation of fish and shellfish, for recreation in or on the nation's waters, and the goal of eliminating the discharge of pollutants into navigable waters by 1985.

Purpose and Authority

The Federal Water Pollution Control Act Amendments of 1972 established a comprehensive program to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters," Section 101(a). By July 1, 1977, existing industrial dischargers were required to achieve "effluent limitations requiring the application of the best practicable control technology currently available" ("BPT"), Section 301(b)(1)(A); and by July 1, 1983, these dischargers were required to achieve "effluent limitations requiring the application of the best available technology economically achievable... which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants" ("BAT"), Section 301(b)(2)(A). New industrial direct dischargers were required to comply with Section 306 new source performance standards ("NSPS"), based on best available demonstrated technology; and new and existing dischargers to publicly owned treatment works ("POTW") were subject to pretreatment standards under Sections 307(b) and (c) of the Act. While the requirements for direct dischargers were to be incorporated into National Pollutant Discharge Elimination System (NPDES) permits issued under Section 402 of the Act, pretreatment standards were made enforceable directly against dischargers to POTW (indirect dischargers).

Although Section 402(a)(1) of the 1972 Act authorized the setting of requirements for direct dischargers on a case-by-case basis, Congress intended that for the most part control requirements would be based on regulations promulgated by the Administrator of EPA. Section 304(b) of the Act required the Administrator to promulgate regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of BPT and BAT. Moreover, Sections 304(c) and 306 of the Act required promulgation of regulations for NSPS, and Sections 304(f), 307(b), and 307(c) required promulgation of regulations for pretreatment standards. In addition to these regulations for designated industry categories, Section 307(a) of the Act required the Administrator to

develop a list of toxic pollutants and promulgate effluent standards applicable to all dischargers of toxic pollutants. Finally, Section 501(a) of the Act authorized the Administrator to prescribe any additional regulations "necessary to carry out his functions" under the Act.

The EPA was unable to promulgate many of these regulations by the dates contained in the Act. In 1976, EPA was sued by several environmental groups, and in a settlement of this lawsuit EPA and the plaintiffs executed a "Settlement Agreement" which was approved by the Court. This Agreement required to EPA to develop a program and adhere to a schedule for promulgating BAT effluent limitations guidelines, pretreatment standards, and new source performance standards for 65 "priority" pollutants and classes of pollutants for 21 major industries. See Natural Resources Defense Council, Inc. versus Train, 9 ERC 2120 (D.D.C. 1976), modified March 9, 1979.

On December 27, 1977, the President signed into law the Clean Water Act of 1977. Although this law makes several important changes in the Federal water pollution control program, its most significant feature is its incorporation of several of the basic elements of the Settlement Agreement program for toxic pollution control. Sections 301(b)(2)(A) and 301(b)(2)(C) of the Act now require the achievement by July 1, 1984, of effluent limitations requiring application of BAT for "toxic" pollutants, including the 65 "priority" pollutants and classes of pollutants which Congress declared "toxic" under Section 307(a) of the Act. Likewise, EPA's programs for new source performance standards and pretreatment standards are now aimed principally at toxic pollutant controls. Moreover, to strengthen the toxics control program Section 304(e) of the Act authorizes the Administrator to prescribe "best management practices" ("BMPs") to prevent the release of toxic and hazardous pollutants from plant site runoff, spillage or leaks, sludge or waste disposal, and drainage from raw material storage associated with, or ancillary to, the manufacturing or treatment process.

In keeping with its emphasis on toxic pollutants, the Clean Water Act of 1977 also revises the control program for non-toxic pollutants. Instead of BAT for "conventional" pollutants identified under Section 304(a)(4) (including biochemical oxygen demand, suspended solids, fecal coliform and pH), the new Section 301(b)(2)(E) requires achievement by July 1, 1984, of "effluent limitations requiring the application of the best conventional pollutant control technology" ("BCT"). The factors considered in assessing BCT for an industry include the cost of attaining a reduction in effluents and the effluent reduction benefits derived compared to the costs incurred by and the effluent reduction benefits from a publicly owned treatment works (Section 304(b)(4)(B)). For non-toxic, nonconventional pollutants, Sections 301(b)(2)(A) and (b)(2)(F) require achievement of BAT effluent limitations within three years after their establishment or by July 1, 1984, whichever is later, but not later than July 1, 1987.

The purpose of these regulations is to provide effluent limitations guidelines for BPT, BAT, and BCT, and to establish NSPS, pretreatment standards for existing sources (PSES), and pretreatment standards for new sources (PSNS), under Sections 301, 304, 306, 307, and 501 of the Clean Water Act.

The United States Environmental Protection Agency (the Agency) was entrusted with the responsibility to carry out the requirements of the Act, and initiated an intensive effort to develop the necessary regulatory means which would achieve the stepwise reduction and elimination of pollutant discharge practices in all major U.S. Industries. For the Inorganic Chemicals Manufacturing Point Source Category, the Agency designed a comprehensive, two phase program to identify the control parameters and establish the technological basis for regulations development. Phase I covered 22 Major Inorganic Chemical Products (1), and the final regulations for these industrial subcategories were published in the Federal Register on March 12, 1974. The regulations included specific numerical effluent limitations and standards of performance for both existing and new sources. Zero-discharge requirements specified for many of the subcategories were to be applied either at the 1977 BPT step or later. Phase II of the Agency's effort resulted in the promulgation of BPT based effluent limitations for an additional group of 27 subcategories referred to as Significant Inorganic Chemical Products (2). The interim final regulations were published on May 22, 1975. Taken together, the two groups of regulations cover 49 inorganic chemical subcategories, many of which include more than one specific chemical product. Although some toxic pollutants were covered in cases where a direct relationship to the process was obvious (e.g., mercury and/or lead in the Chlor-Alkali Industry), the main thrust of the regulations was the control of the pollutant parameters which accounted, in terms of quantity, for most of the pollution loading of navigable waters attributable to the manufacture of inorganic chemicals.

Court Remand of Regulations

On March 10, 1976, the United States Court of Appeals for the Fourth Circuit decided in *E.I. du Pont de Nemours & Company, et al. versus Train*, 541 F. 2d 1018 (4th Cir. 1976), to set aside and remand for reconsideration a number of general definitions and specific discharge regulations promulgated in 1974. These regulations are all within Title 40, Parts 401 and 415 of the Code of Federal Regulations and are listed below:

General Provisions

- 401.11 (i) - Definition of effluent limitations
- 401.11 (q) - Definition of process wastewater
- 401.11 (r) - Definition of process wastewater pollutant

Chlor-Alkali

415.63 - BATEA

Hydrochloric Acid

415.72 - BPCTCA
415.73 - BATEA
415.75 - New sources

Hydrofluoric Acid

415.82 - BPCTCA
415.83 - BATEA
415.85 - New sources

Nitric Acid

415.102 - BPCTCA
415.103 - BATEA
415.105 - New sources

Sodium Carbonate

415.152 - BPCTCA
415.153 - BATEA
415.155 - New sources

Sodium Dichromate

415.173 - BATEA

Sodium Metal

415.182 - BPCTCA
415.183 - BATEA
415.185 - New sources

Sodium Silicate

415.192 - BPCTCA
415.193 - BATEA
415.195 - New sources

Sulfuric Acid

415.210 - Applicability
415.212 - BPCTCA
415.213 - BATEA
415.215 - New sources

Titanium Dioxide

415.220 - Applicability
415.222 - BPCTCA
415.223 - BATEA
415.225 - New sources

For the most part, the main target of the remand was the zero discharge regulations from which the industry petitioners sought relief on grounds of technological infeasibility. During 1975, the Agency funded a special study of the remand issues (3) and was prepared to propose amended regulations.

Following the court remand of the Phase I final regulations, the Agency revoked the Phase II interim final and proposed regulations published in May, 1975, for Aluminum Fluoride, Chrome Pigments, Hydrogen Cyanide, and Sodium Silicofluoride. In this instance, the Agency's intent was to reconsider the specific effluent limitations established for these industries (1977 step) in the light of information made available on process differences between plants and additional data on the actual concentrations and treatability of the regulated discharge constituents. The information was presented to the Agency in the form of various documents prepared by members of the industries concerned. These sources are also cited in the appropriate sections of this report.

The Settlement Agreement

A consent decree was issued in a suit filed by four environmental groups in Natural Resources Defense Council versus Train, 9 ERC 2120 (June 8, 1976) modified 12 ERC 1833 (December 15, 1978). The consent decree contained a Settlement Agreement wherein the Agency agreed to regulate 65 toxic pollutants under Sections 301, 304, 306, and 307 of the Act in accordance with the schedule and provisions stipulated. The original list of 65 chemicals and classes of chemicals attached to the Settlement Agreement was redefined to cover 129 chemical substances, including specific organic compounds, pesticides and their metabolites, polychlorinated biphenyls (PCB's), cyanide, 13 heavy metals and asbestos. Table 3-1 lists the 129 toxic pollutants (sometimes referred to in the literature as "priority pollutants").

The Settlement Agreement also identified 21 point source categories and specified the scope of application of effluent limitations, new source performance standards, and pretreatment standards within each category in terms of the Standard Industrial Classification (SIC) code numbers. For the Inorganic Chemicals Manufacturing Point Source Category, the major industries included are:

- SIC 2182 - Alkalies and Chlorine
- SIC 2813 - Industrial Gases
- SIC 2816 - Inorganic Pigments
- SIC 2819 - Industrial Inorganic Chemicals,
Not Elsewhere Classified

Within these industries, the Agency has identified 63 subcategories listed in Table 3-2 for the initial study. Most of these subcategories, 49 in all, had already been covered by BPT and BAT discharge regulations promulgated in 1974 and 1975. Those regulations established point of discharge control levels for the conventional parameters such as pH, TSS, BOD, and oil and grease. In many cases, specific chemical parameters were regulated, particularly Arsenic, Chromium, Copper, Mercury, Nickel, Lead, Selenium, Zinc, and Cyanide, which are now included in the list of toxic pollutants. Other regulated parameters such as aluminum, barium, iron, ammonia, fluoride and sulfide are not presently listed as toxic chemicals but are to be

treated as nonconventional pollutants under future discharge limitations and standards of performance.

Nearly half of the initial 63 subcategories have been recommended for exclusion from this study on the basis of specific provisions for such exclusion under Paragraph 8 of the Settlement Agreement. The bases for these exclusions are as follows:

- 28 {
- A. No. 63, Ferrous Sulfate, is already covered by the Titanium Dioxide - Sulfate Process subcategory and does not require separate consideration.
 - B. No's. 60, 61 and 62 (Potassium Permanganate, Zinc Oxide, and Lithium Carbonate) have only one plant each (or one plant with a wet process discharge), and represent nonsignificant discharges of toxic pollutants. No's. 27 and 28 (Copper Oxide and Manganese Sulfate) are also single plants, but were covered in screening.
 - C. No's. 36 through 59 have existing BPT or BAT regulations requiring zero discharge of process wastewater to navigable water and there are no known discharges to a POTW. Continued enforcement of the existing regulations will provide adequate control of toxic pollutants.

The remaining 35 nonexcluded subcategories (Table 3-2, No's. 1 through 35) are covered in this report. This group also includes the 11 subcategories whose final regulations were remanded for restudy in E.I. du Pont de Nemours and Company, et al. versus Train, supra, and the four additional subcategories whose interim, final or proposed regulations were revoked and reserved by the Agency.

It was anticipated by the Agency that a substantial number of the 35 industries to be screened would also qualify for exclusion under Paragraph 8 on the basis of the analytical results obtained from the process wastewater toxic pollutant screening program. A preliminary prioritization indicated that the initial detailed study and regulation development would focus on the first 15 subcategories.

This judgment has been substantially supported by the analytical results of the screening programs and a number of additional exclusions are being recommended for subcategories in which nonsignificant toxic pollutant discharges have been determined. A detailed presentation of the analytical results is given under the individual subcategory sections of this report. The additional recommended exclusions include the following:



TABLE 3-1. RECOMMENDED LIST OF TOXIC POLLUTANTS

1. *acenaphthene	*haloethers (other than those listed elsewhere)	85. *tetrachloroethylene
2. *acrolein	40. 4-chlorophenyl phenyl ether	86. *toluene
3. *acrylonitrile	41. 4-bromophenyl phenyl ether	87. *trichloroethylene
4. *benzene	42. bis(2-chloroisopropyl) ether	88. *vinyl chloride (chloroethylene) pesticides and metabolites
5. *benzidine	43. bis(2-chloroethoxy) methane	89. *aldrin
6. *carbon tetrachloride (tetrachloromethane)	*halomethanes (other than those listed elsewhere)	90. *dieldrin
*chlorinated benzenes (other than dichlorobenzenes)	44. methylene chloride (dichloromethane)	91. *chlordane (technical mixture & metabolites)
7. chlorobenzene	45. methyl chloride (chloromethane)	*DDT and metabolites
8. 1,2,4-trichlorobenzene	46. methyl bromide (bromomethane)	92. 4,4'-DDT
9. hexachlorobenzene	47. bromoform (tribromomethane)	93. 4,4'-DDE (p,p'-DDX)
*chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)	48. dichlorobromomethane	94. 4,4'-DDD (p,p'-TDE)
10. 1,2-dichloroethane	49. trichlorofluoromethane ⁽²⁾	*endosulfan and metabolites
11. 1,1,1-trichloroethane	50. dichlorodifluoromethane ⁽²⁾	95. a-endosulfan-Alpha
12. hexachloroethane	51. chlorodibromomethane	96. b-endosulfan-Beta
13. 1,1-dichloroethane	52. *hexachlorobutadiene	97. endosulfan sulfate
14. 1,1,2-trichloroethane	53. *hexachlorocyclopentadiene	*endrin and metabolites
15. 1,1,2,2-tetrachloroethane	54. *isophorone	98. endrin
16. chloroethane	55. *naphthalene	99. endrin aldehyde
*chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)	56. *nitrobenzene	*heptachlor and metabolites
17. bis(chloromethyl) ether ⁽¹⁾	*nitrophenols (including 2,4-dinitrophenol and dinitrocresol)	100. heptachlor
18. bis(2-chloroethyl) ether	57. 2-nitrophenol	101. heptachlor epoxide
19. 2-chloroethyl vinyl ether (mixed)	58. 4-nitrophenol	*hexachlorocyclohexane (all isomers)
*chlorinated naphthalene	59. *2,4-dinitrophenol	102. a-BHC-Alpha
20. 2-chloronaphthalene	60. 4,6-dinitro-o-cresol	103. b-BHC-Beta
*chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)	*nitrosamines	104. g-BHC (lindane)-Gamma
21. 2,4,6-trichlorophenol	61. N-nitrosodimethylamine	105. d-BHC-Delta
22. p-chloro-m-cresol	62. N-nitrosodiphenylamine	*polychlorinated biphenyls (PCB's)
23. *chloroform (trichloromethane)	63. N-nitrosodi-n-propylamine	106. PCB-1242 (Arochlor 1242)
24. *2-chlorophenol	64. *pentachlorophenol	107. PCB-1254 (Arochlor 1254)
*dichlorobenzenes	65. *phenol	108. PCB-1221 (Arochlor 1221)
25. 1,2-dichlorobenzene	*phthalate ethers	109. PCB-1232 (Arochlor 1232)
26. 1,3-dichlorobenzene	66. bis(2-ethoxyhexyl) phthalate	110. PCB-1248 (Arochlor 1248)
27. 1,4-dichlorobenzene	67. butyl benzyl phthalate	111. PCB-1260 (Arochlor 1260)
*dichlorobenzidine	68. di-n-butyl phthalate	112. PCB-1016 (Arochlor 1016)
28. 3,3'-dichlorobenzidine	69. di-n-octyl phthalate	*toxaphene
*dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)	70. diethyl phthalate	114. *antimony (total)
29. 1,1-dichloroethylene	71. dimethyl phthalate	115. *arsenic (total)
30. 1,2-trans-dichloroethylene	*polynuclear aromatic hydrocarbons	116. *asbestos (fibrous)
31. *2,4-dichlorophenol	72. benzo(a)anthracene (1,2-benzanthracene)	117. *beryllium (total)
*dichloropropane and dichloropropene	73. benzo(a)pyrene (3,4-benzopyrene)	118. *cadmium (total)
32. 1,2-dichloropropane	74. 3,4-benzofluoranthene	119. *chromium (total)
33. 1,3-dichloropropylene (1,3-dichloropropene)	75. benzo(k)fluoranthene (11,12-benzofluoranthene)	120. *copper (total)
34. *2,4-dimethylphenol	76. chrysene	121. *cyanide (total)
*dinitrotoluene	77. acenaphthylene	122. *lead (total)
35. 2,4-dinitrotoluene	78. anthracene	123. *mercury (total)
36. 2,6-dinitrotoluene	79. benzo(ghi)perylene (1,12-benzoperylene)	124. *nickel (total)
37. *1,2-diphenylhydrazine	80. fluorene	125. *selenium (total)
38. *ethylbenzene	81. phenanthrene	126. *silver (total)
39. *fluoranthene	82. dibenzo(a,h)anthracene (1,2,3,5,6-dibenzanthracene)	127. *thallium (total)
	83. indeno (1,2,3-cd)pyrene (2,3-phenyleneperylene)	128. *zinc (total)
	84. pyrene	129. *2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

(1) Deleted 92/04/81; 46 FR 10723.

(2) Deleted 91/08/81; 46 FR 2266

*Specific compounds and chemical classes as listed in the consent decree.

TABLE 3-2. SCOPE OF INDUSTRY COVERAGE WITHIN THE INORGANIC
CHEMICALS MANUFACTURING POINT SOURCE CATEGORY

Subcategories Designated for Initial Study

1. Chlor-Alkali	33. Sodium Silicofluoride
2. Hydrofluoric Acid	34. Sodium Thiosulfate
3. Hydrogen Peroxide	35. Sulfur Dioxide
4. Titanium Dioxide	36. Bromine
5. Aluminum Fluoride	37. Calcium Hydroxide
6. Chrome Pigments	38. Chromic Acid
7. Hydrogen Cyanide	39. Fluorine
8. Sodium Dichromate	40. Hydrogen
9. Carbon Dioxide	41. Iodine
10. Carbon Monoxide/Hydrogen	42. Potassium Chloride
11. Copper Sulfate	43. Stannic Oxide
12. Nickel Sulfate	44. Zinc Sulfate
13. Silver Nitrate	45. Calcium Carbide
14. Sodium Bisulfite	46. Calcium Oxide
15. Sodium Hydrosulfite	47. Potassium Metal
16. Hydrochloric Acid	48. Potassium Sulfate
17. Nitric Acid	49. Sodium Bicarbonate
18. Sodium Carbonate	50. Borax
19. Sodium Metal	51. Ferric Chloride
20. Sodium Silicate	52. Lead Monoxide
21. Sulfuric Acid	53. Sodium Fluoride
22. Ammonium Chloride	54. Aluminum Chloride
23. Ammonium Hydroxide	55. Aluminum Sulfate
24. Barium Carbonate	56. Potassium Dichromate
25. Boric Acid	57. Calcium Chloride
26. Calcium Carbonate	58. Sodium Chloride
27. Copper Oxide	59. Sodium Sulfite
28. Manganese Sulfate	60. Potassium Permanganate
29. Strong Nitric Acid	61. Zinc Oxide
30. Oxygen and Nitrogen	62. Lithium Carbonate
31. Potassium Iodide	63. Ferrous Sulfate
32. Sodium Hydrosulfide	

<u>Number</u>	<u>Subcategory</u>
3.	Hydrogen Peroxide
9.	Carbon Dioxide
10.	Carbon Monoxide/Hydrogen
15.	Sodium Hydrosulfite
16.	Hydrochloric Acid
17.	Nitric Acid
18.	Sodium Carbonate
19.	Sodium Metal
21.	Sulfuric Acid
22.	Ammonium Chloride
23.	Ammonium Hydroxide
24.	Barium Carbonate
25.	Boric Acid
26.	Calcium Carbonate
27.	Copper Oxide (one plant)
28.	Manganese Sulfate (one plant)
29.	Strong Nitric Acid
30.	Oxygen and Nitrogen
31.	Potassium Iodide
32.	Sodium Hydrosulfide
34.	Sodium Thiosulfate
35.	Sulfur Dioxide

Silver Nitrate, No. 13, and Sodium Silicofluoride, No. 33, are being deferred for future study under Phase II of the BAT regulation development program for Inorganic Chemicals. This deferrment was caused by problems with plant access during the course of the present study.

General Approach and Methodology

Initiating and undertaking a comprehensive study of the toxic pollutant problem in the Inorganic Chemicals Industry was preceded by an intensive evaluation by the Agency of the kinds of data and supporting information that should be assembled as a basis for the development of regulations. All major decisions on the identity of pollutants and the establishment of effluent limitations and standards of performance for each subcategory had to be suportable by documented evidence collected from operating production facilities. Similarly, the necessary information on production rates, processes, raw materials, water use, waste sources, and treatment technologies in practice has to be acquired with sufficient detail and breadth of coverage to permit an analysis of the engineering and economic variables that are characteristic of each subcategory. Toxic pollutant control regulations would be based on the application of best available technology for treatment and reliable performance evaluations for the removal of specific waste substances.

The following paragraphs briefly describe the major study tasks and their results as they are presented in this report.

Industry Data Base Development and Subcategorization Review

Information from individual manufacturers and previous study documents was reviewed in detail and an evaluation of the appropriateness of subcategorization was performed. Section 4 presents a discussion of the factors considered in subcategorization and presents the rationale for maintaining the present scheme of subcategorization for the industries studied.

The Screening and Verification Sampling Programs

The collection of detailed analytical data on conventional, nonconventional and toxic pollutant concentrations in raw and treated process waste streams was completed in a two-phase sampling program. The first phase, screening, was designed to provide a representative, one-time 72-hour sampling of a plant in each subcategory in order to determine the presence of toxic and other pollutants and to evaluate their potential environmental significance. The sampling and analytical methodology is described in Section 5, along with the basis for making a decision on the need for verification sampling in each subcategory.

Engineering Evaluations

Section 6 describes the procedures and sources used in developing the industry productions and wastewater generation characteristics that form the basis of the model plant concept. The sources of detailed process and waste treatment information are also presented. Section 7 contains an evaluation of treatment technology presently applied in BPT systems and advanced technologies that may be recommended for BAT and NSPS applications. Section 8 provides estimates of the treatability of selected toxic and nonconventional pollutants to be applied in the development of achievable performance characteristics for specific technologies. Section 8 also presents a discussion of the approach taken in statistical analysis of long-term monitoring data. The statistically derived parameters, including variability factors for the 24-hour maximum and maximum 30-day average limitations are presented in Appendix A. Section 9 lays the groundwork for the estimation of pollutant removal performances for each nonexcluded subcategory. The candidate toxic pollutants to be controlled in each subcategory are identified on the basis of the screening and verification data and the rationale for the application of advanced level technologies is presented.

Treatment System Cost Estimates

Section 10 presents the general approach to cost estimating, discusses the assumptions made, and gives the detailed cost estimates for alternative levels of treatment and control. For each subcategory verified, the total estimated installed cost of a typical BPT treatment system is developed on the basis of the model plant design specifications and estimated incremental costs are given for each of

the advanced level treatment alternatives. Costs of RCRA compliance and implementation have not been included in these cost estimates. Figures for RCRA costs are included in a supplementary document, "Contractor Report on RCRA ISS Compliance costs for Selected Inorganic Chemicals Industries". RCRA costs are considered in the Economic Impact Analysis of Pollution Control Technologies for Segments of the Inorganic Chemicals Manufacturing Industry, EPA 440/2-81-023.

Treatability Study

Data was collected through a treatability study to evaluate the achievable performance of proposed BAT for the treatment and control of pollutant discharges, and to provide empirical treatment system performance information applicable to selected inorganic chemical subcategories. The study, completed in July 1980, specifically concentrated on those subcategories in the Inorganic Chemicals Industry for which analytical data on raw wastewaters and treated effluents either did not exist or was deficient, and for which data were needed for purposes of comparison with proposed effluent limitations. Subcategories for which treatability was studied include:

Nickel Sulfate
Hydrofluoric Acid
Copper Sulfate
Chlor-Alkali (Diaphragm Cells)
Titanium Dioxide (Chloride Process)
Chrome Pigments
Sodium Dichromate
Sodium Bisulfite
Sodium Hydrosulfite

General Criteria for Effluent Limitations

BPT Effluent Limitations

The factors considered in defining best practicable control technology currently available (BPT) include the total cost of applying such technology in relation to the effluent reductions derived from such application, the age of equipment and facilities involved, the process employed, non-water quality environmental impacts (including energy requirements), and other factors the Administrator considers appropriate (Section 304 (b) (1) (B)). In general, the BPT technology level represents the average of the best existing performances of plants of various ages, sizes, processes, or other common characteristics. Where existing performance is uniformly inadequate, BPT may be transferred from a different subcategory or category. BPT focuses on end-of-pipe treatment rather than process changes or internal controls, except where such are common industry practice. The cost/benefit inquiry for BPT is a limited balancing, committed to EPA's discretion, which does not require the Agency to quantify benefits in monetary terms. See, e.g., American Iron and Steel

Institute v. EPA, 526 F. 2d 1027 (3rd Cir. 1975). In balancing costs in relation to effluent reduction benefits, EPA considers the volume and nature of existing discharges, the volume and nature of discharges expected after application of BPT, the general environmental effects of the pollutants, and the cost and economic impacts of the required pollution control level. The Act does not require or permit consideration of water quality problems attributable to particular point sources or industries, or water quality improvements in particular water bodies. Therefore, EPA has not considered these factors. See *Weyerhaeuser Company v. Costle*, 590 F.2d 1011 (D.C. Cir. 1978).

BAT Effluent Limitations

The factors considered in assessing best available technology economically achievable (BAT) include the age of equipment and facilities involved, the process employed, process changes, non-water quality environmental impacts (including energy requirements) and such other factors as the Administrator deems appropriate. (Section 304 (b) (2) (B)). At a minimum, the BAT technology level represents the best economically achievable performance of plants of various ages, sizes, processes, or other shared characteristics. As with BPT, uniformly inadequate performance may require transfer of BAT from a different subcategory or category. BAT may include process changes or internal controls, even when these technologies are not common industry practice. The statutory assessment of BAT "considers" costs, but does not require a balancing of costs against effluent reduction benefits (see *Weyerhaeuser v. Costle*, supra). In developing the BAT regulations, however, EPA has given substantial weight to the reasonableness of costs. The Agency has considered the volume and nature of discharges, the volume and nature of discharges expected after application of BAT, the general environmental effects of the pollutants, and the costs and economic impacts of the required pollution control levels. Despite this expanded consideration of costs, the primary determinant of BAT is effluent reduction capability. As a result of the Clean Water Act of 1977, 33 USC 1251 et seq. the achievement of BAT has become the principal national means of controlling water pollution due to toxic pollutants.

BCT Effluent Limitations

The 1977 amendments added Section 301 (b) (2) (E) to the Act, establishing "best conventional pollutant control technology" (BCT) for discharges of conventional pollutants from existing industrial point sources. Conventional pollutants are those defined in Section 304 (b) (4) -BOD, TSS, fecal coliform, and pH. Oil and grease was designated by the Administrator as "conventional" on July 30, 1979, 44 FR 44501. BCT is not an additional limitation, but replaces BAT for the control of conventional pollutants.

Section 304(b)(4)(B) of the Act requires that BCT limitations be assessed in light of a two part "cost-reasonableness" test. American Paper Institute v. EPA, 660 F.2d 954 (4th Cir. 1981). The first test

compares the cost for private industry to reduce its conventional pollutants with the costs to publicly owned treatment works for similar levels of reduction in their discharge of these pollutants. The second test examines the cost-effectiveness of additional industrial treatment beyond BPT. EPA must find that limitations are "reasonable" under both tests before establishing them as BCT. In no case may BCT be less stringent than BPT. EPA published its methodology for carrying out the BCT analysis on August 29, 1979 (44 FR 50732). However, that cost test was remanded by the United States Court of Appeals for the Fourth Circuit. American Paper Institute v. EPA, 660 F.2d 954 (4th Cir. 1981). The Court of Appeals ordered EPA to correct data errors underlying EPA's calculation of the first test, and to apply the second cost test. (EPA had argued that a second cost test was not required). The Agency is currently developing a new methodology.

The proposed regulations had set BCT equal to BPT in all subcategories except for the Chlor-Alkali subcategory (Diaphragm Cell Segment) and the Hydrofluoric Acid subcategory, either because BPT was set equal to BAT or because additional TSS removal failed the Agency's original "cost-reasonableness" test. In the Chlor-Alkali (Diaphragm Cell) and Hydrofluoric Acid subcategories, additional TSS removal passed our original test. Pending formulation by the Agency of a new BCT methodology, the Agency is deferring promulgation of BCT limitations for the Chlor-Alkali (Diaphragm Cell) and Hydrofluoric Acid subcategories. BPT is the minimum level of BCT control required by law. In all other subcategories, we have identified no other economically achievable technologies which result in significant additional removal of conventional pollutants. No possible reassessment of BCT pursuant to the Court's remand could result in BCT limitations different than those promulgated. Accordingly, the Agency is promulgating BCT equal to BPT for all other subcategories.

The cost calculations for the Chlor-Alkali (Diaphragm Cell) and Hydrofluoric Acid subcategories are presented below.

In the diaphragm cell segment of the Chlor-Alkali Subcategory, the cost for removal of additional conventional pollutants is \$0.53 per pound. The calculation is as follows:

$$\frac{\$0.22}{(0.51 \text{ kg/kg} - 0.32 \text{ kg/kg})} = \$0.53 \text{ per pound of TSS removed,}$$

where \$0.22 is the increased cost for BAT filtration over BPT treatment cost in dollars per kkg of production, 0.51 kg/kg is the BPT total suspended solids maximum 30-day average limitation from Table 11-35, and 0.32 kg/kg is the achievable maximum 30-day average TSS loading level with filtration. One kilogram (kg) is 2.2 pounds.

In the Hydrofluoric Acid Subcategory, the cost for removal of additional conventional pollutants is \$0.32 per pound. The calculation is as follows:

$$\frac{\$1.46}{(5.3 \text{ kg/kkg} - 3.2 \text{ kg/kkg})} = \$0.32 \text{ per pound of TSS removed,}$$

where \$1.46 is the increased cost for BAT treatment over BPT treatment cost in dollars per kkg of production from Table 12-16, where 5.3 kg/kkg is the BPT total suspended solids limitation from Table 12-21, and where 3.2 kg/kkg is the effluent TSS loading achievable by application of BAT. See Section 12.

In the Hydrofluoric Acid and Chlor-Alkali subcategories where BCT is deferred, the TSS and pH limitations are the same as BPT.

New Source Performance Standards

The basis for new source performance standards (NSPS) under Section 306 of the Act is the best available demonstrated technology. New plants have the opportunity to design the best and most efficient inorganic chemicals manufacturing processes and wastewater treatment technologies, and Congress therefore directed EPA to consider the best demonstrated process changes, in-plant controls, and end-of-pipe treatment technologies which reduce pollution to the maximum extent feasible.

Pretreatment Standards for Existing Sources

Section 307 (b) of the Act requires EPA to promulgate pretreatment standards for existing sources (PSES) which must be achieved within three years of promulgation. PSES are designed to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of POTWs. The Clean Water Act of 1977 also requires pretreatment for pollutants, such as toxic metals, that limit POTW sludge management alternatives, including the beneficial use of sludges on agricultural lands. Pretreatment is required for toxic pollutants that would pass through a POTW in amounts that would violate direct discharger effluent limitations. EPA has generally determined that there is pass through of pollutants if the percent of pollutants removed by a well-operated POTW achieving secondary treatment is less than the percent removed by the BAT model treatment system. The legislative history of the 1977 Act indicates that pretreatment standards are to be technology-based, analogous to the best available technology for removal of toxic pollutants. The general pretreatment regulations which served as the framework for these pretreatment regulations can be found at 40 CFR Part 403, 43 FR 27736 (June 26, 1978).

The Agency is promulgating PSES for the Chlor-Alkali (Diaphragm Cell) and Chrome Pigments Subcategories and the Agency is amending the existing PSES for the Copper Sulfate and Nickel Sulfate Subcategories. The Agency is excluding the Chlor-Alkali (Mercury cell), Hydrofluoric Acid, Sodium Dichromate, Titanium Dioxide, Hydrogen Cyanide, and Sodium Bisulfite Subcategories from national categorical PSES under the provisions of Paragraph 8(b) of the Settlement Agreement because

the toxic pollutants in discharges to POTWs from sources in those subcategories are below treatable levels or are so insignificant as not to justify developing pretreatment standards. The Agency is not promulgating PSES for the Aluminum Fluoride Subcategory because a well-operated POTW with secondary treatment installed achieves better percent removal of toxic pollutants than is provided by the BAT model treatment system for this subcategory.

Pretreatment Standards for New Sources

Section 307 (c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) at the same time that it promulgates NSPS. New indirect dischargers, like new direct dischargers, have the opportunity to incorporate the best available demonstrated technologies including process changes, in-plant controls, and end-of-pipe treatment technologies, and to use plant site selection to ensure adequate treatment system installation.

the 1990s, the number of people in the world who are under 15 years of age is expected to increase from 1.1 billion to 1.5 billion.

As the world's population grows, the demand for food and other resources will increase. This will put pressure on the environment and on the world's food supply.

One way to meet this demand is to increase the amount of food that is produced. This can be done by using more land for agriculture, by using more water, or by using more fertilizers and pesticides.

Another way to meet this demand is to reduce the amount of food that is wasted. This can be done by improving the way that food is stored and distributed, or by changing the way that people eat.

There are many other ways to meet this demand, and it is important that we find ways to do so that do not harm the environment or the world's food supply.

One of the most important ways to meet this demand is to reduce the amount of food that is wasted. This can be done by improving the way that food is stored and distributed, or by changing the way that people eat.

There are many other ways to meet this demand, and it is important that we find ways to do so that do not harm the environment or the world's food supply.

One of the most important ways to meet this demand is to reduce the amount of food that is wasted. This can be done by improving the way that food is stored and distributed, or by changing the way that people eat.

There are many other ways to meet this demand, and it is important that we find ways to do so that do not harm the environment or the world's food supply.

One of the most important ways to meet this demand is to reduce the amount of food that is wasted. This can be done by improving the way that food is stored and distributed, or by changing the way that people eat.

There are many other ways to meet this demand, and it is important that we find ways to do so that do not harm the environment or the world's food supply.

One of the most important ways to meet this demand is to reduce the amount of food that is wasted. This can be done by improving the way that food is stored and distributed, or by changing the way that people eat.

There are many other ways to meet this demand, and it is important that we find ways to do so that do not harm the environment or the world's food supply.

One of the most important ways to meet this demand is to reduce the amount of food that is wasted. This can be done by improving the way that food is stored and distributed, or by changing the way that people eat.

There are many other ways to meet this demand, and it is important that we find ways to do so that do not harm the environment or the world's food supply.

One of the most important ways to meet this demand is to reduce the amount of food that is wasted. This can be done by improving the way that food is stored and distributed, or by changing the way that people eat.

There are many other ways to meet this demand, and it is important that we find ways to do so that do not harm the environment or the world's food supply.

SECTION 4

SUBCATEGORIZATION REVIEW

Basis for Subcategorization

Factors Considered

The inorganic chemicals industry is very large and diversified and has been segmented into subcategories for the purpose of establishing effluent guidelines. Factors taken into consideration for subcategorization include: raw materials used, product produced, manufacturing process employed, geographical location, size and age of equipment and facility involved, non-water-quality aspects of waste characteristics, water pollution control technology, treatment costs, energy requirements and solid waste disposal. Following is a discussion of each of the general factors considered for this industry.

A. Raw Materials

Different raw materials are used to manufacture a wide variety of products, and vary from raw brines and ores to pure reagent chemicals. Some processes use waste or by product streams from other plants or from other processes within the same plant.

Because of this diversification, raw material characteristics generally do not constitute a logical basis for subcategorization. Variations in raw material quality or purity are not normally sufficient to cause a great difference in wastewater treatment needs, except in the case of trace toxic materials which may occur in some sources but not in others.

B. Dominant Product

Subcategorization by chemical name of the dominant inorganic chemical produced involves the least ambiguity in applying standards to a given point source. This is critical because of the great variety of product mix, manufacturing processes, wastewater constituents, and other factors at existing plants. Subcategorization by product becomes less useful as product mix increases in complexity because multi-product wastewater also becomes more complex and less susceptible to simple uniform treatment.

A subcategory established on the basis of product manufactured might have two or more different processes but, in the majority of cases, the characteristics of the wastewaters are similar and the same treatment technology can be applied for different process wastewater waters. If two or more dissimilar processes

produce wastewater of different quality, and different treatment technologies have to be used, then the subcategory has to be further classified or segmented, for example, the Chlor-Alkali Industry.

C. Manufacturing Process

Typically, inorganic chemicals are manufactured for captive or merchant use in four or more steps starting from raw material to final product. Two or more different products might use the same process but then the raw materials used, process sequence, control, recycle potential, handling, and quality control will vary, producing wastes of different quality. Primary subcategorization, therefore, by process is unlikely to be useful. However, secondary subcategorization by process has been necessary in some cases.

D. Geographical Location

Inorganic chemical plants exist in all parts of the United States but subcategorization on this basis is not appropriate. Geographical location is important in analyzing the feasibility of various treatment alternatives. Evaporation ponds are functional only in areas where evaporation exceeds rainfall. Ocean dumping and deep well disposal are possible only in certain areas, and must be consistent with local, State and Federal laws. The possibility of ground water contamination may preclude the use of unlined holding and settling ponds in many locations.

In the northern regions, climatic conditions may necessitate the inclusion of special provisions to prevent freezing of treatment system components, particularly biological oxidation units, clarifiers, ponds, and open collection systems. The costs of utilizing waste heat sources from the process or providing various types of thermal protection, such as insulation or burial of pipes and tanks and building structural shelters, may add considerably to the capital and O&M cost associated with a treatment technology.

Thus, the influence of geography, climate, geology, etc. is reflected in waste treatment modifications and is primarily manifested in the cost of treatment. This, of itself, is not a good basis for subcategorization.

E. Plant Size

Plant size and production capacity were not found to affect the characteristics of the waste produced. Although plant size can affect treatment cost, this variability can be expressed graphically or mathematically without the need for further segmentation of the category.

F. Plant Age

Plant age can have an important bearing on wastewater volume and quality and is, therefore, a significant factor to consider in evaluating the applicability of treatment technologies and assessing the relative costs of treatment for plants of widely differing age producing the same or similar products. A particular problem with older plants is that their present patterns of water use may have evolved over a long period of time with little consideration for the principles of efficient waste segregation, collection, and treatment. To a limited degree, plant modernization can correct or at least mitigate some of these shortcomings in older facilities, however, only a small proportion of the cost of revamping collection systems or of converting from contact to noncontact cooling systems can be offset by the resulting lower cost of treatment. In general, older plants, even after considerable modernization, normally have a higher volume of wastewater flow and higher waste loadings (although pollutant concentrations may be lower due to poor segregation from noncontact sources) in comparison to relatively new plants. The present and forthcoming requirements for pollution control may impose a severe treatment cost penalty on older plants due to the need for backfitting and replumbing of outdated collection systems. Land availability and land use restrictions are also factors which may translate into higher treatment costs for older facilities which find themselves surrounded by highly developed industrial and residential areas.

Unfortunately, plant age does not readily lend itself to an unambiguous definition where a series of plant modifications has taken place. The extent of modifications also varies greatly among plants within the same product industry. For those plants that have been enlarged or modified from their original status, plant age is not unambiguously calculable and therefore plant age is not a reasonable basis for subcategorization.

G. Non-Water-Quality Characteristics

Airborne emissions from manufacturing operations can be kept within air quality control limits through the use of cyclones, wet scrubbers and other methods. The nature of the air pollution is related to the product(s) manufactured and/or the raw material(s) used. Since both of these elements vary widely within the inorganic chemicals industry, there is no logic in subcategorization on the basis of non-water-quality characteristics.

H. Treatment Cost

From a technical viewpoint, subcategorization by common technological requirements for treatment processes could provide a logical basis for selecting one or more unit processes to accomplish the same treatment function, regardless of the source

of the wastewater. For example, residuals of dissolved heavy metals will respond to lime precipitation and sedimentation at high pH without respect to the specific origin of the metals. This "building block" concept could conceivably result in selecting various combinations of unit processes to meet the treatment requirements. However, if the treatment cost must be expressed in terms of dollars per unit production, this method of subcategorization crosses product lines and interferes with comparison of treatment costs based on the production of a specific chemical. Even if the unit operation is commonly applicable for treating waste flows of different products, the cost of treatment will fluctuate because of variations in quality, loading and flow rates and subcategorization on the basis of treatment cost is not recommended.

I. Energy Cost

Manufacturing processes in the Inorganic Chemicals Industry typically have large energy requirements. In contrast, wastewater treatment processes consume a small fraction of the total energy used. There appears to be no major energy requirements for the wastewater treatment facility and subcategorization on the basis of energy cost is not justified.

J. Solid Waste

Not all inorganic manufacturing processes produce solid wastes. Solid waste producers practice various disposal methods, such as on-site landfills, contract hauling to approved dump sites or incineration. Solid waste disposal becomes very site specific and exhibits a wide range of costs. Because of the lack of uniformity within the industry, solid waste generation and disposal practices are not a satisfactory basis for subcategorization.

General Conclusions

If effluent limitations are to be tied to units of production, only one method of primary subcategorization is broadly applicable to the inorganic chemicals point source category; viz., subdivision by dominant product. However, there are three subcategories, Chlor-Alkali, Titanium Dioxide, and Hydrogen Cyanide which require further subdivision based on the difference in the quantity and quality of the wastewater from the processes, and two others, Hydrofluoric Acid and Aluminum Fluoride, have been reviewed for possible integration (see Section 4.3).

Secondary Subcategorization

Chlor-Alkali

Mercury and diaphragm cells are the two distinct types of electrolytic cells that are used in the production of chlorine and caustic soda. Major process differences between mercury cell and diaphragm cell plants produce corresponding differences in the volume and nature of wastewater generated. A principal difference is the presence of mercury as a contaminant in the wastewaters from the mercury cell process and asbestos in the diaphragm cell plants wastes. The TSS discharges from diaphragm cell plants are generally larger than from mercury cell plants, due to the higher volumes of contact and noncontact water used. Also, in diaphragm cells a large amount of water is produced in the caustic evaporation process. Such water is not produced in mercury cell plants. The quantity of wastewater generated from the diaphragm cell plants is several times that of the mercury cell plants for the same chlorine production capacity. Based on the quantity and characteristics of the wastewater, further subcategorization is justified.

Titanium Dioxide

Two major ores, rutile and ilmenite, are used for the manufacture of titanium dioxide. The ilmenite ore contains 40-70 percent titanium dioxide (TiO_2), up to 35 percent ferrous oxide (FeO), and 25 percent ferric oxide (Fe_2O_3). Rutile ore contains more than 90 percent TiO_2 . Two processing techniques, the sulfate process and the chloride process, are used to extract titanium dioxide from the ores.

The sulfate process uses ilmenite ore and sulfuric acid as raw materials. The chloride process uses rutile ores or ilmenite ores and chlorine, with a different process and wastewater characteristics for each ore. The high grade rutile ore is expensive and its availability is declining. In recent years, new technological advances have alleviated the raw material shortage problem. By upgrading the ilmenite ore quality, the chloride process can be used to produce titanium dioxide of high purity. Because of the difference in quality and quantity of wastewaters generated from the sulfate and chloride processes using the two different ores, the titanium dioxide industry may be further subdivided into three segments as follows:

1. Sulfate process
2. Chloride process using rutile ore
3. Chloride process using ilmenite ore (one step).

The sulfate process generates large amounts of strong and weak sulfuric acid water-borne wastes. Application of pollution control technology to the acid wastes generates about five times as much gypsum as product. The chloride process generates large amount of dissolved metal chlorides and the treatment technology is expensive. Solid wastes from both processes present difficult disposal problems. These solids include ferrous sulfate (FeSO_4) and a hydrated by-product from the sulfate process and heavy metal sludges from the chloride process. Ilmenite ore has to be upgraded before it is used to extract

titanium dioxide by the chloride process, and this beneficiation process step generates additional wastes.

The application of the chloride process to ilmenite ore may proceed in either one or two steps. A patented one-step process accomplishes both beneficiation and chlorination of the ore in a single fluidized bed reactor and generates raw waste loadings which are similar to those from the sulfate process in terms of acidity and metals, and similar to wastes from the chloride-rutile process in terms of spent coke solids and still redissues. In the two-step process, ore beneficiation resulting in either a synthetic rutile or an enriched titanium oxide slag is carried out separately at the mine or the plant. The discharge of wastewater generated by the beneficiation step would be regulated under the Ore Mining and Dressing Point Source Category and will not be considered in this document. The second step of the two-step process generates wastes that are very similar in quantity and quality to those from the chloride-rutile process and will be governed by the discharge regulations for that segment of the TiO_2 subcategory.

Therefore, further subclassification based on the amount and characteristics of the wastewater appears to be justified, and the three process subdivisions indicated above are appropriate for this purpose.

Hydrogen Cyanide

Hydrogen cyanide (HCN) is made from two different processes, the Andrussow process and as a by-product of acrylonitrile manufacture. In the Andrussow process, air, ammonia, and natural gas are reacted to produce the dominant product hydrogen cyanide.

Water-borne wastes from the process consist principally of ammonia and sulfates in addition to cyanide and nitriles.

The primary product in the other process is acrylonitrile ($CH_2=CHCN$) and the hydrogen cyanide is a by-product. Because the hydrogen cyanide is a by-product, it will be covered in the organic chemicals manufacturing category with the primary product.

Review of Possible Integration of Subcategories

Hydrofluoric Acid and Aluminum Fluoride

Aluminum fluoride (AlF_3) usually is produced by the reaction of hydrated alumina ($Al_2O_3 \cdot 3H_2O$) with hydrogen fluoride (HF). One plant produces aluminum fluoride from fluorosilicic acid (H_2SiF_6), a by-product of phosphoric acid (H_3PO_4), and is not covered by the regulation. Two of the aluminum fluoride plants are known to be integrated with hydrogen fluoride (or hydrofluoric acid) production.

The two major uses of hydrogen fluoride are in the fluorocarbon industry and as raw material in the manufacture of aluminum fluoride. A ban on the fluorocarbon propellants has curtailed the use of hydrogen fluoride in that industry and it was completely stopped in 1978. The selling of hydrogen fluoride in the merchant market has declined and the primary use is limited to the production of aluminum fluoride and fluorocarbon plastics until some other major use is found.

For both products (HF and AlF_3), process wastewaters are generated by the various gas scrubbers and by leaks and spills. In both cases, air pollution control scrubber effluents contain mainly fluoride, acidity and sulfate. The fluoride is present as the free ion as well as various complex fluoro anions. Calcium fluoride (CaF_2), generated as a solid waste, is a disposal problem for both the subcategories because of its moderate toxicity. Only one additional solid waste, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is generated from the hydrogen fluoride manufacture alone, and it can be treated and handled independently.

Combining hydrofluoric acid and aluminum fluoride into a single subcategory does not appear to offer any regulatory advantages when the two products are manufactured at the same plant location. The wastewaters associated with the two products are similar and a common treatment facility is normally utilized. In addition, the combined manufacture of these products does not create a unique or unusual situation, either with regard to the wastewater treatment requirements or compliance with discharge regulations. Although the waste gypsum produced at an HF plant supplies enough calcium for adequate fluoride removal from neutralized scrubber wastewaters generated by both HF and AlF_3 production, the applied treatment technology is essentially the same as that applied by manufacturers of either product alone. However, the effluent water quality, wastewater flow, and the toxic pollutant loadings are not the same. Further, the opportunities for drip acid recycle (or the hydrolysis of complex fluorides prior to treatment) and scrubber water recycle are a function of plant design and age, rather than product mix.

In view of these considerations, a recommendation for the creation of an HF/ AlF_3 combined product subcategory is not being made at this time.

Summary

The recommended subcategorization with process subdivisions include the following:

<u>Subcategory</u>	<u>Process Subdivisions</u>
Chlor-Alkali	Mercury Cell Diaphragm Cell
Titanium Dioxide	Sulfate Chloride-Rutile

Hydrogen Cyanide

Chloride-Ilmenite
Andrussow Process
Acrylonitrile By-Product
(Included in the Organic
Chemicals Regulation.)

SECTION 5

SCREENING AND VERIFICATION SAMPLING PROGRAMS

Scope and Methodology

The specific objective of the sampling programs was to establish the extent of the required regulation of toxic pollutant discharges in the inorganic chemical industry in terms of factual information derived from the chemical analysis and flow measurement of representative process raw wastewater streams and treated effluents. Prior to this study, most of the information available on toxic pollutants has been concerned with a relatively small number of known process-related substances contaminating a variety of direct and indirect contact process waters discharged from a production facility. There had been no previous requirement for a comprehensive survey of wastewater chemistry addressing the possibility that a large number of other potentially toxic substances could be present, albeit at extremely low concentrations.

The screening phase of the sampling program was designed to ascertain the presence in each subcategory of any of the 129 listed toxic pollutants at raw waste concentrations or daily loadings which, if untreated, could be environmentally significant. Screening is based on the sampling of one or more typical manufacturing operations in each subcategory. Where significant pollutant concentrations were found, additional plants were sampled during the verification phase for confirmation and further quantification of data on the particular toxic pollutants in question. A goal was set for screening and verification sampling of a sufficient number of plants to account for at least 75 percent of the total U.S. production, in each subcategory having significant concentrations of priority pollutants.

A detailed description of the screening and verification programs are presented in the paragraphs below.

Selecting Plants and Making Preliminary Contacts

In each subcategory, plants were selected for screening on the basis of the following general criteria:

- A. Minimal product mix and no organic product lines which could increase the potential for interprocess cross contamination of wastewaters.
- B. Presence of a physical chemical treatment facility rather than a biological one, or no treatment system. (Biological systems are neither widely used nor generally applicable in the inorganic chemicals industries.)

- C. Manufacture of industrial grade products in volume, rather than low volume reagent grade products.
- D. Median production capacity with the subcategory.
- E. Segregated waste streams to facilitate sampling.
- F. NPDES discharges rather than discharges to POTWs, since treatment for a NPDES discharge is usually more extensive.
- G. Geographical clustering of selected plants to facilitate field logistics, but only to the extent that other factors are equal.

Preliminary phone contacts were made with plant representatives of those facilities which satisfied the above criteria. If requested, a letter was written to describe the objectives of the sampling program and to cite the legal authority of the Agency and its sampling contractor under Section 308 of the Federal Water Pollution Control Act Amendments of 1972. Information provided by industry for which confidential treatment was requested has been handled in accordance with the provisions of 40 CFR Part 2.

Prior to the actual sampling of waste streams, a lead visit to the selected plant was made to gather background information, confirm and update any 308-Questionnaire responses, and to obtain additional technical information regarding processes and waste treatment practices. Sampling sites were selected and described relative to a detailed waste source inventory and a flow diagram of the process and waste treatment system. Arrangements were made for the subsequent sampling visit and the details of the lead visit and sampling point descriptions were documented in an interim report to the Agency.

Screening and Verification Sampling

A. Collection of Samples for Screening

In the screening phase of the sampling program, the specific objective was the detection and quantification of waterborne waste constituents included on the list of 129 toxic pollutants (Table 3-1). Each sample of an individual raw waste stream, a combined waste stream, or a treated effluent was collected where possible by an automatic, time series, compositor over a single 72-hour sampling period. Where automatic compositing was not possible, grab samples were taken at approximately 2-hour intervals during the same sampling period and composited manually.

Each sample was divided into several portions and preserved, as required for different types of analysis, in accordance with the procedure established by EPA (4) for the measurement of toxic pollutants.

Samples were also taken from the composites, or as individual grabs, for the analysis of the conventional and nonconventional pollutants.

Volatile organics were collected in teflon-sealed screw cap vials. Eight 40 ml vials were filled at each sampling site by grab sampling in pairs at approximately 2-hour intervals. The individual vials were cooled to 4°C and shipped to the laboratory where they were used to prepare composites in duplicate just prior to analysis. Three blank vials prepared and sealed in the laboratory accompanied each set of samples during collection, shipment, and storage.

B. Collection of Samples for Verification

The objective of verification sampling was to confirm the first observations from screening and further quantify the concentrations and waste loadings of the toxic pollutants and conventional and nonconventional pollutants. Where any toxic pollutant metals were found during screening sampling of a particular plant, analyses were made for all toxic pollutant metals during the verification sampling.

The established protocol for verification sampling required the collection of three 24-hour composites at each sampling point. Again, where composites could not be taken with automatic samplers, grab samples were taken periodically over the same time period and composited manually.

C. Sample Shipping

All samples, individually labeled, were placed in large plastic bags, which were then placed in a waterproof, insulated shipping container. Enough ice was included to maintain a temperature of approximately 4°C during shipment to the laboratory.

Containers were shipped by the best available route, usually air freight, usually arriving at the laboratory on the same day, but occasionally taking overnight. Upon receipt, all samples were immediately placed in a walk-in refrigerator maintained at 4°C.

In order to maintain the chain of custody and to keep track of samples, sampling personnel kept logs of samples taken in ink in page-numbered, hard-bound books. The data recorded included: date, time, plant code, number, sample type, and sampler. Prior to their arrival at the laboratory, a list of samples shipped, including number, type of samples, and analysis to be performed was sent to each department supervisor to alert him of incoming work.

A master analytical control chart was maintained which included: the date the sample was received, date due, number and type of each sample, and the analysis required.

At the time of analysis, the individual samples were distributed to the analytical chemists along with a list which included: I. D. number of sample, type of sample, analysis required, date samples were received, and due dates.

All samples were kept in a laboratory refrigerator at 4°C when not being handled by the analyst. Upon completion of analysis, the sample was checked back into the Sample Control Department and kept in an identified location in the Sample Control refrigerator. A report of completed samples was then sent to the EPA Sample Control Center.

D. Verification Sampling Plant Selection

After the decision was made to verify the presence of toxic pollutants found in the screening of a subcategory, verification plants were selected. The basis for selection was essentially the same as that used in selecting screening plants.

The screening program results were evaluated to identify those toxic pollutants that were present at potentially treatable concentration or daily loadings. Concentrations or loadings which could be reduced by the highest quality treatment systems were considered significant. Two situations occurred:

1. A subcategory which had a potentially treatable raw waste concentration of any toxic pollutant would be subject to verification sampling, and BAT-based regulations would likely be proposed by the Agency for the treatment and control of that toxic pollutant.
2. A subcategory which had no potentially treatable raw waste concentration of any toxic pollutant would not be subject to verification sampling and would likely be excluded from regulatory coverage in accordance with the provisions for exclusion under Paragraph 8 of the Settlement Agreement.

In analyzing screening data, only those pollutants attributable to process sources were considered. Pollutants which result from cooling tower operations, corrosion or corrosion control, control of biological growth, or any other operation not directly tied to the production process, were not used as a basis for verification.

The number of plants selected for verification in each subcategory was roughly proportional to the number of existing plants in that subcategory with a maximum of five plants selected. In small subcategories (relatively few production facilities), an effort was made to select a sufficient number of plants to account for the majority of the total U. S. production.

When the verification phase of the program was initiated, an important decision was made with regard to metals analysis. First, in view of

the frequent presence of metal contamination in the wastes screened, and the inability in some cases to show a direct relationship between certain metals found and the known process chemicals or the materials of construction, it was decided that all 13 of the toxic metals should be determined again during verification, regardless of whether they were found in screening. This was intended to provide a much more complete data base than would be obtained by running verification analyses for only those metals found in screening to exceed the verification criteria levels at the time of sampling

Analytical Methodology for Toxic Pollutants

The analytical protocol for the screening and verification of toxic pollutants was established in Sampling and Analysis Procedures for Priority Pollutants by U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, April, 1977.

The specified analytical methodologies were employed without modification except where noted below in connection with toxic metals analysis during verification.

Implementation of the methodology and quality assurance provisions required the establishment of special sample handling and control procedures specifically suited to each type of analysis. These procedures, together with a discussion of the achievable detection limits for each parameter or group of similar parameters, are presented in the following paragraphs.

A. Trace Metal Analysis

Figure 5-1 shows a data flow diagram for metals analysis. Atomic absorption methods described in 40 CFR § 136 per Section 304(h) were used. A set procedure was followed in the laboratory to generate the analytical values and the quality control data. The data flow diagram shows the actual sequence employed in verification analysis and the following notes, which are keyed to the diagram, provide additional information on the procedures.

1. Blanks--two for each set of analyses digested.
Duplicates--one every seventh sample.
2. Quality Control at Operator Level (Atomic Absorption):

Blanks--These were run at the beginning and the end of every set analyzed for each metal. Also, air blanks were run on furnace, or heated graphite atomizer (HGA), after any sample with a large positive value.

Standards--Three different concentrations were run at the beginning and end of every set analyzed for each metal.

Standards were also run every tenth sample during the analysis of a set.

Spikes--These were made according to the EPA "Method of Standard Additions," by adding such a volume of standard as to double the apparent concentration of metal present in the sample. Extrapolation backwards of the resultant absorbances allowed correction of absorbance for matrix effects.

Duplicates--For furnace analysis, the sample was run twice wherever a low but positive absorbance was obtained. As well as this, one sample in every seven was run in duplicate routinely. The average of duplicate measurements was the taken value; the difference between duplicate measurements was noted and recorded on control charts. If reproducibility was outside the limits of ± 33 percent, the measurement was repeated.

3. UTD = "Unable to Determine" due to matrix interferences.
4. Criteria Employed in Spike Selection: samples were chosen to be spiked based upon the following criteria:

All samples where there was any suspicion that interference or matrix effect was present

All samples containing a measurable concentration of analyte

In addition, at least one sample in every seven.

The level of spike chosen was controlled by the following factors:

It should approximately double the apparent concentration

If this results in an absorbance greater than that of the highest standard, the spiked sample is suitably diluted with distilled water.

A reagent blank was run with each set of spiked samples prepared.

During the screening phase of the sampling program, the standard protocol followed for metals analysis was:

1. The 13 priority pollutants metals, with the exception of mercury, were determined by AA spectrophotometry in the furnace (HGA) mode.

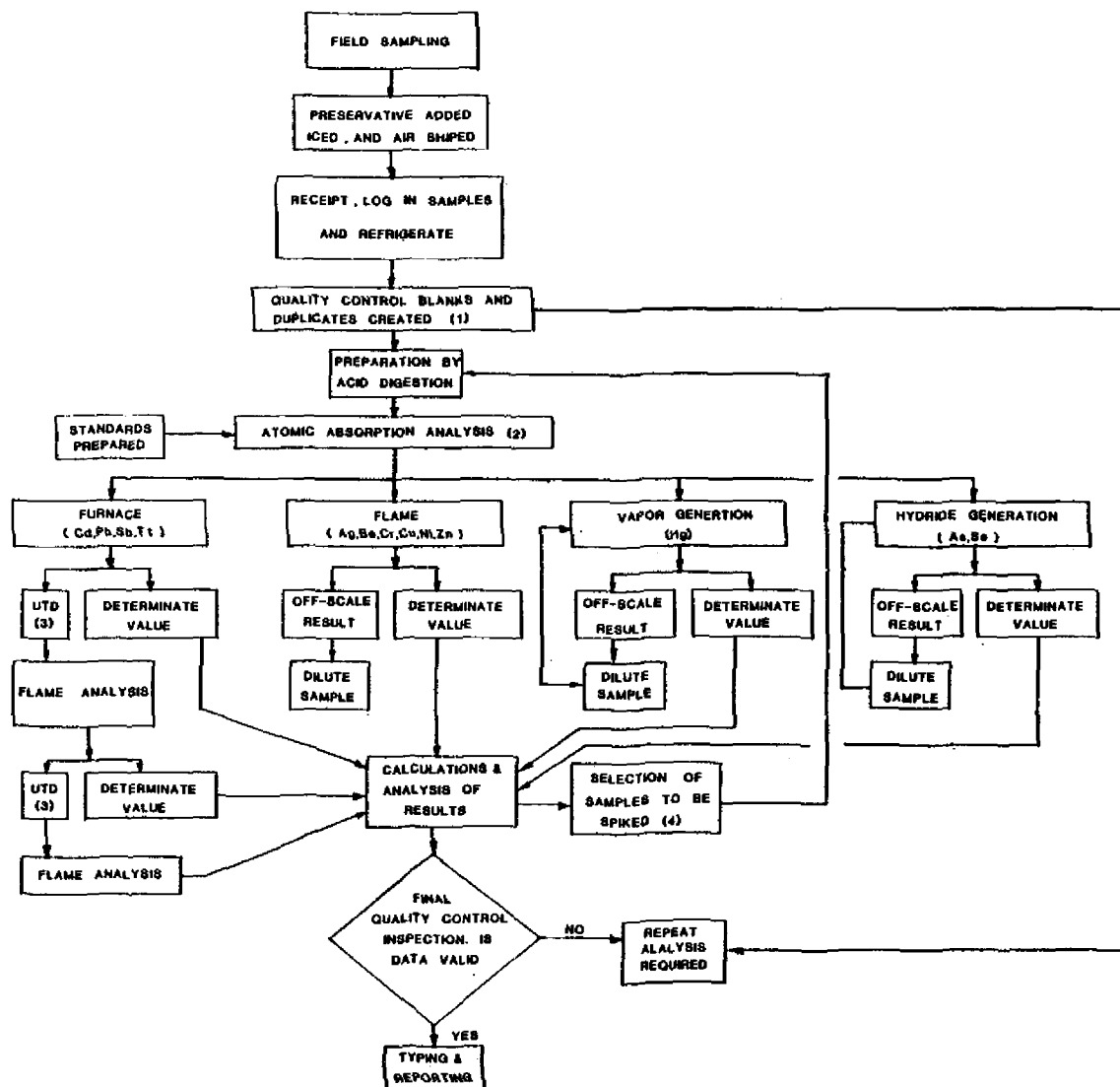


Figure 5-1. Sample flow sheet for metal analysis.

2. If matrix interference was seen, they were spiked and redetermined.
3. If difficulties due to matrix interference persisted, or if metal concentrations appeared high enough, the determination was repeated in the flame mode.
4. Mercury was determined by the standard cold vapor method.

Certain changes in analytical protocol were instituted during verification analysis in order to avoid the excessive matrix interference experienced during screening when the heated graphite atomizer (HGA) was the primary method applied to the analysis of 12 of the metals. The modified protocol for metals was:

1. Six elements were determined by flame only, namely, Ag, Be, Cu, Cr, Ni and Zn.
2. Four elements were determined by furnace (HGA), namely, Cd, Pb, Tl and Sb. If interference occurred, Cd, Pb, Tl and Sb were determined by flame.
3. Hg was still analyzed by the cold vapor method.

This modification reduced the number of preparations per sample from three to two and achieved adequate detection limits which were still well below the verification criteria levels.

Additional modifications were made during the verification program to improve the reproducibility and precision for Hg, As and Se. These were:

1. The cold vapor procedure for Hg was modified to eliminate the pump and allow dilution and rerun from the same sample. This saved time and increased reproducibility.
2. Selenium and arsenic were determined by hydride generation using sodium borohydride (NaBH_4). This greatly minimized problems associated with matrix interference. The method is very reproducible and the detection limits were at levels well below the verification criteria for these two elements.

After the above modifications were adopted, screening samples which originally were unable to be analyzed, or which were recorded as below excessively high detection limits due to the effects of matrix interferences, were rerun. Satisfactory results were then obtained in nearly all cases due to the greatly improved sensitivity and reproducibility.

It should be noted that these modifications of the analytical protocol were in the direction of improved precision and reproducibility and not towards lower detection limits. The original screening procedures generally had a lower detection

limit when it was achievable. However, the methods were too susceptible to giving no result at all with complex industrial matrices, and so the revised protocols sacrificed some sensitivity for precision and reproducibility. The final detection limits were still in the subparts per million range. See Table 5-1 for a summary of these limits, together with those of the original protocol.

B. Organic Compound Analysis

The organic toxic pollutants were determined by the standard protocol (40 CFR § 136 proposed December 3, 1979) which includes sample preparation, extraction, and analytical methodologies. Extractions were carried out using methylene chloride in the case of the acid and base/neutral organic fractions and with hexane/methylene chloride to obtain the pesticide-containing fractions. The acid and base/neutral fractions were reduced in volume and analyzed by gas chromatography-mass spectrometry (GC/MS). The pesticides were analyzed by electron capture gas chromatography followed by GC/MS confirmation of positive results. Volatile organics were analyzed by the purge and trap method of introducing the material into the GC/MS inlet system.

C. Cyanide Analysis

The standard methods for the wet chemical analysis of total cyanide and cyanide amenable to chlorination (Cyanide A) were utilized (40 CFR § 136). Cyanide analysis is subject to several sources of interference, including:

1. Metals-The presence of Fe, Cd, Ca, Ni, Ag, and Zn may cause low results due to the formation of stable complexes with cyanide. The iron complexes may form insoluble precipitates which are particularly difficult to break up both at the time of alkaline chlorination of the sampled wastewater and during the chemical analysis for cyanide.
2. Oxidizing agents-The presence of free chlorine in the wastewater sample will destroy cyanide and cause low analytical results. The addition of ascorbic acid to destroy chlorine at the time of sampling is intended to mitigate this problem. Other oxidizing agents such as peroxides and chromates may also react with cyanides over a period of time and cause low results.
3. Sulfides-Sulfide or bisulfide will interfere in the analysis of cyanide by reacting with the colorimetric reagents.

The presence of sulfur dioxide or bisulfite in the wastewater sample should have no appreciable effect on cyanide results. Detection limits on the order of 1-4 µg/l can be achieved by the analytical

method employed, but the results have to be interpreted with regard to the possible interfering components of the sample.

D. Hexavalent Chromium (Cr VI) Analysis

The determination of Cr VI in wastewater samples is also subject to a number of interferences which can take effect either during sampling and storage or during analysis.

1. Acids-Samples taken and held at a very low pH can experience the conversion of other forms of chromium into Cr VI causing a positive interference.
2. Reducing agents-Samples containing sulfur dioxide, bisulfide, sulfide, ferrous iron, and other reducing agents will result in low values of Cr VI by converting it to trivalent chromium (Cr III). Under these conditions the chromates originally present would be included in the total chromium determination but the analytical results for hexavalent chromium would be proportionately low (see Reference 52).

The detection limits for Cr IV using the diphenylcarbazide colorimetric method are on the order of 1-3 $\mu\text{g/l}$ in the absence of substances which interfere with color development.

E. Asbestos Fiber Analysis

The analysis of selected samples for asbestos fiber (chrysotile) was conducted by the recommended method utilizing transmission electron microscopy with selected area electron diffraction as described by Dr. Charles Anderson (EPA, Athens, Georgia) at the Analytical Protocol Meeting in Denver (November, 1977) (56).

F. Conventional and Nonconventional Pollutants

All techniques used for the analysis of BPT control parameters (conventional and nonconventional pollutants) were those recommended by the Agency. The list of approved test procedures was published in the Federal Register on October 16, 1973 (38 FR 28758) and may also be found in Title 40 of the Code of Federal Regulations (40 CFR 136).

Quality Assurance Provision

The Agency and the contractor's analytical laboratories maintain consistently high standards for accuracy and quality control. As an in-house requirement, a minimum of ten percent of all samples are routinely run in duplicate. Quantitation is based on standards which are prepared in pure water, at concentrations such that all sample measurements are greater than the absorbance of the lowest standard, and less than the absorbance of the highest standard. The standards are also checked by participation in the EPA Reference Sample Program

TABLE 5-1. ANALYTICAL DETECTION LIMITS FOR METALS⁽¹⁾

Element	Original Screening Protocol ⁽²⁾		First Modification of Protocol ⁽³⁾		Second Modification of Protocol ⁽⁴⁾	
	Method	(µg/l)	Method	(µg/l)	Method	(µg/l)
Antimony, Sb	HGA*	10	HGA	10	HGA	10
Arsenic, As	HGA	3	HGA	3	Hydride	10
Beryllium, Be	HGA	0.2	Flame	15	Flame	15
Cadmium, Cd	HGA	1	HGA	1	HGA	1
Chromium, Cr	HGA	1	Flame	25	Flame	25
Copper, Cu	HGA	1	Flame	20	Flame	20
Lead, Pb	HGA	10	HGA	10	HGA	10
Mercury, Hg	Cold Vapor	0.5	Cold Vapor	0.5	New Cold Vapor	0.5
Nickel, Ni	HGA	1	Flame	25	Flame	25
Selenium, Se	HGA	9	HGA	9	Hydride	10
Silver, Ag	HGA	0.5	Flame	15	Flame	15
Thallium, Tl	HGA	2	HGA	2	HGA	2
Zinc, Zn	HGA	1	Flame	25	Flame	1

* Heated Graphite Atomizer

(1) Assuming no matrix interferences requiring dilution of sample.

(2) EPA Contract No. 68-01-4492 (September 29, 1977), Exhibit C, "Protocol for the Measurement of Toxic Substances", Environmental Monitoring and Support Laboratory, Cincinnati, Ohio

(3) June, 1978

(4) August, 1978

that utilizes a double blind technique. (EMSL, Cincinnati, Ohio, Office of Research and Development.)

Additionally, outside laboratories are retained for checks on quality by analyzing split samples and running submitted standards. Accuracy is also insured by analysis of a minimum of fifteen percent of all samples with spikes by the method of standard additions. The spikes are added prior to sample preparation and are carried through the entire sample analysis procedure.

The contractor's laboratories have consistently maintained the standards for laboratory certification which are imposed by the State of California. Certification is dependent upon the accurate performance of routine analyses on check samples submitted by the State, as well as on-site inspections by the State of California's Sanitation and Radiation Laboratory, Department of Fish and Game, and the U. S. Environmental Protection Agency, NEIC, Denver, Colorado.

The quality assurance provisions outlined in the EPA Protocol for GC/MS Analysis of Toxic Pollutants are rigorously adhered to with one added precaution, namely, the use of internal standards as a means of measuring recovery. Although not required by the protocol for pesticide analysis, this technique is utilized as an in-house quality control requirement to ensure the accuracy of results in this analysis.

The high sensitivity of instrumentation used in trace organic chemical analysis dictates that contamination of the samples from any possible source must be diligently guarded against. Accordingly, only glass sample containers with Teflon-lined lids were used and these were subjected to a three-step cleaning procedure prior to use, even though only new liners and glass containers were used. All glassware used for sample preparation and analysis was subjected to a dual cleaning system.

The sample extraction and preparation rooms are dedicated solely to toxic pollutant analysis, and have their own ventilation systems that are isolated from the other sample preparation and receipt areas of the laboratories.

A documented system of existing practices, including calibrations and operational checks, is maintained to assure uniformity of performance and to serve as a basis for alteration of standardization intervals. A chemist is assigned full time to maintain this system, assure strict record formatting and controls, and to direct the quality control program of the laboratories. The primary vehicle of this system is the quality assurance manual containing the detailed procedures used in sample preparation and analysis, and the complete records of all quality control standards, blanks, spikes, and duplicates.

Summary of Analytical Results

The results obtained during the screening and verification sampling program are summarized in Table 5-2 and Table 5-3. These tables show the frequency and distribution of the pollutants according to selected plant groupings, concentration ranges, and subcategories in which the pollutants occur.

Pollutant frequencies as shown in columns 5, 6, 7, and 8 of Table 5-2 are based on the highest individual pollutant concentration found for each plant's raw waste during the screening and verification sampling program.

The toxic pollutant asbestos has not been included in either of the two tables mentioned above. Asbestos concentration is reported in million fibers per liter (MFL) which is not compatible with the concentration units in which the other pollutants have been reported. Asbestos was found in three plants at raw waste concentration levels of $2.1E8$, $2.0E7$, and $9.4E4$ MFL, respectively, where E is exponential on base 10. All three plants belong to the Chlor-Alkali subcategory.

TABLE 5-2. POLLUTANT FREQUENCY BASED ON SAMPLING PROGRAM RESULTS
INCLUDING RAW WASTE *

Pollutants Detected	Pollutant Occurrence Based on Plant Grouping			Pollutant Occurrence Based on Concentration Classification ($\mu\text{g/l}$)			
	5 or <5 Plants	>5 but ≤ 10 Plants	>10 Plants	≤ 50	>50 but ≤ 500	>500 but $\leq 2,500$	>2,500
Antimony			X	28	19	4	1
Arsenic			X	38	12	3	
Beryllium			X	49	4		
Cadmium			X	45	4	4	
Chromium			X	20	13	9	10
Copper			X	21	16	9	7
Cyanide	X						2
Lead			X	25	15	7	6
Mercury			X	46	2		5
Nickel			X	17	20	8	8
Selenium			X	46	7		
Silver			X	45	7	1	
Thallium			X	41	11	1	
Zinc			X	9	18	14	12
Benzene				6	1		
Carbon Tetrachloride				2			
Chlorobenzene				1			
1,2-Dichloroethane				2			
1,1,1-Trichloroethane				4	1		
Hexachloroethane				1			
1,1,2-Trichloroethane				2			
1,1,2,2-Tetrachloroethane	X			3			
Chloroform			X	15	2	1	
1,2-Dichlorobenzene	X			1			
1,1-Dichloroethylene	X			3			
1,2-Dichloropropylene	X				1		
2,6-Dinitrotoluene	X			1			
Ethylbenzene		X		7	1		
Fluoranthene	X			1			
Bis(2-Chloroisopropyl) ether	X			1			
Methylene chloride			X	11	3	1	
Dichlorobromomethane	X			5			
Trichlorofluoromethane	X			2		1	
Chlorodibromomethane	X			2			
Naphthalene	X			1	1		
Nitrophenol	X			1			
Pentachlorophenol	X			2	1	1	1
Phenol	X			2	3		
Bis(2-Ethylhexyl) phthalate	X			20		1	1
Butyl benzyl phthalate	X			3			
Di-n-butyl phthalate			X	15			
Diethyl phthalate	X			5			
Dimethyl phthalate	X			2			
Benzo(a) anthracene	X			1			
Benzo(a) pyrene	X			1			
3,4-Benzofluoroethane	X			1			
Chrysene	X			1			
Anthracene	X			1			
Fluorene	X			1			
Phenanthrene	X			1			
Pyrene	X			1			
Tetrachloroethylene	X			4			
Toluene		X		7		1	
Trichloroethylene	X			3			
Nitrobenzene	X					2	
2,4-Dinitrophenol	X					2	

* Blanks indicate not detected.

TABLE 5-3. DISTRIBUTION OF POLLUTANTS ACCORDING
TO SUBCATEGORY ¹

Pollutants Detected	Subcategory Numbers Where Pollutants Found
Antimony	All ² but 7, 23, 27, 28, 33
Arsenic	" " " " " "
Beryllium	" " " " " "
Cadmium	" " " " " "
Chromium	" " " " " "
Copper	" " " " " "
Cyanide	7
Lead	All ² but 7, 23, 27, 28, 33
Mercury	" " " " " "
Nickel	" " " " " "
Selenium	" " " " " "
Silver	" " " " " "
Thallium	" " " " " "
Zinc	" " " " " "
Benzene	1, 3, 4, 10, 11, 25, 32
Carbon Tetrachloride	1, 2
Chlorobenzene	1, 35
1,2-Dichloroethane	1, 11, 13, 22, 35
1,1,1-Trichloroethane	1
Hexachloroethane	4, 11
1,1,2-Trichloroethane	1, 10, 35
1,1,2,2-Tetrachloroethane	1, 3, 4, 10, 13, 15, 19, 21, 22, 25, 32, 35
Chloroform	24
1,2-Dichlorobenzene	1, 11, 13
1,1-Dichloroethylene	26
1,2-Dichloropropylene	1
2,6-Dinitrotoluene	1
Ethylbenzene	1, 3, 4, 9, 11, 21, 25, 32
Fluoranthene	8
Bis(2-Chloroisopropyl) ether	22
Methylene chloride	1, 4, 8, 9, 12, 13, 19, 21, 22, 25, 26, 32, 35
Dichlorobromomethane	1, 4, 19, 32
Trichlorofluoromethane	1, 4, 25
Chlorodibromomethane	19, 32
Naphthalene	1, 32
4-Nitrophenol	17
Pentachlorophenol	2, 3, 4, 8, 15
Phenol	2, 15, 26, 31, 32
Bis(2-Ethylhexyl) phthalate	1, 4, 7, 8, 10, 11, 12, 13, 15, 18, 24, 25, 26, 30, 31, 35
Butylbenzyl phthalate	1, 2, 12
Di-n-butyl phthalate	1, 4, 8, 11, 17, 18, 19, 21, 22, 30, 31, 34, 35
Diethyl phthalate	8, 10, 11, 19, 31
Dimethyl phthalate	12, 31
Benzo(a) anthracene	8
Benzo(a) pyrene	8

¹ For name of subcategory, refer to Table 3-2.

(Continued)

² "All" means subcategory numbers 1 through 35 of Table 3-2.

TABLE 5-3. Continued

Pollutants Detected	Subcategory Numbers Where Pollutants Found
3,4-Benzofluoranthane	8
Chrysene	8
Anthracene	8
Fluorene	8, 12
Phenanthrene	8
Pyrene	8
Tetrachloroethylene	1, 4, 10, 22
Toluene	1, 3, 4, 10, 11, 15, 18, 32
Trichloroethylene	1, 4, 25

SECTION 6

PROCESS AND WASTE TREATMENT INFORMATION DEVELOPMENT AND EVALUATION

Industry Data Base Description

Information and data on the inorganic chemicals industry were obtained from a number of sources. These sources included literature reviews, plant visits, telephone contacts, industry responses to the Section 308-Questionnaires and information supplied by industry after proposal. The type of material gathered from these sources is discussed below.

Literature Review

A review of the literature was conducted to identify and collect information related to manufacturing processes, raw materials, water use, wastewater sources, wastewater treatment technology, raw waste characteristics, and economic data. Relevant information from reports, books, papers, conference presentations and periodicals were identified by computer search and are presented in the reference section of this report. This information was incorporated into a broad based assessment of process and technology practices aimed at selecting the best available treatment technology and best demonstrated technology for the various industry subcategories. It also provided the background required for evaluating the subcategorization of the industries.

Plant Visits

During the screening and verification phase of this project, much information was gathered from individual plants relating to production capacity, manufacturing processes, waste flows, water reuse, wastewater treatment systems and performance, and best management practices (BMP). The lead visits also provided an opportunity to update and clarify some of the information given in the 308 responses.

Telephone Direct Contact

Numerous contacts were made with knowledgeable persons in both industry and government to gather and exchange information concerning all phases of this study. These sources are cited in the text as personal communications.

308-Questionnaire Responses

The basis for much of the work in this study is the responses from industrial organic chemical firms to the 308 data requests.

Data from 284 manufacturers' responses were utilized by the project team for the development of appropriate guidelines for the inorganic chemicals subcategory. Industrial firms, through their compliance with the needs of the 308-Questionnaire, provided a valuable industry-wide data base used extensively in this analysis.

Essential data elements from each questionnaire were extracted for the purpose of creating a working data base for this report. Specific elements selected for this smaller, more-manageable data base are given in Table 6-1.

These data provided the basis for the subcategory review through a profile of each industry. After compilation of the questionnaire data, industry totals for capacity and derivative quantities such as percent utilization, effluent per ton of product, and conversion to metric units were compiled.

Process Waste Sources and Current Treatment Practices

Data Acquisition

The information presented in this section was obtained from a variety of published sources and the available industry responses to the 308-Questionnaires as well as from plant visits and interviews with industry personnel conducted by the Agency and its contractor during the toxic pollutant screening and verification program. The results of visits and interviews are documented in field notebooks, interim plant visit reports, and telephone communication records which are part of the rule making record.

Plant visits were particularly useful for confirming and updating the detailed technical information contained in the 308-Questionnaire responses. The cooperative attitude displayed by industry greatly facilitated the acquisition of reliable operating data and meaningful sampling results.

Evaluation of Data

Each of the various industrial subcategories in which verification sampling was conducted was the subject of an extensive evaluation to provide the technical basis for selecting candidate advanced treatment technologies and developing the related base and incremental cost estimations.

In the subsections which follow, individual plant descriptions are presented according to the general format for each subcategory:

General Process Description

- Description of process reactions and unit operations.
- Inventory of raw materials used.
- Typical process flow diagram.

Water Use and Waste Source Inventory

TABLE 6-1. 308-QUESTIONNAIRE RESPONSE DATA
DATA ELEMENTS
INORGANIC CHEMICALS GUIDELINES STUDY

Datum Reference	Description	Comments
Manufacturer	Name Location EPA Region	Confidential
Product	Name Subcategory Number of other Products	Inorganic Chemicals
Plant	Capacity Production Age	Fiscal year 1976 1976 1976
Process	Name Volume of Process Effluent Volume of Noncontact Effluent	
Effluent Treatment	Type Permit Major Pollutants	

Description of individual plants visited, sampled and plant information from other sources.
Inventory of raw proces wastewater sources and identification of sampling points.
Process wastewater quality and flow data.
Solid waste generation and disposal.

Control and Treatment Practices

Description of specific treatment technologies and operating facilities.
Description of the total input to the treatment system including sources attributed to other production operations and noncontact water (e.g., cooling water, etc.).

Evaluation of Production and Waste Flow Data

Tabular summary of plant-specific data.
Waste flows per unit of production (unit waste flow) with the range and average values.
Solid waste quantities.
Treatment chemical requirements.

Process Modifications and Technology Transfer Options

Best Management Practices (BMP)

Plant area operations and housekeeping.
Runoff control.
Solid waste handling (e.g., fugitive dust and leachate control, etc.).

Model Plant and BPT Treatment Sytem Specification

The model plant concept plays a central role in both the development of alternative treatment system designs for priority pollutant removal and for estimating the related internal costs of such treatment in each subcategory. In order to be representative of a subcategory, each set of model plant specifications was composited from a profile data summary derived from the available information on production and waste flow.

Based on the typically achievable waste flow rate per unit of production, the model plant was used as a starting point for appropriately designed and sized BPT level wastewater treatment system. Certain assumptions were made regarding the possible process variations and the specific raw waste sources incorporated into each model. In most cases, it was appropriate to assume that the waste flow per unit of production did not vary over the particular range of production capacities covered. Production rates were selected in most subcategories to represent the small, mid-range and large size plants presently in operation. Small subcategories were represented by single mid-range production rates for the model plants. Cost estimates were developed for each set of base level (BPT) and advanced level (BAT/NSPS) treatment system design specifications.

Beginning with Section 11, the model plant and BPT level treatment system descriptions and specifications for each subcategory include the following information:

- Production rates and mode of operation.
- Specific process type and waste sources.
- Waste flow per unit of production.
- Solid waste generation and handling.
- Treatment chemical requirements.

If applicable, the new source model plant is also described and the design specifications given for its waste treatment system.

The model plants do not represent exemplary or specific existing plants, but are typical plants of adequate design derived from the range of plants and treatment facilities found in the entire subcategory. For the purpose of cost estimating, it is necessary to specify cost rationale, define a set of initial assumptions, and consider the variability of factors such as wastewater flows, pollutant load, unit treatment process, plant age, etc. General assumptions have been detailed under Section 10 of this report and are employed as the basis for developing baseline model plant cost estimates presented in the subsequent sections dealing with individual industries.

Dissolved Solids in Wastewater Effluents

Many waste treatment plants discharge final effluent into watercourses which feed fresh water streams used as sources of water supply by downstream agencies or industries. Groundwater aquifers which underlie large portions of the country are tapped to supply fresh water through wells serving public and industrial water needs. Saline wastes discharged into streams or into unlined lagoons can significantly alter the salt content (total dissolved solids) of the fresh water. Although Federal regulations seldom limit the total dissolved solids or the various ions such as chloride, sulfate, bicarbonate, and nitrate, these constituents can be of serious concern to local water users.

To protect the mineral quality of ground and surface waters State and local water pollution control agencies typically establish limits on the discharge of substances which contribute sodium, potassium, hardness, chloride, sulfate, or conductivity, which is a measure of total solids in solution. This restriction can affect the chemicals chosen for waste treatment. For example, alkaline precipitation can be accomplished by using lime, which forms an insoluble calcium sludge, or by adding caustic soda, forming a soluble sodium salt.

In choosing an acid for neutralization of alkaline wastes, it is important to weigh the overall effects of chloride (from hydrochloric acid) and sulfate (from sulfuric acid), particularly with respect to irrigational use of the receiving water.

Chemicals used in the model plant processes were selected on the basis of best performance, including consideration of scaling problems, which can be severe when calcium and sulfate are at saturation levels. It may be necessary to alter the nature of chemicals used at a specific plant, in order to meet local water quality requirements.

SECTION 7

ASSESSMENT OF TECHNOLOGY FOR ADVANCED TREATMENT AND CONTROL

Introduction

In the inorganic chemicals industry, pollution abatement practices vary and a wide range of treatment technologies can be found, ranging from no treatment to the application of highly advanced technologies for the removal of specific pollutants.

Until the NRDC Settlement Agreement, industry attention was primarily directed towards general pollution problems including removal of trace metals, but not towards treatment of over 100 individual specific organic compounds now listed as toxic pollutants. Even with the classical (conventional and nonconventional) pollutants, treatment technology has been directed to removal down to the part per million level, whereas now the thrust is towards part per billion level requirements. For both these reasons, higher level technologies are often not in place in the inorganic chemicals industry, and it is necessary to look into technologies that have been applied in other industries or developed at the laboratory or pilot plant scale specifically for the removal of these toxic substances from industrial wastewater, and determine whether they can be adopted as viable technological options.

A list of candidate technologies was compiled from the literature, in-house expertise, and industry contacts. These were evaluated with respect to:

1. Treatment effectiveness
2. Cost
3. Nonwater pollution environmental effects
4. Applications in the inorganic chemicals industry or on other industrial wastes with similar wastewater characteristics.

The anticipation that few of the organic toxic pollutants would be found in inorganic chemical wastes was justified by the results of the analytical programs. Only one industrial subcategory, namely, Chlor-Alkali production using graphite anodes, had potentially significant levels of organic toxic pollutants. As a result, the initial search for candidate BAT technologies became limited to treatment technologies for the thirteen metals, cyanide, and asbestos.

The technologies finally adopted were not new or untried technologies since it was found that most treatment requirements could be met by taking conventional techniques--for example, chemical

precipitation--and developing them to a higher degree of engineering and design sophistication, so that optimum removal efficiencies could be achieved.

The following pages describe the theoretical basis for treatment systems adopted for BAT application.

Hydroxide Precipitation

Hydroxide precipitation is the most widely used technology for removing trace metals from wastewaters, with lime or caustic soda commonly used to supply the hydroxide ions. Under suitable conditions the metals form insoluble metal hydroxides which can be separated from solution.

The chemistry of the process is not simple, and must be understood for each metal. Many metals are amphoteric, the optimum pH for precipitation varies, and organic complexes can interfere. A simple form of the reaction may be written as:



Metal ion + two hydroxyl ions = insoluble metal hydroxide

If the pH is below the optimum for hydroxide precipitation soluble complexes form:



Metal ion + hydroxyl ion = soluble metal complex

If the pH is above the optimum for hydroxide precipitation, the metal hydroxide may redissolve by forming soluble complex hydroxides:



Insoluble metal hydroxide + hydroxyl ion = soluble
metal complex

Since most metals have the capability of coordinating with other ions or molecules, these simple equations assume that the hydroxonium ion is the coordinated species. However, if organic radicals are present, they can form chelates and mask the typical precipitation reactions:



Metal ion + hydroxyl ion = soluble metal
+ organic ions chelate

Such complexes may require unusual treatment to hydrolyze them, and their presence often explains why some treatment practices yield relatively poor results.

Assuming the absence of organic complexing agents, the treatment levels attainable by hydroxide precipitation can be forecast from a knowledge of the pH of the system. Figure 7-1 shows the theoretical solubility of those toxic metals which form insoluble hydroxides, while Table 7-1 shows the solubility product constants. For comparison, the values for sulfides are also given in Table 7-1.

It is clear from the range of optimum pH's illustrated that for wastewaters containing more than one metal, no single optimum pH exists, and problems arise at the threshold of the alkaline range (circa pH 10) where some metals have least solubility, while others are at the point of redissolving as an anionic species. For successful application as a wastewater treatment technology, careful control of pH must be practiced if the best removals are to be achieved.

In practice the solubility of metallic hydroxides, and the tendency for fine insolubles to remain in suspension, may yield effluents which will not meet $\mu\text{g/l}$ standards, and hydroxide precipitation is often supplemented by the use of coagulating agents to improve solids removal, or sulfide coprecipitation to reduce ultimate solubilities.

In practice, the technology uses unit process steps which are simple, well-established, and well-understood by the industry.

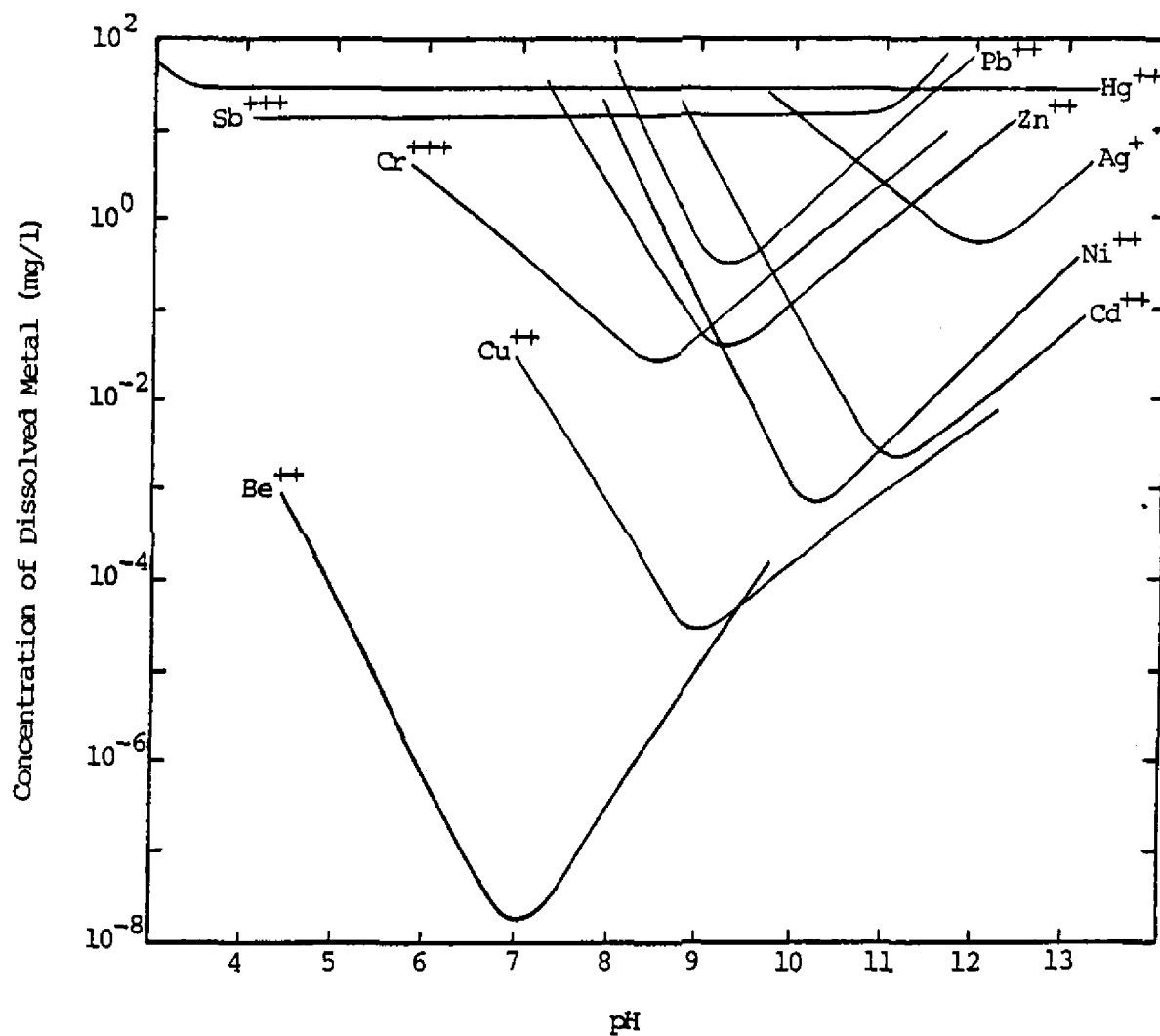
Depending on the quantity of waste flow, the treatment can either be a batch or continuous operation, with batch treatment being favored when waste flows are small. In batch treatment the equipment usually consists of two tanks, each with a capacity to treat the total wastewater volume expected during the treatment period. These systems can be economically designed for flows up to 50,000 gallons per day (5).

The treatment tanks serve the multiple functions of equalizing the flow, acting as a reactor and as a settler. During operation the wastewater is stirred, and a homogeneous sample is taken and analyzed to determine the chemical dosage requirements. The chemicals are added, mixed and stirred for about 10 minutes. After the reaction is complete, the solids are allowed to settle for a few hours. The clear liquid is then decanted and discharged. Settled sludge is retained to serve as a seed for crystal growth for the next batch, but must be drawn off periodically and disposed of, usually in a chemical landfill.

For larger daily flows a typical continuous flow treatment scheme consists of a flash mixer, flocculator, settling unit with sludge storage tank, and, in some cases, a filtration system.

The ability to separate the solids from the wastewater is important. Metallic hydroxides tend to be gelatinous and separate poorly in gravity separators. Finely suspended solids tend to pass out with the effluent and increase the total metal content. Thus, improvements in precipitation applications have been directed toward fine solids removal, and this is reflected in the addition of various filtration

Figure 7-1. Theoretical solubilities of toxic metal hydroxides/oxides as a function of pH.



NOTE: Solubilities of metal hydroxides/oxides are from data by M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, Oxford, 1966.

TABLE 7-1. SOLUBILITY PRODUCTS OF TOXIC METALS

Metal	Solubility Product Constant (K_{sp})	
	Metal Hydroxide	Metal Sulfide
Antimony (III)	--	--
Arsenic	--	--
Beryllium	1.6×10^{-22} (1)	--
Cadmium	2.5×10^{-14} (1)	3.6×10^{-29} (2)
Chromium (III)	6.3×10^{-31} (1)	--
Copper	2.2×10^{-20} (1)	8.5×10^{-45} (2)
Lead	1.2×10^{-15} (1)	3.4×10^{-28} (2)
Mercury	3.0×10^{-26} (1)	2.0×10^{-49} (2)
Nickel	2.0×10^{-15} (1)	1.4×10^{-24} (2)
Selenium	--	--
Silver	2.0×10^{-8} (1)	1.6×10^{-49} (2)
Thallium (I)	--	5.0×10^{-21} (1)
Zinc	1.2×10^{-17} (1)	1.2×10^{-28} (2)

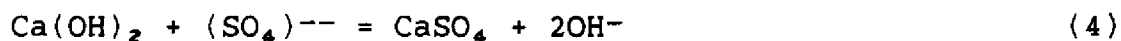
NOTE: References for above values are shown below.

- (1) Dean, J.A., Ed., Lange's Handbook of Chemistry, 12th ed., McGraw-Hill Book Co., New York, 1979.
- (2) Weast, R.C., Ed., Handbook of Chemistry and Physics, 57th ed., CRC Press, Cleveland, Ohio, 1976.

systems and the use of flocculant aids as improved levels of treatment.

Soda ash (sodium carbonate, Na_2CO_3) is sometimes found to be the reagent of choice particularly for lead removal. Lead carbonate, PbCO_3 , and lead hydroxide/carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, (basic carbonate) are formed which may afford improved settling properties for a particular waste. This practice is found in Chlor-Alkali (Diaphragm Cell) waste treatment.

Hydrated lime suspensions are more commonly used than soda ash or caustic soda as the hydroxide source because they are cheaper. However, if there is sulfate ion present in the wastewater, gypsum will be formed:



Hydrated lime + sulfate ion = calcium sulfate (gypsum)
+ hydroxyl ions

This increases the sludge produced, may cause scaling problems in pipelines, and may clog a dual-media filter. Using caustic soda is more expensive, but it generally eliminates the scaling problem. Total dissolved solids in the form of sodium salts are increased in the caustic soda treated wastewaters. Although low concentrations of sodium are not regarded as polluting, high levels can make drinking water unpalatable, limit the use of water for agriculture, and promote degradation of the structure of arable soils. Thus, where high total dissolved solids are of concern, lime would be the preferred neutralizing agent.

This treatment technology is widely applied in treating industrial wastewaters. Industries that are using hydroxide precipitation include:

- Inorganic Chemicals
- Plating and Metal Finishing
- Mining
- Textiles
- Steel and Iron
- Non-Ferrous Metal Processing and
- Electronics

Better than 99 percent removal of trace metals have been reported in the literature with final concentrations in the treated effluents ranging from sub ppm to low ppm (see Table 8-1 through 8-10).

Ferrite Coprecipitation

An interesting variation on the theme of hydroxide precipitation is a process developed in Japan for the removal of heavy metals from acidic wastewater. The process, known as ferrite coprecipitation, has the potential for producing a marketable residual by converting the metal

ions in solution into insoluble ferromagnetic oxides or ferrites which can be removed magnetically or by filtration (5). The treatment is applied by adding a ferrous salt to the metal-bearing wastewater, then neutralizing and oxidizing the complex heavy metal-ferrite coprecipitate. Particle sizes are reported to be relatively large and sludges formed can be safely disposed of by landfilling.

Although extensive performance data have not been developed, the information available indicates that very high removal efficiencies can be achieved for most of the common heavy metals, including mercury and hexavalent chromium. The method has not been considered here as an available technology due to the lack of sufficient information on chemical dosing requirements, energy requirements, and performance in situations similar to those found in the inorganic chemicals industry. In connection with wastewater treatment in the Titanium Dioxide Subcategory for the sulfate process, the wastes contain considerable amounts of ferrous iron from the processing of ilmenite ore and the practice of neutralization and aeration may involve the same chemistry as the ferrite coprecipitation process.

Sulfide Precipitation

The basic principle of sulfide treatment technology is similar to that of hydroxide precipitation. Sulfide is added to precipitate the metals as metal sulfides and the sludge formed is separated from solution by gravity settling or filtration. Sodium sulfide and sodium bisulfide are the two chemicals commonly used, with the choice between these two precipitation agents being strictly an economic consideration.

Metal sulfides form according to the following equation:



Metal ion + sodium sulfide = insoluble metal sulfide
+ sodium ions

In order to calculate the theoretical solubilities of the metal sulfides as a function of pH, the equilibria involved in solid metal sulfide dissociation are taken into account:



Metal sulfide = metal ion + sulfide ion and, depending on pH, the sulfide ion can react with hydrogen ions to form the bisulfide ion and hydrogen sulfide.



Sulfide ion + hydrogen ion = bisulfide ion



Bisulfide ion + hydrogen ion = hydrogen sulfide

The concentration of metal ion in solution will equal the concentration of sulfide ion, bisulfide ion and hydrogen sulfide. Knowing the metal sulfide solubility product (Table 7-1) and the acid dissociation constants of hydrogen sulfide, $K_1 = 9.1 \times 10^{-8}$, $K_2 = 1.1 \times 10^{-12}$ (see Reference 2 in Table 7-1) the solubility of the metal ion can be calculated as a function of the hydrogen ion concentration and, therefore, as a function of pH.

For a divalent metal ion the equation is:

$$(M^{++}) = [K_{sp} (1 + (H^+)/1.1 \times 10^{-12}) + ((H^+)^2/1 \times 10^{-19})]^{1/2}$$

Using the above information, the theoretical solubilities of the toxic metal sulfides were calculated and are shown in Figure 7-1.

The major problem in applying sulfide precipitation techniques is associated with the toxicity of sulfides. This warrants both care in application and post treatment systems to remove excess sulfide. Pretreatment involves raising the pH of the waste stream to minimize evolution of hydrogen sulfide gas.

A recently developed and patented process to eliminate the potential hazard of excess sulfide in the effluent and the formation of gaseous hydrogen sulfide uses ferrous sulfide as the sulfide source (6). The fresh ferrous sulfide is prepared by adding sodium sulfide to ferrous sulfate. The ferrous sulfide slurry formed is added to a wastewater to supply sufficient sulfide ions to precipitate metal sulfides which have lower solubilities than ferrous sulfide. Typical reactions are:



Ferrous sulfide + copper ion = insoluble copper sulfide
+ iron ion

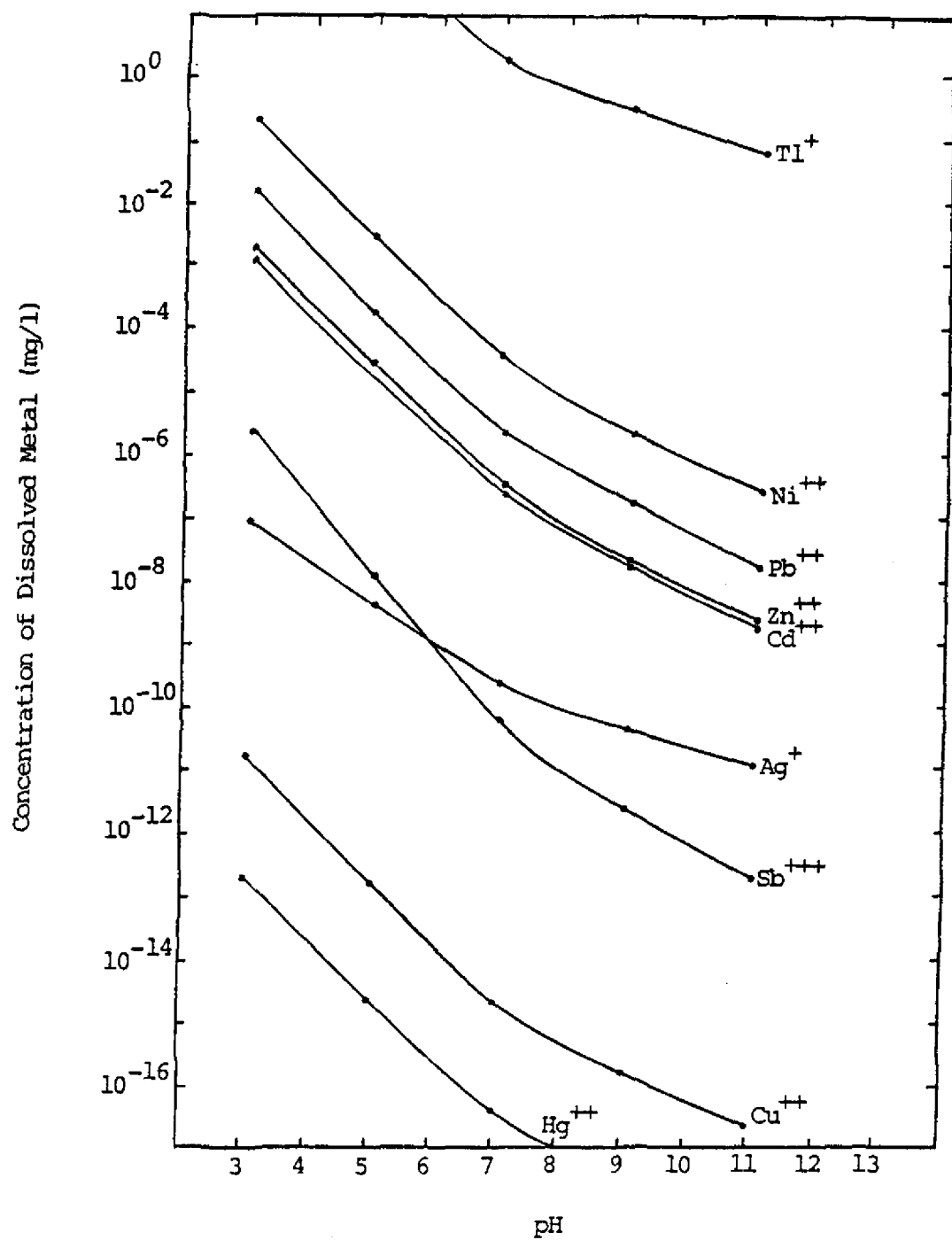


Ferrous sulfide + = ferrous hydroxide +
nickel hydroxide insoluble nickel sulfide

A detention time of 10-15 minutes is sufficient to allow the reaction to go to completion (7). Ferrous sulfide itself is also a relatively insoluble compound. Thus the sulfide ion concentration is limited by the solubility of ferrous sulfide, which amounts to about 0.02 mg/l, and the inherent problems associated with conventional sulfide precipitation are minimized (8).

One other advantage of this process is that if chromium (VI) is present, it will also be reduced at the pH of normal operation (8 to 9) and precipitate as the trivalent hydroxide (Cr III).

Figure 7-2. Theoretical solubilities of toxic metal sulfides as a function of pH.



Treatment systems for sulfide precipitation are similar to those used for hydroxide precipitation. A continuous treatment scheme generally consists of a pH adjustment tank, flash mixer, flocculator, settling units with sludge storage, and a dual media filter.

Before the addition of sodium sulfide or bisulfide the pH of the incoming wasteflow is adjusted to pH of 7-8 in the first reaction tank to reduce the formation of obnoxious hydrogen sulfide gas. The chemicals are then added to the flash mixer where they are thoroughly mixed with the wastewater.

After the flash mix, the wastewater passes through a flocculating basin where the floc agglomerates and settles in the settling unit. The overflow from the settling unit generally passes through a filter to remove any fine precipitates. Any excess sulfide will need to be removed before final discharge. This can be achieved either by aeration or other chemical oxidation techniques.

Sulfide precipitation is being practiced in the inorganic chemicals industry, mining industry, textile industry, and nonferrous metal processing industry. Most of the Chlor-Alkali industry is applying this technology to remove mercury from its waste streams.

Literature citations on the efficiency of sulfide precipitation (9, 10, 11) indicate that most results are in the sub ppm range, and that sulfide treatment is superior to hydroxide treatment for the removal of several trace metals. A recent report concluded that, with no complexing agents in the waste, the following effluent quality can be achieved (11).

Metals Concentration

Cadmium	0.01 mg/l
Copper	0.01 mg/l
Zinc	0.01 mg/l
Nickel	0.05 mg/l
Chrome (total)	0.05 mg/l

Adding ferrous sulfide as a polishing step to remove residual metals appears to be a promising, economical technology. Although there is no full-scale treatment system using ferrous sulfide operating in the inorganic chemicals industry, pilot studies on chrome pigment waste indicate that this process is superior to sulfur dioxide reduction followed by hydroxide precipitation (12).

The Xanthate Process

The use of xanthates for the removal of metals from waste streams appears to be a new, promising technology for treating metal-bearing wastewaters. Xanthates contain functional groups capable of forming insoluble complexes with metals, and the sludge so formed can be separated by conventional means.

Xanthates can be generated by mixing starch or cellulose with carbon disulfide in a caustic medium. Three types of xanthates have been proven in bench pilot scale studies to be effective in removing cadmium, chromium (III), copper, iron, lead, mercury, nickel, silver and zinc from industrial wastewaters (13-20). These are:

Soluble starch xanthate with a cationic polymer,

Insoluble starch xanthate, and

Fibrous cellulose xanthate

The general removal mechanism is as follows:



Xanthate + metal ion = insoluble metallic xanthate
+ sodium ions

where R = starch or cellulose.

Unlike hydroxide precipitation, this process is reported to be effective in removing metals over a wide pH range of 3 to 11, with an optimum range between 7 and 9.

Brass mill wastewaters, lead battery effluent, circuit board rinse waters, electroless copper plating rinse waters, pyrophosphate electroplating rinse waters, and copper etching rinse waters were studied in a pilot plant with insoluble starch xanthate as the complexing agent (20). This pilot study demonstrated that the xanthates can either be added to a reactor to mix with the wastewaters or be applied as a precoat on a pressure filter (20). Results of these pilot studies showed that metals were reduced to below 50 µg/l (ppb).

Another study indicated cellulose xanthate is as effective as starch xanthate in removing trace metals. The following table summarizes the result of the study with a cellulose xanthate dosage of 90 mg/l and a contact time of 30 minutes (18-19).

Concentration, mg/l

<u>Metals</u>	<u>Influent</u>	<u>Effluent</u>
Cadmium	1.35	0.027
Chromium	0.30	0.022
Copper	1.6	0.06-0.14
Iron	3.1	0.08-0.36
Lead	3.9	0.008-0.021
Nickel	2.4	0.077
Zinc	1.0	0.03-0.04

This study also concluded that cellulose xanthate is superior to starch xanthate in terms of sludge settling characteristics, filterability, and handling.

Xanthate may also be used as a complexing agent to prevent the formation of soluble anions from insoluble amphoteric metal hydroxides.

The xanthate process is a relatively new technology, and the reagent compounds are not yet available in commercial quantities. More information is needed on dosage rates in continuous flow operations. Potentially the metals can be recovered by leaching the xanthate complex with nitric acid, but metal recovery has not been demonstrated yet. Sludge disposal problems may arise if the sludge complex is unstable and, if xanthates are to be generated on site, care will be needed in handling the hazardous carbon bisulfide.

Ion Exchange

Ion exchange is a chemical reaction between the ions in solution and the ionic sites on an exchange resin. Many natural solids (e.g., soils, proteins, and zeolites) exhibit such exchange characteristics. However, synthetic resins are the predominant ones used for ion exchange applications in modern industrial technology. These resins contain functional groups that can react with the ions in solution. Depending on these functional groups, the resins can be classified into:

- Strongly acidic cation exchanger,
- Weakly acidic cation exchanger,
- Strongly basic anionic exchanger, and
- Weakly basic anionic exchanger.

Cation exchangers are capable of exchanging with cations in solution. Strongly acidic cation exchangers contain functional groups such as sulfonates, ($-\text{SO}_3\text{H}$ and $-\text{SO}_3\text{Na}$), while weakly acidic exchangers have functional groups derived from carboxylic acids, ($-\text{COOH}$ and $-\text{COONa}$).

Anionic exchangers are used to exchange with the anions in solution. In general, strongly basic exchangers contain amine functional groups ($-\text{R}_3\text{NOH}$ and $-\text{R}_3\text{NCl}$), and weakly basic exchangers contain ammonia functional groups ($-\text{NH}_3\text{OH}$ and $-\text{NH}_3\text{Cl}$).

When the functional groups are used up in the reaction, the resins can usually be regenerated. Cationic resins can be regenerated by sodium chloride, hydrochloric acid, sulfuric acid or sodium hydroxide. Anionic resins are regenerated by sodium hydroxide, ammonium hydroxide, sodium carbonate, sodium chloride, or hydrochloric acid.

The exchanger can either be added to the wastewaters in batch operations or be packed in a fixed bed or column. Fixed bed is by far the more effective and hence more popular. The operation generally

follows a four-step cycle: exchange (service), backwash, regeneration, and rinse.

During the exchange step, the reaction between the ions in solution and the ionic sites in the resin takes place as the wastewater passes down the bed. The reaction is generally regarded as a result of electrostatic attraction (20). Therefore, the size of the hydrated ion and the charge on the ion are the determining factors for the exchange reaction. A trivalent ion is attracted more strongly than a bivalent ion which is in turn attracted more strongly than a monovalent ion. For ions with the same charge, the smaller hydrated ion is capable of moving closer to the exchange site, and is thus favored.

Many synthetic resins contain functional groups that are selective to certain metals. For example, a resin manufactured by a European company reacts preferentially with mercury (Hg^{++}) and mercuric chloride (HgCl^+) ions according to the following equations:



Resin + mercury ion = insoluble resin complex
+ hydrogen ions



Resin + mercuric chloride ion = insoluble resin complex
+ hydrogen ions

The exchange reaction is governed by the law of mass action. During the reaction, the affinity of the resin for the two ions is so great that essentially all the mercury or mercury chloride-resin complex formation equilibria are shifted toward the formation of Hg^{++} and HgCl^+ which are rapidly removed. A 5 ppb residual mercury concentration in the effluent is achieved by this process (22).

After all the exchangeable sites in the resin are used up, the bed is backwashed by passing clean water through to loosen up the bed and to remove any fine particulates that are trapped inside the bed.

After the backwash cycle the resins can be regenerated with the appropriate regenerant.



Insoluble resin complex = regenerated resin
+ hydrochloric acid + mercuric chloride

One attractive feature of the ion exchange process is that it concentrates the metals in the regeneration step, and thus provides a potential for their recovery. However, if recovery is not feasible, this creates a secondary stream which needs to be treated.

A recent study found that sodium aluminosilicates (zeolites) might be a low-cost exchanger that can be discarded after a one-time use (22). This would eliminate the regeneration step. On a batch study with a five-minute contact time, cadmium and mercury were removed to below 10 ppb. Thermodynamic considerations show this exchanger to have a high affinity for cadmium, copper, mercury, nickel, silver, zinc, cesium, and barium.

Ion exchange is a proven technology that can reduce metal concentrations down to low levels. However this technology is used only in limited industrial pollution abatement applications because of the high cost associated with the process. Consequently, ion exchange has not been recommended in this report for BAT technology.

Reduction Processes

Many metals can exist in solution in several oxidation states, and it may be necessary to convert from a higher valency state to a lower one in order to apply a given chemical reaction. The classic example is chromium, which as the trivalent chromic ion will precipitate as the hydroxide in alkaline solution, while the hexavalent chromate or dichromate ion will not. The latter needs to be reduced if precipitation is to occur.

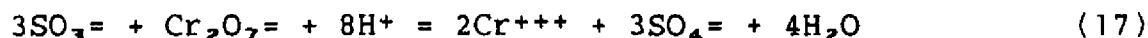
Hexavalent chromium (e.g., CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) is toxic and soluble. The most efficient way of removing this from solution is a two-step process of reduction followed by precipitation.

Chromium (III) is much less toxic than chromium (VI), and forms an insoluble hydroxide which can be removed from solution by settling and filtration.

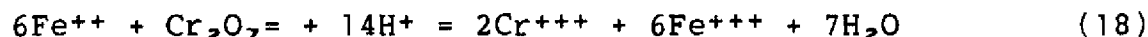
A number of chemicals are used for the reduction of chromium. Most common are sodium bisulfite, sodium metabisulfite, sulfur dioxide and ferrous salts. The reduction is accomplished readily at low pH with these reagents. Typical reduction reactions are:



Sulfur dioxide + dichromate ion = trivalent chromium ion
+ hydrogen ion + sulfates and water



Sulfite ion + dichromate ion = trivalent chromium ion
+ hydrogen ion + sulfate + water



Ferrous ion + dichromate ion = trivalent chromium ion
+ hydrogen ion + ferric ion + water

The reduced chromium and the ferric ions produced in the third equation will exist as the soluble sulfate at acid pH's. If the pH is above 5, the reaction rate is drastically reduced, and although dithionite will effect reduction at neutral pH's, it is very costly and its use may be contraindicated.

After the reduction step, lime or caustic soda is added to raise the pH to 8.5-9.0. Trivalent chromium will be precipitated.



Trivalent chromium = insoluble chromium hydroxide
+ hydroxide ion

The theoretical solubility limit of chromium hydroxide is above 0.02 mg/l (8). It is reported that applying sulfur dioxide to a pigment waste consistently reduced Cr (VI) and Cr(T) to 0.5 mg/l and 1.5 mg/l respectively as 30-day averages (9) (10). By applying ferrous sulfide to a plating waste with an initial Cr(VI) concentration of 128 mg/l and Cr(T) concentration of 153 mg/l, an effluent quality of less than 0.05 mg/l of either species is achieved (12).

A one-step precipitation-reduction process using sodium bisulfide was used in a dichromate plant to remove chromium from its wastewater. An effluent quality with less than 1 mg/l Cr(VI), and less than 5 mg/l Cr(T) was reported (3).

One other common reduction process is the application of sodium borohydride to reduce metals in waste streams. Sodium borohydride is a mild but effective reducing agent (3), and is currently used in some chlor-alkali plants to reduce the soluble mercury ion to metallic mercury which is removed from solution by carbon adsorption:



Mercury ion + borohydride ion = insoluble mercury metal
+ hydroxyl ion + borate ion + water

A mercury level of 0.01 mg/l in the final effluent has been reported (3).

Sodium borohydride is also reported to be effective in removing silver, mercury, gold, lead, and cadmium (5). However, this technology is only being applied in limited cases, the cost of the chemical being the major drawback. The cost of sodium borohydride was \$16.00 per pound in 1978 (23).

Oxidation Processes

The oxidation of organic substances is generally carried out by thermal processes such as wet oxidation and incineration, or by

biological processes such as the activated sludge process, trickling filters, biodiscs, and aerated lagoons.

Incineration is actually a combination of oxidation and pyrolysis. Both involve chemical changes resulting from heat. Oxidation involves actual reaction with oxygen, while pyrolysis refers to rearrangement or breakdown of molecules at high temperatures in the absence of oxygen. There are five types of incinerators available commercially. These are rotary kiln, multiple hearth, liquid injection, fluidized bed, and pyrolysis (24). A minimum temperature of 1000 degrees C and a residence time of two seconds is required for the reaction to proceed. This process has been shown to be successful in reducing pesticides to harmless molecules (25).

Wet oxidation is a process in which an aqueous waste can be oxidized in the liquid phase in a closed, high-temperature, high pressure vessel. This reduces some of the problems (such as air pollution from exhaust gas) inherent in incineration. Wet oxidation has been used for a variety of wastes including pulping waste and acrylonitrile liquor (26). A percent reduction in excess of 99.8 of some of the toxic pollutants has been reported (27).

Thermal oxidation processes are not expected to have much application in the inorganic chemicals industry, mainly because of the high energy cost required and the low level of organic contamination found in the wastes.

The application of chemical oxidation to industrial wastes is well established for cyanides, sulfite, ammonia, and other harmful species in dilute waste streams (phenols, mercaptans, polysulfides, etc.). Common chemicals used as oxidizing agents included chlorine, hypochlorite, hydrogen peroxide, potassium permanganate, ozone, and chlorine dioxide. Air and oxygen are also used.

The most widely used chemical oxidation technology applicable to the inorganic chemicals industry is the oxidation of cyanide. The oxidation reaction between chlorine and cyanide is believed to proceed in two steps as follows:



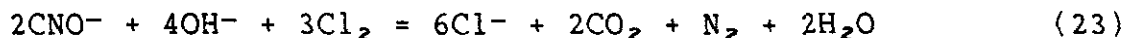
Cyanide + chlorine = cyanogen chloride + chloride ion



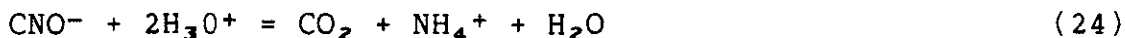
Cyanogen chloride = cyanate ion + chloride
+ hydroxyl ion ion + water

The formation of cyanogen chloride (CNCl) is essentially instantaneous. The second reaction, the formation of cyanate, is accomplished most rapidly and completely at a pH of 10 or higher (9,28). A detention time of 30 minutes to two hours is usually allowed.

The cyanates can be further decomposed into nitrogen and carbon dioxide by excess chlorination or acid hydrolysis.



Cyanate + hydroxyl ion = chloride ion + carbon dioxide
+ chlorine + nitrogen + water



Cyanate + hydronium ion = carbon dioxide + ammonium ion
+ water

The first reaction can be accomplished in about one hour if the pH is adjusted to 8.0-8.5. Acid hydrolysis usually takes place at pH 2-3 and care must be taken to avoid the liberation of the toxic cyanogen chloride as a gas. Hydrolysis is not usually the chosen option.

Other common chemicals used to oxidize cyanide include sodium hypochlorite, ozone, and hydrogen peroxide. The reaction for sodium hypochlorite is essentially the same as for chlorine. For ozone and hydrogen peroxide, the oxidation step proceeds as follows:



Ozone + cyanide = oxygen + cyanate ion



Hydrogen peroxide + cyanide = cyanate ion + water

The advantage of using these two oxidizing reagents is that no dissolved solids are added to the wastewater. In addition, excess chlorine is not discharged.

A patented process uses hydrogen peroxide and formaldehyde to decompose cyanide at about 120°F. This has the advantage of precipitating cadmium and zinc simultaneously (9).

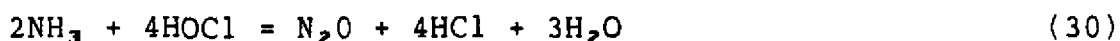
Laboratory studies in one plant currently practicing alkaline chlorination indicated that the presence of ammonia in the wastewater reduces the efficiency of cyanide removal. It is well known that ammonia reacts with chlorine or hypochlorous acid to form chloramines:



Ammonia + hypochlorous acid = monochloramine + water, etc.



If excess chlorine is added, chloramines can be converted into nitrogen oxides(s):



This equation is not exact because the final form of nitrogen oxide is believed to be a mixture of nitrous oxide, nitrogen dioxide and nitric oxide.

The treatment of cyanide by chemical oxidation is currently practiced in the following industries:

Inorganic Chemical (Hydrogen Cyanide Production)

Mining

Plating

The free cyanide level after treatment is generally below 0.1 mg/l (9).

Membrane Processes

Membrane processes have emerged in the last decade as a promising new technology for the treatment of saline water and wastewaters. A membrane is a semi-permeable barrier which allows the transport of some molecules (ions) and retains others. The driving force can either be electropotential differences (electrodialysis) or pressure difference (reverse osmosis and ultrafiltration). The major application of these processes has been the desalination of brackish water and sea water. More recently, these have also found application in a number of industries, including:

Mining

Electroplating

Metal Finishing

Printed Circuit Board Manufacturing

Battery Manufacturing

Pulp and Paper

Food Processing

In electrodialysis, an even number of alternating anion and cation selective membranes are placed between two electrodes. When current is applied the anions are attracted to the anode, and cations are attracted to the cathode. In the process of migration, the cations pass through the cation-permeable membrane and are blocked by the anion-permeable membrane. Likewise, the anions pass through the anion-permeable membrane and are blocked by the cation membrane. This results in alternating paths of purified water and concentrated reject (Figure 7-3).

The electrodialysis membranes are made very thin and are assembled in stacks. The flow path is the active portion of the cells.

Pretreatment to remove suspended materials is absolutely essential. Other materials in the waste feed that may lead to membrane fouling include high organic content, calcium sulfate, and certain complex ions such as ZnCl^- which can partially convert the anion membrane to the cation form, with significant loss in system performance (28).

As ionic concentration decreases, the electroconductivity of the water also decreases, making it less efficient to remove the remaining salt. Most operations do not produce a product water of less than 500 mg/l total dissolved solids.

Reverse osmosis (RO) and ultrafiltration (UF) are similar in basic concepts. Both are pressure-driven separation processes that employ high-flux semi-permeable membranes operating under dynamic flow conditions (29). In contrast to electrodialysis, these involve the transport of solvent, not solute, across the membrane.

Osmosis is a process in which solvent from a dilute solution is transported spontaneously across a semi-permeable membrane into a concentrated solution. By applying enough pressure to overcome this osmotic pressure, reverse osmosis, i.e., the passage of solvent from a concentrated solution to a dilute solution through a semi-permeable membrane, occurs. The operating pressure of reverse osmosis units is usually between 350 and 600 psi. Ultrafiltration usually operates at a much lower pressure (5 to 100 psi). The predominant transport mechanism is selective sieving through pores. The membrane retains high molecular weight dissolved solids such as synthetic resins, colloids, and proteins. The upper and lower molecular weight limit is generally defined as 500,000 and 500, respectively.

Membranes are usually fabricated in flat sheets or tubular forms. The most common material is cellulose acetate but other polymers such as polyamides are used. There are four basic module designs: plate-and-frame, tubular, spiral-wound, and hollow fiber. Table 7-2 is a comparison between the various reverse osmosis modules. Membrane processes are effective in removing (concentrating) inorganic and organic substances from a wastestream. Usually extensive pretreatment is required to reduce the suspended solids and control pH. There are uncertainties about operation efficiency, membrane lifetime, rejection specificity, and other factors. If recovery is not feasible, the concentrated reject must be disposed or treated by other methods. The high operation and capital cost limits the widespread application of these technologies. For these reasons membrane technique is not recommended as a BAT technology for this industry.

Adsorption

Adsorption is a surface phenomenon in which a substance is accumulated on the surface of another substance. Sorption of a solute on a solid surface is widely used in pollution abatement practices. The term "adsorbate" refers to the substance being concentrated, and the term "adsorbent" refers to the material that provides the surface.

Activated carbon is the prevalent adsorbent used. Both inorganic and organic substances are known to be removed effectively by activated carbon. Certain chlor-alkali plants are currently using activated carbon as a polishing step to remove mercury.

Activated carbon is made by charring basic substrates, such as wood, coke, coal, shell, husks, etc., at 600°C in a controlled atmosphere, where oxygen is kept low by adding carbon dioxide or steam. This process drives out volatiles, leaving a porous carbon lattice in an "activated" state.

Activated carbon can be obtained in powdered and granular form. Powdered carbon is about 50-70 microns in diameter, and 90 percent should pass through a 300-mesh screen. Granular carbon is about 0.1-1 mm in diameter, and because of this is three times more expensive than powdered carbon.

The application involves the passage of the wastewaters through a contact bed. When the bed is exhausted, the carbon is either regenerated or sent to landfill. It is economical for large plants to regenerate the carbon. This can be done either by thermal regeneration in a rotary kiln or multihearth incinerator, or by chemical regeneration by using oxidizing agents such as hydrogen peroxide or acids and bases.

The application of carbon adsorption has been mainly in organic waste treatment. Recently, there are studies indicating the effectiveness of carbon adsorption in removing mercury, cadmium, cyanide, chromium, lead, nickel, zinc, arsenic, and copper (30, 31).

An interesting development in carbon technology is its use after the wastewater is ozonized. This combination (known as Bacteriologically Activate Carbon or BAC) has proved effective in treating otherwise biologically inactive organic compounds. The process involves chemical modification of the organics by the ozone. Maintenance of an aerobic region on the carbon allows a biologically activated film to develop and the modified organics are further treated by a mixed process of biological oxidation and carbon adsorption. The system has the advantage of being a potential add-on to existing BPT systems, and should be cost effective since it has been found that the carbon only needs regeneration at infrequent intervals.

No industrial applications of this technology are known, although research is under way (32).

Bacteriologically Activated Carbon is a very attractive potential BAT technology for the removal of organic toxic pollutants from waste streams, although no application to the inorganic chemical industry subcategories studied in this report was found.

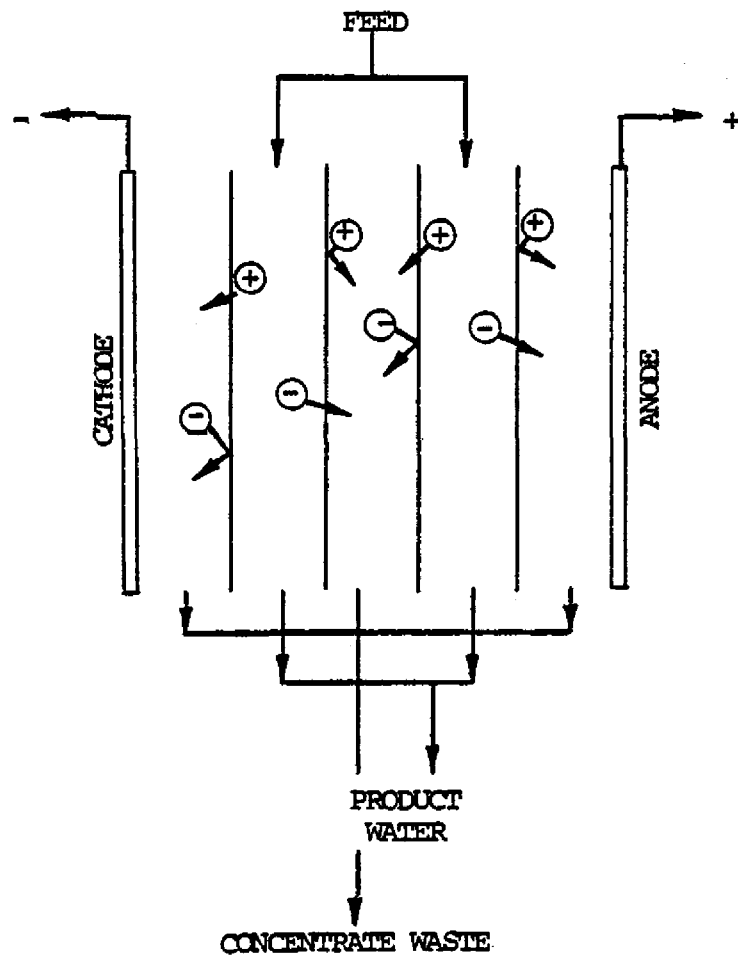


Figure 7-3. Electrodialysis process.

TABLE 7-2. COMPARISON OF REVERSE OSMOSIS CONCEPTS

	Packing Density (ft ² /ft ³)	Water Flux at 600 psi (gal/ day/ft ²)	Water Output Per Unit Volume (gal/ day/ft ²)	Sodium Chloride Rejection	Parasitic Pressure Losses (psi)		Useful pH Range	Ease of Cleaning
					Feed Channel	Product Channel		
Plate-and-Frame	150	10	1500	Very good	30	30	2-8	Fair
Large tubes	50	10	500	Very good	50	10	2-8	Very good
Spiral	250	10	2500	Very Good	10	50	2-8	Good to very good
Polyamide hollow fine fibers	5000	1 (400 psi)	5000	Fair	10	50	0-12	Fair
Cellulose acetate hollow fine fibers	2500	3 (250 psi)	7500	Good	10	50	3-7	Fair

Source: Weber, Physicochemical Processes, 1972.

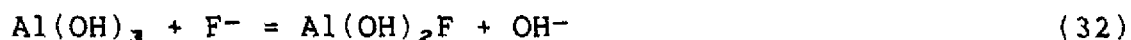
Fluoride Removal

The conventional method of treating fluoride-bearing wastes is to precipitate the fluoride as calcium fluoride by the addition of lime. The reaction is:

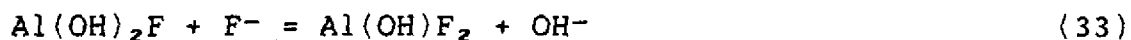


Hydrated lime + fluoride ion = insoluble calcium fluoride
+ hydroxyl ion

Using this process alone, it is difficult to remove fluoride to below 8 mg/l due to the solubility of calcium fluoride (9, 33). Adding alum with the lime generally improves the removal efficiency. Fluoride ions are removed as follows:



Aluminum hydroxide = aluminum monofluorohydroxide
+ fluoride ion + hydroxyl ion, etc.



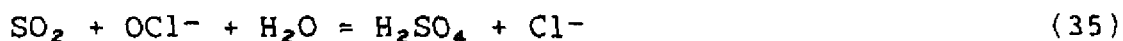
Complexed fluorides are also adsorbed to some extent on the aluminum hydroxide surface and removed in the coagulation process (33). Large amounts of alum (5000 mg/l) are required to reduce the fluoride concentration to below 1 ppm.

Activated alumina has been shown to be effective in removing fluoride and arsenic in wastewater (34) and fluoride from drinking water in municipal water treatment practice (35-38). Typically, the fluoride content of raw water can be reduced from about 8 to 1 ppm (38). Application of activated alumina to high fluoride industrial wastes shows that a low ppm effluent can be achieved (39), although high capital and operation costs generally limit the wide application of this process.

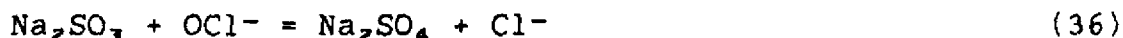
Certain process operations used in the manufacture of inorganic fluoride compounds involve the use of sulfuric acid and starting materials which contain silicate or borate impurities. This may lead to the formation of waste containing fluorosulfonate, hexafluorosilicate or tetrafluoroborate complex ions. Although tetrafluoroborate is usually a very minor constituent and the hexafluorosilicate is readily hydrolyzed in treatment systems, the fluorosulfonate ion is fairly stable and presents a serious problem where low levels of total fluoride are required. The lime precipitation method is not effective in removing the fluorosulfonate and the effectiveness of adsorption techniques is not known.

Chlorine Removal

The removal of residual chlorine (in the form of hypochlorite) in industrial wastewater is normally accomplished by the addition of sulfur dioxide or a related reducing agent such as sodium bisulfite or sodium metabisulfite. Typical reactions are shown in Equations 35 and 36.



Sulfur dioxide + hypochlorite ion = sulfuric acid
+ water + chloride ion



Sodium sulfite + = sodium sulfate +
hypochlorite ion chloride ion

Alternatively, hydrogen peroxide, although relatively expensive, may also be used for dechlorination according to Equation 37.



Hydrogen peroxide + hypochlorite ion = water + oxygen +
chloride ion

In the chlor-alkali industry, certain wastewater streams may have a sufficiently high loading of chlorine to warrant recovery of the product by air stripping, steam stripping, or extraction by carbon tetrachloride. In some locations, a market exists for sodium or calcium hypochlorite solutions which can be generated by treating the tail gases with caustic soda or lime. This may serve as a means for disposing of waste chlorine which cannot otherwise be economically recovered. As alternatives for waste chlorine disposal, the streams may be treated to form the hypochlorite and then decomposed thermally or catalytically. These technologies are discussed in Section 11 dealing with the chlor-alkali industry. Chlorine residuals remaining after the recovery and/or decomposition steps have been taken would be amenable to treatment with reducing agents such as sulfur dioxide, bisulfite, or hydrogen peroxide as described above.

SECTION 8

TREATABILITY ESTIMATES AND LONG-TERM DATA ANALYSIS

The Development of Treatability Estimates

Preliminary Analysis

The review of technological treatment options applicable to the removal of toxic pollutants has led to the conclusion that the particular contaminants found in the raw process wastewaters of the subject industries can be effectively controlled by the proper application of fairly well-known and demonstrated techniques. In order to proceed from a general discussion and description of techniques to a detailed evaluation for each subcategory of the levels of removal that can be expected, a summary is now presented of selected treatability data for the 13 toxic metals.

The treated waste concentrations and removal efficiencies reported in the literature are assumed to represent the best performance characteristics that can be obtained under the specified operating conditions. The treatment technologies considered can thus be assigned a set of optimum conditions and best performance estimates for removal of the particular toxic metals that are amenable to treatment. Taking each metal in turn, Tables 8-1 through 8-10 give the initial and final concentrations, the removal efficiencies, and the pH conditions for different treatment technologies. The best performance estimates for metal removal are derived from the tabulated data and are utilized in turn as the bases for making estimates of average achievable performance. The sequence of analytical steps is:

1. Review and analyze applicable performance data.
2. Estimate best performance under optimum treatment conditions.
3. Estimate average achievable performance under expected industrial operating conditions.

The third step involves the consideration of treatment system variables under full-scale operating conditions in industrial situations where the design objective would be the simultaneous removal of several waste load constituents. Each industry designs for maximum removal and/or recovery of the major process-related waste substances and utilizes an appropriate technology which is both reliable and cost effective. Optimum treatment conditions for the removal of a particular pollutant can rarely be achieved consistently and any given set of conditions will be somewhat less than optimum for most, if not all, of the treatable constituents. In any well-operated production facility the normal variations in production rates, raw material quality, the desired product mix in some cases, and contact water use requirements may cause severe hydraulic and pollutant load

TABLE 8-1. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
ANTIMONY AND ARSENIC REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
<u>Antimony</u>					
Lime/Filter	11.5	0.6	0.4	28	40
Ferric chloride/Filter	6.2	0.5	0.2	65	40
Alum/Filter	6.4	0.6	0.2	62	40
<u>Arsenic</u>					
Lime Softening	-	0.2	0.03	85	9, 10
Sulfide/Filter	6-7	-	0.05	-	9, 10
Lime (260 mg/l)/Filter	10.0	5.0	1.0	80	41
Lime (600 mg/l)/Filter	11.5	5.0	1.4	72	41
Ferric sulfate	5-7.5	0.05	0.005	90	42
Ferric sulfate	6.0	5.0	0.5	90	41
Lime/Ferric Chloride/ Filter	10.3	3.0	0.05	98	9, 10
Activated alumina (2 mg/l)	6.8	0.4-10	<0.4	96-99+	43
Activated carbon (3 mg/l)	3.1-3.6	0.4-10	<4.0	63-97	43
Ferric Chloride	-	0.3	0.05	98	9, 10
Ferric Chloride	-	0.6-0.9	<0.13	-	9, 10

TABLE 8-2. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
BERYLLIUM AND CADMIUM REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
<u>Beryllium</u>					
Lime/Filter	11.5	0.1	0.006	99.4	40
<u>Cadmium</u>					
Lime (260 mg/l)/Filter	10.0	5.0	0.25	95	41
Lime (600 mg/l)/Filter	11.5	5.0	0.10	98	41
Lime Softening	5-6.5	0.44-1.0	0.008	92-98	8
Lime/Sulfide	8.5-11.3	0.3-10	0.006	98+	44
Ferrous Sulfide (Sulfex)	8.5-9.0	4.0	<0.01	99+	7,8,11
Ferrite coprecipitation/ Filter		240	0.008	99+	5

TABLE 8-3. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
COPPER REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
Lime/Filter	8.5-9.0	3.2	0.07	98	8
Lime (260 mg/l)/Filter	10.0	5.0	0.4	92	41
Lime (600 mg/l)/Filter	11.5	5.0	0.5	91	41
Ferric sulfate/Filter	6.0	5.0	0.3	95	41
Lime	>8.5	10-20	1-2	90	9,10
Lime	9.5	3.0	0.2	93	45
Alum	6.5-7.0	3.0	0.2	93	45
Lime/Sulfide	5.0-6.5	50-130	<0.5	-	44
Ferrous sulfide (Sulfex)	8.5-9.0	3.2	0.02	99	8
Ferrous sulfide (Sulfex)	8.5-9.0	4.0	0.01	99+	7,8,11
Ferrite Coprecipitation/ Filter	-		0.01	99+	5

TABLE 8-4. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
CHROMIUM III AND CHROMIUM VI REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
<u>Chromium</u>					
Lime (260 mg/l)/Filter	10.0	5.0	0.1	98	41
Lime (600 mg/l)/Filter	11.5	5.0	0.1	98	41
Reduction/Lime	7-8	140 (as Cr VI)	1.0	—	9,10
Reduction/Lime	7-8	1300 (as Cr VI)	0.06 CrIII	—	3,9,10
Lime Softening	10.6-11.3	—	0.15	98+	46
Lime/Filter	7-9	—	0.05	—	47
Lime	9.5	15	0.1	—	45
Lime	9.5	3.2	<0.1	—	45
Ferrite coprecipitation/Filter	—	25	0.01	—	5
Ferric sulfate	6.5-9.3	—	—	98+	46
Ferric sulfate/Filter	—	5.0	0.05	99	41
<u>Chromium VI</u>					
Activated carbon (pulverized, Pittsburgh type RC)	3.0	10	1.5	85	48
Same as above	2.0	10	0.4	96	48
Activated carbon (granular)	6.0	3	0.05	98	41
Ferrite coprecipitation	—	0.5	not detectable	—	5
Sulfur dioxide reduction	—	—	0.01-0.1	—	9,10
Bisulfite reduction	—	—	0.05-1.0	—	9,10

TABLE 8-5. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
LEAD REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
Lime (260 mg/l)	10.0	5.0	0.25	95.0	41
Lime/filter	8.5-9.0	189	0.1	99.9	5
Lime (260 mg/l)/Filter	10.0	5.0	0.075	98.5	41
Lime (600 mg/l)/Filter	11.5	5.0	0.10	98.0	41
Ferrous sulfate/Filter	6.0	5.0	0.075	98.5	41
Sodium hydroxide (1 hour settling)	5.5	—	1.6	—	10
Sodium hydroxide (24 hour settling)	7.0	—	0.04	—	10
Sodium hydroxide/Filter	10.5	1700	0.60	99+	49
Sodium carbonate/Filter	10.1	1260	0.60	99+	49
Sodium carbonate/Filter	6.4-8.7	10.2-70.0	0.2-3.6	82-99+	10
Sodium carbonate/Filter	9.0-9.5	5.0	0.01-0.03	99+	9,10
Ferrous sulfide (Sulfex)	8.5-9.0	189	0.1	99.9	8
Ferrite coprecipitation/ Filter	—	480	0.01-0.05	99.9	5

TABLE 8-6. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
MERCURY II REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
Sulfide	-	0.3-50.0	0.01-0.12	-	9,10
Sulfide	10.0	10.0	1.8	96.4	50
Sulfide/Filter	5.5	16.0	0.04	99	50
Sulfide/Filter	4.0	36.0	0.06	99.8	50
Sulfide/Filter	5.8-8.0	0.3-6.0	0.01-0.125	87-99.2	50
Ferrite coprecipitation/ Filter	-	6.0-7.4	0.001-0.005	99.9	5
Activated Carbon	-	0.01-0.05	<0.0005	-	9,10
Activated Carbon/Alum	-	0.02-0.03	0.009	-	46
Activated Carbon	-	0.06-0.09	0.006	-	50

TABLE 8-7. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
NICKEL REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
Lime	8.5-9.0	75	1.5	98	8
Lime (260 mg/l)/Filter	10.0	5.0	0.3	94	41
Lime (600 mg/l)/Filter	11.5	5.0	0.15	97	41
Caustic Soda/Filter	11.0	-	0.3	-	49
Ferrous sulfide (Sulfex)	8.5-9.0	75	0.05	99.9	8,11
Ferrite coprecipitation	-	1000	0.20	99.9	5

TABLE 8-8. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
SILVER REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
Sodium hydroxide	9.0	54	15	72	13
Ferric sulfate (30 mg/l)	6-9	0.15	0.03-0.04	72-83	46
Lime Softening	9.0-11.5	0.15	0.01-0.03	80-93	46
Chloride precipitation (alkaline chlorination in the presence of cyanide)	-	105-250	1.0-3.5	97+	9,10
Ferric chloride/Filter	6.2	0.5	0.04	98.2	40
Sulfide precipitation	5-11	-	-	very high	9,10

TABLE 8-9. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
SELENIUM AND THALLIUM REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
<u>Selenium</u>					
Ferric chloride/Filter	6.2	0.1	0.03	75	40
Ferric chloride/Filter	6.2	0.05	0.01	80	40
Alum/Filter	6.4	0.5	0.26	48	40
Ferric sulfate	5.5	0.10	0.02	82	51
Ferric sulfate	7.0	0.10	0.03	75	51
Lime/Filter	11.5	0.5	0.3	35	40
Lime/Filter	11.5	0.06	0.04	38	40
<u>Thallium</u>					
Lime/Filter	11.5	0.5	0.2	60	40
Ferric chloride/Filter	6.2	0.6	0.4	30	40
Alum/Filter	6.4	0.6	0.4	31	40

TABLE 8-10. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY -
ZINC REMOVAL

Treatment Technology	pH	Initial Concen- tration (mg/l)	Final Concen- tration (mg/l)	Removal (%)	References
Lime/Filter	8.5-9.0	3.6	0.25	93	8
Lime (260 mg/l)	10.0	5.0	0.85	83	41
Lime (260 mg/l)/Filter	10.0	5.0	0.80	84	41
Lime (600 mg/l)	11.5	5.0	0.35	93	41
Lime (600 mg/l)/Filter	11.5	5.0	1.2	77	41
Lime/Filter	-	16	0.02-0.23	-	5
Sodium hydroxide	9.0	33	1.0	97	13
Sulfide	-	42	1.2	97	5
Ferrous sulfide (Sulfex)	8.5-9.0	3.6	0.02	99+	8,11
Ferrite coprecipitation	-	18	0.02	99+	5

input excursions which at best can be moderated by effective equalization in the treatment system. This is considerably less of a problem in batch treatment than with a continuously operating system. The latter requires continuous feedback monitoring for pH control and chemical dosage in order to maintain the effluent quality within acceptable limits for a number of parameters. Under these conditions, the 30-day averages derived from the actual treated effluent monitoring data (NPDES, etc.) would equate to what has been identified in Step 3 above as the estimated 30-day achievable performance using the same general treatment technology.

The estimated ranges of average achievable performance are presented in Table 8-11. In formulating the proposed regulations, these values were used as maximum 30-day averages in cases where there were insufficient data from sampling or long-term monitoring of the actual industry discharges.

Statistical evaluation of long-term monitoring data is described in Section 8.3 and the results are presented in Appendix A where various derivative quantities such as long-term averages and standard deviations are tabulated.

Final Analysis

Following publication of the proposed regulations on July 24, 1980 (45 FR 49450) additional data on performance of the BPT and BAT options for several subcategories were evaluated and eventually incorporated into the basis for the final regulations. The sources of additional data include the following:

A. Treatability Study for the Inorganic Chemicals Manufacturing Point Source, EPA 440/1-80-103, July, 1980.

B. Industry comments on the proposed regulations - The written comments received by EPA as well as comments given orally at the public hearing on proposed pretreatment standards (October 15, 1980) are part of the official public record of the rule making. The comments are summarized and responses are given in "Responses to Public Comments, Proposed Inorganic Chemicals Manufacturing Effluent Guidelines and Standards," which is a part of the Record for this rule. Individual comment documents or letters are cited in this report where they are used as sources of information.

C. Treatability Manual, Volume III, Technologies for Control/Removal of Pollutants, EPA 600/8-80-042c, July, 1980.

Table 8-12 presents tabular summaries of the available industry treatment performance data for most of the priority toxic metals. These include estimated long-term averages in cases where there were sufficient data given to utilize the Maximum Likelihood Estimation method for calculating statistical parameters as indicated in the footnotes. Overall arithmetic medians and averages are also given for metals where five or more individual data sets were available.

TABLE 8-11. ESTIMATED ACHIEVABLE MAXIMUM 30-DAY AVERAGES FOR THE APPLIED TECHNOLOGIES

	Final Concentrations (mg/l)						
	Lime Settling	Lime Filter	Sulfide Filter	Ferrite Coprecip- itation Filter	Soda Ash Settling	Soda Ash Filter	Alum
Antimony, Sb	0.8-1.5	0.4-0.8					
Arsenic V	0.5-1.0	0.5-1.0	0.05-0.1				
Beryllium, Be	0.1-0.5	0.01-0.1					
Cadmium, Cd	0.1-0.5	0.05-0.1	0.01-0.1	<0.05			
Copper, Cu	0.5-1.0	0.4-0.7	0.05-0.5	<0.05			
Chromium III, Cr ⁺³	0.1-0.5	0.05-0.5		0.01			
Lead, Pb	0.3-1.6	0.05-0.6	0.05-0.4	0.20	0.4-0.8	0.1-0.6	
Mercury II, Hg			0.01-0.05	<0.01			
Nickel, Ni	0.2-1.5	0.1-0.5	0.05-0.5				
Silver, Ag	0.4-0.8	0.2-0.4	0.05-0.2				
Selenium, Se	0.2-1.0	0.1-0.5					
Thallium, Tl	0.2-1.0	0.1-0.5					0.2-0.5
Zinc, Zn	0.5-1.5	0.4-1.2	0.02-1.2	0.02-0.5			

(continued)

TABLE 8-11 continued

	Ferric Chloride	Activated Carbon	Final Concentrations (mg/l)			Lime/FeCl ₂ Filter ²	Alkaline Chlori- nation
			SO ₂ Reduction	Bisulfite Reduction			
Arsenic V, As	0.05-0.5	0.3				0.02-0.1	
Chromium VI, Cr+6		0.1	0.01-0.1	0.05-0.5			
Mercury II, Hg		0.01					
Silver, Ag	0.05-0.1						
Selenium, Se	0.05-0.1						
Thallium, Tl	0.7						
Cyanide (Free), CN _A							0.1-0.5

An industry long-term average effluent concentration was then estimated for each pollutant/treatment option combination for which sufficient data were available. For copper and nickel, the average values for lime/settling were adjusted upward from 0.32 to 0.40 mg/l in order to show a larger decrease when filtration is added. In the case of chromium, the average with filtration was adjusted to 0.16 mg/l. Plants presently practicing filtration are generally those with higher raw waste concentrations of metals in comparison to plants which can achieve adequate treatment without filtration. This tends to reduce the observed differences in performance with and without filtration and, therefore, understates the potential benefit of adding filtration to a particular lime/settling system. The estimated achievable long-term average concentrations, as shown in Table 8-13, generally fall within the estimated range of the corresponding maximum 30-day averages in Table 8-11 which were derived from literature data. Thus, there is substantial agreement between the two sets of estimates and there is good reason to conclude that the lower limits of the treatability ranges in Table 8-11 are actually more like long-term averages than maximum 30-day averages for the inorganic chemicals industry. The final toxic metal regulations are based on the estimated achievable long-term average concentrations in Table 8-13 in cases where there are insufficient industry specific performance data available. The numerical limitation in each case was obtained by multiplying the long-term average concentration by the model plant unit flow rate and an appropriate variability factor. The variability factors are selected to represent as accurately as possible the actual full-scale treatment system's variability under normal operating conditions.

It is understood that in each subcategory plant treatment system conditions, particularly where chemical precipitation is involved, are usually optimized for the removal of only one metal. Other metals may be removed incidentally under the same conditions although their removal efficiencies may not be optimal. An example is the prevalent use of sulfide precipitation/filtration technology for the removal of mercury. The precipitation is normally carried out under neutral to moderately-acid conditions in order to limit the amount of residual sulfide in the system and, depending on specific raw waste characteristics, to obtain desirable solid properties for filtration. Under these conditions, the incidental removals of other metals such as nickel and zinc are not at their maximum efficiencies, but are still effective.

The industry performance data summarized in Table 8-12 for many of the toxic metal/treatment combinations express an observed incidental removal rather than an optimum removal. This provides an empirical basis for estimating practical control levels for metals under off-optimum pH conditions in either alkaline precipitation or sulfide precipitation systems. The Agency does not regard the implementation of more than one optimized metal removal step as necessary to meet the final BPT/BAT regulations.

TABLE 8-12. INDUSTRIAL WASTE WATER TREATMENT SYSTEM PERFORMANCE —
SUMMARY OF EFFLUENT CONCENTRATION DATA ON TOXIC METALS ⁽¹⁾

	Lime/Clarification ⁽²⁾ (mg/l) Source ⁽⁴⁾		Lime/Filtration ⁽²⁾ (mg/l) Source ⁽⁴⁾		Sulfide/Filtration ⁽³⁾ (mg/l) Source ⁽⁴⁾			Lime/Clarification ⁽²⁾ (mg/l) Source ⁽⁴⁾		Lime/Filtration ⁽²⁾ (mg/l) Source ⁽⁴⁾		Sulfide Filtration ⁽³⁾ (mg/l) Source ⁽⁴⁾		
Antimony	0.18	PM ⁽⁵⁾		ND	0.23	CAM ⁽⁶⁾		Copper	0.030	IS ⁽⁵⁾	0.035	CP ⁽⁷⁾	0.033	CAM ⁽⁶⁾
Arsenic	0.080	NFM ⁽⁵⁾	0.30	CP ⁽⁷⁾	0.17	CAM ⁽⁹⁾			0.030	CAD ⁽¹⁴⁾	0.13	CP ⁽²¹⁾	0.056	CAM ⁽⁹⁾
			0.038	CS ⁽⁸⁾	0.096	CAM ⁽⁶⁾			0.038	OMD ⁽⁵⁾	0.17	CS ⁽¹⁵⁾	0.24	CAM ⁽¹⁷⁾
Beryllium	ND			ND		ND			0.060	OMD ⁽⁵⁾	0.23	CS ⁽¹⁵⁾	0.43	CAM ⁽¹⁷⁾
Cadmium	0.060	TDS ⁽¹⁰⁾	0.076	MF ⁽¹¹⁾		ND			0.070	NFM ⁽⁵⁾	0.25	IS ⁽⁵⁾		
	0.080	NFM ⁽⁵⁾							0.070	SEP ⁽⁵⁾	0.37	MF ⁽¹¹⁾		
	0.12	MF ⁽¹¹⁾							0.080	OMD ⁽⁵⁾	0.90	MF ⁽¹¹⁾		
Mercury	ND			ND	0.020	CAM ⁽⁹⁾			0.090	OMD ⁽⁵⁾				
					0.022	CAM ⁽¹²⁾			0.10	OMD ⁽⁵⁾				
					0.036	CAM ⁽⁹⁾			0.14	MF ⁽¹¹⁾				
					0.057	CAM ⁽¹³⁾			0.54	CAD ⁽¹⁷⁾				
Selenium	ND			ND		ND			0.70	NFM ⁽⁵⁾				
Silver	ND			ND	0.070	CAM ⁽⁹⁾			1.1	CS ⁽¹⁵⁾				
Thallium	ND			ND		ND			1.5	CS ⁽¹⁵⁾				
Chromium III	0.040	IS ⁽⁵⁾	0.037	CP ⁽¹⁵⁾		ND		Lead	0.085 median		0.23 median		NA	
	0.050	NFM ⁽⁵⁾	0.046	TDC ⁽¹⁵⁾					0.32 average		0.30 average			
	0.050	CAD ⁽¹⁴⁾	0.072	SDC ⁽¹⁸⁾										
	0.070	TDS ⁽¹⁰⁾	0.20	SDC ⁽¹⁵⁾					0.017	HF ⁽¹⁹⁾	0.038	MF ⁽¹¹⁾	0.032	CAD ⁽¹³⁾
	0.071	CAD ⁽¹⁵⁾	0.28	MF ⁽¹¹⁾					0.10	MF ⁽¹¹⁾	0.11	CP ⁽⁷⁾	0.12	CAM ⁽⁹⁾
	0.072	TDC ⁽¹⁶⁾	0.33	CP ⁽⁷⁾					0.15	OMD ⁽⁵⁾	0.41	CP ⁽²¹⁾	0.16	CAM ⁽⁶⁾
	0.080	TM ⁽⁵⁾	0.44	CP ⁽²¹⁾					0.19	NFM ⁽⁵⁾			0.46	CAD ⁽¹⁵⁾
	0.15	MF ⁽¹¹⁾							0.20	NFM ⁽⁵⁾				
	0.18	TDC ⁽¹⁵⁾							0.15 median		NA		NA	
	0.26	SDC ⁽¹⁵⁾							0.13 average					
	0.35	CAD ⁽¹⁷⁾												
	0.36	IS ⁽⁵⁾												
	0.43	CP ⁽¹⁵⁾												
	0.81	SDC ⁽¹⁵⁾												
	1.8	IS ⁽⁵⁾												
	0.15 median		0.20 median			NA								
	0.32 average		0.20 average											

(Continued)

TABLE 8-12 continued

	Lime/Clarification ⁽²⁾ (mg/l) Source ⁽⁴⁾		Lime/Filtration ⁽²⁾ (mg/l) Source ⁽⁴⁾		Sulfide/Filtration ⁽³⁾ (mg/l) Source ⁽⁴⁾			Lime/Clarification ⁽²⁾ (mg/l) Source ⁽⁴⁾		Lime/Filtration ⁽²⁾ (mg/l) Source ⁽⁴⁾		Sulfide/Filtration ⁽³⁾ (mg/l) Source ⁽⁴⁾	
Nickel	0.020	IS ⁽⁵⁾	0.090	SDC ⁽¹⁸⁾	0.022	CAM ⁽⁹⁾	Zinc	0.020	OMD ⁽⁵⁾	0.018	CS ⁽⁸⁾	0.090	TM ⁽⁵⁾
	0.050	CAD ⁽¹⁴⁾	0.11	CS ⁽¹⁵⁾	0.074	CAM ⁽⁶⁾		0.040	OMD ⁽⁵⁾	0.058	CP ⁽⁷⁾	0.13	CAM ⁽⁹⁾
	0.10	NFM ⁽⁵⁾	0.13	CS ⁽¹⁵⁾				0.040	FI ⁽⁵⁾	0.11	SDC ⁽¹⁸⁾	0.15	CAM ⁽⁶⁾
	0.17	HF ⁽¹⁹⁾	0.19	NS ⁽¹⁵⁾				0.10	CAD ⁽¹⁴⁾	0.25	MF ⁽¹¹⁾		
	0.20	CS ⁽¹⁵⁾	0.20	CS ⁽⁸⁾				0.11	TM ⁽⁵⁾	0.57	MF ⁽¹¹⁾		
	0.20	SDC ⁽¹⁸⁾	0.59	MF ⁽¹¹⁾				0.15	TDS ⁽¹⁰⁾				
	0.25	CS ⁽¹⁵⁾	0.80	NS ⁽²⁰⁾				0.20	NFM ⁽⁵⁾				
	0.26	CAD ⁽¹⁷⁾						0.24	IS ⁽⁵⁾				
	0.31	MF ⁽¹¹⁾						0.25	IS ⁽⁵⁾				
	0.33	IS ⁽⁵⁾						0.35	OMD ⁽⁵⁾				
	0.50	NFM ⁽⁵⁾						0.39	MF ⁽¹¹⁾				
	1.4	NS ⁽¹⁵⁾						0.54	CAD ⁽¹⁷⁾				
								0.55	HF ⁽¹⁹⁾				
								0.60	NFM ⁽⁵⁾				
	0.23 median		0.19 median		NA			8.2	FM ⁽⁵⁾				
	0.32 average		0.30 average										
								0.20 median		0.11 median		NA	
								0.78 average		0.20 average			

NOTES:

- (1) Influent or raw waste concentrations of metals are at treatable levels; i.e., higher than the corresponding treatability ranges given in Table 8-11. All effluent concentrations are measured off treatment and are expressed as total (dissolved plus suspended) for each metal.
- (2) Lime/Clarification and Lime/Filtration treatment means equalization of raw waste influent stream(s) followed by alkaline precipitation using lime or caustic soda, solids removal by sedimentation or clarification, and either discharge of the clarified effluent directly or discharge of the filtrate after passage of the clarified effluent through a dual media filter or its equivalent.
- (3) Sulfide/Filtration refers to a direct treatment of the equalized raw waste influent by sulfide addition (usually in the form of sodium sulfide or bisulfide) under conditions ranging from pH 5 to 11 followed by settling and/or filtration by filter press or activated carbon column.
- (4) Source Codes:
- | | | | | | |
|-----|-------------------------------|-----|--|-----|-------------------------------------|
| CAD | Chlor-Alkali, Diaphragm Cells | IS | Iron and Steel | SEP | Steam Electric Power Generating |
| CAM | Chlor-Alkali, Mercury Cells | MF | Metal Finishing (including electroplating) | SDC | Sodium Dichromate |
| CS | Copper Sulfate | NFM | Nonferrous Metals | TDC | Titanium Dioxide - Chloride Process |
| CP | Chrome Pigments | NS | Nickel Sulfate | TDS | Titanium Dioxide - Sulfate Process |
| FI | Foundry Industry | OMD | Ore Mining and Dressing | TM | Textile Mills |
| HF | Hydrofluoric Acid | PM | Paint Manufacturing | | |

(5) U.S. Environmental Protection Agency, Treatability Manual, Vol. III, Technologies for Control/Removal of Pollutants, EPA 800 8-80 042 c, July, 1980.

(6) This document, Table 11-16.

(7) This document, Table 16-9.

(8) This document, Table 21-11.

(Continued)

TABLE 8-12 continued

NOTES: continued

- (9) Olin Corporation, Chemicals Group, Charleston, TN. Letter to Mr. Elwood E. Martin, U.S. EPA, Effluent Guidelines Division, Washington, D.C., October 20, 1980. Maximum likelihood estimates of the long term averages from Olin mercury treatment effluent data by Jacobs Engineering Group, Inc.
 - (10) This document, Table 14-30.
 - (11) Hamilton Standard, Division of United Technologies Corp., Windsor Locks, CT. Letter to Mr. Richard Kinch, U.S. EPA, Effluent Guidelines Division, Washington, D.C., November 25, 1980. Tabulations of statistical parameters derived from historical data on the metal finishing industry.
 - (12) The Chlorine Institute, Inc., New York, N.Y. Letter to Mr. G. E. Stigall, U.S. EPA, Effluent Guidelines Division, Washington, D.C., May 28, 1979. Attachment "C", a tabular summary of mercury treatment effluent data.
 - (13) PPG Industries, Inc., Pittsburgh, PA. Letter to Mr. Elwood E. Martin, U.S. EPA, Effluent Guidelines Division, Washington, D.C., January 2, 1981. Maximum likelihood estimates of the long term averages from PPG mercury and lead treatment effluent data by Jacobs Engineering Group, Inc.
 - (14) This document, Table 11-37.
 - (15) U.S. Environmental Protection Agency, Treatability Studies for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-80/103, July, 1980. Maximum likelihood estimates of long term averages from treatability data by Jacobs Engineering Group, Inc.
 - (16) This document, Table 14-12.
 - (17) Diamond Shamrock Corporation, Dallas, TX. Letter to Mr. Elwood E. Martin, U.S. EPA, Effluent Guidelines Division, Washington, D.C., October 22, 1980. Tabular summary of highest values from treatment effluent during one month of monitoring.
 - (18) This document, Table 18-13.
 - (19) This document, Table 12-22.
 - (20) This document, Table 22-10.
 - (21) This document, Appendix A.
 - ND = No data available
 - NA = Not applicable
-

TABLE 8-13. ESTIMATED ACHIEVABLE LONG TERM AVERAGE
CONCENTRATIONS FOR TOXIC METALS WITH
BPT OR BAT TREATMENT OPTIONS

Toxic Metal	Lime/Clarification (mg/l)	Lime/Filtration (mg/l)	Sulfide/Filtration (mg/l)
Antimony	ID ⁽¹⁾	ND ⁽²⁾	ID
Arsenic	ID	ID	0.15
Beryllium	ND	ND	ND
Cadmium	0.10	ID	ND
Chromium	0.32	0.16	ND
Copper	0.40	0.30	0.20
Lead	0.15	ID	0.10
Mercury	ND	ND	0.034
Nickel	0.40	0.30	ID
Selenium	ND	ND	ND
Silver	ND	ND	ID
Thallium	ND	ND	ND
Zinc	0.80	0.20	0.12

(1) ID: Insufficient data for a reliable estimate

(2) ND: No data available

Selection of Toxic Metal Control Parameters

Control Parameters for Hydroxide Precipitation

Section 7.2 of this report describes hydroxide precipitation as the most widely-used technology for removing trace metals from wastewaters. Out of the thirteen toxic metal pollutants, two have hydroxide/oxide solubilities independent of the pH range (selenium and thallium) and two have minimum hydroxide/oxide solubilities over a wide pH range (antimony at pH 2-10.4 and mercury at pH 4-12). Arsenic is removable by precipitation with lime (probably as calcium arsenate) in the presence of excess calcium ion under neutral to alkaline conditions. The remaining eight toxic metals have minimum hydroxide/oxide solubilities only over narrow pH ranges (see Figure 7-1). Lead may also be effectively treated with carbonate (soda ash, Na_2CO_3) to form insoluble basic lead carbonate precipitates.

It is clear from the range of optimum pH's illustrated in Figure 7-1 that no single pH exists which can effectively provide optimum removal of all eight of these metals. Relatively effective removal can be obtained by dividing the eight metals into two groups. Group A consists of beryllium, chromium, copper, lead, and zinc. Group B consists of cadmium, nickel and silver. Because they rarely occur at treatable levels and, therefore, rarely require removal, one metal from each group (beryllium and silver) can be eliminated from the selection of an optimum pH range for each group. The information in Figure 7-1 was used to determine the solubility of the six remaining metals at unit pH increments from 8.5 to 11.5. These data are presented in Table 8-14.

Table 8-14 indicates that control of any metal of Group A in the 8.5-9.5 pH range should control the other members of the group. Control of any metal of Group B in the 10.5-11.5 pH range should control the other members of the group. Control of metals from different groups will depend on the details of each case. Possible approaches to controlling metals from different groups might involve the use of the intermediate 9.5-10.5 pH range or the control of one metal in one group when the theoretical solubilities of the metal or metals in the other group are low throughout the 8.5-11.5 pH range.

Control Parameters for Sulfide Precipitation

Section 7.2 of this report describes sulfide precipitation as superior to hydroxide treatment for the removal of several toxic metals. The main application of sulfide precipitation is in mercury removal and mercury, therefore, is the obvious choice as the control metal for this technology. Figure 7-2 points out, however, that mercury is the most insoluble of the toxic metal sulfides and that the solubilities of the metal sulfides are strongly dependant upon pH. Control of mercury in the acid pH range may result in less than optimum control of the least insoluble metal sulfides. Therefore, control of a second metal that is present in treatable concentrations

TABLE 8-14. THEORETICAL SOLUBILITIES OF TOXIC METAL
HYDROXIDES/OXIDES AT VARIOUS pH VALUES

pH	8.5	9.5	10.5	11.5
Metal	Concentration (mg/l)			
Group A				
Cr ⁺⁺⁺	0.030 ⁽¹⁾	0.20	1.0	9.0
Cu ⁺⁺	0.00010	0.000080 ⁽¹⁾	0.00050	0.0020
Pb ⁺⁺	8.0	0.50 ⁽¹⁾	4.0	>10
Zn ⁺⁺	0.60	0.070 ⁽¹⁾	0.50	3.0
Group B				
Cd ⁺⁺	>10	1.0	0.010	0.0010 ⁽¹⁾
Ni ⁺⁺	1.0	0.010	0.0010 ⁽¹⁾	0.010

(1) Lowest value

and that is among the least insoluble of the toxic metal sulfides could give greater assurance that the metals without effluent limitations were also being removed. However, it could also result in higher mercury discharges. Operation of sulfide precipitation in the neutral or slightly alkaline range should result in acceptable removal of all toxic metal sulfides as well as minimizing the problem of hydrogen sulfide evolution. Soluble polysulfide formation can be prevented by avoiding the very alkaline pH range and by close control of excess sulfide.

The Use Of Historical Pollutant Data

Determination of Effluent Limitation Guidelines Based Upon Historical Performance

In cases where there has been long-term monitoring of the pollution levels in the effluent stream discharged by a plant, it is possible to assess in-plant treatment performance through analysis of historical data that has been collected for this purpose. The appropriateness of standards constructed from data collected from a single plant performance is, of course, dependent on the plant's current performance in relation to the performance of other plants in the manufacturing subcategory. As economically feasible alternative waste treatment technologies become available, pollutant discharge guidelines need to be reviewed and revised to reflect these advances.

Statistical analysis of historical monitoring data is required to assess a plant's ability to discharge within set guidelines. To perform this analysis certain assumptions must be made regarding the nature of applicable statistical or probabilistic models, the constancy of the operation of the treatment facility, and the quality of the monitoring methods.

The statistical analyses contained in this development document belong to either of two principal types: those for daily observations of pollutant concentrations, and the others for 30-day average pollutant levels.

Tables in Appendix A provide a summary of traditional descriptive measures, i.e., number of observations(No), minima(Min), arithmetic average(Avg), maxima(Max), and coefficient of variation(CV). In addition, a descriptive statistic, the variability factor, pertinent to the development of performance standards for pollution monitoring, is included. These tables, prepared for both daily measurements as well as 30-day averages, are statistical summaries derived from data offered by industry in response to Section 308-Questionnaires, and offered in comments on the proposed regulations. Data in these tables are representative of currently achieved pollutant discharge performance levels in the several plants presented.

Formulation of variability factors to be used in determination of limitation guidelines based upon historical performance was accomplished by employing standard statistical analysis of the data

resulting from long-term monitoring of effluent stream discharges of plants in the inorganic chemical manufacturing subcategory. In the following paragraphs are presented details of the theory and derivation of these statistical procedures, and of the resulting formulae which relate variability factors to estimated long-term parameter averages, standard deviations, coefficients of variation, and "Z-values" computed from the normal probability distribution. These details are given both for the analysis applying to daily maxima criterion and for that applying to 30-day averages.

The term "variability factor" is used in referring to the multiple of the long-term average which is used in formulating performance standards. This factor allows for variation in pollution level measurements due to sampling error, measurement error, fluctuations in the amount of the pollutant in raw materials, and other process variations.

In the recording of actual data, as reported by industrial point sources in their responses to 308 Questionnaires, certain data values were entered as "less than" detectability limits. In these cases, the sample of monitoring data has been "censored" in the process of data recording since only the threshold value has been retained (i.e., if a pollutant concentration was reported as <0.050 mg/l, the value of 0.050 mg/l was used). In the statistical analysis of monitoring data, censored values were included with measured values in the sample. This practice provides a reasonable approach, both for assessing industry's capability to perform and environmental concerns for valid pollutant limitations.

First, since censoring was done only for "less than" bounds, any bias from their inclusion would cause a slight increase in the long-term average, moderately affecting (in the direction of leniency toward industry) the estimate of long-term average pollution levels.

On the other hand, the use of censored values combined with measured values tends to reduce the variability slightly (or in the direction of less leniency toward industrial point sources). For illustration, if the sample consisted solely of censored values, the estimated long-term average might be slightly overstated. Nevertheless, the point source ought have no difficulty with the threshold or detectability limit as a performance guideline, since none of the historical data exceeded that limit.

Assumptions Concerning Daily Pollutant Level Measurements

In the formulation and calculation of the following performance standards, individual sample measurements of pollutant levels were assumed to follow the lognormal distribution, a well known and generally accepted statistical probability model used in pollution analyses. Under this assumption the logarithms of these measurements follow a normal probability model. It was also assumed that monitoring at a given plant was conducted responsibly and in such a way that resulting measurements can be considered statistically

independent and amenable to standard statistical procedures. A final assumption was that treatment facilities and monitoring techniques had remained substantially constant throughout the monitoring period.

As an indication of the appropriateness of assuming a lognormal distribution for daily measurements, the plot of the cumulative distribution of logarithms of daily effluent concentration data on normal probability paper is illustrated in Figure 8-1.

The linearity of the cumulative plot indicates the degree to which actual monitoring data are in agreement with the theoretical lognormal model for their distribution.

In addition, Figure 8-2, reproduced here from a report prepared by industry for consideration by EPA, also demonstrates the validity of the lognormal assumption for daily data.

In the analysis of daily data, the inherent variability of measured pollutant levels in the effluent stream from inorganic chemical manufacturing processes must be incorporated in calculating upper limits for daily pollutant discharge levels. Even well treated and controlled plants may experience some days when an atypically high level of pollutant discharge is present in their waste stream. To allow for this variability, performance standards must necessarily be set above the plant's long-term average performance. However, guideline limitations must be established at a level low enough to ensure adequate control. Establishing effluent guidelines that balance these factors means that occasional, infrequent instances of non-compliance are statistically predictable at well-operated and maintained treatment facilities. Since pollutant discharge is often expressed in terms of average level, it is convenient to describe standards of performance and allow variability in term of multiples of this average. Such a method of computing standards as functions of multiples of average level performance is explained below. The ratio of the pollutant standard level to the estimated long-term average is commonly called the "variability factor".

This factor is especially useful with lognormally distributed pollutant levels because its value is independent of the long-term average, depending only upon the day-to-day variability of the process and the expected number of excessive discharge periods. For a lognormal population, the variability factor (P/A), the performance standard P, and the long-term average A, are related by:

$$\ln(P/A) = S'(Z - S'/2)$$

where

- A. "ln" represents the natural logarithm (base e) of a numerical quantity.

- B. S' is the estimated standard deviation of the logarithms of pollutant level measurements. In the calculations which follow, S' is computed by the statistical procedure known as the "method of moments".
- C. Z is a factor derived from the standard normal distribution. Z is chosen to give performance limitations which provide a balance between appropriate consideration of day to day variation in a properly operating plant and the necessity to ensure that a plant is functioning properly.

The value of Z used for determining performance standards for daily measurements of pollutant concentration is chosen as $Z=2.33$. This Z -value corresponds to the 99th percentile of the lognormal distribution meaning that only 1 percent of the pollutant observations taken from a plant with proper operation of treatment facilities would be greater than the performance standard, P . Use of this percentile statistically predicts one incident of non-compliance for every 100 samples for a plant in normal operation. Many plants in this industry are required by their NPDES permits to self-monitor once per week. At this frequency, there will be 260 samples analyzed over the 5 year life of the permit. The use of the 99th percentile to establish daily maximum limitations statistically predicts 2 to 3 incidents of non-compliance per pollutant in 5 years. This percentile has been used to establish daily maximum limitations in all other guidelines proposed or promulgated, and has been used for daily maximum limitations in Inorganic Chemicals manufacturing.

A. Calculation of Variability Factors

As mentioned above, development of variability factors for daily pollution level measurements was based on the assumption that these data, (X_1, X_2, \dots, X_n) , follow a lognormal distribution. When this distribution is not a precise model, lognormally based procedures tend to somewhat overestimate variability and produce liberal standards which act to the benefit of permittees.

Following this assumption, if $Y_i = \ln(X_i)$, where $\ln(X_i)$ represents the natural logarithm or log base e of the pollution measurement, then the Y_i ; $i=1, 2, \dots, n$ are each normally distributed. If A' and S' are the mean and standard deviation of $Y = \ln(X)$ respectively, then the probability is k percent that an individual Y will not exceed $A' + ZS'$, where Z is the k -th percentile of the standard normal distribution, e.g. $Z=2.33$ is the 99th percentile of the standard normal distribution. It follows that $A' + ZS'$ is the natural logarithm of the k -th percentile of X and that the probability is k percent that X will not exceed a performance standard $P = \exp(A' + S'(Z - S'/2))$. The variability factor VF , is obtained by dividing P by A , hence,

$$VF = P/A = \exp(S'(S'/2)), \text{ and}$$

$$\ln(VF) = \ln(P/A) = S'(Z - S'/2)$$

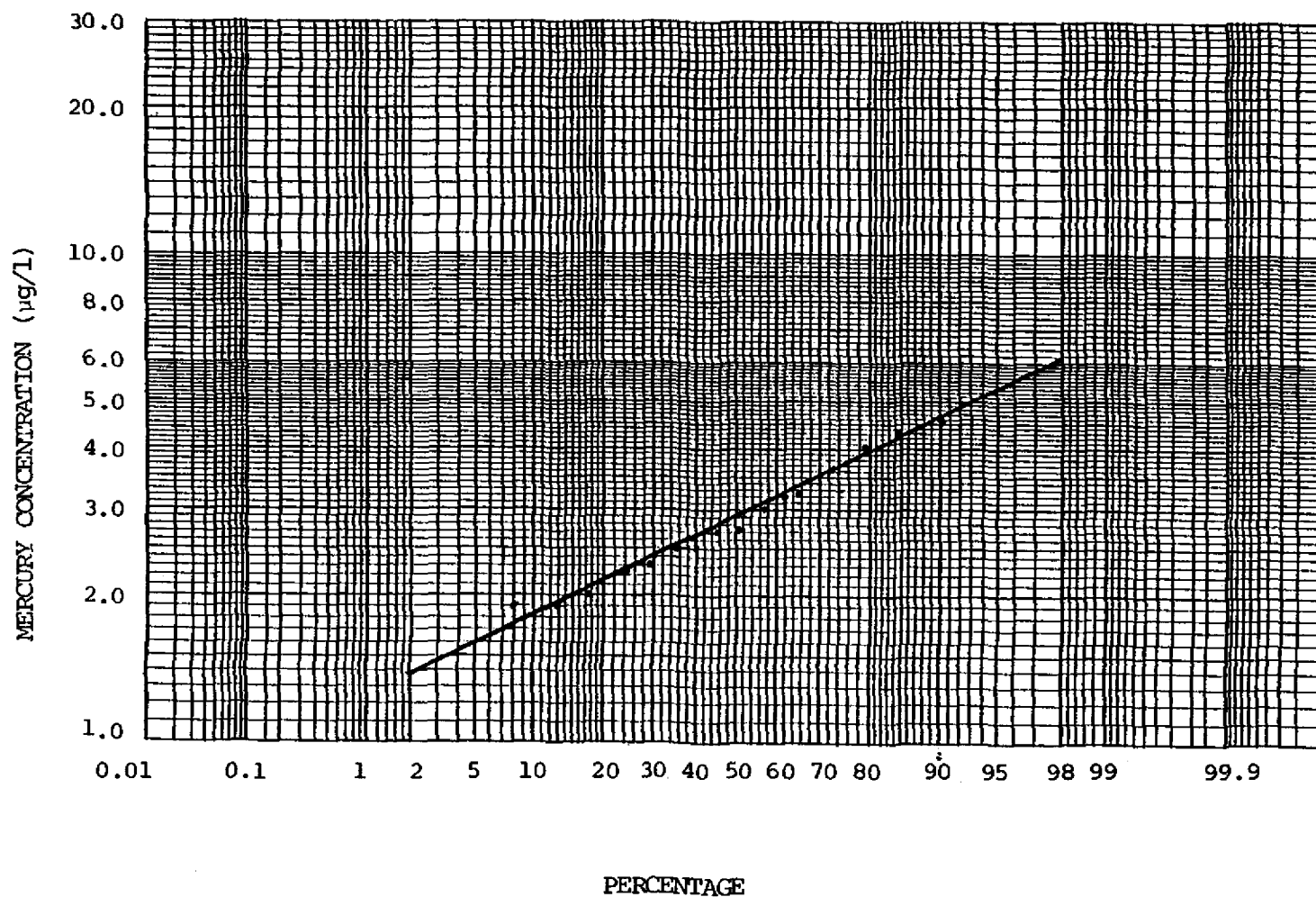


Figure 8-1. Cumulative distribution of daily concentrations of mercury in treated effluent from plant #251.

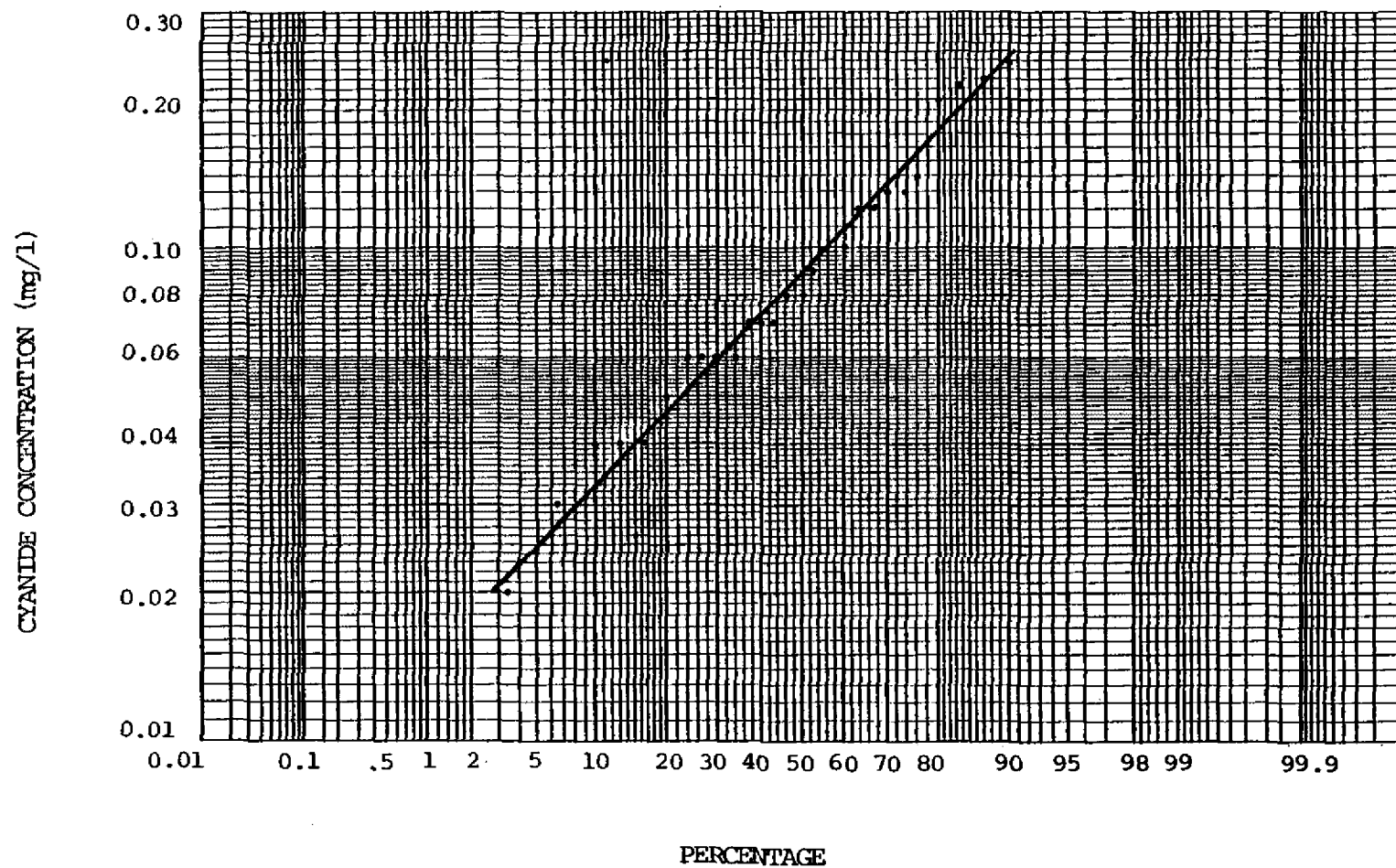


Figure 8-2. Cumulative distribution of daily concentrations of cyanide in treated effluent from plant #765.

To estimate the VF for a particular set of monitoring data, where the method of moments is used, S' is calculated as the square root of $\ln(1.0 + (CV)^2)$, where the sample coefficient of variation, $CV = S/X$, is the ratio of sample standard deviation to sample average.

B. Example Calculation of Variability Factors From Long-Term Data

Given the following descriptive statistics for a particular parameter, as might be found for lead (mg/l) in Appendix A.

No	Min	Avg	Max	CV
128	0.002	0.068	0.100	0.609

Calculate the estimated standard deviation of logarithms

$$(S')^2 = \ln(1.0 + 0.609^2) = 0.315$$

$$S = 0.56$$

Then

$$\ln(P/A) = 0.56(2.33 - 0.56/2) = 1.148$$

The variability Factor VF is,

$$VF = P/A = \exp(1.148) = 3.15$$

The performance standard P;

$$P = A(VF) = A(P/A) = (0.068)(3.15) = 0.21$$

That is, using the descriptive statistics for a pollutant presented above and the statistical approach just described, the daily maximum limitation established for that pollutant in a guideline would be 0.21 mg/l.

The statistical distributions relevant for the analysis of daily data are shown in Figure 8-3.

The statistical interpretation of P, the performance standard, is that one estimates that 99 percent (for the selected $Z=2.33$ value corresponding to the 99th percentile) of the daily pollution level measurements will not exceed P. For large data sets, P is roughly equivalent to an upper 99 percent confidence bound for an individual daily measurement.

Assumptions Concerning 30-Day Average Pollutant Level Observation

While individual pollution level measurements should be assumed lognormally distributed, that assumption is not appropriate when

analyzing 30-day averages. These averages generally are not distributed as lognormal quantities. However, for averages of daily (lognormal) measurements, a statistical principle, the "Central Limit Theorem", provides the basis for using the normal probability model. Therefore, the methods used in computing historical performance characteristics for 30-day averages differ from those used for daily samples. In this case, the sample coefficient of variation is the primary determinant of the variability factor, and there is no need to resort to logarithmic transformation. Examples of the appropriateness of this assumption is the cumulative distribution of 30-day averages shown in Figure 8-4 and 8-5. A straight line plot here on normal probability paper indicates the validity of this model.

Under these conditions, the 30-day average values (X_1, X_2, \dots, X_m), for m months behave approximately as random data from a normal distribution with mean A and standard deviation S . Therefore, the probability is k percent that a monthly X will not exceed the performance standard P , where

$$P = A + Z(S)$$

The variability factor is

$$VF = P/A = 1.0 + Z(S/A) \text{ and will be estimated by}$$

$$VF = 1.0 + Z(CV)$$

Where

- A. Z is a factor derived from the standard normal distribution. If one wishes a performance standard based upon expecting 95 percent of monthly averages to be within guidelines, then $Z=1.64$ should be used.
- B. CV is the estimated coefficient of variation of the 30-day averages and is computed by S_x/X , the ratio of standard error of sample means to overall or grand average of monthly averages.

Calculation of Variability Factors

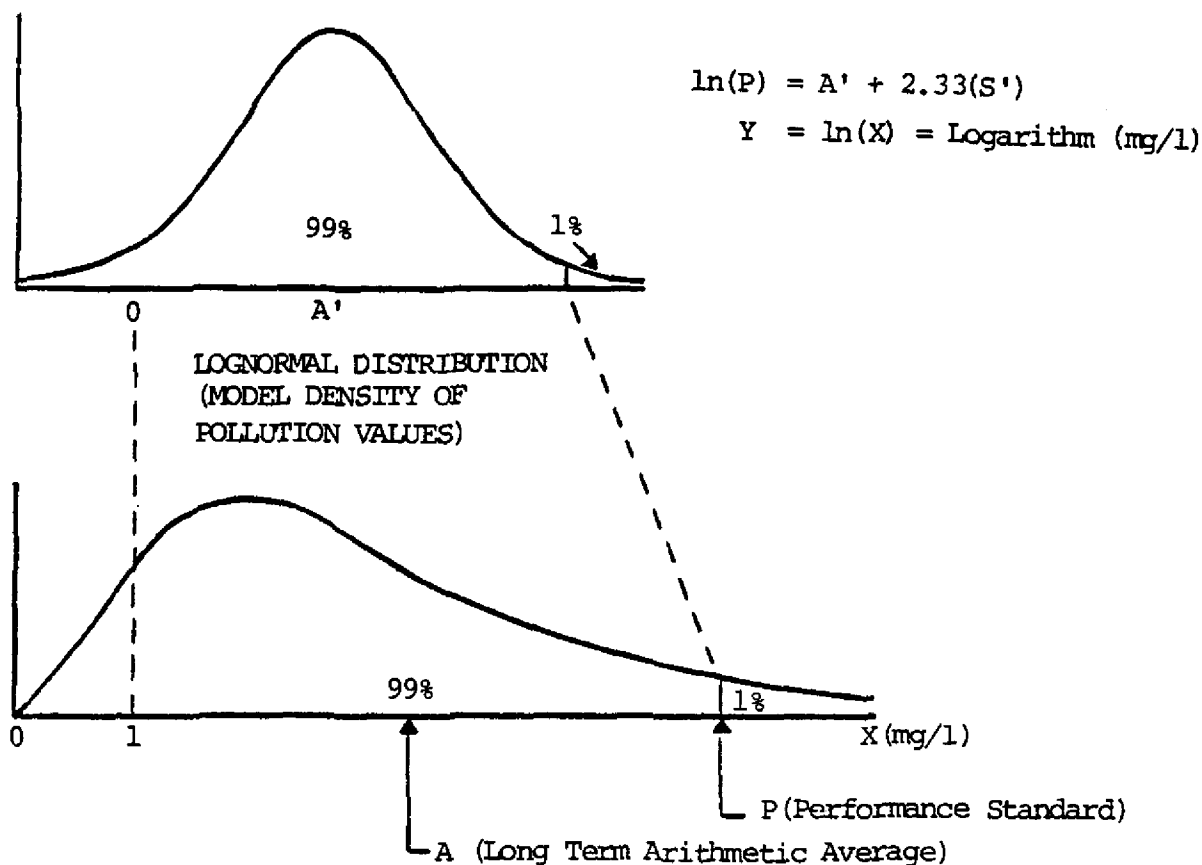
A sample calculation of 30-day average variability factor is shown below. The descriptive statistical data is for zinc (mg/l) from Appendix A.

No	Min	Avg	Max	CV
30	0.010	0.151	0.815	1.03

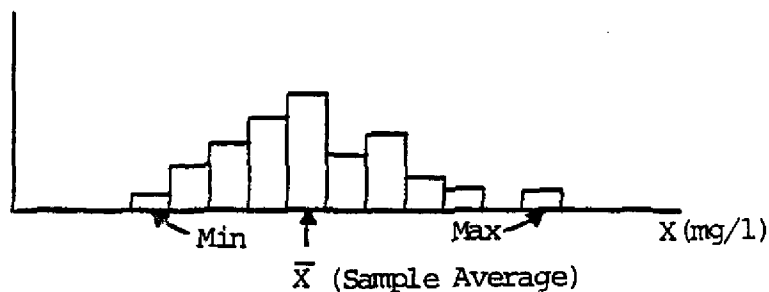
$$VF = 1 + Z(CV) = 1.0 + 1.64(1.03) = 2.7$$

$$P = A(VF) = (0.151)(2.7) = 0.41$$

NORMAL DISTRIBUTION
(MODEL DENSITY OF LOGARITHMS OF POLLUTION VALUES)



SAMPLE DISTRIBUTION OF N MEASUREMENTS
(LONG TERM MONITORING DATA)



Note: (a) S' is estimated as $(S')^2 = [\ln(1 + CV^2)]$

$$CV = S/\bar{X}$$

$$S^2 = \sum (X - \bar{X})^2 / (N-1)$$

$$\bar{X} = \sum X / N$$

Figure 8-3. Statistical distribution for daily pollution measurements.

That is, the maximum 30-day average effluent limitation derived from the descriptive statistics above would be 0.41 mg/l for that pollutant.

Given the previous descriptive statistics for a particular sample, one obtains the performance standard P , by multiplying the mean of the 30-day averages in the data set by VF . An appropriate statistical interpretation is that, for the selected value of $Z=1.64$ corresponding to the 95th percentile of a normal distribution, one estimates that 95 percent of the 30-day average pollution level measurements will not exceed P , or in other words, the statistics predict up to 3 incidents of non-compliance with the 30-day average per pollutant over the 5 year (60 month) life of a permit at a well-operated and maintained treatment facility. This is essentially the same number of predicted incidents of non-compliance as was predicted for daily maximum limitations derived using the 99th percentile confidence level (see above).

In developing the statistical derivatives for monthly averages, in many cases, a full 30 days of daily average determinations were not available. In the above example, the monthly average is based on four data points taken during the month. The standard deviation is then derived from these "monthly" averages assuming a normal distribution for the population of averages. Permits are usually written on the basis of monthly averages obtained from fewer than 30 data points per month. The use of "monthly" averages rather than 30-day averages results in a higher variability and, hence, a higher performance standard than would be attained using 30-day averages based on 30 data points per month.

Figure 8-6 shows the relationship between the normal probability model and frequency distribution of 30-day averages.

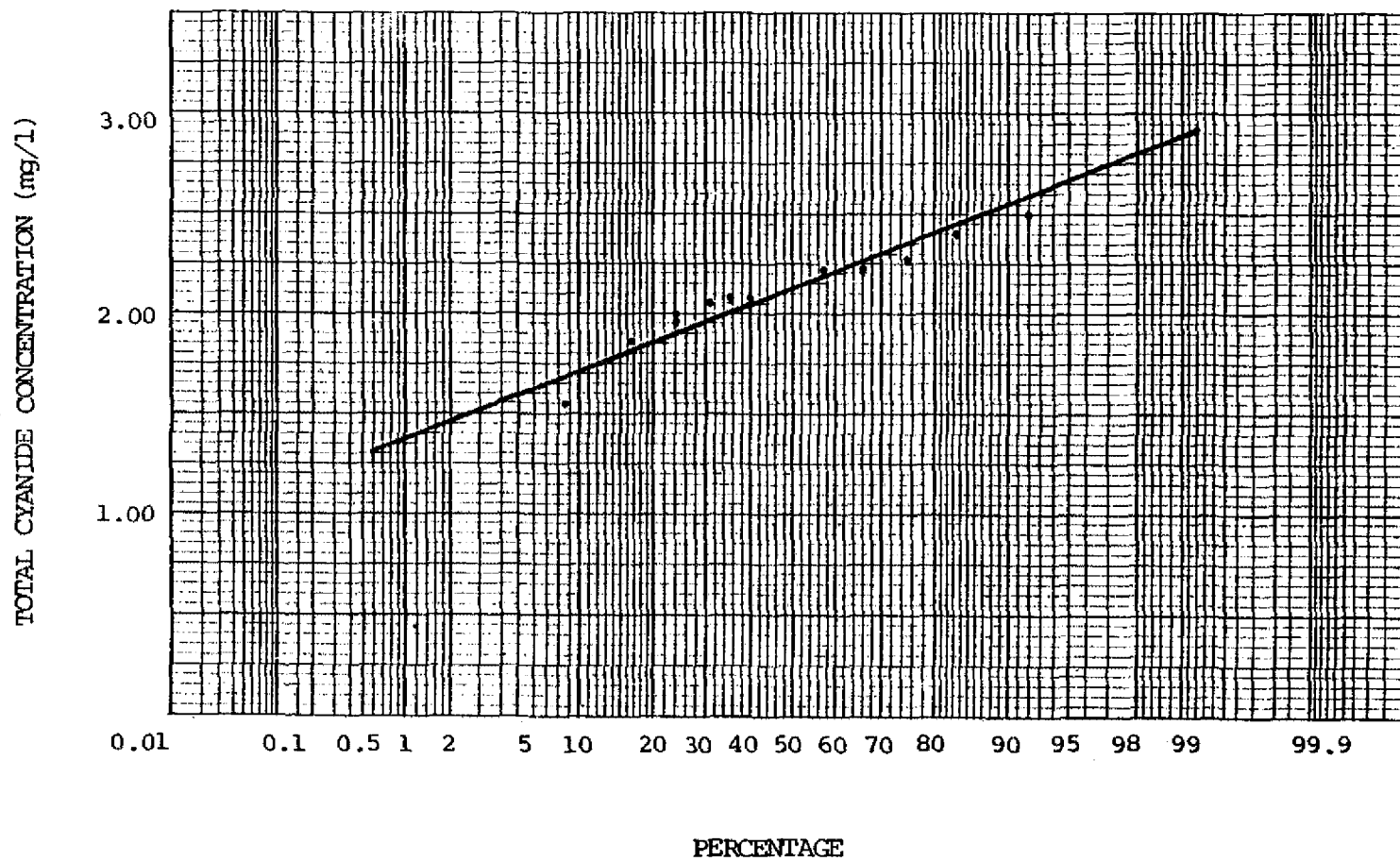


Figure 8-4. Cumulative distribution of 30-day averages of total cyanide in treated effluent from plant #782.

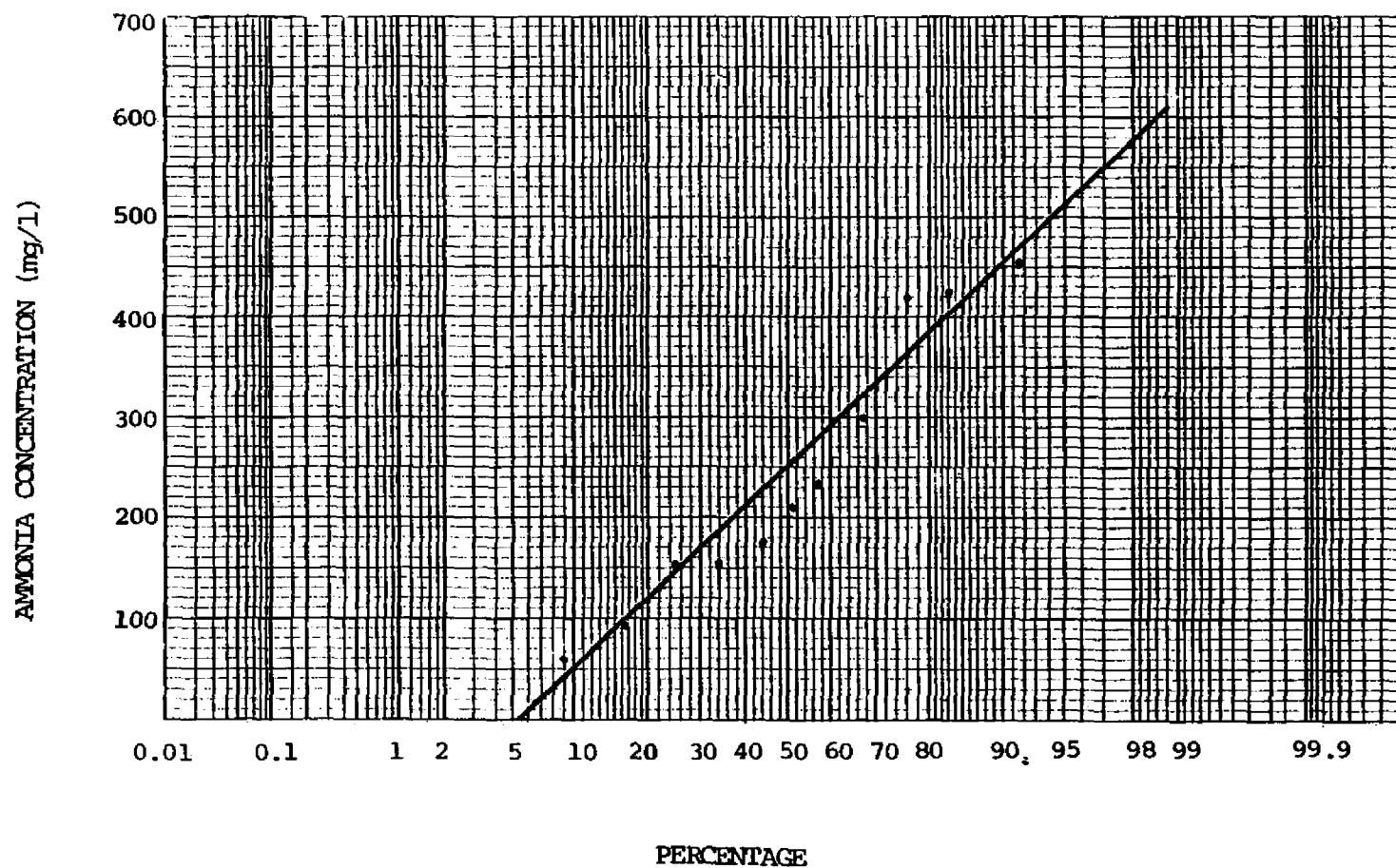
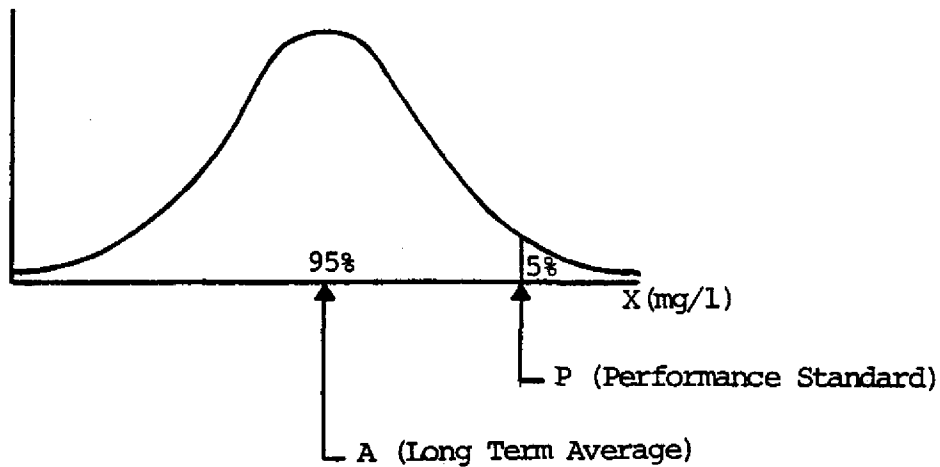
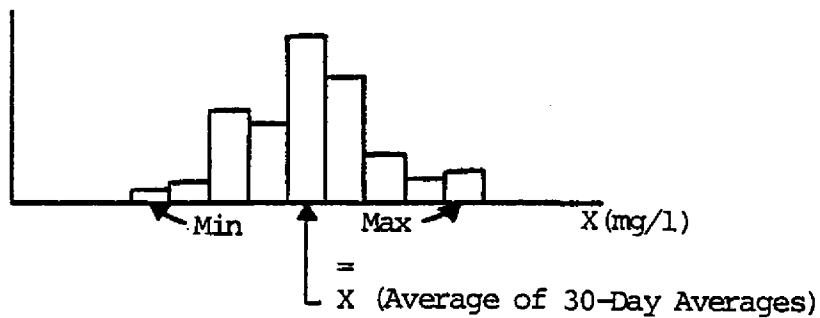


Figure 8-5. Cumulative distribution of 30-day averages of ammonia in treated effluent from plant #782.

NORMAL DISTRIBUTION
(MODEL DENSITY OF 30-DAY AVERAGE POLLUTION MEASUREMENTS)



SAMPLE DISTRIBUTION OF M MONTHLY AVERAGES
(LONG TERM MONITORING DATA)



Note: (a) $P/A = 1 + 1.64 (CV)$

$$CV = S_{\bar{X}} / \bar{X}$$

$$(S_{\bar{X}})^2 = (\sum (\bar{X} - \bar{\bar{X}}) / (M-1))$$

$$\bar{\bar{X}} = \sum \bar{X} / M$$

Figure 8-6. Statistical distributions for 30-day average pollution measurements.

SECTION 9

TREATMENT TECHNOLOGY APPLICATIONS FOR TOXIC POLLUTANT REMOVAL

Selection of Pollutants to be Controlled

In order to determine which toxic pollutants, if any, may require effluent limitations, the pollutants observed in each subcategory were evaluated with regard to their treatability and potential environmental significance on the basis of the raw waste concentrations and mass loadings found during screening and verification. In an attempt to prioritize the need for regulation the toxic metals were divided into two groups:

Group 1 - Those priority pollutants which appear at concentration levels that are readily treatable using available technology.

Group 2 - Other treatable and/or potentially treatable priority pollutants observed in the subcategory. These include toxic metals which exist at concentrations below the minimum treatability limit and above the minimum detection level. The Group 2 pollutants would be controlled by the same treatment technology used to control the Group 1 pollutants.

Table 9-1 presents the significant toxic pollutant metals found in each group. In general, those metals occurring in the first group are of prime concern and require regulation, while those occurring in the second group are of somewhat less concern and are not expected to require regulation. Metals in Group 2 are effectively controlled by the technologies used to control the metals in Group 1, which are the two or three dominant metals in the raw waste load and are directly related to the particular product or process involved.

Application of Advance Level Treatment and Control Alternatives

General Design Objectives

Beginning with Section 11 of this document, the selection and application of toxic pollutant treatment and control technology for model plant systems for each of the regulated subcategories are described. Several levels of treatment are indicated. Level 1 represents existing BPT treatment systems and the advanced levels (Level 2, 3, etc.) are the selected technologies for step-wise improvements in toxic pollutant removal over that achieved by the BPT system. Flow diagrams show BPT components as a starting point for advanced level treatment additions and incremental cost estimates.

For both existing and new sources, the advanced level technology options are selected as candidates for BAT with toxic pollutant removal as the primary objective. Although the advanced level systems chosen also give improved performance over the Level 1 (BPT) systems

TABLE 9-1. PRIORITIZATION OF TOXIC POLLUTANTS FOUND IN EACH SUBCATEGORY

SUBCATEGORY	Group 1(1)	Group 2(2)
Chlorine-diaphragm cell	Copper Lead Nickel	Antimony Arsenic Cadmium Chromium Mercury Selenium Thallium Zinc
Chlorine-mercury cell	Mercury	Antimony Arsenic Cadmium Chromium Copper Lead Nickel Silver Thallium Zinc
Hydrofluoric Acid	Nickel Zinc	Antimony Arsenic Cadmium Chromium Copper Lead Mercury Selenium Thallium
Titanium Dioxide - Chloride Process	Chromium	Lead Nickel Zinc
Titanium Dioxide - Sulfate Process and Chloride Ilmenite Process	Chromium Nickel	Antimony Arsenic Cadmium Copper Lead Selenium Thallium Zinc

(1) Group 1 - dominant raw waste pollutants selected as control parameters for the effluent limitations or guidance.

(2) Group 2 - secondary raw waste pollutants found less frequently and at lower concentrations. These pollutants have not been selected as control parameters but are expected to receive adequate treatment as a result of controlling the Group 1 pollutants.

TABLE 9-1 Continued

SUBCATEGORY	Group 1	Group 2
Aluminum Fluoride	Copper Nickel	Arsenic Cadmium Chromium Mercury Zinc
Chrome Pigments	Chromium Lead Zinc	Antimony Cadmium Copper Cyanide Mercury Nickel
Hydrogen Cyanide	Cyanide	None
Sodium Dichromate	Chromium Nickel	Copper Selenium Silver Zinc
Copper Sulfate	Copper Nickel Selenium	Antimony Arsenic Cadmium Chromium Lead Zinc
Nickel Sulfate	Copper Nickel	Antimony Arsenic Cadmium Chromium Lead Mercury Selenium Thallium Zinc
Sodium Bisulfite	Chromium Zinc	Antimony Cadmium Copper Lead Mercury Nickel

for the removal of conventional and nonconventional pollutants, this is regarded as a secondary design objective.

Pretreatment Technology

Since untreated heavy metal ions will either pass through the treatment provided in a typical POTW, or will be precipitated with the POTW solid residue, pretreatment of wastes containing significant amounts of heavy metals is necessary. As a general rule, alkaline precipitation, followed by settling and removal of the solids will suffice. In certain subcategories, such as the chlorine industry, specific treatment will be required for highly critical constituents (such as mercury and lead). Normally the Level 1 and 2 model treatment processes shown in the following subsections will be appropriate for pretreatment prior to discharge to a POTW. Pass-through would occur in the absence of pretreatment when BPT and BAT treatment would reduce toxic metal concentrations by a greater percent than is achieved by a POTW.

New Source Performance Standards

New Source Performance Standards are at least equal to BAT. In a few cases where new plants have the opportunity to design systems for better toxic removal performance without expensive retrofitting the higher technology systems have been used as a basis.

Estimated Achievable Performance Characteristics for Advanced Level Applications

Advanced level control and treatment alternatives for reduction of pollutant discharges and their applicability to each subcategory are presented in the sections dealing with individual products. With few exceptions, these alternatives were selected specifically for removal of priority pollutants and were designed for end-of-pipe treatment.

Treatment technologies practiced outside the industry are recommended when appropriate and, in most cases, apply to the removal of toxic pollutant metals. The estimated 30-day average treatability levels (Section 8, Table 8-11), long-term data parameters, and the screening and verification results are all utilized in the development of estimated performance characteristics for the indicated treatment applications in each subcategory.

Advanced Level Removal of BPT Pollutants

Performance estimates for these systems, when possible, were based on effluent quality achieved at plants currently practicing these technologies. However, in most cases, the advanced levels are not currently being practiced within the specific subcategory of concern, and performance information from other appropriate sources is necessarily utilized.

When established wastewater treatment practices, such as clarification or filtration, form a part of advanced treatment alternatives, the specified achievable effluent quality has been based on concentrations accepted as achievable through proper design and control. The prime example of this is suspended solids reduction by filtration.

Advanced Level Removal of Toxic Pollutants

Performance estimates for toxic pollutants were also based, when possible, on effluent quality achieved at plants currently practicing these technologies. However, in most subcategories, toxic pollutant analyses are not conducted unless a specific pollutant is regulated and requires monitoring. Where transfer of technology is applied as a treatment alternative, performance estimates for toxic pollutant removals were based on the demonstrated performances in other industries while incorporating allowances for specific differences in process waste characteristics and operating conditions. Statistically derived long-term monitoring data parameters were described in Section 8 and are compiled in tabular form in Appendix A. The screening and verification data are used to supplement the available long-term data applied to each subcategory. A judgment is made whether the screening and verification data represent a well-performing system or one which is not performing at its technological potential. For a well-performing system, the data are regarded as representative of long-term averages and are compared with the estimated treatability ranges from Table 8-11, as well as the 30-day averages developed from the long-term data. In this manner, the performance estimates for each pollutant, at each treatment level for the nonexcluded subcategories, are developed and presented in tabular summaries. By starting with the estimated achievable long-term averages, the specific variability factor ratio derived for each pollutant is used to estimate the maximum 30-day average and daily maximum values.

The model plant waste flow per unit of production is then taken to calculate the estimated mass emission values of the 30-day average and daily maximum limits for each pollutant to be controlled.

Pollution Control Parameters to be Regulated

Conventional Pollutants

Wastewater quality parameters which are identified as conventional pollutants include the following:

- pH
- Total Suspended Solids (TSS)
- Biochemical Oxygen Demand, 5-Day (BOD-5)
- Fecal Coliform
- Oil and Grease

Only the first two parameters (pH and TSS) in this group have been selected for regulation in the Inorganic Chemicals Manufacturing Point Source Category. For direct dischargers, the pH range of 6 to 9 has

been established as the general control limitation and the permissible frequency and duration of excursions beyond this range is to be specified in individual plant discharge permits. The limitations of TSS are specified for both BPCTA and NSPS-based regulations, the former being largely a function of industry performance and the latter stemming from treatability estimates with the appropriate technologies.

Nonconventional Pollutants

The wastewater quality parameters classified as nonconventional pollutants include the nontoxic metals such as aluminum, boron, barium, and iron along with chemical oxygen demand (COD), total residual chlorine, fluoride, ammonia, and nitrate, etc. Of these, only iron, COD, total residual chlorine, fluoride, and ammonia are considered for regulation in the inorganic chemicals industry. Due to its toxicity, chlorine would be controlled in direct discharges, but it is excluded from control in pretreatment regulations because influent to POTW's is often chlorinated. A similar argument is made for the control of ammonia, that is, POTW's can use ammonia as a source of essential nutrients. However, since many POTW's are only capable of about 20 percent ammonia removal, both direct discharge and pretreatment regulations would specify ammonia limitations. Similarly, the type of COD found in inorganic chemical industry discharges may not be amenable to biochemical oxidation in a POTW. In addition, compounds which contribute to the COD are likely to create odor and corrosion problems in sewer systems. Therefore, its control would also be retained in pretreatment regulations. Fluoride control is also required for both direct and indirect discharges largely because the most practical technology for fluoride removal (precipitation as calcium fluoride) must be applied to relatively concentrated wastewater sources. This treatment method achieves removal levels which at best are still unacceptable for direct municipal or agricultural water uses. POTW's are not effective for fluoride removal and unless sufficient dilution occurs prior to the reuse of the water, special techniques (e.g., adsorption on activated alumina) would have to be applied for further fluoride removal.

Toxic Pollutants

The toxic pollutants found at significant levels during screening and verification are listed by subcategory in Table 9-1. Out of these, toxic pollutant control parameters were selected largely on the basis of treatability. Since several toxic pollutants may be controlled by a common treatment technology, it is possible to select one or more control parameters which will act as a surrogate for others exhibiting the same treatability characteristics. Treatment system operating conditions would normally be optimized for the removal of the specified control parameters which would be monitored on a regular basis. The other toxic pollutants would be monitored much less frequently as a periodic check of the effectiveness of surrogate control.

The following toxic pollutants have been designated as control parameters in this point source category:

- Cadmium
- Chromium (Total)
- Copper
- Cyanide (amenable to chlorination)
- Lead
- Mercury
- Nickel
- Selenium
- Zinc

The specific control parameters selected for each subcategory are presented in the tables entitled "Effluent Limitations" in the sections of this report dealing with the individual industries. Some general comments about them are given here.

The most common technology applied in industry for the removal of chromium from wastewaters involves a reduction step, whereby Cr (VI) in solution is converted to the less toxic Cr (III) form which can then be removed by alkaline precipitation. The efficiency of this treatment depends upon the presence of an excess reducing agent and pH control to drive the reduction step to completion. When treated effluent samples are taken to monitor residual Cr (VI) and total chromium levels, the analytical results for Cr (VI) are subject to several factors which adversely affect the accuracy and reproducibility of the diphenylcarbazide (DPC) colorimetric method. The problem is not so much one of analytical interferences with the Cr (VI) - DPC color development, but rather the actual changes in Cr (VI) concentration that can take place during sampling, sample preservation and storage, and analysis. The major cause of such changes is the presence of an excess reducing agent in the treated effluent. This tends to give false low readings for Cr (VI) although in some cases the opposite may occur as a result of sample preservation and storage under acidic oxidizing conditions.

Thus, in view of the questionable reliability of the presently accepted Cr (VI) monitoring procedure, total chromium, Cr (T), is recommended as the control parameter to be used in the inorganic chemicals industry. The adequacy of Cr (T) as a control parameter is predicated on its effectiveness as a surrogate for Cr (VI) control. Since the concentration of Cr (T) represents the summation of all forms of chromium normally found in solution or suspension including Cr (VI), the final concentration of Cr (T) in a treated effluent is dependent on the effectiveness of both the reduction and the alkaline precipitation steps. In this way, the use of Cr (T) as the control parameter assures that adequate removal of Cr (VI) is being achieved as a direct consequence of the treatment technology required.

SECTION 10

COSTS OF TREATMENT AND CONTROL SYSTEMS

Introduction

Purpose of Cost Data

More complex treatment methods and higher levels of pollutant removal are reflected in increased costs of equipment, energy, labor and chemicals. At some point, the increasing costs of treatment will outweigh the benefits of such treatment. Therefore, it is important that for each subcategory the Agency know the base cost and the incremental costs of each level of treatment which it might prescribe. These "options" of internal costs, which are the industry's annual costs of providing the necessary waste treatment, will result in related increases in product costs, which are termed external costs. Thus annual costs of waste treatment are expressed in terms of dollars per unit of annual production of the principal product.

Plant visits revealed very few treatment plants serving a single product manufacturing line, therefore, it was not feasible to seek actual waste treatment facilities which could serve as real models for estimating purposes. Accordingly, the cost data were taken from similar construction projects by the contractor, and from unit process equipment costs assembled from vendors and other commercial sources. Based on the level of supporting details and scope definition, the accuracy range of the cost estimates is expected to be minus 15 to plus 25 percent.

Actual costs incurred by individual plants may be more or less than the presented model plant costs. The major causes of variability are:

- Wastewater treatment combined with the treatment of other product effluents.

- Site dependent conditions, as reflected in piping lengths, climate, land availability, water and power supply and the location of the points of final discharge and solids disposal.

- Material (reagent) costs, due to variation in availability and distance from the source.

- Flow rate of wastewater to be treated.

The construction costs are expressed in mid-1978 dollars. The investment costs and the annual costs given in the preamble to the regulation are expressed in 1981 dollars, and were updated from 1978 dollars using the Department of Commerce Composite Index for Construction Costs.

General Approach

Since few single product waste treatment plants were available for detailed study, the costs presented in this section are based on model plants which closely resemble the types and capacities of waste treatment facilities needed for each separate product subcategory. The model plant selections are based on review of Section 308-Questionnaire responses, plant visits, development documents, contacts with the industries to verify treatment practices and to obtain data on size, wastewater flow, and solid waste disposal systems. Thus, each model is synthesized from actual data as a typical plant in its subcategory with a level of waste treatment equivalent to BPT. Variations in treatment plant capacity are accounted for by selecting sets of models which represent the range of existing production plant capacities in the subcategory; large, medium, and small. Thus, the model plants are not set up as exemplary plants, but as typical plants of adequate design which represent the range of plants and treatment facilities found in the subcategory.

Cost References and Rationale

Cost information contained in this report was obtained directly from industry, engineering firms, equipment suppliers and current experience of the contractor. Costs are based on similar industrial installations or engineering estimates. Cost estimates have been developed from either current costs for similar plants or from general cost estimates.

Treatment costs are based on model production plant characteristics which determine the treatment processes selected for each operation. Under set effluent limitations, treatment costs are primarily functions of the pollutant load (i.e., kg/kg of product) and wastewater flow rate (i.e., cubic meters/day). Available data indicate that both pollutant loads and flow rates can vary significantly among plants manufacturing the same product.

Definition of Levels of Treatment and Control Cost Development

For the purpose of establishing the base level treatment costs, each industry is assumed to be practicing Best Practicable Control Technology Currently Available (BPT), for the EPA pollutants (conventional and nonconventional, as well as some of the toxic metal pollutants) which are specified for each subcategory. The investment costs and annual costs of such BPT systems are shown in this report as either the Base Level, Level 1, or BPT costs. This level of treatment may also provide incidental removal of additional toxic pollutants not previously specified in the regulations.

The advanced treatment level (BAT) is aimed primarily at reduction of toxic pollutants to levels considered acceptable for July 1, 1984 performance, utilizing Best Available Technology Economically Achievable (BAT) at incremental investment and annual costs beyond those shown for Level 1 (BPT). For example, for Level 2 (BAT)

treatment, the incremental cost as given in the table is directly added to Base Level 1 or BPT cost to obtain the total cost of the treatment system. The wastewater treatment flow diagrams for the advanced treatment levels, as given in this report, also include the flow diagram for Level 1 (BPT) treatment.

Treatment and Disposal Rationale Applied to Cost Development

The following assumptions are employed in the cost development:

- A. Noncontact cooling water generally is excluded from treatment (and treatment costs) provided that no pollutants are introduced.
- B. Water treatment, cooling tower and boiler blowdown discharges are not considered process wastewater unless such flows contain significant amounts of pollutants.
- C. Sanitary sewage flow is excluded.
- D. The plants are assumed to operate 24-hours per day, 350 days a year, except where otherwise noted.
- E. Manufacturing plants are assumed to be single product plants.
- F. The inorganic chemical industry extensively uses in-plant control techniques such as in-process abatement measures, housekeeping practices, and recycling of process wastewaters to recover valuable materials or use these materials as feed for other by-products. Segregation of uncontaminated cooling and other waters prior to treatment and/or disposal, and other similar measures can contribute to waste load reduction. All such costs have not been included in the cost estimates.
- G. Excluded from the estimates are any costs associated with environmental permits, reports or hearings required by regulatory agencies.

Expression of Costs

The estimated costs for all treatment systems are expressed in mid-1978 dollars to construct appropriate facilities for each single product manufacturing subcategory at various production rates. Total costs are given for the BPT and NSPS systems while incremental costs are given for a BAT system.

Where a single product plant produces more than one waste stream requiring treatment, the respective investment and annual costs are the combined costs of all treatment.

Total annual costs per metric ton of product are shown in the summaries for each product subcategory.

A. Direct Investment Costs for Land and Facilities

Types of direct investment costs for waste treatment facilities and criteria for estimating major components of the model plants are contained in the following subsections:

1. Site Development Costs - These include clearing the site, all earthwork and site improvements. The lagoon costs are based on the excavation and backfill required to construct multiple rectangular lagoons with common dikes to permit alternate dewatering for sludge removal by the clamshell method. They are also based on reasonably level sites being available, consisting of sandy loam with high clay content, and no large rocks or rock formations. Lagoons are unlined, excepting where contents are highly acidic. Where lining is required, hypalon or clay is used.

Site improvements include local drainage, fencing, and roads. Road costs are based on graded and graveled service roads only within the boundaries of the plant and not for access. Perimeter fencing is supplied for the lagoons and for the sludge disposal site.

2. Equipment Costs - This is the installed cost of all equipment except the monitoring system (considered elsewhere). Depending upon the method of treatment, equipment for wastewater treatment consists of a combination of items such as pumps, aerators, chemical feed systems, agitators, flocculant feed systems, tanks, clarifiers, thickeners, filters, etc. Costs for these items were obtained from vendors' verbal quotations and were based on contractors' experience with procurement of similar items. Enclosures are provided for critical equipment and controls.

Chemical storage, feeders and feedback equipment include such items as probes, instruments, controls, transmitters, valves, dust filters and accessories. Bulk chemical storage bins are designed to hold a standard bulk truck load, plus five day's needs, between ordering and delivery. Critical pumps are furnished in duplicate and when clarifiers are used, the flow is split between two units, permitting one to be bypassed for repairs. Single units are used for small flows, batch treatment and intermittent service.

Added to the cost of the equipment itself, is the corresponding installation labor, as well as the material and labor costs for concrete, structural steel, piping, instrumentation, and electrical work. The labor costs include all pro-ratable elements of "indirect" costs such as fringe benefits, payroll insurance and taxes, construction equipment, temporary construction facilities, field staff, etc. The hours and unit costs for the labor are based on

Los Angeles or Gulf Coast type productivity using union craft labor.

In some subcategories, a portion of the wastewater is returned to the process from an intermediate treatment step. In such cases, the estimated investment cost of the reuse pumps are included as part of the equipment cost. However, the return piping, accessories, operating and maintenance costs are considered as water supply costs.

3. Monitoring Equipment - In this report, it is assumed that flow and pH monitoring equipment will be installed at the treated effluent discharge point. It will consist of an indicating sensor and recorder, alarms and controls and an automatic sampler.
4. Land - Land availability and cost of land can vary significantly, depending upon geographical location, degree of urbanization and the nature of adjacent development. Land for waste treatment, and in some cases for inert solids disposal, is assumed to be contiguous with the production plant site and reasonably convenient to a waterway which can receive permitted discharges of wastewater. Where inert solids are retained at the plant site, enough land is included in the base level model plant investment cost to accept residual solids for a normal operating period of ten years at the same production rate for which the plant is sized.

For the purpose of this report, land for lagoons, treatment facilities, and on-site residual waste disposal is valued at \$30,000 per hectare (\$12,000 per acre).

B. Investment Costs for Supporting Services

1. Contractor's Overhead and Profit - The construction contractor's fixed or "overhead" expenses and profit are estimated as fifteen percent of the installed plant cost.
2. Engineering - This includes the design and inspection services to bring a project from a concept to an operating system. Such services broadly include laboratory and pilot plant work to establish design parameters, site surveys to fix elevations and plant layout, foundation and ground water investigations, and operating instructions; in addition to design plans, specifications and inspection during construction. These costs, which vary with job conditions, are often estimated as percentages of construction cost, with typical ranges as follows:

Preliminary survey and construction
surveying

1 to 2%.

Soils and groundwater investigation	1 to 2%
Laboratory and pilot process work	2 to 4%
Engineering design and specifications	7 to 12%
Inspection and engineering support during construction	2 to 3%
Operation and maintenance manual	1 to 2%

From these totals of 14 percent to 25 percent, a midvalue of 20 percent of in-place construction (installed equipment and construction) costs has been used in this study to represent the engineering and design costs applied to model plant cost estimates. These costs include, in addition to the professional service hours, the costs for expenses such as telephone, reproductions, computer services, and travel fees.

3. Contingency - This is an allowance of 10 percent applied to the estimated total investment cost, excluding land, based on the status of engineering, design and specifications, quality of prices used, and the anticipated jobsite conditions. This covers design development, (but not scope), errors and omissions, impact of late deliveries and unusually adverse weather conditions, variations in labor productivity and other unforeseen difficulties during construction.

C. Operation and Maintenance Costs

Annual operation and maintenance costs are described and calculated as follows:

1. Labor and Supervision Costs - Plant operations are assumed to be conducted 24-hours per day 350 days per year, with attendance for only part of each working day. For batch wastewater treatment systems, adjustments are made for the number of working days in a year. Personnel costs are based on an hourly rate of \$20.00. This includes fringe benefits and an allocated portion of costs for management, administration, and supervision.

Personnel are assigned for specific activities as required by the complexity of the system, usually 4 to 12 hours per day.

2. Energy Costs - Energy (electricity) costs are based on the cost of \$306.00 per horsepower operating 24 hours per day and 350 days per year. For batch processes, appropriate

adjustments are made to suit the production schedule. The cost per horsepower year is computed as follows:

$$Cy = 1.1 (0.7457 \text{ HP} \times \text{Hr} \times \text{Ckw}) / (E \times P) \quad (1)$$

Where:

Cy = Cost per year
 HP = Total horsepower rating of motor (1 hp = 0.74557 kw)
 E = Efficiency factor (0.9)
 P = Power factor (1.00)
 Hr = Annual operating hours (350 X 24 = 8400)
 Ckw = Cost per kilowatt-hour of electricity (\$0.040)

The 1.1 factor in equation (1) represents allowance for incidental energy used such as lighting, etc. It is assumed that no other forms of energy are used in the waste treatment system.

3. Chemicals - Prices for the chemicals were obtained from vendors and the Chemical Marketing Reporter. Unit costs of common chemicals delivered to the plant site are based on commercial grade of the strengths of active ingredient percentages as follows:

Hydrated Lime (Calcium Hydroxide)	Bulk	\$ 80/metric ton
	Bag	\$ 85/metric ton
Quicklime	Bulk	\$ 70/metric ton
Ground limestone		\$13.20/metric ton
Soda Ash (58% Bulk)		\$ 85/metric ton
Caustic Soda (58% NaOH)		\$200/metric ton
Sodium Sulfide (60-62%)		\$435/metric ton
Sulfuric Acid		\$ 75/metric ton
Hydrochloric Acid (32%)		\$ 70/metric ton

Aluminum Sulfate (56% Alumina)	\$250/metric ton
Flocculant (Polymer)	\$2.00/kg
Sulfur Dioxide (Ton Containers)	\$335/metric ton
Chlorine (Ton Containers)	\$220/metric ton
Sodium Bisulfide (72-74%)	\$385/metric ton
Ferrous Sulfate	\$ 70/metric ton
Diatomaceous Earth	\$0.30/kg
Activated Carbon	\$2.00/kg

4. Maintenance - The annual cost of maintenance is estimated as 10 percent of the investment cost, excluding land.
5. Taxes and insurance - An annual provision of three percent of the total investment cost has been included for taxes and insurance.
6. Residual waste disposal - Sludge disposal costs can vary widely. Chief cost determinants include the amount and type of waste, and the choice of either on-site disposal or contract hauling which depends on the size of the disposal operation and transport distances. Off-site hauling and disposal costs are taken as \$13.00 per cubic meter (\$10.00 per cubic yard) for bulk hauling, with appropriate increases for small quantities in steel containers. For on-site disposal from lagoons, a clamshell at \$600.00 and front end loader at \$300.00 per disposal day are used. For very large sludge quantities, lower unit costs have been assumed. The computed sludge quantities are spread on land valued at \$12,000 per acre.
7. Monitoring, analysis, and reporting - The manpower requirements covered by the annual labor and supervision costs include those activities associated with the operation and maintenance of monitoring instruments, recorders, and automatic samplers as well as the taking of periodic grab samples. Additional costs for analytical laboratory services have been estimated for each subcategory assuming that sampling takes place three times a week at the point of discharge and that an analytical cost of \$20.00 per constituent is incurred. Approximately 10 percent of the total analytical cost has been added for quality control and water supply samples. Unless otherwise stated, continuous compliance monitoring at the BPT level are based on the determination of four constituents. At the advanced (BAT) levels, the determination of six constituents is assumed. A reporting cost of \$1,500 per year is added for clerical

support. Monitoring costs for periodic batch treatments are reduced in proportion to the number of days per year when discharges occur.

D. Amortization

Annual depreciation and capital costs are computed as follows:

$$CA = B (r(1 + r)^n)/((1 + r)^n - 1) \quad (2)$$

Where:

- CA = Annual Cost
- B = Initial amount invested excluding cost of land
- r = Annual interest rate (assumed 10 %)
- n = Useful life in years

The multiplier for B in equation (2) is often referred to as the capital recovery factor, and is 0.1627 for the assumed overall useful life of 10 years. No residual or salvage value is assumed.

E. Items Not Included in Cost Estimates

Although specific plants may encounter extremes of climate, flood hazard and availability of water, the costs of model plants have been estimated for average conditions of temperature, drainage and natural resources. It is assumed that any necessary site drainage, access roads, water development, security, environmental studies and permit costs are already included in production facilities costs.

Therefore, the model costs are only for facilities, supplies and services directly related to the treatment and disposal of waterborne wastes, including land needed for treatment and on-site sludge disposal. Air pollution control equipment required by the Clean Air Act is not included. It was also assumed that all required utilities are provided at the edge of the plant site and the existing plant's capacities are capable of supplying the requirements. RCRA costs have not been included. RCRA costs are considered in the Economic Impact Analysis of Pollution Control Technologies for Segments of the Inorganic Chemicals Manufacturing Industry, EPA 440/2-81-023, which were developed in part from information in "Contractor Report on RCRA ISS Compliance Costs for Selected Inorganic Chemicals Industries."

Dust collectors normally associated with package treatment, chemical transfer and feeding systems are included. Raw wastes from various sources are assumed to be delivered to the treatment facility at sufficient head to fill the influent equalization basin, and final effluent is discharged by gravity. Costs of pumps, pipe lines, etc., necessary to deliver raw wastewater to the treatment plant or to deliver the treated effluent to the point of discharge are not included in the cost estimates.

Since the treatment models are designed to serve single product manufacturing plants, no emergency holding basins or internal bypasses are provided. Any such necessary facilities are more appropriately furnished as part of a combined waste treatment system serving several product lines.

Cost Estimates For Each Subcategory

Estimated costs for the wastewater treatment plants for the different annual productions and at various levels of treatment are calculated in terms of total annual costs. The total annual cost is the summation of the annual amortization of the investment costs and the annual operation and maintenance costs.

The types of costs shown for each model plant are:

1. Investment
2. Annual operation and maintenance
3. Annual amortization of investment costs (excluding land)

The total annual costs per metric ton of product have been calculated.

For the purpose of the cost estimate, the first level (BPT or NSPS) is expressed as the total cost of the treatment system. The other level (BAT) represents the incremental cost above the base cost. The actual additional costs a plant would incur in implementing the described treatment processes depend on current treatment practices, and to some extent, on the availability of land.

In some cases, land for economical on-site sludge disposal for a ten year period has been provided in the BPT model plant costs. Since land cost is not amortized, its value appears in the investment cost, but not in the total annual costs.

For the purpose of cost estimating, a set of generally representative model plant specifications are given for each nonexcluded subcategory starting with the Chlor-Alkali industry in Section 11. These specifications together with the basic assumptions on cost estimating in this section, form the basis of the cost estimates for alternative treatment systems. These cost estimates are presented in a tabular format in the cost development portion of each applicable subcategory section. In order to take into account more fully the wide range of

plant specific variables, additional cost elements which may add to the baseline costs are then considered on a case-by-case basis.

SECTION 11

CHLOR-ALKALI INDUSTRY

Industry Profile

General Description

Chlorine and its co-product caustic soda (alkali) are used in large quantities in the production of plastics, organic and inorganic chemicals, in the pulp and paper industry, in water and wastewater treatment and in a number of other industries.

The production rate in the United States is approximately 9 million metric tons (10 million short tons) of chlorine per year and over 95 percent of that production is by the electrolysis of a sodium or potassium chloride solution via one of two major processes, mercury cell and diaphragm cell.

Other processes for chlorine production such as the recently developed membrane process are not addressed here because only pilot-scale production exists or no data are available from fully operating facilities.

Subcategorization

The factor chosen for the primary subcategorization of the inorganic chemicals point source category was dominant product (see Section 4). Other factors considered for subcategorization include: raw materials used, manufacturing process employed, geographical location, size and age of equipment and facility involved, non-water-quality aspects of waste characteristics, water pollution control technology, treatment costs, energy requirements and solid waste disposal. The chlor-alkali subcategory was further subdivided on the basis of differences in cell design and in the quantity and quality of wastewater generated.

Mercury and diaphragm cells are the two distinct types of electrolytic cells that are used in the production of chlorine and caustic soda. Major process differences between mercury cell and diaphragm cell plants produce corresponding differences in the volume and nature of wastewater generated. A principal difference is the presence of mercury as a contaminant in the wastewaters from the mercury cell process and asbestos in the diaphragm cell plant wastes. The TSS discharges from diaphragm cell plants are generally larger than from mercury cell plants, due to the higher volumes of contact and noncontact water used. Also, in diaphragm cells a large amount of water is used and an appreciable quantity of wastewater is produced in the caustic evaporation process. Such water is not produced in mercury cell plants. The quantity of wastewater generated from the diaphragm cell plants may be more than four times that of the mercury

cell plants for the same chlorine production capacity. Based on the quantity and characteristics of the wastewater, further subcategorization is justified.

Mercury Cell Process Industry Profile

General Description

Approximately 30 percent of the U.S. production of chlorine is by mercury cell plants. In 1978 of 27 known plants, 308 data were available for 15. Table 11-1 presents a summary profile of the subcategory. Table 11-2 presents the status of discharge regulations for mercury cell chlorine plants prior to promulgation of these regulations. Control of pH in the 6.0 to 9.0 range was also included in those regulations.

General Process Description

A. Brine System

The sodium chloride solution (brine or salt dissolved in water) is treated with sodium carbonate and sodium hydroxide to precipitate impurities such as calcium, magnesium, and iron. Precipitated hydroxides and carbonates are then settled usually in a clarifier and the underflow, known as brine mud, is sent to a lagoon or filtered. Brine muds from mercury cell plants usually contain small amounts of mercury because the spent brine from the cells is recycled. Consequently brine mud filtrate is recycled or treated before discharge and solids are disposed of in secure landfills.

Before it is sent to the cells, the treated brine is filtered and then pH adjusted. Spent or depleted brine from the cells is acidified and dechlorinated using vacuum and/or air stripping before being saturated with salt and recycled.

B. Mercury Cell Process

The mercury cell, in general, consists of two sections: the electrolyzer and the decomposer or denuder. The electrolyzer is an elongated steel trough that is inclined slightly from the horizontal. Mercury flows in a thin layer at the bottom forming the cathode of the cell, and the brine flows concurrently on top of the mercury. Parallel graphite or metal anode plates are suspended from the cover of the cell. Electric current flowing through the cell decomposes the brine, liberating chlorine at the anode and sodium metal at the cathode. The metallic sodium forms an amalgam with mercury.



TABLE 11-1. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	CHLORINE MERCURY CELL
Total subcategory capacity rate	3,550,000 kkg/year
Total subcategory production rate	2,750,000 kkg/year
Number of plants in this subcategory	27
308 Data on file for	15
With total capacity of	1,280,000 kkg/year
With total production of	1,090,000 kkg/year
Representing capacity	36 percent
Representing production	40 percent
Plant production range:	
Minimum	19,100 kkg/year
Maximum	198,000 kkg/year
Average production	77,900 kkg/year
Median production	70,400 kkg/year
Average capacity utilization	75 percent
Plant age range:	
Minimum	2 years
Maximum	26 years
Waste water flow range:	
Minimum	4 cubic meters/day
Maximum	2,100 cubic meters/day
Volume per unit product:	
Minimum	< 1 cubic meters/kkg
Maximum	11 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978, and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

TABLE 11-2 STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY CHLORINE MERCURY CELL

SUBPART F (40 CFR 415.60, 3/12/74)

STANDARDS

Product Process	Parameters	BPCTCA		BATEA*		NSPS	
		Max. (1)	Avg. (2)	Max.	Avg.	Max.	Avg.
		(kg/kkg)	(kg/kkg)	(kg/kkg)	(kg/kkg)	(kg/kkg)	(kg/kkg)
Mercury Cell Process	TSS	0.64	0.32	No discharge of pwwp ⁽³⁾		0.64	0.32
	Hg	0.00028	0.00014	No discharge of pwwp		0.00014	0.00007

* Section 415.63 was remanded and reserved (41 FR 51601, November 23, 1976).

(1) Max. = Maximum of any one day.

(2) Avg. = Average of daily values for thirty consecutive days shall not exceed.

(3) pwwp = Process wastewater pollutant.

The amalgam from the electrolyzer flows to a denuder and the spent brine is recycled to the brine purification process. In the denuder, the amalgam becomes an anode to a short-circuited iron or graphite cathode. Deionized water is added to the denuder which reacts with the amalgam to form hydrogen and caustic soda. In modern mercury cells, the denuder or decomposer is a horizontally or vertically laid graphite-packed bed. The water and the amalgam flow countercurrently. Mercury is then returned to the electrolyzer.

C. Product Purification

Chlorine from the cell is cooled to remove water and other impurities. The condensate is usually steam stripped for chlorine recovery and returned to the brine system or discharged. After cooling, chlorine gas is dried further by scrubbing with sulfuric acid. The diluted acid is then usually regenerated, sold or used for nonbrine system pH control. When chlorine gas is compressed and liquified, it leaves behind noncondensable gases known as tail or sniff gas. The tail gas is usually scrubbed with caustic or lime, generating a hypochlorite solution which is then decomposed, used on-site, sold or discharged with or without treatment.

The sodium hydroxide or caustic product formed at the denuder has a concentration of 50 percent NaOH. Some of the impurities present in the caustic can be removed or reduced by the addition of certain chemicals, and the caustic is then filtered. In most cases it is sent to storage or is evaporated if a more concentrated product is required.

Hydrogen gas is cooled by refrigeration to remove water vapor and mercury, and can be treated further by molecular sieves or carbon. Condensate from hydrogen cooling is then discharged or recycled to the denuder after mercury recovery.

Figure 11-1 presents a general process flow diagram of chlorine production by mercury cell.

Water Use And Wastewater Source Characteristics

Water Use

Water is used at mercury cell plants for noncontact cooling, tailgas scrubbing, cell washing, equipment maintenance, floor washings and in the decomposition of sodium-mercury amalgam in the denuder to produce sodium hydroxide. Because most brine systems at mercury cell plants are closed systems, water use in the brine system is minimal. The total water usage at plants was found to range from 7.6 to 204 cubic meters per metric ton (1800 to 49,000 gallons per short ton), with noncontact cooling water, which is not covered by this effluent guideline, comprising approximately 70 percent of the total.

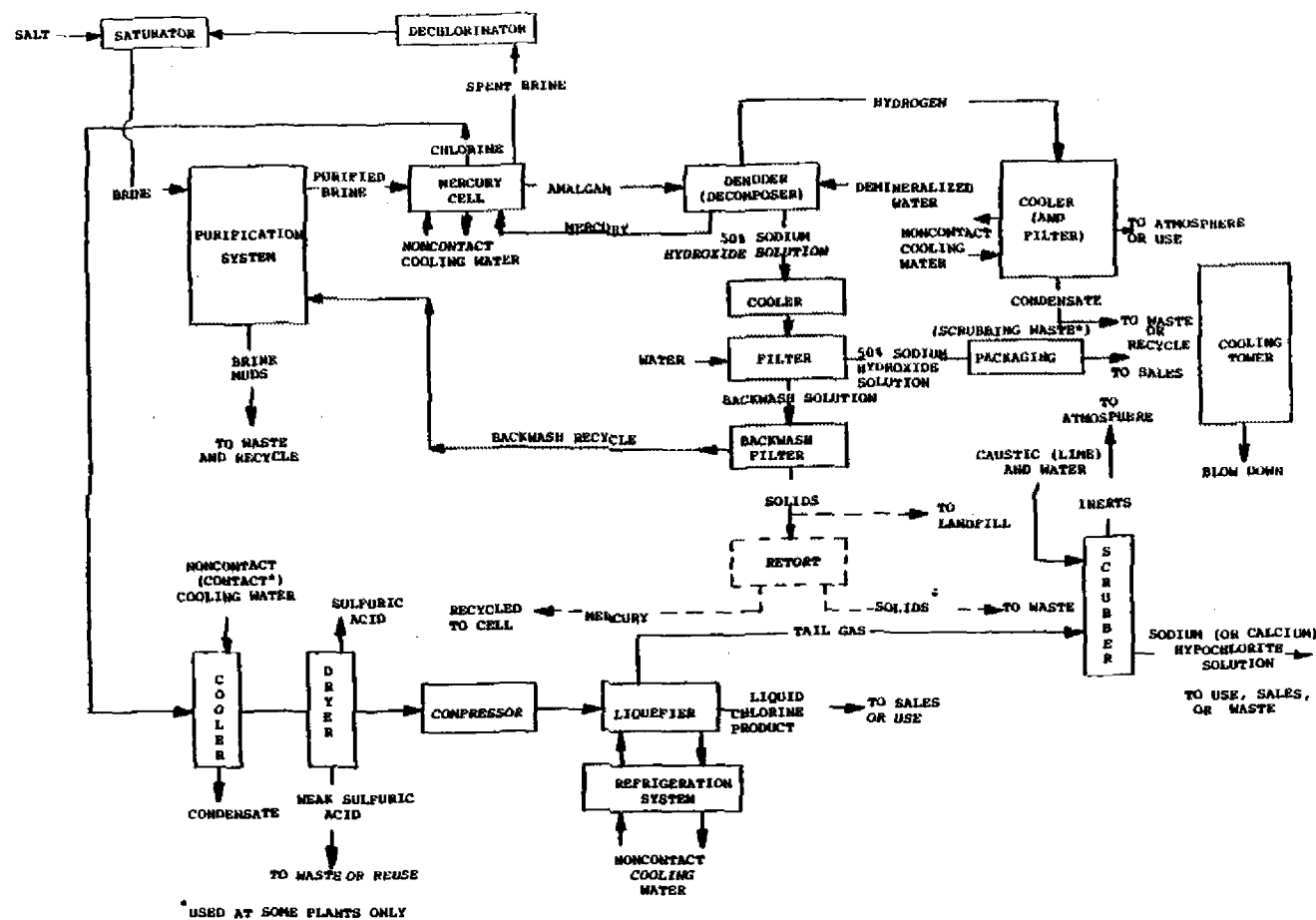


Figure 11-1. General process diagram for production of chlorine/caustic by mercury cells.

Waste Sources

The following waste sources are or can be contaminated with mercury and would therefore require treatment if discharged.

A. Brine Mud

This is the waste produced during the purification of brine before it is introduced into the cell for electrolysis. The metals commonly removed during purification are magnesium, calcium, iron and other trace metals such as titanium, molybdenum, chromium, vanadium and tungsten. Calcium and iron are removed as hydroxides. Brine mud is the major portion of the waste solids produced from the process. The solids content of the stream varies from 2 to 20 percent and the volume varies from 0.04 to 1.5 cubic meters per metric ton of chlorine produced. The waste is either sent to a pond for settling or is filtered. The overflow from the pond or the filtrate is recycled to the process as makeup water for the brine. In the mercury cell process, only 16 percent of the brine is recycled to the purification unit after dechlorination. This recycled brine is contaminated with mercury so the resulting brine mud contains small amounts of mercury.

B. Cell Room Wastes

The major components of this stream include leaks, spills, area washdown and cell wash waters. The amount varies from plant to plant and depends largely on housekeeping practices. Data indicate a range of from 0.01 to 1.5 cubic meters per metric ton of chlorine produced. Cell room waste constitutes the major stream requiring treatment because of the high levels of mercury present in these wastes. If graphite anodes are used in the cells, the wastes may also contain lead (used as an electrical contact at the anode) and chlorinated organics. However most mercury cell plants have converted to metal anodes.

C. Chlorine Condensate

Condensation from the cell gas is contaminated with chlorine. At some plants, the condensates are recycled to the process after chlorine recovery. Both contact and noncontact water is used for chlorine cooling and for removal of water vapor. Because of this, the amount and type of wastewater varies from plant to plant. Data from one plant indicates a waste condensate flow of approximately 0.01 cubic meter per metric ton of chlorine produced.

D. Spent Sulfuric Acid

Concentrated sulfuric acid is used in the dryer to remove the residual water from the chlorine gas after the first stage of cooling. In most cases, the acid is used until a constant

concentration of 50-70 percent is reached. The spend acids can be regenerated for reuse, used for pH control in a nonbrine treatment system, or sold.

E. Tail Gas Scrubber Liquid

The tail gas containing the uncondensed chlorine gas from the liquefaction stage, ~~along with some air and other gases,~~ is scrubbed with sodium/calcium hydroxide to form sodium/calcium hypochlorite solution. When the equipment is purged for maintenance, the tail gas is also absorbed in calcium or sodium hydroxide, producing the corresponding hypochlorite solution. The hypochlorite can be used in another process on site, sold, discharged to treatment or decomposed before discharge or treatment. The amount of tail gas scrubber water varies from 0.04 to 0.58 cubic meter per metric ton of chlorine.

F. Caustic Filter Washdown

The 50 percent caustic produced at the denuder is filtered to remove salt and other impurities. The filters are backwashed periodically as needed, and the backwash can be discharged to treatment or filtered with the filtrate recycled to the brine system and the solids sent for disposal or mercury recovery. Wastewater volume from caustic filter backwashing is variable and no flow data are available.

G. Hydrogen Condensate

Hydrogen produced at the denuder is cooled to remove mercury and water carried over in the gas. The condensate is either sent to treatment facilities or to mercury recovery after which it can be returned to the denuder. Data on the volume of this waste stream are not available.

H. Summary of Wastewater Flow

Summing the flow ranges presented above for specific waste sources results in a maximum mercury-contaminated waste flow of 2.1 cubic meters per metric ton (m^3/kg) for plants where specific stream data were available. This does not include brine mud flows which are reused instead of discharged, and therefore do not affect total flow.

Data available on total discharges at 13 mercury cell plants are presented in Table 11-3. The average discharge volume indicated is also $2.1 \text{ m}^3/\text{kg}$, although flows as high as $6.3 \text{ m}^3/\text{kg}$ do exist.

Description of Specific Plants

The following descriptions of specific plants includes those that were sampled during the screening and verification program. The discussion primarily covers plant practices in wastewater control and treatment.

Screening Program

Plant #299 was visited in the screening and verification phase of the program. The mercury-contaminated waste streams include outlet end-box wash water, spills and cleanup water, brine mud saturator sludge, and pump seals wastewater. The combined wastewater is sent to a surge pond. The effluent from the surge pond is mixed with sodium hydroxide and sent to a settling pond. The overflow from the pond is pH adjusted, filtered (in a filter press) and passed through activated carbon towers before discharge. In the sampling program wastewater influent to the surge pond and the overflow from the settling pond were sampled. Figure 11-2 gives the general process diagram and shows all the waste streams sampled. Table 11-4 presents major pollutant concentrations and loads for the sampled streams.

Verification

Four more plants (#747, #167, #106 and #317) producing chlorine/caustic by mercury cells were visited and sampled in the verification program. Table 11-5 presents pollutant concentrations for the sampled streams and loads for TSS and mercury.

At Plant #747, the brine dechlorination system has been converted from barometric condensers to a steam ejector system. The conversion resulted in increased chlorine recovery and reduced contact wastewater. By providing settling and secondary filter facilities, the brine filter backwash has been eliminated. The tail gas scrubber liquid (hypochlorite solution) is offered for sale and if not marketed, is treated for removal of chlorine and discharged. Mercury bearing wastewaters are treated with sodium sulfide (Na_2S) and filtered. Solids are retorted for mercury recovery and the filtrate is mixed with the other process wastewaters and the pH adjusted before discharge. A flow diagram of the manufacturing process, including the wastewater treatment facility, is given in Figure 11-3.

At Plant #167, the wastewater streams, consisting of filter backwash, cell room wash, rain water runoff, and leaks and spills, are combined and treated for mercury removal. The water is sent to a holding lagoon and the overflow is reduced by reaction with ferrous chloride, which precipitates mercury. The reacted solution is sent to a clarifier and the underflow from the clarifier is disposed of in a landfill. The overflow is filtered and the filtrate is passed through activated carbon and an ion exchange column prior to discharge to a lagoon. The effluent from the lagoon is pH adjusted and discharged. Figure 11-4 shows the simplified process flow diagram for Plant #167, including the sampling locations.

TABLE 11-3. SUMMARY OF WASTE WATER FLOW DATA FOR CHLORINE
MERCURY CELL PLANTS

SUBCATEGORY	CHLORINE MERCURY CELL
Plant Number	Waste Water Flow (m ³ /kg Chlorine)
917	0.36
907	0.36
299	1.6
103	0.36
747	0.67
343	1.6
106	0.67
131	1.7
589	5.8
898	0.98
741	0.51
553	1.0
769	6.3
Average of 13 plants	2.1

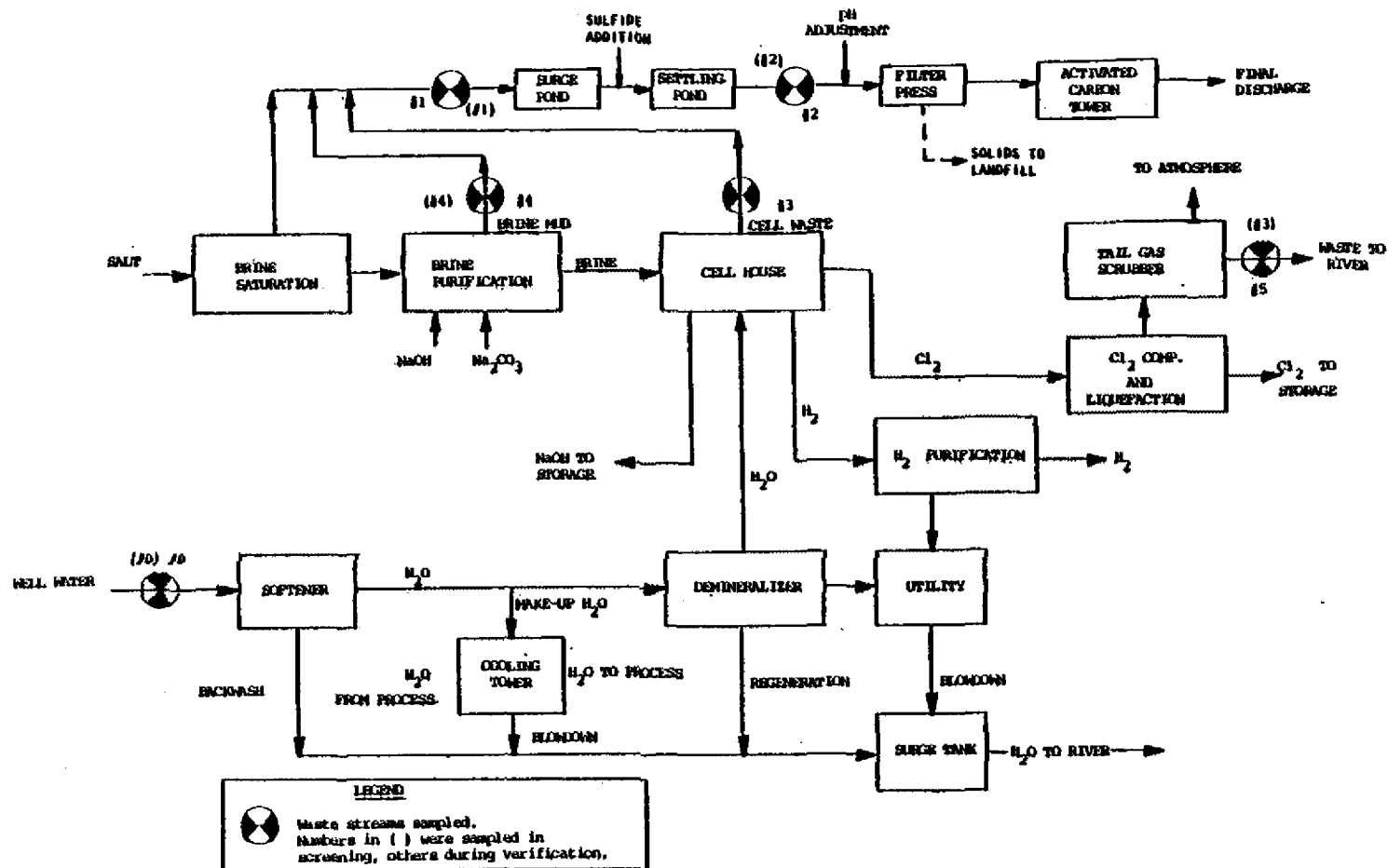


Figure 11-2. General process flow diagram at plant #299 showing the sampling points: Chlorine/caustic (mercury cell) manufacture.

TABLE 11-4. POLLUTANT CONCENTRATIONS AND LOADS AT PLANT # 299

SUBCATEGORY		CHLORINE (MERCURY CELL)			
Stream Number	Stream Description	TSS (mg/l)	TSS (kg/kkg)	Mercury (mg/l)	Mercury (kg/kkg)
Screening Phase: (1)					
1	Cell Waste	12	0.016	0.15	0.0002
2	Mercury Treatment Effluent	5.0	0.0070	0.029	0.00004
3	Tail Gas Scrubber	NA	NA	0.11	NA
Verification Phase: (2)					
1	Mercury Treatment Influent	91	0.13	5.9	0.080
2	Mercury Treatment Effluent	18	0.026	0.20	0.0003
3	Cell Waste	120	0.17	11.	0.015
4	Brine Mud	13,000	NA	0.54	NA
5	Tail Gas Scrubber	180	0.022	0.17	0.00002

NA = Not available.

(1) = Data based on one 72-hour composite sample of each stream.

(2) = Data based on three 24-hour composite samples of each stream.

TABLE 11-5. POLLUTANT CONCENTRATIONS AND LOADS AT VERIFICATION PLANTS (1)

SUBCATEGORY		CHLORINE (MERCURY CELL)			
Stream Number	Stream Description	TSS		Mercury	
		(mg/l)	(kg/kg)	(mg/l)	(kg/kg)
Plant 747					
1	Cell Waste	700	1.6×10^{-1}	18	4.3×10^{-3}
2	Treated Waste	60	1.4×10^{-2}	0.10	2.3×10^{-5}
3	Acid Input	NA	NA	0.023	3.5×10^{-6}
4	Acid Output	NA	NA	0.0030	7.2×10^{-7}
5	Dechlor System	9.0	0.0037	0.035	1.5×10^{-5}
6	Cl ₂ Condensate	2.0	2.7×10^{-5}	0.27	1.8×10^{-6}
7	Tail Gas Scrubber	NA	NA	0.039	8.0×10^{-7}
Plant 167					
5	All Cl ₂ Wastes	560	1.9	3.8	1.3×10^{-2}
6	Cell Wash	57	5.7×10^{-4}	0.72	6.7×10^{-6}
7	Brine Process	4.0	7.1×10^{-3}	0.0050	9.0×10^{-6}
8	Treated Waste	2.0	1.3×10^{-2}	0.32	1.8×10^{-3}
9	Clarifier Underflow	5,900	4.0	10.4	8.7×10^{-5}
Plant 317					
1	Cell Waste	45	NA	14	NA
2	Brine Mud Filtrate	520	NA	34	NA
3	Tank Car Wash	18	NA	0.033	NA
4	Collection Tank	21,000	8.6	123	5.0×10^{-2}
5	Treated Effluent	110	4.4×10^{-2}	0.10	4.3×10^{-5}
6	Deionizer Effluent	18	5.2×10^{-3}	0.0010	2.9×10^{-7}
7	N-C Cooling	16	2.2	0.0010	1.4×10^{-4}
8	Final Effluent	18	2.4	0.0020	3.6×10^{-4}
Plant 106					
1	Cell Wash	79		3.9	
2	Treated Cell Wash	20		0.015	
4	Final Effluent	2.0		<0.00050	NA

NA = Not available.

(1) = Data based on the average of three 24-hour composites.

At Plant #317, the brine purification mud is mixed with spent sulfuric acid and sodium hypochlorite solution. The treatment removes mercury from the mud and transfers it to the solution. The solution is filtered and the solids landfilled. The filtrate is mixed with other mercury-contaminated wastewaters, which includes the brine purge, cell room liquid wastes and plant area wash water. This is then reacted with sodium hydrosulfide to precipitate the mercury as mercury sulfide and then filtered. The solids are sent to a mercury recovery unit and the filtrate is sent to a holding tank. The effluent from the holding tank is mixed with de-ionizer waste and noncontact cooling water before discharge. The process flow diagram showing the waste streams sampled is given in Figure 11-5.

At Plant #106, mercury-bearing wastes are segregated from other wastewaters and combined for batch treatment. Mercury-bearing leaks, spills, and precipitation are contained and collected by curbing around the cell room and collecting the wastes in a common sump. From the sump the combined waste is pumped to treatment. In the treatment system, the pH is initially adjusted using waste sulfuric acid and 20 percent caustic solution as required. Sodium sulfide and filter aid are added and the waste agitated in fiberglass reaction tanks. The effluent from the tanks is filtered and the filter cake is retorted for mercury recovery. The residual waste, after mercury recovery, is placed in a lined solid waste disposal area. The filtrate is sent to the first of two lined lagoons. Primary pH adjustment is made using waste sulfuric acid and 20 percent caustic before entry into the first lagoon; final pH adjustment is made between the first and second lagoons.

Descriptions of Plants Not Sampled

At Plant #589, the wastewater going to the mercury treatment system consists of cell room washdown, brine filter backwash, leaks, spills, cleanup water, and hydrogen cooling condensate. The wastewaters are reacted with hydrochloric acid and sodium bisulfide and then sent to a settling basin where mercury sulfide precipitates. The overflow is passed through a series of effluent filters before discharge.

At Plant #343, the cell room wash water, brine purification sludge, and chlorine cooling condensate are combined and sent to a pond. The suspended solids settle in the pond and are dredged out once a year. The dredged sludge is "Chem Fixed" and disposed of in an appropriate landfill. The overflow from the pond is reacted with Na_2S and the reacted solution is sent to a clarifier. The clarifier underflow, consisting mainly of mercury sulfide, is returned to the pond. The clarifier overflow is discharged.

All contact wastewater at Plant #907 is treated for mercury removal in a patented process involving reduction of mercury to the metallic state using sodium borohydride. Previously contaminated wooden flooring in the cell room has been removed and replaced with fiberglass gratings to reduce the amount of mercury in the effluent and for better waste control. Molecular sieves have been installed on

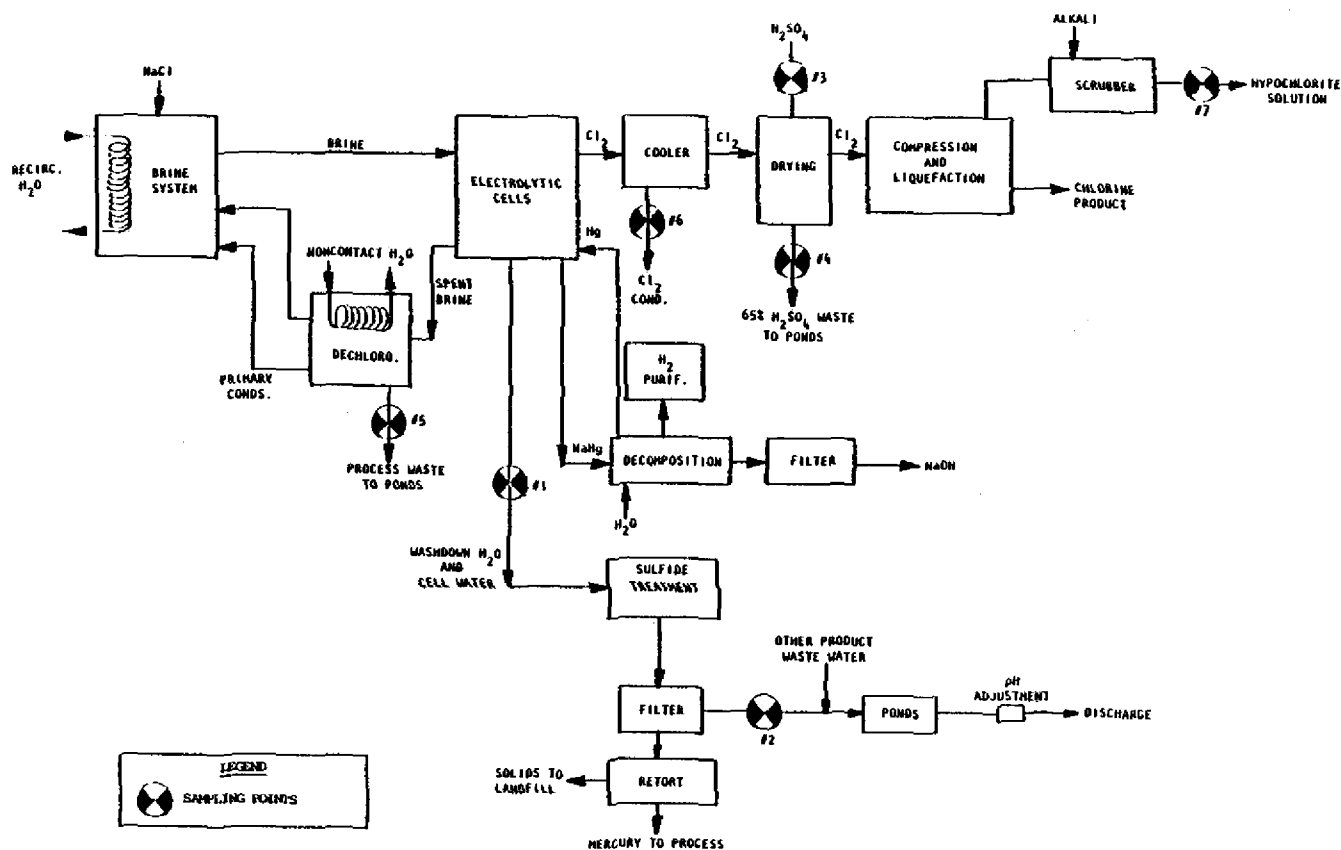


Figure 11-3. General process flow diagram at plant #747 showing the sampling points. Chlorine/caustic (mercury cell) manufacture.

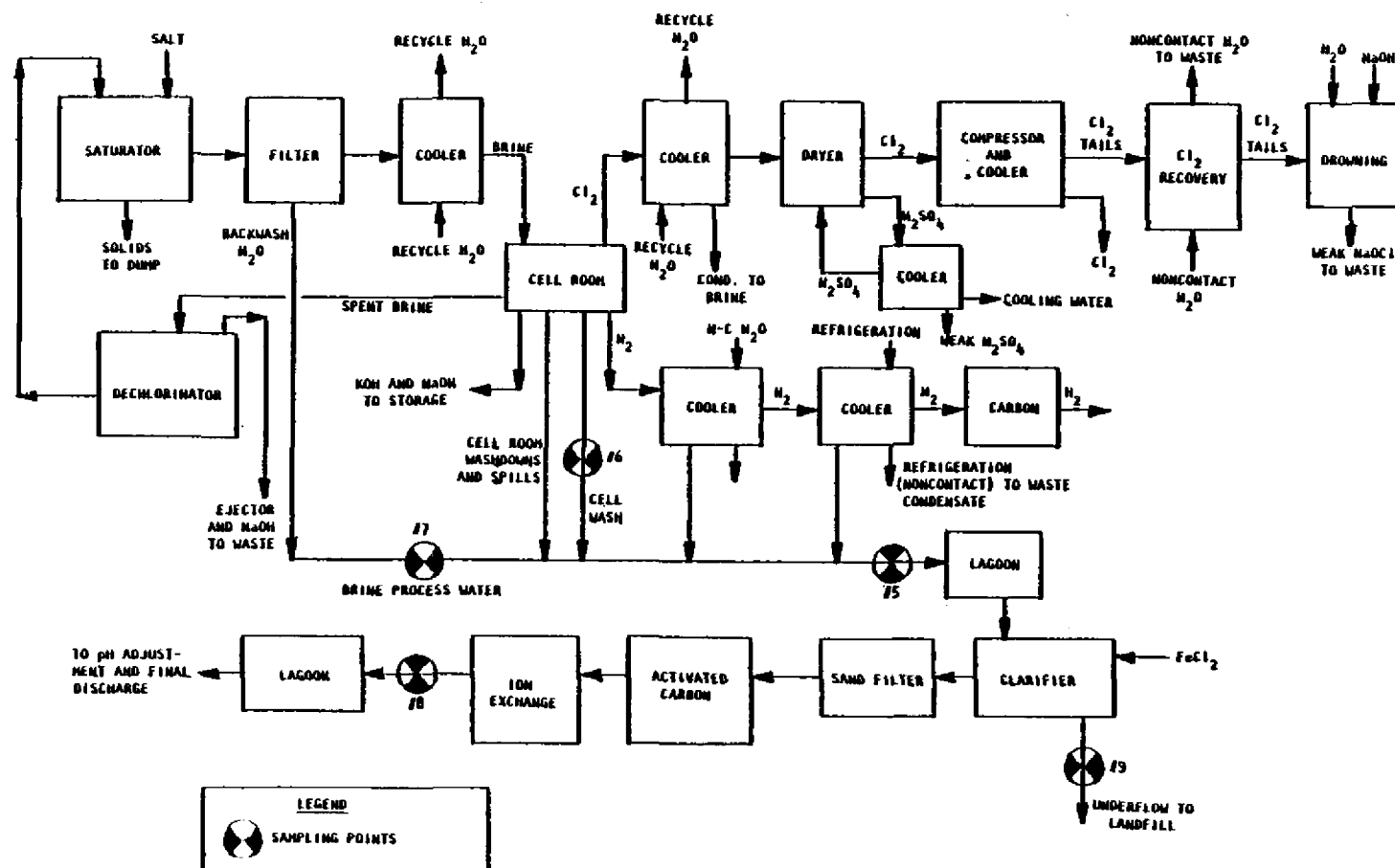


Figure 11-4. General process flow diagram at plant #167 showing the sampling points. Chlorine/caustic (mercury cell) manufacture.

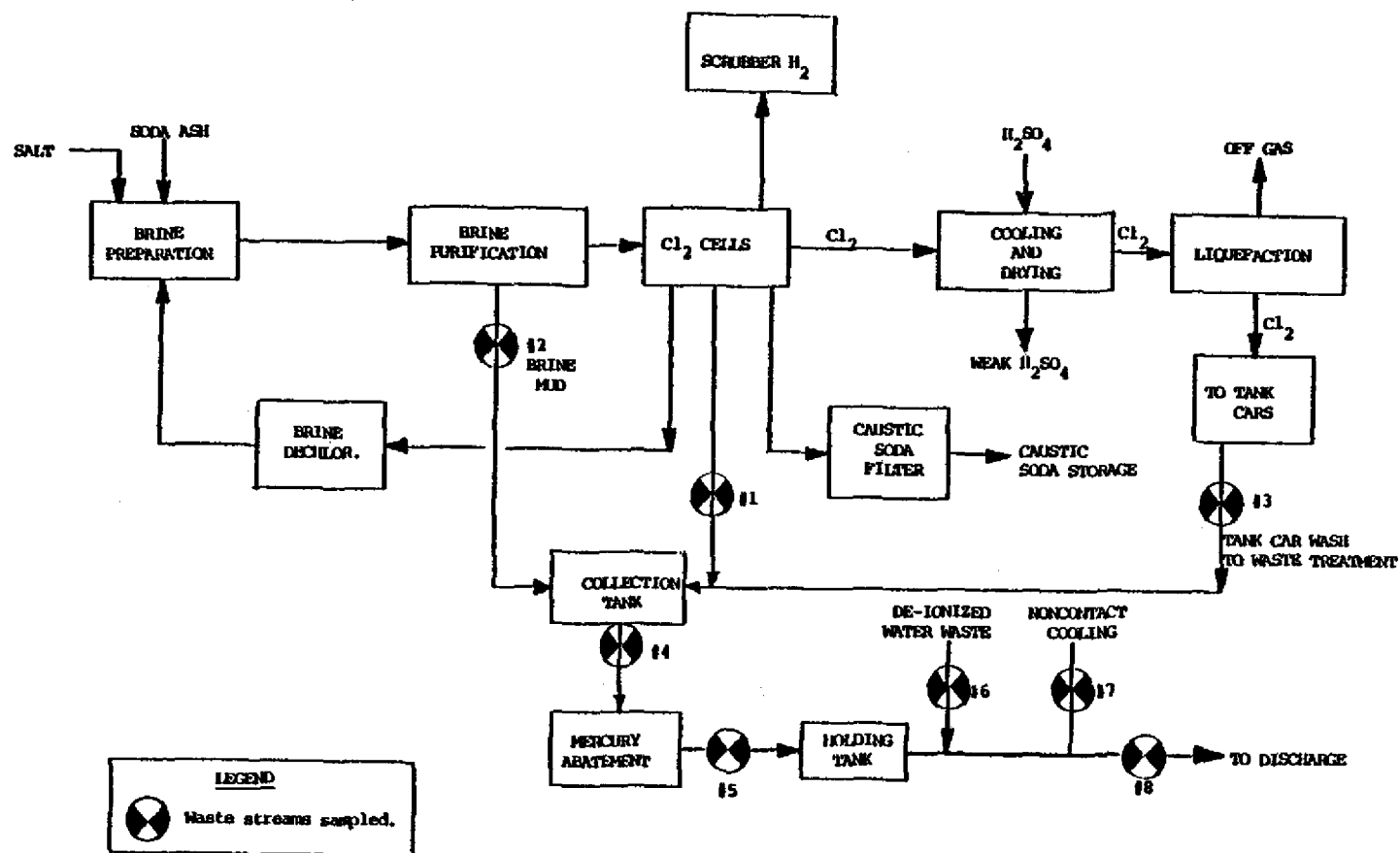


Figure 11-5. General process flow diagram at plant #317 showing the sampling points. Chlorine/caustic (mercury cell) manufacture.

cell end boxes to reduce the mercury content in the air vented from the cells. The treatment not only cleans the air but is also believed to reduce mercury in the plant area runoff.

In the treatment system, the mercury-contaminated wastewater is reacted with sodium borohydride to reduce dissolved mercury to the metallic form. The reacted solution is filtered prior to delivery to one of the banks of three columns packed with anthracite coal. After passing through three absorption columns in series, the treated wastewater is delivered to large holding tanks, from which it may be discharged or returned to treatment, depending on its mercury content. Filter cake, resulting from the filtration of the waste prior to the coal absorption step, is retorted for mercury recovery.

Waste solids at this facility, including mercury treatment sludges and brine muds, are deposited in an on-site disposal area. Chlorine discharges are essentially eliminated by three significant waste management practices: the chlorine condensate is collected and returned to the brine system, tail gas scrubbing effluents are used in the manufacture of another product, and spent sulfuric acid from chlorine drying is dechlorinated in an air stripper and shipped off-site for the manufacture of another product. Gases from the air stripper are returned to the chlorine purification header.

At Plant #324, the barometric condenser on the brine dechlorination was replaced with an indirect cooler, resulting in a reduction of chlorinated wastewater. The tail gas scrubber effluent is used for the manufacture of another product, and the brine muds are sent to a pond. Small amounts of mercury, when detected in the brine mud, are leached with water and treated with other mercury-contaminated wastewaters which include the cell room wash water, caustic filter backwash, and brine leaks. The combined wastewater is mixed with hydrogen processing wastewater, reacted with sulfuric acid, sodium borohydride, and sodium sulfide, and then filtered. The filtrate is adjusted for pH and recycled to process.

At Plant #385, the brine mud sludge is sent to a retention pond where it accumulates. All process contact wastewater is collected in an unlined pond where it is treated and the treated effluent is used as the scrubber liquid for tail gases. The spent scrubber solution is sent to an adjacent paper plant for use.

At Plant #416, the cell room wastes are used for bleach manufacture. The wastewater streams from the chlorine/caustic plant are sent to an adjacent paper company.

At Plant #784, the wastewater, consisting of KCl brine filter backwash and area washdown and spills, is sent to a basin. The basin equalizes the flow and the overflow is treated with sulfuric acid prior to reaction with NaHS and clarification. The clarifier overflow passes through an activated carbon filter and to a final tank where it undergoes pH adjustment before discharge.

The wastes are segregated at Plant #674. The clarification pond is used for waste streams containing suspended solids. The streams going to the pond include brine purification muds and spent chlorinated lime. The mercury-contaminated wastewaters are treated separately. These include the brine saturation waste, brine filter backwash, cell room sumps, and tank car washes. The combined mercury-laden wastewater is sent to a collection pond and the overflow from the pond is pH adjusted before the addition of Na_2S . The reacted solution is sent to another pond and the pond overflow is passed through a carbon adsorption column before final discharge. A part of the treated effluent is reinjected into the brine well.

At Plant #012, the brine treatment area is paved to trap all spills, leaks, and rain runoff from that area. The contaminated wastewaters from the plant are re-injected into the brine wells to keep the hydraulic balance and maintain pressure in the salt deposits.

Summary of the Toxic Pollutant Data

Presented below are the toxic pollutants found in the raw wastes during screening and verification.

Because several waste streams usually contribute to the total raw waste at mercury cell plants, a calculation was often necessary to determine the pollutant concentrations that would exist in the streams before they were mixed prior to treatment. An example of this calculation is the "mixing" of the following hypothetical streams:

Stream A: 100 gallons per minute, 15 mg/l

Stream B: 10 gallons per minute, 60 mg/l

$$\frac{(\text{Flow} \times \text{concentration}) + (\text{Flow} \times \text{concentration})}{\text{Total Flow}}$$

= concentration of mixed streams

$$= \frac{(100 \text{ gpm})(15 \text{ mg/l}) + (10 \text{ gpm})(60 \text{ mg/l})}{110 \text{ gpm}} = 19 \text{ mg/l}$$

The maximum raw waste concentrations observed during any single 24-hour sampling period were:

Maximum Raw Waste Concentrations Observed
($\mu\text{g/l}$)

Pollutant	Screening Plant (#299)	Verification Plants (#299, #747, #167, #206, #317)
Antimony	< 250	770
Arsenic	< 10	400
Cadmium	< 1	790
Chromium	8	180
Copper	350	2,300
Lead	1	1,900
Mercury	150	180,000
Nickel	< 100	2,400
Silver	< 1	870
Thallium	140	440
Zinc	230	34,000

Section 5 of this report describes the methodology of the screening and verification sampling program. In the chlorine mercury cell industry, a total of 18 days of sampling were conducted at Plants #299, #747, #167, #317 and #106. Thirty-two different sampling points were involved covering various raw waste streams and the treated effluents at these plants. The evaluation of toxic metal content of these process related waste streams was based on 949 analytical data points. The screening for toxic organic pollutants at Plants #299 and #167 generated an additional 490 analytical data points. The daily raw waste loads were calculated from the waste stream flow rates measured or estimated at the time of sampling and the measured pollutant concentration.

The daily loading is determined by:

$$\text{Daily loading (as kg of pollutant = } \frac{(C)(Q)}{1000} \text{ per day)}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: $\text{kg/m}^3 = 1000 \text{ mg/l}$), and

Q is the waste stream flow rate expressed in units of m^3/day (m^3 , a cubic meter, is equal to 264.2 U.S. gallons).

Similarly, the unit loadings were calculated from the reported chlorine production rate, the waste stream flow rate, and the measured pollutant concentration:

$$\text{Unit loading (as kg of pollutant per kkg of chlorine)} = \frac{(C)(Q)}{1000P}$$

where C and Q are the same as described above, and P is the chlorine production rate expressed in units of kkg/day (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs.)

The minimum, average, and maximum values are based on data from those plants where the particular pollutant was found at a concentration greater than the analytical detection limits and considered a "significant concentration". The term "significant concentration" means an observed concentration in any 24 or 72-hour composite raw waste sample that is above the analytical detection limit, and potentially treatable.

In Table 11-6, the toxic pollutant raw waste data are presented as the average daily concentrations and the unit loadings found at the individual plants. These averages were derived by averaging the concentrations and loads based on three 24-hour composite samples from each plant.

In Table 11-7 daily loadings (in kg/day) and unit loadings in (in kg/kkg) are presented as minimum, average and maximum values based on the data presented in Table 11-6.

Based on the total annual production of this subcategory and the average waste load generated per unit product, the estimated total pollutant raw waste loads generated each year by this subcategory are as follows:

<u>Pollutant</u>	<u>Raw Waste load</u> <u>(kg/year)</u>
Antimony	1,400
Arsenic	1,000
Cadmium	210
Chromium	360
Copper	960
Lead	880
Mercury	44,000
Nickel	820
Silver	850
Thallium	770
Zinc	7,200

Pollution Abatement Options

Toxic Pollutants of Concern

Mercury is the major toxic pollutant of concern in the production of chlorine by the mercury cell process. Other toxic metals often found in significant concentrations in raw wastes include arsenic, antimony,

cadmium, chromium, copper, lead, nickel, silver, thallium and zinc. Sources of these metals are assumed to be impurities in the raw salt or brine and corrosion products from the reaction between chlorine and process equipment materials of construction. No toxic organics were found at treatable levels.

Prevailing Control and Treatment Practices

Specific control and treatment practices at 14 plants were described above. All known mercury cell plants practice treatment of mercury-bearing wastes, but control practices such as recycling of brine mud filtrate or pond overflow, chlorine condensates, hydrogen condensates and caustic filter backwash, and solids handling vary from plant to plant. Although all known treatment facilities precipitate mercury and separate the solids formed by clarification and/or filtration, sampling data has shown that some treatment systems, including those with more advanced technologies such as adsorption or ion exchange, are not operating efficiently.

Process Modifications and Technology Transfer Options

The following process modifications are being practiced at one or more mercury cell plants and can significantly reduce pollutant loads discharged.

A. Anode Material

Nearly all mercury cell plants now use metal anodes. Their use, as opposed to graphite anodes, improves the power efficiency of the cells and reduces the potential pollutant load.

B. Liquefaction of Chlorine

Utilization of high pressure and refrigeration for chlorine recovery will reduce the chlorine content of tail gases.

C. Brine Recycling

Although practiced at many facilities not all plants are using a closed-loop brine system which eliminates a significant waste volume requiring mercury treatment.

D. Mercury Emissions

Hydrogen gas produced in the denuder can be refrigerated and passed through treated carbon or molecular sieves to remove the mercury escaping with gas. This will reduce the mercury emissions and reduce atmospheric fallout in the neighborhood of the plant. This in turn will reduce mercury concentrations in storm runoff. Two plants are practicing this control technology.

TABLE 11-6. AVERAGE TOXIC POLLUTANT RAW WASTE CONCENTRATIONS AND LOADS AT VERIFICATION PLANTS (1)

$\left(\frac{\text{mg/l}}{\text{kg/kg}}\right)$						
SUBCATEGORY	CHLORINE (MERCURY CELL)					
Pollutant	Plant #					Average Load
	299	747	167	317	106	
Antimony	0.48 0.00077	0.11 0.000076	*	*	0.49 0.00033	.000392 (2 plants)
Arsenic	0.23 0.00037	0.030 0.000021	0.33 0.0018	0.10 0.000051	*	.000306 (4 plants)
Cadmium	0.010 0.000016	0.020 0.000014	*	0.46 0.00023	0.031 0.000021	.000007 (4 plants)
Chromium	0.063 0.00010	0.10 0.000069	0.12 0.00067	0.080 0.000041	0.013 0.0000087	.000177 (5 plants)
Copper	0.30 0.00048	0.38 0.00026	0.075 0.00042	1.2 0.00061	0.12 0.000080	.00037 (5 plants)
Lead	0.060 0.000096	0.16 0.00011	0.072 0.00040	1.4 0.00071	0.33 0.00022	.000307 (5 plants)
Mercury	5.9 0.0094	18 0.012	3.8 0.021	123 0.063	3.9 0.0026	.0216 (3 plants)
Nickel	*	0.093 0.000064	0.060 0.00034	1.4 0.00071	0.17 0.00011	.000306 (4 plants)
Silver	*	0.047 0.000032	*	0.11 0.000056	0.58 0.00039	.000159 (3 plants)
Thallium	0.18 0.00029	0.022 0.000015	*	*	0.38 0.00025	.000185 (3 plants)
Zinc	0.27 0.00043	0.69 0.00048	0.17 0.00095	20 0.010	0.96 0.00064	.0005 (5 plants)

* - Concentration below treatable level.

(1) Data based on the average of three 24-hour composites.

TABLE 11-7. SUMMARY OF RAW WASTE LOADINGS AT
VERIFICATION PLANTS

SUBCATEGORY		CHLORINE (MERCURY CELL)					
Pollutant	Daily Loadings (kg/day)			Unit Loadings (kg/kg)			Number of Plants Averaged*
	min.	avg.	max.	min.	avg.	max.	
Antimony	0.044	0.17	0.30	0.000076	0.00039	0.00077	3
Arsenic	0.0054	0.11	0.27	0.000021	0.00056	0.0018	4
Cadmium	0.0062	0.013	0.025	0.000014	0.000070	0.00023	4
Chromium	0.0043	0.037	0.098	0.0000087	0.00018	0.00067	5
Copper	0.045	0.10	0.18	0.000080	0.00037	0.00061	5
Lead	0.036	0.070	0.12	0.000096	0.00031	0.00071	5
Mercury	1.6	3.1	5.1	0.0026	0.022	0.063	5
Nickel	0.037	0.056	0.075	0.000064	0.00015	0.00071	4
Silver	0.0059	0.082	0.22	0.000032	0.00016	0.00039	3
Thallium	0.0090	0.086	0.14	0.000015	0.00019	0.00029	3
Zinc	0.14	0.41	1.1	0.00043	0.0025	0.010	5

* - Only those plants where the pollutant was observed at "significant concentrations" are included in the averaging. "Significant concentrations" is defined in 11.4.4.

E. Tail Gas Emission Control

When chlorine gas produced from the cell is compressed and cooled, chlorine separates as liquid chlorine, and noncondensable gases (tail or sniff gas containing residual chlorine vapor) are produced at the discharge end of the condenser. The amount of chlorine present in the tail gas is significant and has to be removed and treated or recovered before the tail gas is vented to the atmosphere. The common industrial practice is to scrub the gas with caustic soda or lime solution thus producing the corresponding hypochlorite. The hypochlorite solution is either sold, used on-site, sent to a wastewater treatment plant, or discharged without treatment. Treatment of this waste is a relatively recent practice. Decomposition is a common method of treatment using catalytic, thermal, and chemical methods as described below.

Catalytic decomposition involves the addition of small quantities of cobalt, nickel, and iron chloride to the waste streams, followed by retention in reaction tanks for periods up to several days. Of the two plants employing this technology, one reports zero discharge of chlorine, and the other reports respective average and maximum chlorine discharge rates of 0.015 and 0.14 kg per metric ton of chlorine produced.

Thermal decomposition occurs when the temperature of the solution containing hypochlorite reaches 175 degrees F. Lime reacts with chlorine exothermically, producing heat and calcium hypochlorite. If the hypochlorite solution is not cooled, thermal decomposition occurs. One chlorine/caustic plant is using this treatment method and another is planning to use it. The plant using thermal decomposition reports complete conversion of hypochlorite to chloride.

Chemical decomposition takes place by reacting the hypochlorite solution with a chemical reactant which is usually sodium sulfite or hydrogen peroxide. Chemical decomposition is expensive but complete and rapid.

When chlorine is present in a dissolved form (hypochlorous acid) in water, a stripping technique may be applied to recover the chlorine. Chlorine condensate streams and spent chlorine-drying acid are most commonly treated by steam or vacuum stripping, with the chlorine frequently returned to process for purification and recovery as a product. The tail gas is not generally scrubbed with water because water does not effectively remove chlorine and the chlorine concentration in the exhaust will reach 0.1 to 4.5 percent by volume after scrubbing with water. One effective method of chlorine recovery from the tail gas is by the passage of the gas through an absorbing material such as carbon tetrachloride and subsequent recovery of the chlorine. The process is proprietary and little information is available on its design or performance.

Best Management Practices

A. Area Runoff

Provisions can be made to divert and contain storm runoff from plant areas. Collected runoff can then be sent to the wastewater treatment system.

B. Leaks and Spills

The brine treatment area and the cell room areas can be paved with fiberglass gratings, and provision should be made to collect the leaks and spills from the operation.

C. Mercury Contaminated Solids

The precipitated mercury waste should be stored in a lined pond, disposed of in a secured landfill or sent to mercury recovery operations. Brine mud should be discharged to a lined pond or a secure landfill after filtration. The brine mud contains small amounts of mercury which can leach into the ground water if proper safety precautions are not taken.

D. Transportation, Handling and Abnormal Operations

Provisions should be made to remove chlorine from air emissions resulting from abnormal operating conditions such as start up and shut down, or from vents on returned tank cars, cylinders, storage tanks, and process transfer tanks during handling and loading of liquid chlorine.

Advanced Treatment Technologies

Methods available for the removal of elemental mercury or mercuric salts from plant wastewaters include precipitation with sodium sulfide to form insoluble mercuric sulfide, adsorption by activated carbon, adsorption by ion-exchange and other resins, reduction by borohydride, hydrazine, sulfite, hypophosphite, or iron, and biological reduction (57). All of these methods are patented; many of these methods have been proven on a pilot scale only. Sulfide precipitation and adsorption techniques will also provide for the removal of other toxic metals.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

Following the evaluation of significant toxic pollutants found in raw wastewaters, current industry treatment practices and applicable treatment alternatives, two levels of end-of-pipe treatment were selected as alternatives for application in the mercury cell chlorine subcategory.

A. Level 1 (BPT)

This treatment consists of sulfide precipitation of mercury-bearing wastewater followed by pressure filtration. This level of treatment, which will also reduce other heavy metals, includes recycle of the brine mud overflow or filtrate back to process, and the settling and storage of brine muds. Mercury-bearing solids can be sent to mercury recovery or disposal. The flow diagram for this treatment level is shown in Figure 11-6.

B. Level 2

The filtered Level 1 effluent is passed through a granular activated carbon bed where residual metal sulfides and any metallic mercury will be removed. The flow diagram for this treatment level is shown in Figure 11-7. Cost estimates for this level can be obtained from the proposed Development Document (60).

Equipment for Different Treatment Levels

A. Equipment Functions

In Level 1, typical of existing treatment facilities, mercury-bearing wastes are equalized in a surge tank, and following chemical mixing, sulfide precipitates are removed in a conventional plate and frame filter press followed by final pH adjustment of the filtrate before discharge. In Level 2 a conventional granular activated carbon filter is added for further removal of residual metals before pH adjustment.

B. Chemical Handling

Sodium bisulfide is used with filter aid after pH adjustment to pH 5-7. Care is needed to prevent escape of toxic and obnoxious H_2S fumes at neutral and acid pH level. At Level 2 no additional chemicals are used since the activated carbon bed is not regenerated but is periodically removed and replaced. The handling of granular carbon may cause temporary dust problems but it causes no special hazards.

C. Separation and Removal of Solids

Conventional settling and filtration methods are used, but because of the toxicity of mercury, precipitated sludges should be disposed of in a safe chemical waste area.

D. Monitoring Requirements

Both levels of treatment include provisions for sampling and monitoring of the wastewater discharge. Monitoring of heavy

metals is done by atomic absorption methods at a qualified commercial laboratory. Simple field tests for heavy metals as a group are available for routine process control.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed. The model plant characteristics are:

A. Wastewater Flow

Data presented in Table 11-3 indicate an average wastewater flow of $2.1 \text{ m}^3/\text{kgg}$ for 13 plants, while the average of the five plants surveyed during this study averaged $1.7 \text{ m}^3/\text{kgg}$.

For effluent limitation calculations (see 11.8.2) and for cost estimation the more conservative unit flow from the larger data base ($2.1 \text{ m}^3/\text{kgg}$) has been used.

B. Chlorine Production

Approximately 50 percent of the production data for all the chlorine/caustic plants using mercury cells is available on file. Production ranges from 19,000 to 198,000 kkg of chlorine/year. Three model plants with productions of 19,100 kkg/yr, 95,500 kkg/yr and 191,000 kkg/yr were selected to represent the subcategory production range. The flow per unit of production is assumed to be the same for each size of model plant. Seventy-seven percent of the plants for which flow data was available have flows per unit of production equal to or less than the average unit flow (Table 11-3).

C. Solid Waste Produced

Brine mud constitutes the major source of solid waste generated at chlorine plants. Although flows and solids content vary considerably from plant to plant, an average flow of $0.42 \text{ m}^3/\text{kgg}$ at 10 percent suspended solids gave an estimated solids load of 42 kg/kgg to be used for cost estimating purposes. The implementation of RCRA regulations has not been included in these estimates, but RCRA costs are considered in the Economic Impact Analysis of Pollution Control Technologies for Segments of the Inorganic Chemicals Manufacturing Industry, EPA 440/2-81-023.

Chlorine Bearing Wastes

In the selection of model plants, the following assumptions have been made for the chlorine contaminated waste streams. The chlorine condensate waste stream has not been included in the waste streams going to the treatment facility. In the majority of the

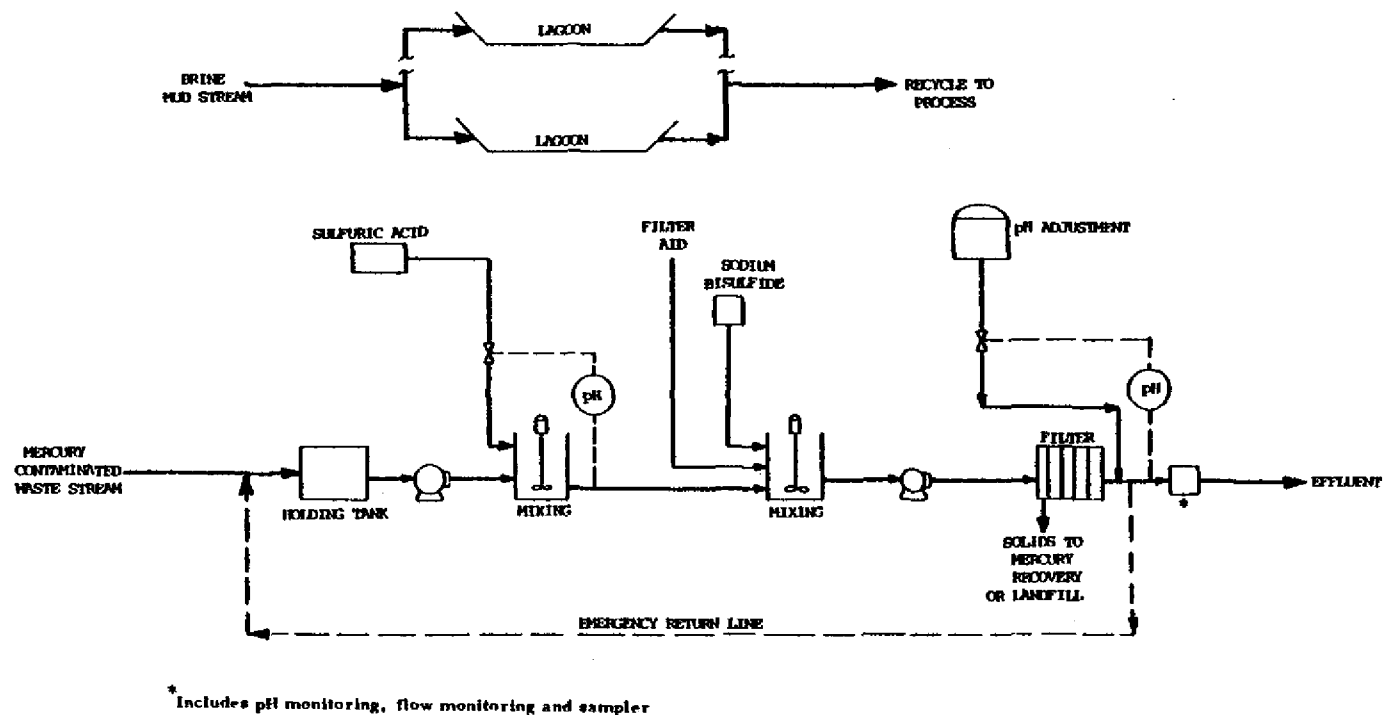


Figure 11-6. Level 1 waste water treatment for chlorine - mercury cell subcategory.

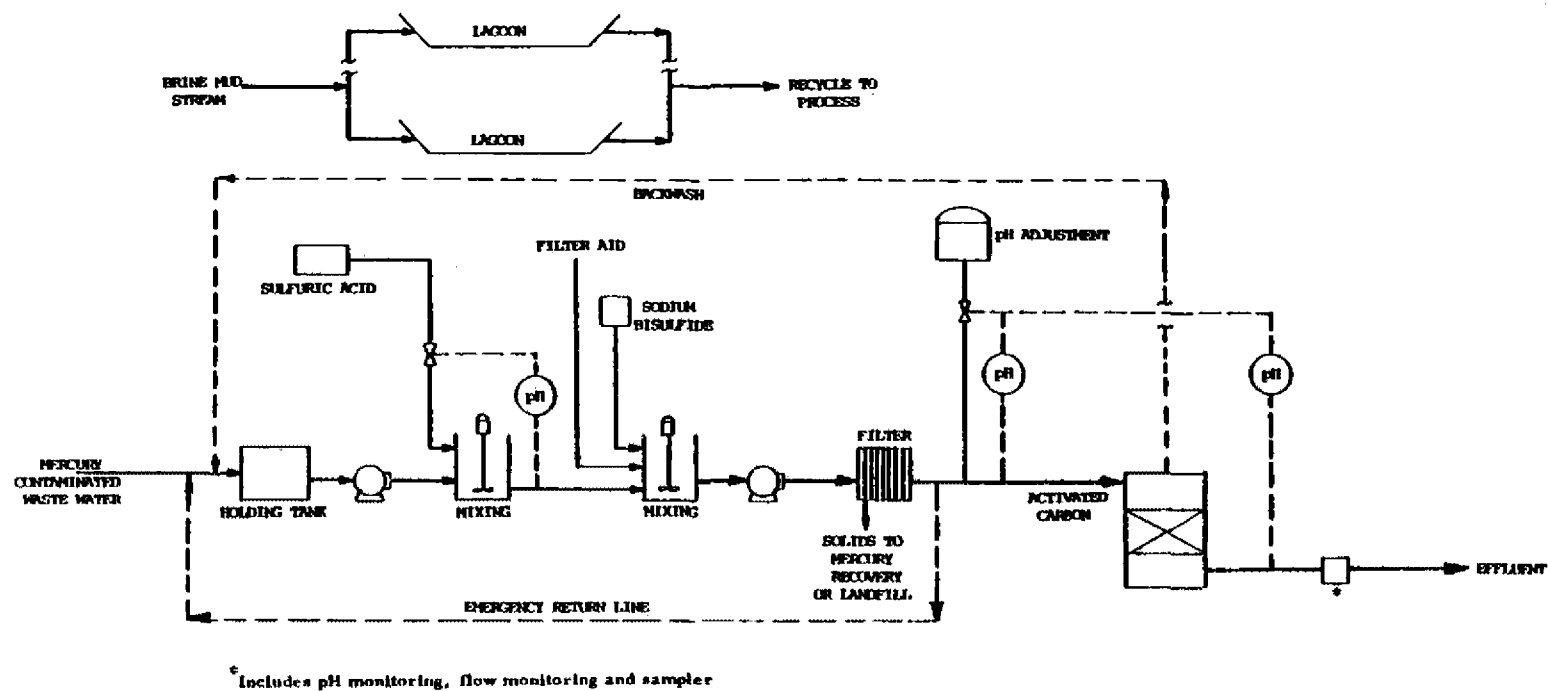


Figure 11-7. Level 2 waste water treatment for chlorine - mercury cell subcategory.

chlorine/caustic plants, this stream is stripped of chlorine by steam or vacuum and the chlorine is recycled to the purification operation. The wastewater is then returned to the process and introduced to the brine purification unit or sent to the treatment unit. The quantity of wastewater generated by this operation is small and does not significantly affect the flow determination. In some cases the chlorine gas from the cells is contact cooled with water and the scrubbed liquid, after steam stripping, is reused. The stripping operation in the recovery of chlorine is part of the process and, therefore, its cost is not included in the treatment cost. The spent tail gas scrubber solution, which contains mainly calcium or sodium hypochlorite, is assumed to be used or decomposed before it is discharged or sent to treatment. Thermal decomposition can be practiced at no additional cost at some facilities, while another efficient treatment method is catalytic decomposition. The cost estimates for decomposition are not included here because at many plants the hypochlorite stream is sold, used on-site or only infrequently discharged depending on market demand.

However, because of the environmental effects of high levels of chlorine in process wastewater discharges, the cost for the dechlorination of such streams using sulfur dioxide has been included because this is the treatment method on which control of total residual chlorine is based.

Model Plant Treatment Costs

On the basis of the model plant specifications and design concepts presented earlier, the estimated costs of treatment for three models having different production levels are shown in Tables 11-8, 11-9 and 11-10. The costs of BAT treatment are incremental over BPT costs. Table 11-11 presents a summary of the unit cost distribution between amortization and operation and maintenance components.

Basis for Regulations

Basis for BPT Limitations

A. Technology Basis

Existing mercury cell chlorine plants are controlling mercury in their wastewaters in accordance with existing BPT regulations which require a discharge of less than 0.00014 kg/kg of product as a 30-day average. The BPT regulations presently in effect (40 CFR 415.62 (a)) will not be revised. Pollutants regulated include TSS, pH and mercury. The technology basis of sulfide precipitation and filtration of mercury bearing streams (Level 1) is currently being applied at 24 plants in this subcategory. Other plants in the industry use mercury control methods that are different in detail but with the same objective.

The existing regulations apply at the treatment system effluent for TSS and mercury and at the plant effluent for pH. These regulations are presented in Table 11-2 and are sustained by the fact that plants having properly operated BPT technology have demonstrated the achievability of the effluent limitations based on available long-term monitoring data. Table 11-12 presents data from eleven mercury cell plants, seven of which are meeting the 30-day average limitations. The other four plants have mercury control technology installed but are not meeting BPT limits.

B. Flow Basis

The existing regulations contain only load limitations, kg/kkg, and no flow basis or concentration limit was provided. But the regulations did consider the inclusion of noncontact cooling water in determining discharge load limitations.

Basis for Final BAT Effluent Limitations

The original BAT limitations for this subcategory required zero discharge of process wastewater pollutants. These regulations were remanded and are not in effect. The final regulations allow for the discharge of process wastewater following treatment.

A. Technology Basis

Utilizing the cost estimates presented in this report, the Agency has analyzed the cost effectiveness of Level 1 and Level 2 treatment options for pollutant removal. The economic impact on the mercury cell chlorine subcategory has been evaluated in considering the technology basis for final BAT limitations.

For BAT, the Agency is promulgating limitations based on BPT technology (Level 1) with the addition of dechlorination. Dechlorination is being included in BAT because the toxicity of chlorine to aquatic life is well documented (59) and it is a pollutant of concern to the Agency. Dechlorination, currently practiced by at least two plants, may be required only at fewer than half of the plants in the subcategory because hypochlorite produced in tail gas scrubbers is often sold or used in other operations while residual chlorine in condensates is usually stripped or recovered. Table 11-13 presents residual chlorine discharges at plants that have reported the use, sale or treatment of chlorine-bearing wastewaters. This data indicates that some plants will be able to meet the residual chlorine limitations without the application of additional technology.

The Agency considered the addition of carbon adsorption for additional mercury removal but rejected its use because of high cost and questionable performance in this industry.

B. Flow Basis

The flow basis for BAT limitations is 2.1 m³/kkg based on the average of discharge data of 13 plants presented in Table 11-3. The order of magnitude of this unit flow volume was supported by data obtained during sampling visits to five plants at which flows ranged from 0.5 m³/kkg to 5.6 m³/kkg with an average of 1.7 m³/kkg.

C. Selection of Toxic Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are promulgated is based on the evaluation of raw waste concentrations found during the sampling program and on the treatability of toxic pollutants using BAT technology.

Table 11-14 presents the achievable concentrations of toxic pollutants using the BAT technology of sulfide precipitation followed by filtration. The first column gives the literature based treatability data presented in Section 8 and summarized in Table 8-11 and reflects the lowest level achievable by this technology. The second column gives actual industrial wastewater treatment system performance as presented in Tables 8-12 and 8-13 of Section 8. Also presented in Table 11-14 are the maximum and average raw waste concentrations of toxic pollutants found during the sampling program with an indication of the number of plants where the literature-based treatability concentration was exceeded.

Based on the occurrence of treatable levels of specific toxic metals in raw wastes and the fact that the sulfide precipitation technology is already utilized as BPT in the chlorine mercury cell subcategory, all the metals in Table 11-14, with the exception of chromium and thallium for which no sulfide/filter treatment data are available, are candidates for BAT regulation. Consideration of Section 8 on the control parameters for sulfide precipitation, however, leads to the selection of mercury as the toxic pollutant to be regulated. Antimony, arsenic, cadmium, chromium, copper, lead, nickel, silver, thallium and zinc are included for guidance but no limits are set because control of mercury will control these other metals.

D. Basis of Pollutant Limitations

Limitations are presented as unit loadings (kg/kkg) and/or concentrations (mg/l) for each pollutant. The relationship between the two is based on the unit flow rate. Although actual unit flow rates at plants vary by an order of magnitude due to such factors as raw materials and plant control practices, the Agency has determined that the unit loading effluent limitations (kg/kkg) can be met by well-operated treatment facilities.

TABLE 11-8. MODEL PLANT TREATMENT COSTS

Subcategory	Chlorine - Mercury cell Production 19,100 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	26,500	0
Equipment	93,000	23,000
Monitoring equipment	20,000	0
Subtotal	139,500	23,000
Contractor's O & P ^b	20,925	3,450
Subtotal	160,425	26,450
Engineering	32,085	5,290
Subtotal	192,510	31,740
Contingencies	19,251	3,174
Subtotal	211,761	34,914
Land	21,000	0
TOTAL INVESTMENT COST	232,761	34,914
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	112,000	14,000
Energy	1,300	500
Chemicals	500	1,500
Maintenance	21,176	3,491
Taxes and insurance	6,983	1,047
Residual waste disposal	4,500	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	161,459	28,039
C. AMORTIZATION OF INVESTMENT COST	34,454	5,681
TOTAL ANNUAL COST	195,912	33,719

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 11-9. MODEL PLANT TREATMENT COSTS

Subcategory	Chlorine - Mercury cell	
Production	95,500 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	79,500	0
Equipment	163,000	40,000
Monitoring equipment	20,000	0
Subtotal	262,500	40,000
Contractor's O & P ^b	39,375	6,000
Subtotal	301,875	46,000
Engineering	60,375	9,200
Subtotal	362,250	55,200
Contingencies	36,225	5,520
Subtotal	398,475	60,720
Land.....	63,000	0
TOTAL INVESTMENT COST	461,475	60,720
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	112,000	21,000
Energy	3,700	700
Chemicals	2,500	7,500
Maintenance	39,848	6,072
Taxes and insurance	13,844	1,822
Residual waste disposal	21,500	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	208,392	44,594
C. AMORTIZATION OF INVESTMENT COST	64,832	9,879
TOTAL ANNUAL COST	273,224	54,473

^a Represents the incremental cost above that for BPT treatment^b Overhead and Profit

TABLE 11-10. MODEL PLANT TREATMENT COSTS

Subcategory	Chlorine - Mercury cell Production 191,000 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	130,000	0
Equipment	246,000	60,000
Monitoring equipment	20,000	0
Subtotal	396,000	60,000
Contractor's O & P ^b	59,400	9,000
Subtotal	455,400	69,000
Engineering	91,080	13,800
Subtotal	546,480	82,800
Contingencies	54,648	8,280
Subtotal	601,128	91,080
Land	123,000	0
TOTAL INVESTMENT COST	724,128	91,080
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	112,000	28,000
Energy	6,500	1,300
Chemicals	5,000	15,000
Maintenance	60,113	9,108
Taxes and insurance	21,724	2,732
Residual waste disposal	42,500	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	262,837	63,640
C. AMORTIZATION OF INVESTMENT COST	97,804	14,819
TOTAL ANNUAL COST	360,640	78,459

^a Represents the incremental cost above that for BPT treatment^b Overhead and Profit

TABLE 11-11. MODEL PLANT UNIT TREATMENT COSTS

Subcategory Chlorine - Mercury cell

		Annual Treatment Costs (\$/kkg)	
		LEVEL OF TREATMENT	
COST ITEM	PRODUCTION (kkg/yr)	BPT	BAT*
Annual Operation and Maintenance	19,100	8.45	1.47
	95,500	2.18	0.47
	191,000	1.38	0.33
Annual Amortization	19,100	1.80	0.30
	95,500	0.68	0.10
	191,000	0.51	0.08
Total Annual Cost	19,100	10.26	1.77
	95,500	2.86	0.57
	191,000	1.89	0.41

*Represents the incremental cost above BPT

TABLE 11-12. MERCURY DISCHARGES FROM SELECTED CHLOR-ALKALI MERCURY CELL PLANTS*

SUBCATEGORY	CHLORINE (MERCURY CELL)		
	Mercury Waste Load (kg/kg)		
Plant	Average	Daily Maximum	Maximum 30-day Average
#343	0.000025	0.00094	0.00029
#907	0.000020	0.00026	0.000030
#898	0.000060	0.0025	0.00043
#195	0.000040	0.00073	0.00015
#106	0.000065	0.00022	0.000096
#589	0.000055	0.00086	0.00049
#299	0.000040	0.00019	0.000056
[REDACTED]	[REDACTED]	0.000093	0.000065
#317**	0.0000054	0.000048	0.000010
#195**	0.000022	0.00066	0.00010
#324**	0.00086	0.0022	0.0018

* See Reference 3

** From Plant Long Term Monitoring Data presented in Appendix A.

BAT limitations, which apply at the treatment system effluent for toxic metals and at the plant effluent for residual chlorine, are presented in Table 11-15.

1. Chlorine - Total residual chlorine limits are based on an evaluation of long-term monitoring data for total residual chlorine as presented in Appendix A (Tables A-1a and c). The long-term average concentration is 0.64 mg/l. The average variability factor for daily measurements of total residual chlorine is 2.3 and the average variability factor for 30-day averages is 1.4.

The 24-hour maximum concentration is:

$$(0.64 \text{ mg/l}) (2.3) = 1.5 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.64 \text{ mg/l}) (1.4) = 0.90 \text{ mg/l}$$

The load limitations for total residual chlorine (kg/kkg) are calculated based on the unit flow rate of 2.1 m³/kkg, thus:

$$(1.5 \text{ mg/l}) (2.1 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 0.0032 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.90 \text{ mg/l}) (2.1 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 0.0019 \text{ kg/kkg}$$

2. Toxic Pollutants

The effluent limitations and guidelines for the selected toxic pollutants are derived from three sources of information: industrial wastewater treatment system performance data (Table 8-12 and 8-13), verification sampling data, and literature based treatability estimates (Table 8-11).

The results of analysis of treated effluent represent plant performance observed during three days of screening or verification sampling. The effluent data for toxic pollutants found above treatable concentrations in raw wastes are summarized in Table 11-16. Data are presented from four plants practicing BPT technology (sulfide precipitation followed by filtration). Sampling data for the fifth plant, #299, reflect effluent quality prior to filtration.

a. Mercury

TABLE 11-13. RESIDUAL CHLORINE DISCHARGES AT SELECTED
CHLOR-ALKALI PLANTS*

Plant	Chlorine Waste Load (kg/kg)	
	Average	Range
#207	0.33	1.4 maximum
#014	0.040	0 to 1.29
#819	ND ⁽¹⁾	0.016 to 0.14
#747	0.0020	0 to 0.0060
#106	0.0010	0 to 0.14
#589	0.0030	0.0010 to 0.011
#747 ⁽²⁾	0.0025	ND
#324 ⁽²⁾	3.72	0.38 to 12.2

* See Reference 3

(1) - ND = No data

(2) - From Plant Long-Term Monitoring Data

TABLE 11-14. COMPARISON OF RAW WASTE CONCENTRATIONS OF TOXIC POLLUTANTS WITH TREATABILITY

SUBCATEGORY		CHLORINE (MERCURY CELL)			
Pollutant	Literature-Treatability ⁽¹⁾ (mg/l)	Industrial Waste Water Treatment System Performance (mg/l)	Maximum Plant Average (mg/l)	Average of 5 Plants (mg/l)	Number Plants out of Five Exceeding Literature-based Treatability Level
Antimony	ND	0.23 ⁽²⁾	0.49	<0.28	ND
Arsenic	0.050	0.15 ⁽³⁾	0.33	0.14	3
Cadmium	0.010	0.19 ⁽⁴⁾	0.46	0.11	3
Chromium	ND	ND	0.12	0.075	ND
Copper	0.050	0.20 ⁽³⁾	1.2	0.41	5
Lead	0.050	0.10 ⁽³⁾	1.4	0.40	3
Mercury	0.010	0.034 ⁽³⁾	123	30.9	5
Nickel	0.050	0.022 ⁽⁴⁾	1.4	0.35	2
Silver	0.050	0.070 ⁽⁴⁾	0.58	0.15	2
Thallium	ND	ND	0.38	0.17	ND
Zinc	0.020	0.12 ⁽³⁾	20	4.4	5

(1) Estimates from Section 8.1, Table 8-11, given as the lower limit of treatability.

(2) Data from Table 11-16 (average effluent concentration from verification sampling).

(3) Estimated achievable long-term average concentrations from Table 8-13.

(4) Data from Table 8-12 (recently submitted by Olin Corporation).

ND = No data available on treatability with sulfide/filter.

The BAT limitations for mercury, although based on the same technology, are more stringent than BPT limitations. The estimated achievable long-term average concentration for mercury from Table 8-13 is 0.034 mg/l and is obtained from recently submitted industry data. A daily variability factor of 3.1 and a 30-day average variability factor of 1.4 are estimated from data in Appendix A and from the recently submitted industry data.

The 24-hour maximum concentration is:

$$(0.034 \text{ mg/l}) (3.1) = 0.11 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.034 \text{ mg/l}) (1.4) = 0.048 \text{ mg/l}$$

The load limitations for mercury (kg/kkg) are calculated based on the unit flow rate of 2.1 m³/kkg, thus:

$$(0.11 \text{ mg/l}) (2.1 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 0.00023 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.048 \text{ mg/l}) (2.1 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 0.00010 \text{ kg/kkg}$$

Comment from 3 companies operating 10 plants stated that the plants can achieve these limitations.

b. Zinc

The zinc guidance is based on the estimated achievable long-term average concentration of 0.12 mg/l which is obtained from Table 8-13. A daily variability factor of 7.6 and a 30-day average variability factor of 1.5 are obtained from the recently submitted industry data on zinc effluent concentrations.

The 24-hour maximum concentration is:

$$(0.12 \text{ mg/l}) (7.6) = 0.91 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.12 \text{ mg/l}) (1.5) = 0.18 \text{ mg/l}$$

c. Antimony

TABLE 11-15. EFFLUENT LIMITATIONS
Chlorine-Mercury Cell
Best Available Technology
Wastewater Flow: 2.1 m³/kg

SUBCATEGORY		CHLORINE MERCURY CELL				
Pollutant	Subcategory Performance (mg/l)	Daily Variability Factor	Concentration Basis (mg/l)		Effluent Limit (kg/kg)	
		30-day Avg. Variability	Max.	24-hr.	Max.	24-hr.
		Factor	Avg.	Max.	Avg.	Max.
<u>Nonconventional Pollutants:</u>						
Total Residual Chlorine ⁽⁷⁾	0.64 ⁽¹⁾	2.3/1.4	0.90	1.5	0.0019	0.0032
<u>Toxic Pollutants:</u>						
Antimony	0.23 ⁽²⁾	7.6/1.5	0.35	1.7	--(5)	--(5)
Arsenic	0.15 ⁽³⁾	6.7/1.4	0.21	1.0	--(5)	--(5)
Cadmium	0.050 ⁽²⁾	7.6/1.5	0.075	0.38	--(5)	--(5)
Chromium	0.044 ⁽²⁾	7.6/1.5	0.066	0.33	--(5)	--(5)
Copper	0.20 ⁽³⁾	7.6/1.5	0.30	1.5	--(5)	--(5)
Lead	0.10 ⁽³⁾	4.1/1.3	0.13	0.41	--(5)	--(5)
Mercury ⁽⁶⁾	0.034 ⁽³⁾	3.1/1.4	0.048	0.11	0.00010	0.00023
Nickel	0.10 ⁽⁴⁾	5.7/1.4	0.14	0.57	--(5)	--(5)
Silver	0.067 ⁽²⁾	7.6/1.5	0.10	0.51	--(5)	--(5)
Thallium	0.17 ⁽²⁾	7.6/1.5	0.26	1.3	--(5)	--(5)
Zinc	0.12 ⁽³⁾	7.6/1.5	0.18	0.91	--(5)	--(5)

- (1) Long-term average concentration from Appendix A.
- (2) Average effluent concentration from verification sampling.
- (3) Estimated achievable long-term average concentration from Table 8-13.
- (4) Lower limit of literature treatability for sulfide/filter technology according to Table 8-11.
- (5) No load limits; concentration limits are provided for guidance purposes.
- (6) Limits are also applicable to PSNS, and NSPS.
- (7) Limits are also applicable to NSPS.

Because no industry data is available, the antimony guidance is based on the average effluent concentration from the verification sampling. The value of 0.23 mg/l is used as a long-term average. The variability factors established for zinc are applied to antimony since these would approximate the situation where a metal is incidentally controlled.

The 24-hour maximum concentration is:

$$(0.23 \text{ mg/l}) (7.6) = 1.7 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.23 \text{ mg/l}) (1.5) = 0.35 \text{ mg/l}$$

d. Arsenic

The arsenic guidance is based on the estimated achievable long-term average concentration of 0.15 mg/l which is obtained from Table 8-13. A daily variability factor of 6.7 and a 30-day average variability factor of 1.4 are obtained from the recently submitted industrial data on arsenic effluent concentrations.

The 24-hour maximum concentration is:

$$(0.15 \text{ mg/l}) (6.7) = 1.0 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.15 \text{ mg/l}) (1.4) = 0.21 \text{ mg/l}$$

e. Cadmium

Because no industry data are available, the cadmium guidance is based on the average effluent concentration from the verification sampling. The value of 0.050 mg/l is used as a long-term average. The variability factors established for zinc are applied to cadmium since these would approximate the situation where a metal is incidentally controlled.

The 24-hour maximum concentration is:

$$(0.050 \text{ mg/l}) (7.6) = 0.38 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.050 \text{ mg/l}) (1.5) = 0.075 \text{ mg/l}$$

f. Chromium

TABLE 11-16. EFFLUENT CONCENTRATIONS OF TOXIC POLLUTANTS
FROM VERIFICATION SAMPLING

SUBCATEGORY		CHLORINE (MERCURY CELL)					
Pollutant	Plant Effluent Concentrations (mg/l)						Treatability ⁽¹⁾ (mg/l)
	Plant						
	#299	#747	#317	#106	#167	Avg.	
Antimony	0.15	<0.25	<0.25	<0.45	<0.065	<0.23	(2)
Arsenic	0.063	<0.010	0.020	<0.0050	0.38	<0.096	0.050
Cadmium	0.073	0.12	<0.025	0.016	0.010	<0.050	0.010
Chromium	<0.060	<0.050	<0.050	<0.010	<0.050	<0.044	(2)
Copper	0.038	<0.025	<0.030	0.043	<0.025	<0.033	0.050
Lead	<0.050	0.073	0.17	0.38	0.12	<0.16	0.10
Mercury	0.029	0.10	0.19	<0.00050	0.32	<0.13	0.010
Nickel	<0.050	<0.050	<0.067	0.14	<0.050	<0.074	0.10
Silver	<0.015	<0.015	<0.015	0.26	<0.015	<0.067	0.050
Thallium	0.20	<0.045	<0.25	0.26	0.090	<0.17	(2)
Zinc	0.10	<0.025	0.51	0.088	<0.025	<0.15	0.020

(1) Lower limit from literature-based treatability estimates from Section 8.1.

(2) No data available for treatability with sulfide/filter.

Because no industry data are available, the chromium guidance is based on the average effluent concentration from the verification sampling. The value of 0.044 mg/l is used in place of a long-term average. The variability factors established for zinc are applied to chromium since these would approximate the situation where a metal is incidentally controlled.

The 24-hour maximum concentration is:

$$(0.044 \text{ mg/l}) (7.6) = 0.33 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.044 \text{ mg/l}) (1.5) = 0.066 \text{ mg/l}$$

g. Copper

The copper guidance is based on the estimated achievable long-term average concentration of 0.20 mg/l which is obtained from Table 8-13. A daily variability factor of 7.6 and a 30-day average variability factor of 1.5 are obtained from the recently submitted industry data on copper effluent concentrations.

The 24-hour maximum concentration is:

$$(0.20 \text{ mg/l}) (7.6) = 1.5 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.20 \text{ mg/l}) (1.5) = 0.30 \text{ mg/l}$$

h. Lead

The lead guidance is based on the estimated achievable long-term average concentration of 0.10 mg/l which is obtained from Table 8-13. A daily variability factor of 4.1 and a 30-day average variability factor of 1.3 are obtained from the recently submitted industry data on lead effluent concentrations.

The 24-hour maximum concentration is:

$$(0.10 \text{ mg/l}) (4.1) = 0.41 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.10 \text{ mg/l}) (1.3) = 0.13 \text{ mg/l}$$

i. Nickel

The industrial wastewater treatment system performance data in Table 8-12 show values for nickel below the lower limit of literature treatability estimated in Table 8-11. Because of this, the lower limit, 0.10 mg/l, is used in place of a long-term average as a basis for the nickel guidance. A daily variability factor of 5.7 and a 30-day average variability factor of 1.4 are obtained from the recently submitted industry data on nickel effluent concentrations.

The 24-hour maximum concentration is:

$$(0.10 \text{ mg/l}) (5.7) = 0.57 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.10 \text{ mg/l}) (1.4) = 0.14 \text{ mg/l}$$

j. Silver

Because no industry data are available, the silver guidance is based on the average effluent concentration from the verification sampling. The value of 0.067 mg/l is used in place of a long-term average. The variability factors established for zinc are applied to silver since these would approximate the situation where a metal is incidentally controlled.

The 24-hour maximum concentration is:

$$(0.067 \text{ mg/l}) (7.6) = 0.51 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.067 \text{ mg/l}) (1.5) = 0.10 \text{ mg/l}$$

k. Thallium: Because no industry data are available, the thallium guidance is based on the average effluent concentration from the verification sampling. The value of 0.17 mg/l is used in place of a long-term average. The variability factors established for zinc are applied to thallium since these would approximate the situation where a metal is incidentally controlled.

The 24-hour maximum concentration is:

$$(0.17 \text{ mg/l}) (7.6) = 1.3 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.17 \text{ mg/l}) (1.5) = 0.26 \text{ mg/l}$$

Basis for BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. The dechlorination technology added to BPT for BAT does not remove additional conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for New Source Performance Standards

For NSPS, the Agency is promulgating limitations equal to BPT for TSS and pH and BAT for other pollutants because of the prohibitive cost of additional technology. Pollutants to be limited are pH, TSS, mercury, and total residual chlorine.

Basis for Pretreatment Standards

For pretreatment standards for new sources, the Agency is promulgating limitations based on BAT technology excluding dechlorination. Dechlorination is unnecessary for discharges to POTWs because influent to POTWs is often chlorinated. The pollutant to be limited is mercury. The PSNS limitations are based on BAT because this provides better mercury removal than is achieved by a well-operated POTW with secondary treatment installed and, hence, mercury will pass through a POTW in the absence of pretreatment.

The Agency is not promulgating PSES for this subcategory. Instead, the subcategory is excluded from categorical PSES under the provisions of paragraph 8(b) of the Settlement Agreement because the discharge of total toxic metals to POTWs from the two existing sources combined is below treatable levels and amounts to only 40 pounds per year. Both existing sources have installed and are operating treatment facilities equivalent to BPT/BAT to control mercury.

Diaphragm Cell Process Industry Profile

General Description

Approximately 65 percent of the U.S. production of chlorine is by diaphragm cell plants. Of 40 known plants in 1978, Section 308 data are available for 19. Table 11-17 presents a summary profile of the subcategory. Table 11-18 presents the status of discharge regulations prior to promulgation of this regulation for diaphragm cell chlorine plants.

General Process Description

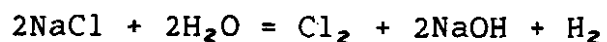
A. Brine System

As in the mercury cell process, the sodium chloride solution (brine or salt dissolved in water) is purified before it is sent to the electrolytic cells. Precipitation of major impurities with sodium carbonate and sodium hydroxide followed by clarification generates a brine mud waste which is then sent to a lagoon or filtered. The settled brine is saturated further by the addition of salt from caustic evaporators and then is sent to the cells.

The fundamental difference between diaphragm and mercury cell brine systems is that unconverted sodium chloride in diaphragm cell processes is carried with the sodium hydroxide (caustic) from the cell and is then removed as a solid in caustic evaporators. In mercury cells, the unconverted sodium chloride is discharged through the brine system.

B. Diaphragm Cell

The treated brine solution is electrolyzed in the diaphragm cell to form chlorine, hydrogen, and sodium hydroxide according to the reaction:



The diaphragm cell contains a porous asbestos diaphragm separating the anode from the cathode. Chlorine is liberated at the anode and hydrogen and hydroxyl ions (caustic) are produced at the cathode. In the past, the predominant material used for anodes was graphite with some cell designs using lead to provide an electrical contact and support. The lead was joined to the graphite anode by an organic binder. In recent years, many graphite anodes have been replaced by stabilized metal anodes made of titanium with a platinum or ruthenium oxide coating. (An industry association estimate is that approximately 49 percent of U.S. diaphragm cell capacity still involves graphite anodes.) The advantages of using metal anodes compared to graphite anodes are increased power efficiency of the cells, longer anode life and a reduction in potential pollutant loads of lead and chlorinated organics.

C. Product Purification

As with mercury cell plants, chlorine liberated at the anode must be cooled and dried to remove moisture and other impurities. The cooling generates a chlorine condensate stream which can be stripped to recover chlorine and then returned to the brine system or discharged. Drying the chlorine gas is accomplished by scrubbing with sulfuric acid. The resulting diluted acid can subsequently be regenerated, sold, or used for nonbrine system pH

TABLE 11-17. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	CHLORINE (DIAPHRAGM CELL)
Total subcategory capacity rate	8,270,000 kkg/year
Total subcategory production rate	6,430,000 kkg/year
Number of plants in this subcategory	40
308 Data on file for	19
With total capacity of	6,400,000 kkg/year
With total production of	4,200,000 kkg/year
Representing capacity	77 percent
Representing production	66 percent
Plant production range:	
Minimum	14,700 kkg/year
Maximum	1,500,000 kkg/year
Average production	221,000 kkg/year
Median production	103,000 kkg/year
Average capacity utilization	67 percent
Plant age range:	
Minimum	4 years
Maximum	74 years
Waste water flow range:	
Minimum	1,100 cubic meters/day
Maximum	7,100 cubic meters/day
Volume per unit product:	
Minimum	1 cubic meters/kkg
Maximum	23 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

TABLE 11-18. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY CHLORINE (DIAPHRAGM CELL)

SUBPART F (40 CFR 415.60, 3/12/74)

STANDARDS

Product	Parameters	BPCTCA		BATEA		NSPS	
		Max ¹	Avg. ²	Max.	Avg.	Max.	Avg.
Process		(kg/kg)	(kg/kg)	(kg/kg)	(kg/kg)	(kg/kg)	(kg/kg)
Diaphragm							
Cell							
Process	TSS	0.64	0.32	No discharge of pwwp ⁽³⁾		0.64	0.32
	Pb	0.005	0.0025	No discharge of pwwp ⁽³⁾		0.00008	0.00004

* Section 415.63 was remanded and reserved (41 FR 51601, November 23, 1976).

(1) Max. = Maximum of any one day.

(2) Avg. = Average of daily values for thirty consecutive days.

(3) pwwp = Process wastewater pollutant.

control. When the chlorine gas is compressed and liquified, noncondensable gases known as tail or sniff gases remain. These are usually scrubbed with caustic soda or lime generating a hypochlorite solution which can be sold, used on-site, or discharged, with or without decomposition or treatment.

The sodium hydroxide or caustic from the diaphragm cell has a concentration of about 11 percent NaOH and a sodium chloride content as high as 17 percent. The caustic is evaporated to 50 percent NaOH by multiple effect evaporators. Sodium chloride remains as a solid salt which is then separated from the caustic and returned to the brine system. Further purification of the caustic is necessary for some applications (such as rayon production) and extraction or adsorption techniques have been used to remove small amounts of impurities. The caustic can be evaporated further if more concentrated products are required. The vapor evolved from the last of multiple effect evaporators is condensed in barometric condensers generating contact cooling water, or in surface condensers using noncontact cooling water.

The hydrogen gas generated in the process can be vented or cooled by refrigeration to remove water vapor before sale or use as a fuel.

Figure 11-8 is a general flow diagram for the manufacture of chlorine by the diaphragm cell process.

Water Use and Wastewater Sources

Water Use

Water use at diaphragm cell plants is similar to that at mercury cell plants with one exception. Common uses include noncontact cooling, tail gas scrubbers, cell wash, equipment maintenance, floor washings and filter backwashing. The exception at diaphragm cell plants is the use of water for barometric condensers in the evaporation of caustic.

Waste Sources

A. Brine Mud

As with mercury cells, this is the waste produced during purification of brine before it is introduced into the cells for electrolysis. It consists of precipitated hydroxides and carbonates of calcium, magnesium, iron, and other metals. The mud can be a major source of solid waste depending on the purity of the raw salt used. At diaphragm cell plants, brine muds are filtered or settled in lagoons. The solids are landfilled and the filtrate or overflow is discharged or recycled to the brine system.

Brine mud is the major source of solid waste at chlorine plants, and discharges range from 0.04 to 1.5 cubic meters per metric ton (m^3/kg), with a solids content of from 2 to 20 percent.

B. Cell Room Wastes

These wastes include leaks, spills, area washdown and cell wash waters. At diaphragm cell plants, cell wash waters are heavily laden with asbestos and are therefore settled and/or filtered before chemical treatment or discharge. At some plants using graphite anodes in the cells, the cell room wastes also contain lead. Data from diaphragm cell plants indicate a waste flow from 0.02 to 1.2 m^3/kg from cell room operations.

C. Chlorine Cooling Condensate

Condensate from the indirect cooling of cell gas is contaminated with chlorine. The chlorine is removed (stripped) or recovered from the stream before discharge or recycle. Condensate flows from three plants range from 0.16 to 0.9 m^3/kg .

D. Spent Sulfuric Acid

Concentrated sulfuric acid is used to dry chlorine gas after the first stage of cooling. Once diluted to 50 to 70 percent, the spent acid can be regenerated, sold, or used for nonbrine system pH control.

E. Tail Gas Scrubber Liquid

The uncondensed chlorine gas from the liquefaction stage is scrubbed with sodium or calcium hydroxide producing the corresponding hypochlorite. The hypochlorite can be used in other processes, sold, decomposed, or discharged. The amount of tail gas scrubber water generated at diaphragm cell plants ranges from 0.1 to 0.29 m^3/kg .

F. Filter Backwashes

Backwashing of filters used to treat brine before it is sent to the cells at one graphite anode diaphragm cell plant generated a wastewater flow of 0.45 m^3/kg . Backwashing of filters used to clarify caustic product at the same plant resulted in an average flow of 5.4 m^3/kg . At some diaphragm cell plants, these wastewaters are partially recycled to process.

The relatively high flow of caustic filter backwash is due to the need to remove sodium sulfate, an impurity in the caustic. Sulfate ions, if allowed to accumulate in the brine system at graphite anode plants will interfere with cell performance.

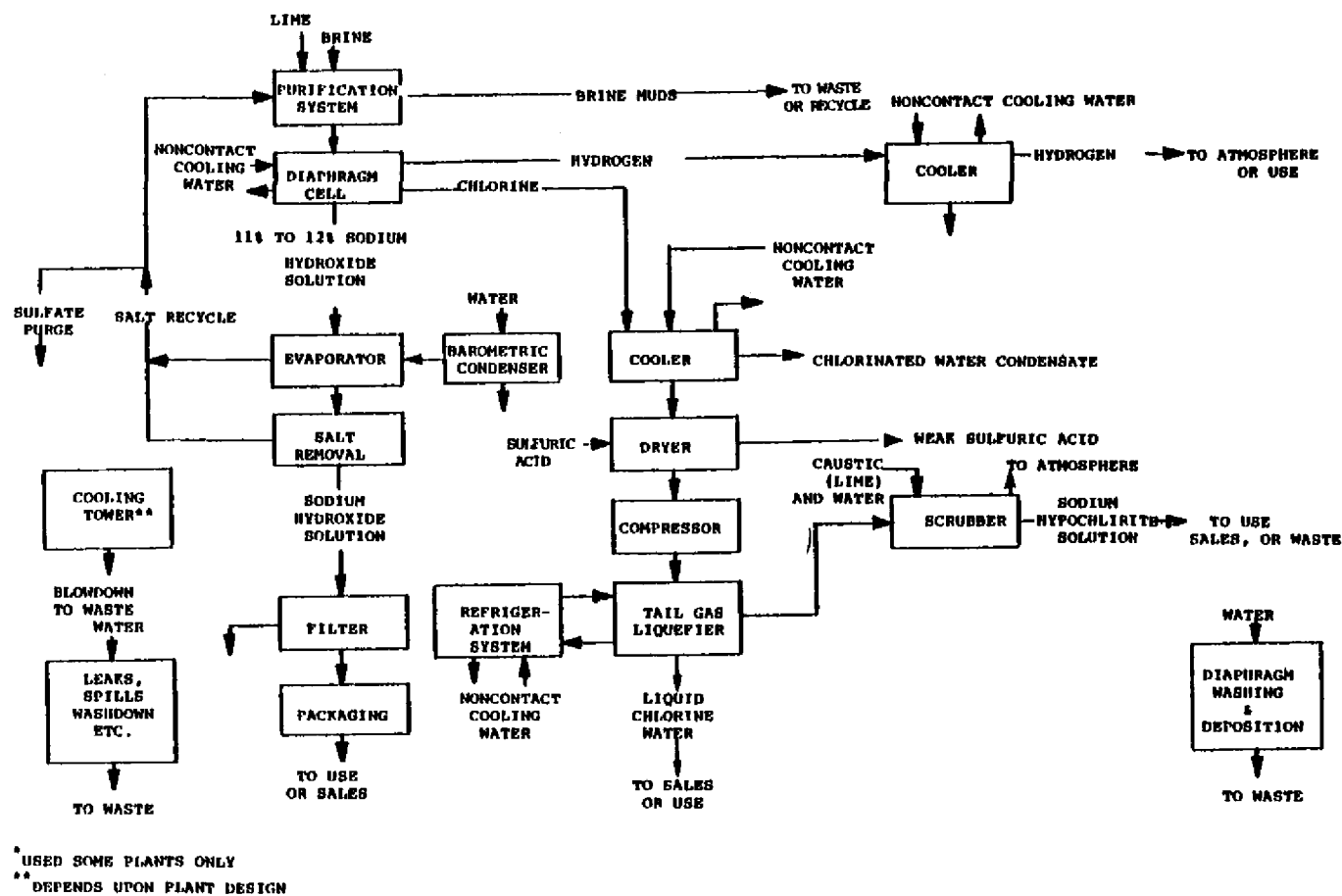


Figure 11-8. General process flow diagram for production of chlorine/caustic by diaphragm cells.

G. Hydrogen Condensate

Cooling of hydrogen gas for use or sale produces a condensate stream which can be discharged. Although no data are available on the volume of this flow, it is small.

H. Barometric Condenser Wastewater

When vapors from caustic evaporators are contact-cooled, a significant amount of wastewater can be generated. Flows of from ~~90 to 300~~ m^3/kg have been reported at facilities where barometric condenser water is "once through" and not recirculated. Recirculation of barometric condenser water requires a cooling step and a blowdown discharge. A number of facilities are accomplishing this with a corresponding reduction in water use. The necessary blowdown of recirculating barometric condenser wastewater at two plants ranges from a flow of $0.82 \text{ m}^3/\text{kg}$ to $0.89 \text{ m}^3/\text{kg}$.

I. Summary of Wastewater Flows

Table 11-19 summarizes unit wastewater flow data available by specific sources. A separate list of flows at one graphite anode plant is presented to compare wastewater generation between metal anode and graphite anode plants.

Descriptions of Specific Plants

The following description of plants includes those plants that were sampled during the screening and verification program. The discussion primarily covers plant practices in wastewater control and treatment. Plants were selected for screening and verification sampling because they were representative of the industry in that they included a wide range of sizes and variation in process detail.

Screening

At Plant #014, visited during the screening program, the chlorine condensate is stripped with steam to remove and recover chlorine. Brine precipitates (muds) are land disposed, while the spent sulfuric acid and the scrubber solutions are used at an adjacent plant. The condensate from the hydrogen cooler is used as makeup water for a cooling tower system, and the condensate from the evaporative concentration of sodium hydroxide is used to dissolve salt reclaimed from the concentration process. The cell washings are sent to a collection pond where asbestos and other suspended solids are removed. In Figure 11-9, the general process flow sheet is presented. The waste streams sampled and their waste loadings are presented in Table 11-20. The only process waste stream discharged is once-through barometric condenser cooling water.

Verification

Four plants were visited and their waste streams sampled during the verification program. The results of analysis of the wastewaters are presented in Table 11-20.

At Plant #261, the cathode wash water is passed through a filter and the asbestos drummed and disposed of in an off-site landfill, while the filtrate goes to the sewer. Brine purification muds at this facility are utilized for their alkalinity on-site and then they are settled prior to discharge of the supernatant. Spent sulfuric acid is used for neutralization of wastewaters. Dechlorination of the drying acid by reaction with sodium bisulfite is planned in the near future. Figure 11-10 shows the process flow diagram and sampling points.

Plant #738 has two production lines, 738A and 738B, that are almost identical. At the new plant (738B) the NaOH is not concentrated nor is the waste from the chlorine disposal system scrubbed. In addition, the inert gases from the liquefaction step are put through the chlorine disposal system. The process flow sheets are shown in Figures 11-11 and 11-12.

Plant #736 has installed demisters to control the vapors evolved from the last stage of the evaporator during the concentration of caustic soda. In this treatment, the steam evolved from the concentration of cell liquors passes through metal wool filters to reduce entrained solids. The cell room washings are sent to a settling chamber and the settled asbestos is sent to a landfill. The other wastewaters, consisting of caustic evaporator washings and wastes from salt separation, brine purification operations, and caustic filtration backwash waters, are combined and sent to one of two settling ponds. Skimming devices on the settling ponds remove any oil that separates, while the settled solids in the ponds are dredged and disposed of in an abandoned brine well. Figure 11-13 shows the process flow diagram and sampling points.

Plant #967 uses graphite anodes in its diaphragm cells. The cell washings at this plant are sent to an asbestos pond that has a continuous cover of water. Periodically, the settled solids are removed, sealed in drums and disposed of in a landfill. The overflow from the pond is treated with soda ash to precipitate lead, and then filtered. Sulfuric acid is used to bring the pH down to the 6 to 9 range. Figure 11-14 is a general process flow diagram for Plant # 967.

Descriptions of Plants Not Sampled

At Plant #999, brine mud and other streams with high suspended solids are collected and filtered with leaf filters. The cake is disposed of in a landfill and the filtrate returned to the brine system.

At Plant #326, wastewater from the diaphragm cell process is combined with other process wastewaters. The combined wastewater is sent to

TABLE 11-19. WASTE WATER FLOWS AT DIAPHRAGM CELL CHLORINE PLANTS

Stream Description	Flow (m ³ /kg)			
	Plants with Metal Anodes			Plant with Graphite Anodes
	min.	avg.	max.	
Cell room wastes and cell wash	0.020	0.38	0.67	1.2
Chlorine Condensate	0.16	0.49	0.90	0.78
Spent Sulfuric Acid		0.010		NA
Tail Gas Scrubber	0.10	0.17	0.29	0.11
Caustic Filter Wash		NA		5.4
Brine Filter Backwash		NA		0.45
Caustic Cooling Blowdown	0.82	0.86	0.89	NA
Brine Mud	0.040	0.42	1.5	NA

NA: Not Available

two settling tanks in series. In one of the settling tanks, skimmers have been installed to remove oil and the overflow from the second is filtered before discharge.

At Plant #589, the brine mud from the clarifier underflow is sent to a brine mud settling pond. The overflow, which is mostly brine, is returned to the process. The cell room washings are sent to a settling pit and the settled asbestos fibers are removed by the use of a vacuum truck, and disposed of in a landfill. The chlorine from the cells is contact-cooled with the tail gas scrubber water. The resulting wastewater is steam stripped for chlorine recovery before discharge.

At Plant #741, chlorine, caustic soda, and potassium hydroxide are produced using both mercury and diaphragm cells. Mercury-bearing effluent at this facility is treated by sulfide precipitation. Tail gas absorption wastes are treated by catalytic decomposition by a process which consists of scrubbing with caustic soda solution and treating the resulting hydrochlorite solution with nickel chloride and iron chloride. Consumption of iron and nickel chloride is approximately equal and consists of 0.01 kilogram per metric ton of chlorine produced. The catalytic decomposition proceeds relatively slowly, and wastes are retained in the treatment tanks for approximately three days, after which time no residual chlorine is reported to be present (3).

Toxic Pollutant Concentrations

A. Analytical Data Base

Section 5 of this report describes the methodology of the screening and verification sampling program. In the chlorine diaphragm cell industry, a total of 15 days of sampling were conducted at Plants #014, 261, 738, 967, and 736. Thirty-seven different sampling points were involved covering various raw waste streams and the treated effluents at these plants. The evaluation of the toxic metal content of these process related waste streams was based on 975 analytical data points. The sampling for toxic organic pollutants at Plants #014 and 967 generated 2300 analytical data points. Analysis of waste for asbestos generated an additional 13 data points.

B. Asbestos

Asbestos, used as a diaphragm separating the cell anode and cathode, is the major toxic pollutant consistently found in process wastewater from diaphragm cell plants. It occurs primarily in wastes resulting from activities such as cell room washdown and cell repair and cleaning.

Table 11-21 presents the results of asbestos determinations of supply water and wastewaters at three diaphragm cell plants.

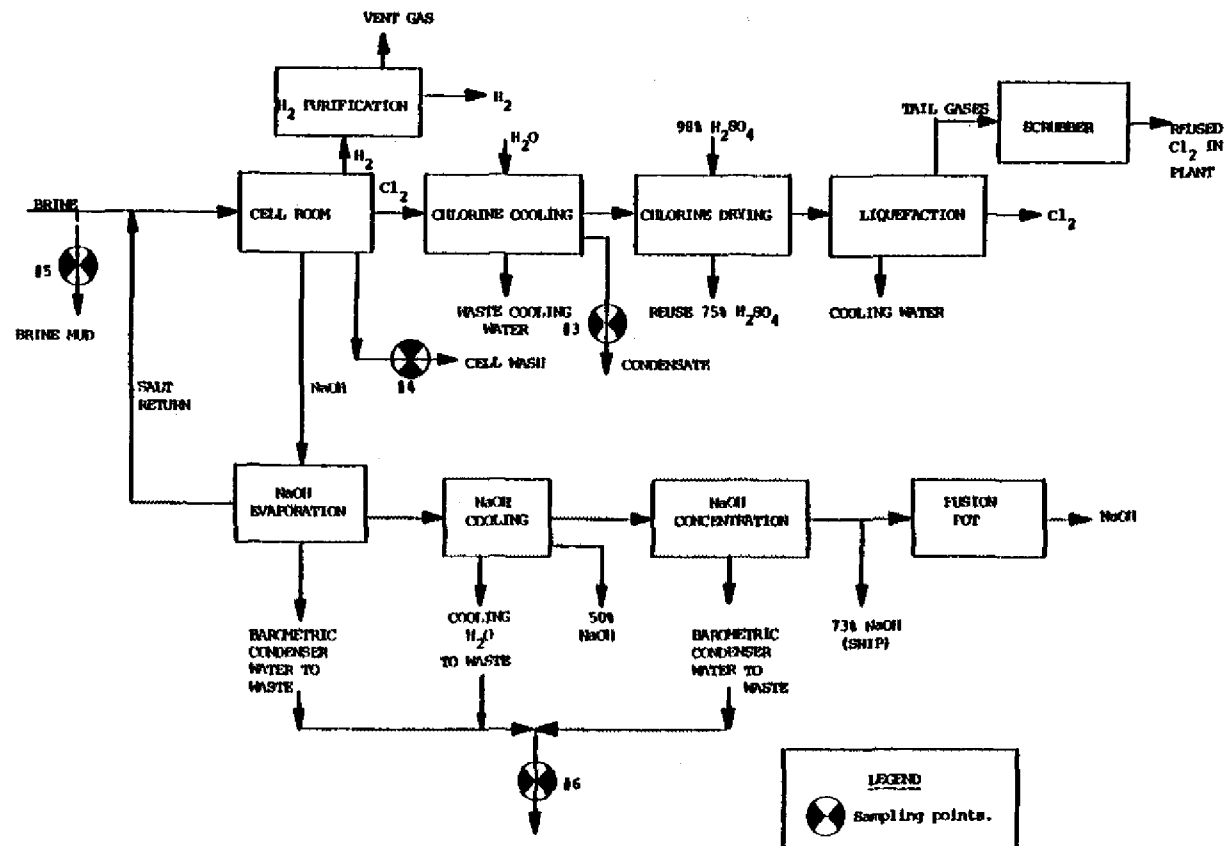


Figure 11-9. General process flow diagram at plant #014 showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture.

TABLE 11-20. POLLUTANT CONCENTRATIONS AND LOADS AT
SCREENING AND VERIFICATION PLANTS

SUBCATEGORY		CHLORINE DIAPHRAGM CELL			
Plant & Stream No.	Stream Description	(mg/l)	TSS (kg/kkg)	Lead (mg/l)	Lead (kg/kkg)
#014					
3	Cl ₂ condensate	.20	1.4×10^{-3}	0.0055	5.0×10^{-6}
4	Cell wash	1600	2.4×10^{-2}	0.26	3.9×10^{-6}
5	Brine mud	NA	NA	0.72	1.3×10^{-5}
6	Bar. condenser	7.0	3.6	0.0050	1.5×10^{-3}
#261					
1	Brine mud	NA	NA	0.36	3.0×10^{-4}
2	Cell wash	4800	1.8×10^{-1}	2.0	7.6×10^{-5}
3	Asbestos filtrate	9.0	NA	0.075	NA
4	Filter cake	NA	NA	42	NA
5	Bar. condenser	6.0	NA	< 0.010	NA
#738A1					
	Cell room waste	27	1.4×10^{-3}	0.077	3.9×10^{-6}
2	Asbestos wash	57	7.0×10^{-3}	0.031	3.8×10^{-6}
3	Hypo scrubber	290	2.7×10^{-2}	0.18	1.7×10^{-5}
4	Cl ₂ cooling water	35	2.2×10^{-1}	0.28	1.3×10^{-4}
5	Caustic cooling tower	48	4.3×10^{-2}	0.51	4.5×10^{-4}
#738B6					
	Cell room waste	95	4.5×10^{-3}	0.067	3.2×10^{-6}
7	Asbestos wash	72	8.3×10^{-3}	0.13	1.5×10^{-5}
8	Hypo scrubber	160	1.4×10^{-2}	0.20	1.7×10^{-5}
9	Cl ₂ cooling water	20	1.7×10^{-2}	0.20	1.7×10^{-5}
10	Caustic cooling tower	4.7	3.8×10^{-3}	< 0.010	< 8.2×10^{-6}
11	Chlorate sump	32.	7.0×10^{-3}	< 0.010	< 2.3×10^{-6}
12	Plant effluent(B)	63	5.7×10^{-1}	0.12	1.1×10^{-3}
13	Final effluent (Total)	58	NA	0.078	NA
14	Brine mud	270	NA	0.10	NA

(Continued)

TABLE 11-20 (continued)

Plant & Stream No.	Stream Description	TSS		Lead	
		(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)
#736					
1	Cell wash	934	6.0×10^{-2}	0.014	9.1×10^{-6}
2	Cell room drain	284	4.6×10^{-3}	0.17	2.8×10^{-6}
3	Brine mud	20,000	33	0.019	3.1×10^{-5}
4	50% Bar. condenser	32	NA	0.010	NA
5	70% Bar. condenser	21	NA	0.010	NA
6	95% Bar. condenser	90.3	NA	0.010	NA
7	Chlorine condensate	2.4	3.9×10^{-4}	0.010	1.6×10^{-6}
#967					
1	Cell bldg wastes	1000	1.8×10^{-1}	680	1.2×10^{-1}
2	Lead pond effluent	54	3.0×10^{-2}	29	1.6×10^{-2}
3	Caustic backwash	160	8.6×10^{-1}	0.32	1.7×10^{-3}
4	Brine backwash	13,000	5.8	0.52	2.3×10^{-4}
5	Cell wash	310	5.6×10^{-2}	48	8.6×10^{-3}
6	Condensate and H_2SO_4	1100	8.7×10^{-1}	0.92	7.3×10^{-4}
7	Scrubber waste	270	1.2×10^{-2}	0.67	2.9×10^{-5}

NA: Not Available

7

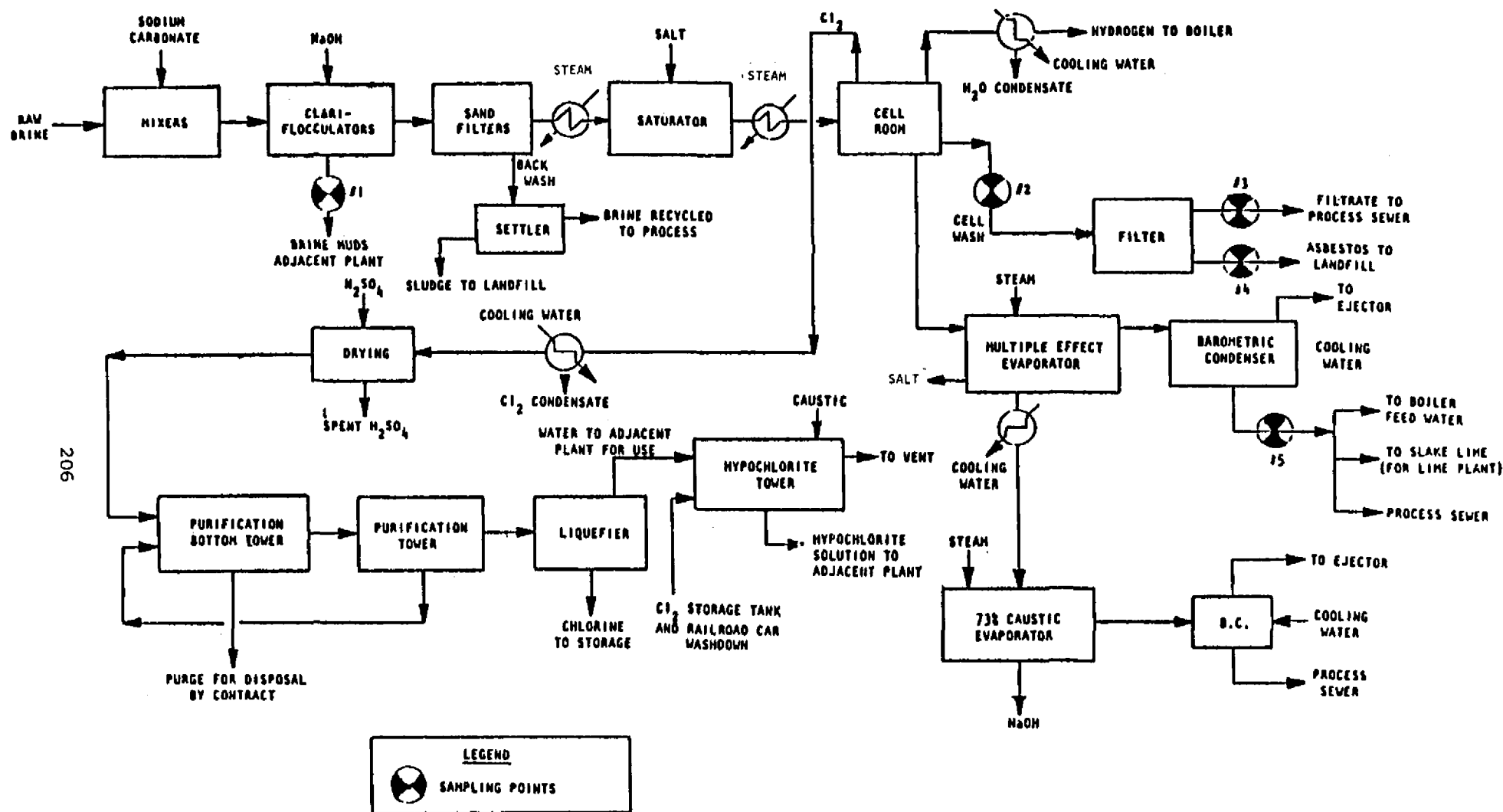


Figure 11-10. General process flow diagram at Plant #261 showing the sampling points. Chlorine/Caustic (Diaphragm Cell) manufacture

Figure 11-11. General process flowsheet at plant #738-A showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture.

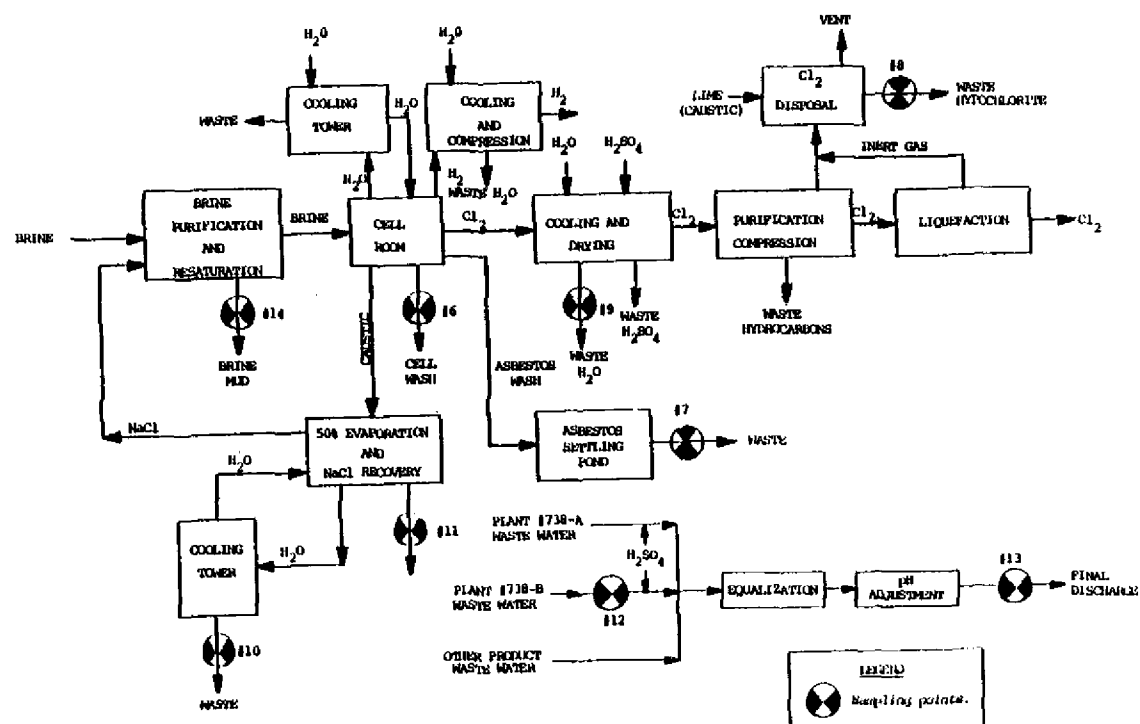


Figure 11-12. General process flow diagram at plant #738-B showing the sampling points. Chlorine/caustic (diaphragm cell) manufacture.

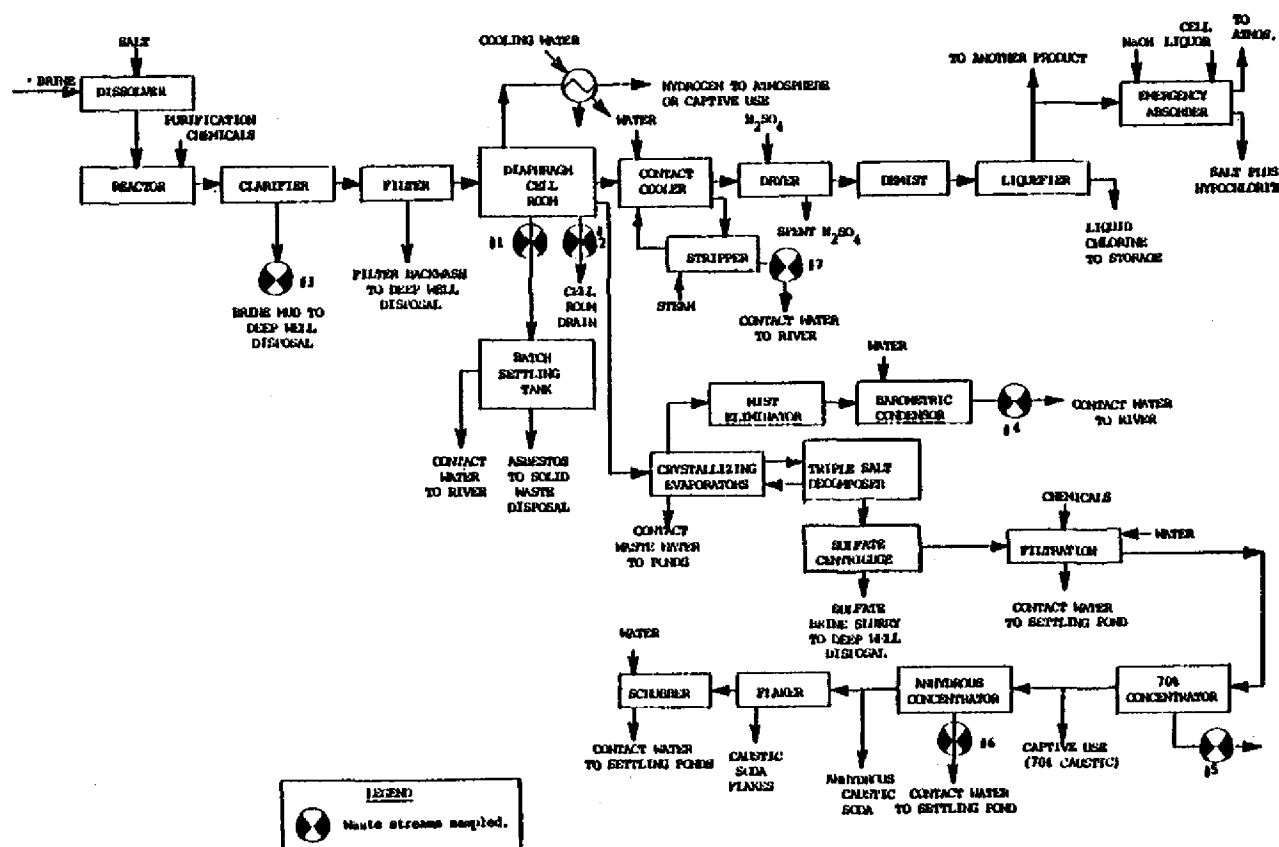


Figure 11-13. General process flow diagram at Plant #736 showing the sampling points. Chlorine/Caustic (Diaphragm Cell) manufacture

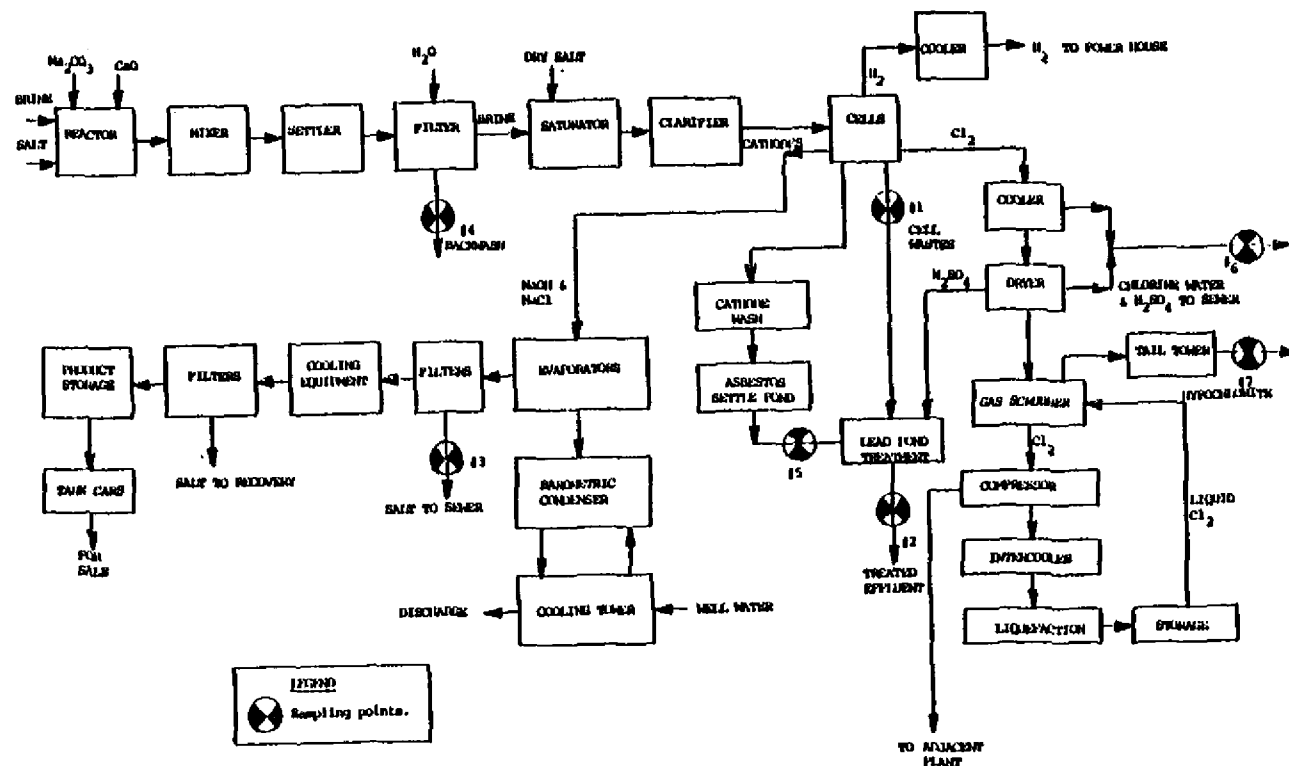


Figure 11-14. General process flow diagram at Plant #967 showing the sampling points. Chlorine/Caustic (Diaphragm Cell) manufacture

Results are expressed as total fibers per liter (in millions) as well as Chrysotile and Amphibole fibers per liter.

There is no standardized 304(h) analytical method for asbestos in water and because of this, EPA is excluding limitations for asbestos from these regulations and deferring regulation to a later date.

C. Toxic Metals

Table 11-22 presents maximum daily concentrations of toxic metals found in raw waste samples during the screening and verification of diaphragm cell chlorine plants. Maximum concentrations observed at one graphite anode plant are presented separately. It is clear that except for lead, toxic metals concentrations at the graphite anode plant are essentially no higher than at the metal anode plants.

Because several waste streams usually contribute to the total raw waste at chlorine plants, a calculation was often necessary to determine the pollutant concentrations that would exist when the streams were mixed prior to treatment. An example of this calculation is the "mixing" of the following hypothetical streams:

Stream A: 100 gallons per minute, 15 mg/l of pollutant

Stream B: 10 gallons per minute, 60 mg/l of pollutant

The weighted average for the mixed streams is given by:

$$\frac{(\text{Flow A} \times \text{Concentration A}) + (\text{Flow B} \times \text{Concentration B})}{(\text{Flow A} + \text{Flow B})}$$

= concentration of mixed streams

Substituting numerical values gives:

$$\frac{(100 \text{ gpm}) (15 \text{ mg/l}) + (10 \text{ gpm}) (60 \text{ mg/l})}{(110 \text{ gpm})} = 19 \text{ mg/l}$$

This method was used to calculate raw waste concentrations of pollutants as presented in Table 11-22. Barometric condenser wastewater when "once through" was not included because of the high dilution effect of these large flows. Brine mud flows were also not included.

The daily raw waste loads were calculated from the waste stream flow rates measured or estimated at the time of sampling and the measured pollutant concentration.

That is,

$$\text{Daily loading (as kg of pollutant per day)} = \frac{(C) (Q)}{1000}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: $\text{kg/m}^3 = 1000 \text{ mg/l}$) and

Q is the waste stream flow rate expressed in units of m^3/day (m^3 , a cubic meter, is equal to 264.2 U.S. gallons).

Similarly, the unit loadings were calculated from the reported chlorine production rate, the waste stream flow rate, and the measured pollutant concentration.

$$\text{Unit loading (as kg of pollutant per kkg of chlorine)} = \frac{(C) (Q)}{1000P}$$

where C and Q are as described above, and P is the chlorine production rate expressed in units of kkg/day (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs).

The minimum, average and maximum values were calculated based on data from those plants where the particular pollutant was found at a detectable concentration.

In Table 11-23, the toxic pollutant raw waste data are presented as the average daily concentrations (based on three 24-hour samples) and the unit loadings found at the individual plants. Beryllium, selenium, and thallium are not included in the table because average concentrations were below detectable limits.

In Table 11-24, plant average daily and unit loadings are presented as minimum, average, and maximum values based on data presented in Table 11-23 for metal anode plants only. (The graphite anode plant is considered separately due to its particular waste source characteristics.)

Based on the average waste loads generated per unit of product at metal anode plants and one graphite anode plant, and the estimated total subcategory production, the estimated total pollutant raw waste loads generated each year by this subcategory are as follows:

TABLE 11-21. RESULTS OF ASBESTOS SAMPLING AT DIAPHRAGM CELL PLANTS

Plant	Stream	Total Asbestos Fibers (MFL) *	Chrisotile MFL	Amphibole MFL
# 261	Supply	8.0	7.5	0.40
	Cell Wash	2.1×10^8	2.1×10^8	0
	Filtered Discharge	1.6×10^3	1.6×10^3	0
	Barometric Condenser	0.40	0.40	0
# 736	Supply	0.70	0.70	0
	Cell Wash	2.0×10^7	2.0×10^7	0
	Cell Room Waste	2.9×10^2	2.8×10^2	8.0
	Barometric Condenser	1.8	0	1.8
	Barometric Condenser	5.3	5.3	0
	Barometric Condenser	1.4×10^2	1.4×10^2	0
# 967	Supply	9.7×10^2	9.7×10^2	0
	Cell Waste	2.4×10^4	2.4×10^4	8.0×10^2
	Pond Effluent	2.4×10^3	2.4×10^3	0
	Caustic Wash	7.8×10^3	7.8×10^3	0
	Brine Filter Backwash	8.0×10^2	6.2×10^2	1.8×10^2
	Cathode Wash Waste	3.2×10^5	3.2×10^5	0
	Condensate & Spent Acid	2.7×10^2	1.8×10^2	8.9×10
	Neutralizer Waste	2.1×10^3	2.1×10^3	0

*Million fibers per liter

TABLE 11-22. MAXIMUM RAW WASTE CONCENTRATIONS OF TOXIC METALS OBSERVED AT DIAPHRAGM CELL CHLORINE PLANTS (mg/l)

SUBCATEGORY CHLORINE DIAPHRAGM CELL		
Toxic Metal	Plants with Metal Anodes	Plant with Graphite Anode
Antimony	<0.25	<0.065
Arsenic	0.17	0.59
Beryllium	<0.014	<0.0010
Cadmium	0.037	0.017
Chromium	7.4	<0.048
Copper	17	0.27
Lead	2.0	44
Mercury	<0.0030	0.0040
Nickel	22	0.070
Selenium	<0.020	<0.030
Silver	0.018	<0.016
Thallium	<0.25	<0.050
Zinc	3.0	0.25

Raw Waste Load

<u>Pollutant</u>	<u>kg/year</u>
Antimony	483
Arsenic	6,300
Cadmium	41
Chromium	3,100
Copper	4,400
Lead	470,000
Mercury	48
Nickel	3,600
Silver	5
Zinc	5,100

Because cell room wastes including cell or cathode wash wastes, leaks, spills and washdown are usually treated separately at diaphragm cell plants and because other process wastes such as filter backwashes, condensates and caustic evaporation wastes are usually discharged after settling, these two waste mixes were evaluated separately. Table 11-25 presents average raw waste concentrations and loads of toxic metals found in cell room wastes at the six diaphragm cell plants sampled. Table 11-26 presents the similar data from the sampling of other process wastes at these plants.

D. Toxic Organic Pollutants

The use of graphite anodes at chlorine plants results in the generation of a variety of simple chlorinated hydrocarbon compounds as a result of the attack of chlorine on the anodes. These compounds are carried out of the cell with the chlorine and find their way into the various waste streams which originate from the chlorine cooling, drying, compression, and liquefaction steps.

Table 11-27 presents the toxic organics that were observed in measurable concentrations in the raw wastes at Plant #967. The concentrations presented in the table were calculated as a mixture of all raw waste streams weighted on a flow basis as previously described.

Table 11-28 presents the concentrations of toxic organics by individual raw waste streams at Plant #967. It is clear from the table that the highest concentrations of organics occur in wastes from chlorine treatment (condensate, drying acid and tail gas scrubber water) and they account for 83 percent of the total organic waste load.

TABLE 11-23. TOXIC METAL CONCENTRATIONS AND LOADS AT SCREENING AND VERIFICATION PLANTS (1)

		$\frac{(\text{mg/l})}{(\text{kg/kg})}$				
SUBCATEGORY		CHLORINE DIAPHRAGM CELL				
POLLUTANT	014	261	Plant #		736	967**
			738A	738B		
Antimony	*	*	*	*	0.010	0.011
	*	*	*	*	0.0000033	0.00015
Arsenic	*	0.17	*	0.011	0.057	0.30
	*	0.0000064	*	0.000021	0.000014	0.0021
Cadmium	0.0020	0.037	*	*	0.025	*
	0.0000018	0.0000014	*	*	0.0000061	*
Chromium	0.019	1.9	0.52	0.066	0.18	0.0040
	0.000017	0.000071	0.0046	0.0012	0.000044	0.000032
Copper	0.015	17	0.045	0.12	0.43	0.16
	0.000014	0.00064	0.00039	0.00023	0.00011	0.0011
Lead	0.0060	2.0	0.082	0.11	0.016	21
	0.0000045	0.000075	0.00060	0.000021	0.0000039	0.15
Mercury	0.0020	*	*	*	0.0030	0.0020
	0.0000018	*	*	*	0.0000070	0.000014
Nickel	0.90	22	0.21	0.067	0.22	0.68
	0.00081	0.00081	0.0018	0.00013	0.000054	0.00049
Silver	*	0.018	*	*	*	*
	*	0.00000070	*	*	*	*
Zinc	*	1.5	0.29	0.093	3.0	0.19
	*	0.000054	0.0021	0.00018	0.00074	0.0014

* Below measurable concentrations.

** Graphite Anode plant.

(1) Based on one 72-hour composite or the average of three 24-hour composites.

Sample 1960 source (P. 227)

Plant specific data (P. II. 5-72)
says "0.15"

TABLE 11-24. SUMMARY OF RAW WASTE LOADINGS AT SCREENING AND VERIFICATION METAL ANODE PLANTS

SUBCATEGORY		CHLORINE DIAPHRAGM CELL					
Pollutant	Loading (kg/kg)			Unit Loading (kg/kg)			*Number of Plants Averaged (out of 5)
	min.	avg.	max.	min.	avg.	max.	
Antimony	0.00077	0.00077	0.00077	0.0000033	0.0000033	0.0000033	1
Arsenic	0.0019	0.0084	0.020	0.0000064	0.000017	0.000030	3
Cadmium	0.00041	0.00076	0.0014	0.0000014	0.0000032	0.0000061	3
Chromium	0.0042	0.59	2.8	0.000017	0.00096	0.0046	5
Copper	0.0035	0.12	0.19	0.000014	0.00020	0.00064	5
Lead	0.00090	0.094	0.37	0.0000039	0.00016	0.00060	5
Mercury	0.00016	0.00030	0.00044	0.0000007	0.0000012	0.0000018	2
Nickel	0.0066	0.31	1.1	0.000010	0.00057	0.0018	5
Silver	0.00021	0.00021	0.00021	0.0000017	0.0000007	0.0000007	1
Zinc	0.016	2.1	8.0	0.000054	0.00078	0.0021	4

* Only those plants where the pollutant was observed at measurable concentrations.

Pollution Abatement Options

Toxic Pollutants of Concern

Lead occurs in high concentrations in the cell room wastewaters of chlorine plants using lead anchored graphite anodes. Other toxic metals often found in significant concentrations at diaphragm cell plants include arsenic, cadmium, chromium, copper, nickel, and zinc. Antimony, mercury, and silver were also detected but at concentrations that are not treatable. These metals are not considered further. The sources of these metals may be raw material impurities or corrosion products from the reaction between chlorine or acid and the process equipment materials of construction.

Toxic organic compounds also occur in wastewaters from graphite anode plants because of the attack of chlorine on the anode material. They appear primarily in waste streams associated with the purification of chlorine.

Asbestos occurs in all wastewaters from diaphragm cell plants, and in large quantities in cell room wastewaters when cells are cleaned and repaired.

Prevailing Control and Treatment Practices

Specific control and treatment practices at ten plants were described above. The prevailing practices at diaphragm cell plants are to control asbestos wastes by settling or filtering cell wash waters and to neutralize and settle all wastewaters before discharge. The recycle or reuse of waste streams is practiced to varying degrees in the industry depending on plant-specific factors such as raw material quality and type of anodes used.

Plants using lead anchored graphite anodes are treating lead-bearing wastes by chemical precipitation and settling and/or filtration before discharge.

The control of toxic organic compounds in the waste streams at graphite anode plants also varies in the industry. At Plant #967 where the end use of the chlorine is captive, involving its direct application to the manufacture of a chlorinated organic product, the bulk of chlorinated organic impurities are not removed.

At Plant #195, where a more purified product is required, the organics are accumulated in the reboiler of the chlorine scrubber. The residues are treated batchwise for separation and recovery of the organic phase materials which are then sold as feedstock for the manufacture of related products. Prior to discharge the aqueous phase is vacuum stripped to remove additional organics and chlorine for recycle. Normally, one batch of organics is treated per week. After separating each batch of organics and stripping the residual aqueous phase, the quantity of wastewater discharged is approximately 5.7 m³/day. The organic loading in this waste is not known, however, if

TABLE 11-25. TOXIC METAL CONCENTRATIONS AND LOADS IN CELL ROOM WASTE WATERS AT SCREENING AND VERIFICATION PLANTS $\left(\frac{\text{mg/l}}{\text{kg/kgg}}\right)$ (1)

Pollutant	Plant #					
	014	261	738A	738B	736	967**
Antimony	*	*	0.050 0.0000081	*	0.038 0.0000031	0.41 0.00015
Arsenic	0.010 0.0000001	0.17 0.0000064	*	*	0.17 0.000014	0.45 0.00017
Cadmium	*	0.037 0.0000014	*	*	*	0.016 0.0000059
Chromium	0.94 0.000014	1.9 0.000071	*	0.075 0.000012	0.54 0.000044	0.086 0.000032
Copper	0.53 0.0000075	17 0.00064	0.24 0.000042	0.38 0.000061	1.1 0.000090	2.4 0.00089
Lead	0.26 0.0000039	2.0 0.000075	0.044 0.0000077	0.11 0.000018	0.047 0.0000038	370 0.14
Mercury	*	*	0.0030 0.0000005	*	0.0020 0.0000002	0.0010 0.0000004
Nickel	54 0.00081	22 0.00081	*	0.061 0.0000098	0.67 0.000055	0.36 0.00013
Silver	*	0.018 0.0000007	*	*	*	*
Zinc	*	1.5 0.000054	0.046 0.0000080	0.46 0.000074	0.58 0.000048	0.92 0.00034

* Below detection limits

** Graphite anode plant

(1) Based on one 72-hour composite or the average of three 24-hour composites.

TABLE 11-26. RAW WASTE TOXIC METALS CONCENTRATION AND LOADS IN PROCESS STREAMS OTHER THAN CELL ROOM WASTES FROM SCREENING AND VERIFICATION PLANTS (1)

Pollutant	#014	#738A	Plant#	#736	#967	Avg
			#738B (mg/l) (kg/kg)			
Antimony	*	*	*	*	*	*
Arsenic	*	*	0.011 0.000019	*	0.29 0.0020	0.15 0.0010
Cadmium	0.0020 0.0000018	*	*	0.038 0.0000062	*	0.020 0.0000040
Chromium	*	0.53 0.0046	0.065 0.00011	*	*	0.29 0.00014
Copper	0.0040 0.0000036	0.041 0.00035	0.094 0.00016	0.090 0.000015	0.030 0.00020	0.043 0.00014
Lead	*	0.083 0.00060	0.11 0.00019	*	0.40 0.0027	
Mercury	0.0020 0.0000018	*	*	0.0030 0.0000005	0.0020 0.000014	0.0020 0.0000054
Nickel	0.0030 0.0000027	0.21 0.0018	0.067 0.00012		0.052 0.00035	0.088 0.00072
Silver	*	*	*	*	*	*
Zinc	*	0.29 0.0021	0.058 0.00010	4.3 0.00070	0.15 0.0010	1.5 0.0037

* Below detection limits

(1) Based on one 72-hour composite or the average of three 24-hour composites.

TABLE 11-27.

RAW WASTE TOXIC ORGANICS AT A GRAPHITE ANODE PLANT

SUBCATEGORY

CHLORINE DIAPHRAGM CELL

Pollutant	Average Concentration* (mg/l)	Load (kg/day)
benzene	0.00040	0.0011
carbon tetrachloride	0.023	0.066
1,2-dichloroethane	0.079	0.23
1,1,1-trichloroethane	0.00014	0.00040
hexachloroethane	0.010	0.029
1,1,2-trichloroethane	0.00040	0.0011
1,1,2,2-tetrachloroethane	0.000044	0.00013
chloroform	0.085	0.24
1,1-dichloroethylene	0.000026	0.000074
2,6-dinitrotoluene	0.000026	0.000074
methylene chloride	0.00056	0.0016
bromoform	0.000063	0.00018
dichlorobromomethane	0.035	0.10
chlorodibromomethane	0.0020	0.0057
hexachlorobutadiene	0.0040	0.011
bis(2-ethylhexyl)phthalate	0.00075	0.0022
di-n-butyl phthalate	0.00078	0.0022
tetrachloroethylene	0.036	0.10
toluene	0.0030	0.0086
trichloroethylene	0.020	0.0057

* Flow-proportioned concentration

TABLE 11-28. RAW WASTE TOXIC ORGANICS BY WASTE WATER SOURCE AT A GRAPHITE ANODE PLANT

CHLORINE DIAPHRAGM CELL			
SUBCATEGORY			
Stream	Total Toxic Organics (mg/l)	Total Toxic Organics (kg/day)	Percent of Total Toxic Organics
Cell building wastes	0.126	0.0093	1.1
Caustic filter backwash	0.057	0.12	14
Brine filter backwash	0.0030	0.00050	0.06
Cell wash	0.20	0.014	1.6
Chlorine condensate and Spent H ₂ SO ₄	2.2	0.70	81.5
Scrubber waste	0.81	0.015	1.7
Totals	0.30 *	0.86	100

* Flow-proportioned concentration

the assumption is made that the discharge is saturated with carbon tetrachloride (CCl_4) (800 mg/l & 20 degrees C), the waste load would be 0.5 kg/day.

Although the daily mass emissions from the two plants are likely to be similar and both would require additional treatment to achieve acceptable discharge levels, the wide difference in concentrations of the chlorinated organics as well as the manner in which they are handled would necessitate the application of an advanced treatment technology specifically suited to each case.

Where the flow is large and the concentrations are low, the application of activated carbon adsorption to the collected organic-bearing waste stream at Plant #967 would be capable of reducing a CCl_4 mass emission from 0.066 kg/day to approximately 0.03 kg/day, assuming an achievable treatability level of 0.10 mg/l.

In the case of Plant #195, where the volume of wastewater is small but the concentrations of residual chlorinated organics can be on the order of several hundred parts per million, a more appropriate removal technology would be stream stripping with an overhead return to the process. Assuming a treatability level of 10 mg/l for CCl_4 using this technology, its mass emission could be reduced to approximately 0.001 kg/day.

Process Modifications and Technology Transfer Options

A. Anode Material

The use of metal anodes rather than graphite anodes increases cell power efficiency and greatly reduces the pollutant loads of toxic organics and, in many cases, lead in plant wastewaters. Approximately half of the diaphragm cell production of chlorine is now by metal anodes.

B. Caustic Evaporation Water

The vapors from the evaporative concentration of caustic soda are either contact-cooled or cooled in surface condensers. Plants practicing contact cooling through barometric condensers generate large amounts of wastewater contaminated with caustic soda and salt. By changing from contact cooling of the vapors to noncontact cooling, or by recirculating barometric condenser water, the amount of wastewater generated can be reduced considerably. If the change is considered too expensive or is not feasible, demisters or similar control devices can be installed to reduce the salt and caustic carryover in the vapors.

C. Diaphragm Material

Although not in full scale use at any U.S. chlorine plants, modified diaphragms have been developed which can reduce power

consumption and minimize asbestos discharges. The polymer modified asbestos diaphragm consists of a polymer treated asbestos diaphragm baked into place on the cathode. Its usage results in power savings and has an environmental benefit, since, at the time of diaphragm replacement, the discarded material is produced in stabilized pieces instead of loose asbestos fibers. Final disposal is thus safer and easier.

D. Liquefaction of Chlorine

Utilization of high pressure and refrigeration for chlorine recovery will reduce the chlorine content in tail gases.

E. Tail Gas Emission Control

As with mercury cell plants, chlorine in tail gases has to be removed and treated or recovered before venting to the atmosphere. The common practice is to scrub the gas with caustic soda producing a hypochlorite solution. This hypochlorite can then be sold, used on-site or discharged. Decomposition is a common method of removing the chlorine in this stream prior to discharge. Catalytic, thermal and chemical methods of decomposition, described in Section 11, are effective.

Best Management Practices

The following Best Management Practices are common industry practices and are provided for guidance purposes although they may not meet the requirements of the Resource Conservation and Recovery Act (as amended, 42 USC 6901 et seq.).

A. Area Runoff

Provisions can be made to divert and contain storm runoff from areas where lead or asbestos contamination could occur. Collected runoff can then be treated with other wastes.

B. Leaks and Spills

Provisions can be made in cell room areas to control and collect the leaks or spills contaminated with lead or asbestos.

C. Contaminated Solids

Asbestos waste and precipitated metals wastes should be stored in a lined pond or disposed of in a secure landfill.

Advanced Treatment Technologies

The methods available and currently used in the industry for the removal of lead and other toxic metals from plant wastewaters include hydroxide or carbonate precipitation followed by settling or

filtration. Further removal of metals can be effected using sulfide precipitation, adsorption and ion exchange.

Removal of asbestos from cell wastes is improved with the addition of coagulating agents prior to filtration of these wastes.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT)

Level 1 treatment addresses the waste characteristics associated with diaphragm cell plants using graphite anodes. The data from graphite anode plants were used because the pollutant load is greater than for metal anode plants. Existing plants that have changed from graphite anodes to metal anodes will have residual effects for an extended time after the change--possibly as long as two years. The asbestos contaminated cell room wastes are treated with a flocculating agent and a filter aid prior to filtration. The solids are removed to a landfill and the filtrate is sent to a holding tank where it is combined with any other process waste sources containing treatable levels of lead and other toxic metals. Alkaline precipitation of the toxic metals is accomplished by the addition of soda ash. The solids are removed by settling and the filtrate is combined with other process waste streams such as chlorine condensate, tail gas scrubber water, caustic filter backwash and barometric condenser blowdown waters found to be contaminated with toxic metals at levels usually below the limits of treatability by alkaline precipitation. The combined flow is sent to a polishing pond for additional clarification prior to discharge. At all levels of treatment, the brine mud is collected in lagoons and the effluent recycled to process. The flow diagram for Level 1 treatment is shown in Figure 11-15.

Level 1 treatment was ultimately selected as the basis for BPT because it represents a typical and viable industry practice for the control of asbestos fiber, lead, and other toxic metals in wastewaters associated with diaphragm cell plants using graphite anodes. Note that the industry is concerned about the discharge of asbestos and has taken steps to reduce this discharge. Treatment level 1 has the effect of reducing total asbestos discharges even though we do not set specific limits. Plants utilizing metal anodes or nonlead containing graphite anode cells are expected to have lower levels of toxic metal emissions and may not require alkaline precipitation to meet the proposed BPT limitations. All direct discharge plants in the industry presently have BPT or equivalent treatment technology or meet the limits without treatment.

B. Level 2 (BAT)

The objective of Level 2 treatment technology is to achieve, at a reasonable cost, a greater degree of toxic metals removal than provided by Level 1. Thus, Level 2 adds dual-media filtration to the combined effluent from Level 1 treatment excluding noncontact waste streams. Dechlorination of the filtered process wastewater discharge is also included in Level 2 (BAT) treatment. This assumes treatment by sulfur dioxide or bisulfite to remove total residual chlorine.

Level 2 was finally selected as the basis for BAT regulations on the strength of technology transfer options within the inorganic chemicals industry and because four out of five plants sampled were meeting BAT limits derived from published treatability data. In addition, two plants are known to practice dechlorination of their effluent. The flow diagram for Level 2 is shown in Figure 11-16.

C. Level 3

The practice of sulfide precipitation of mercury in the mercury cell segment of the chlor-alkali industry suggested the application of this technology for achieving greater removal of toxic metals in diaphragm cell plants. Level 3 adds sulfide precipitation to Level 2 as shown in Figure 11-17. This option was not selected due to its relatively high cost per pound of additional metal removal obtained. Cost estimates for this level can be obtained from the Development Document (60).

Equipment for Different Treatment Levels

A. Equipment Functions

Conventional sludge dewatering by filter press is used for asbestos sludge before disposal and dual-media filter backwash is returned to the influent surge tank. Level 3 treatment requires the addition of a reagent mixing tank and chemical solution feeder to introduce ferrous sulfide ahead of the Level 2 dual-media filter. All equipment is conventional and readily available.

B. Chemical Handling

Nonhazardous solutions of aluminum sulfate and sodium carbonate are the only solutions used at Levels 1 and 2. Inert filter aid used in the alum sludge filter process presents no unusual hazard. At Level 3 the potential hazard of handling sodium sulfide is nullified by reacting it with ferrous sulfate to form ferrous sulfide. Any excess ferrous sulfide will oxidize to a ferric sulfide precipitate. At the point where sodium sulfide is

reacted with ferrous sulfate, good ventilation is essential to avoid the hazards associated with hydrogen sulfide gas.

C. Solids Handling

For all three levels of treatment, brine mud solids are accumulated in lined lagoons on-site. Abestos solids and precipitated metals wastes are to be sent to suitable chemical landfills.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed. Because higher pollutant loads and larger unit flows exist at graphite anode plants as opposed to metal anode plants the characteristics associated with these plants were used when possible for the model plant characteristics as discussed below.

A. Chlorine Production

Approximately 60 percent of the production data for all chlorine plants using diaphragm cells is available on file. Production ranges from 15,000 to 1,500,000 kkg of chlorine per year. Three model plants with production rates of 19,000, 95,500, and 191,000 kkg per year were selected to represent the subcategory production range.

B. Wastewater Flow

Based on industry flow data (Table 11-19), waste streams in the model plants are segregated into brine mud, cell wash and cell room wastes, and other process wastes such as filter backwashes, condensates and tail gas scrubber wastes. For treatment cost estimates at all levels of treatment the following flow basis was used.

1. A brine mud flow of 0.45 m³/kkg is sent to lagoons for solids removal. Solids are disposed of on-site and the clarified effluent is recirculated to the process.
2. Cell room wastes consisting of leaks, spills, and area washdown contaminated with lead and other metals are combined with treated cell wash waters for a total flow of 1.2 m³/kkg to be treated for metals removal. Included in this flow is the cathode or cell wash waters which are heavily laden with asbestos. These wash waters are sent to asbestos removal at a flow rate of 0.07 m³/kkg, and then to treatment with the other wastewaters.
3. Other process wastewater sources account for an additional 7.6 m³/kkg which is combined with effluent from the

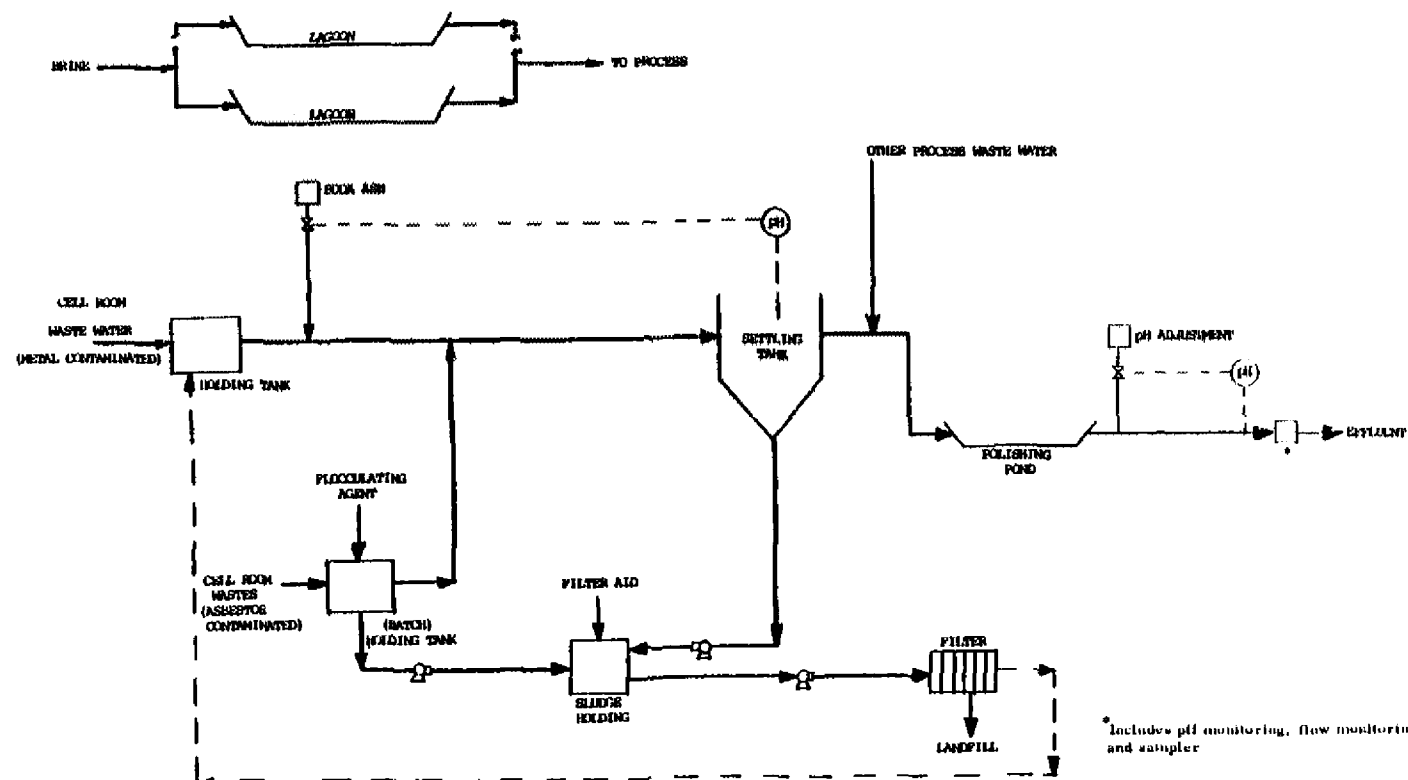


Figure 11-15. Level 1 waste water treatment for chlorine - diaphragm cell subcategory.

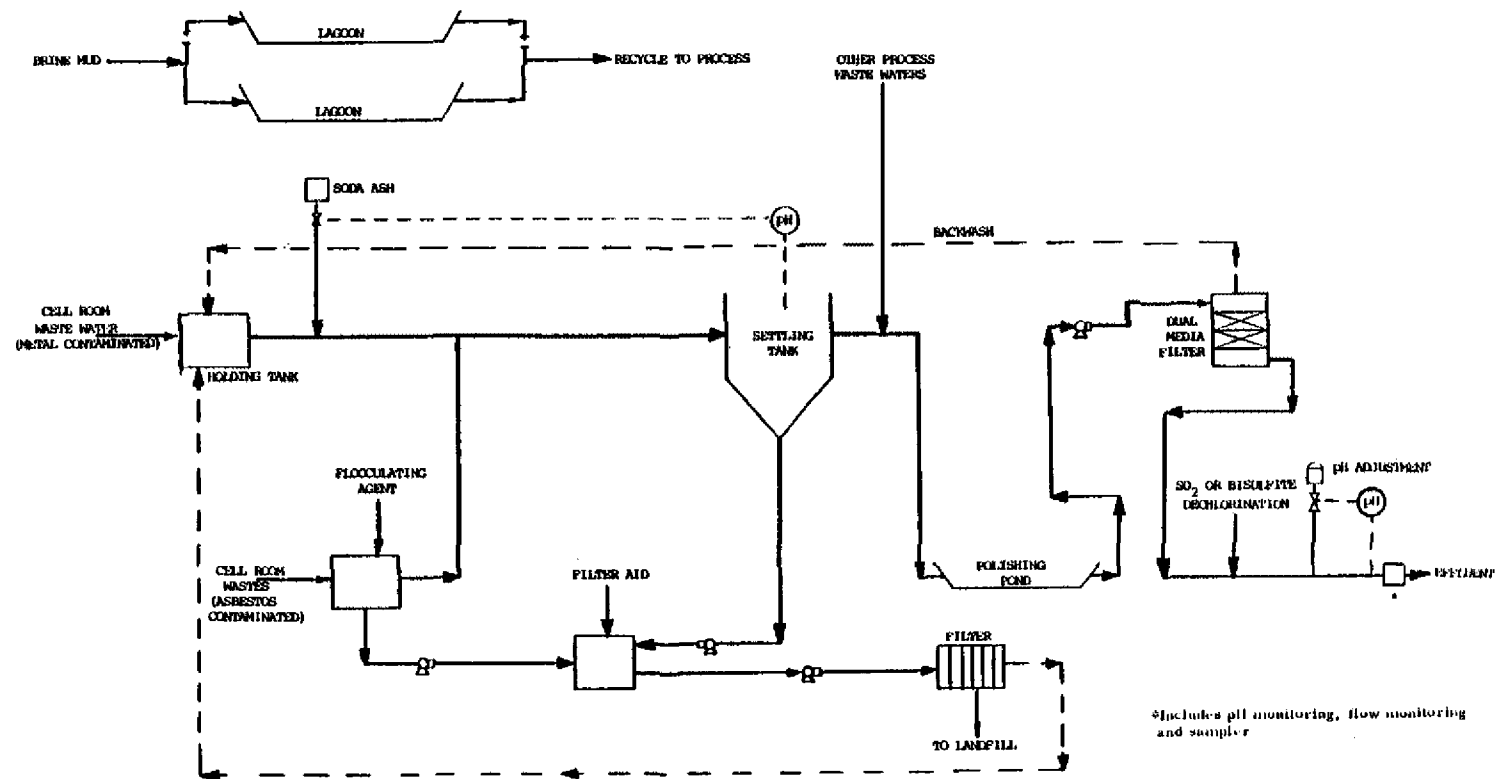


Figure 11-16. Level 2 waste water treatment for chlorine - diaphragm cell subcategory.

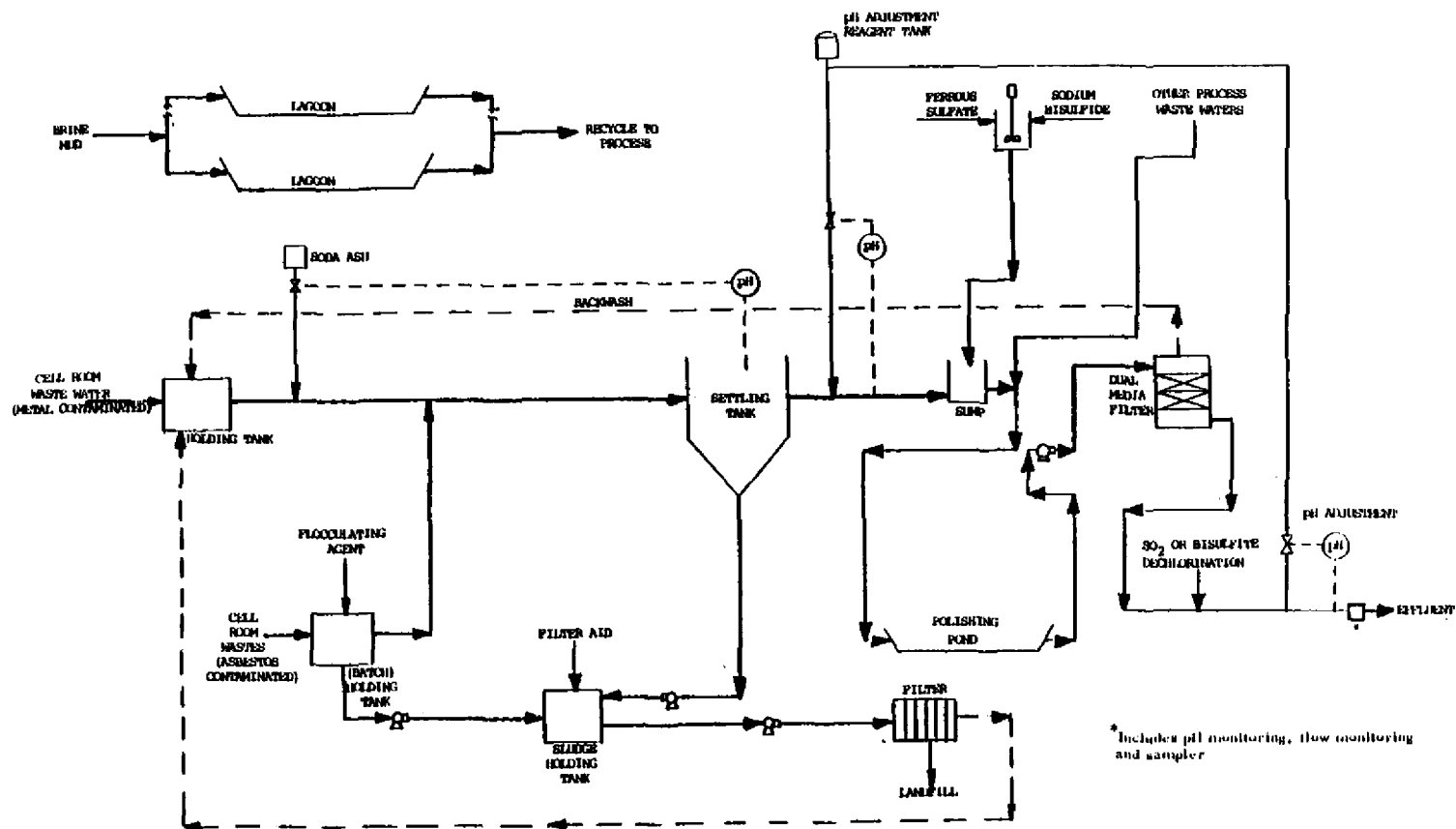


Figure 11-17. Level 3 waste water treatment for chlorine - diaphragm cell subcategory.

treatment of wastes from the cell room and cathode wash areas. This brings the model plant total flow rate to an estimated $8.8 \text{ m}^3/\text{kg}$. The final, combined process waste flow is either clarified and discharged as in Level 1 (BPT) treatment or clarified, passed through dual-media filtration, and dechlorinated prior to discharge as in Level 2 (BAT) treatment.

C. Solid Waste Produced

Brine mud constitutes the major source of solid waste generated at chlorine plants. Although solids content varies from plant to plant, an average of ten percent solids was used for the model resulting in a solids load of 42 kg/kg which is disposed of on-site. Asbestos from cell wash operations and precipitated solids from metal treatment generate a solid waste of 0.83 kg/kg that is disposed of off-site.

D. Chlorine Bearing Wastes

In the selection of model plants, the following assumptions have been made for the chlorine contaminated waste streams.

The chlorine condensate waste stream has not been included in the waste streams going to the treatment facility. In the majority of the chlorine/caustic plants, this stream is stripped of chlorine by steam or vacuum and the chlorine is recycled to the purification operation. The wastewater is then returned to the process and introduced to the brine purification unit or sent to the treatment unit. The quantity of wastewater generated by this operation is small. In some cases the chlorine gas from the cells is contact-cooled with water and the scrubbed liquid, after steam stripping, is reused. The stripping operation in the recovery of chlorine is part of the process and, therefore, its cost is not included in the treatment cost.

The spent tail gas scrubber solution, which is mainly calcium/sodium hypochlorite, is assumed to be used or decomposed before it is discharged. Thermal decomposition can be practiced at no additional cost at some facilities, while another efficient method is catalytic decomposition. The cost estimates for decomposition are not included here because at many plants the hypochlorite stream is sold, used on-site or only infrequently discharged, depending on market demand.

However, because of the environmental effects of high levels of chlorine in process wastewater discharges, the cost for the dechlorination of such streams using sulfur dioxide has been included because this is the treatment method on which control of total residual chlorine is based.

1. Chlorinated Organic Wastes

The chlorine-bearing waste streams at graphite anode plants are also those streams carrying the highest concentrations of toxic organics as indicated in Table 11-28. Section 11 discussed the techniques used to recover and remove organics from waste streams at Plant #195 and the fact that organic contaminated streams can exist as either high volume-low concentration or low volume-high concentration depending on plant specific factors. Costs for removing organics (including implementation of RCRA regulations) are not included in the model plant cost estimates because organics are not limited in the regulation. Organics occur at low levels at most of the plants and when they are present the appropriate treatment method is site specific. Although the costs are not included the following information is provided as guidance. The additional costs for steam stripping in a plant (such as Plant #195) which already has a vacuum vaporizer, would be under \$10,000 for modification of the existing equipment. Steam costs could vary from \$1,000 to \$5,000 per year. If a vaporizer is not in place, a steam stripper to process 5 to 30 m³/week would cost roughly \$50,000 to \$100,000, depending on the input concentrations to be handled. The corresponding steam costs would range from \$2,000 to \$10,000 per year.

The capital costs of an activated carbon adsorption unit for handling the relatively high volume wastes with a low influent organic loading (as found at Plant #967) cannot be reliably estimated in the absence of specific treatability data on the waste streams in question.

Alternatively, incineration of the chlorinated organic residuals is an effective means of destroying and disposing of this material provided that adequate measures are taken to control the release of HCl to the atmosphere.

A process evaluation should be made to determine the most efficient means for isolating and collecting the organic bearing waste streams prior to treatment.

Incidental removal of chlorinated organics will occur with the application of model plant treatment levels previously presented. Such removal, however, is expected to be erratic and therefore cannot be predicted. Because raw waste concentrations of these organics vary considerably depending on plant practices and are marginally treatable at times, applicable control and treatment technologies will need to be assessed on a case-by-case basis.

For these reasons, the Agency is not providing specific numerical discharge limitations for organic pollutants, but is providing guidance for evaluating control options that could be applied in the industry.

Model Plant Treatment Costs

On the basis of the model plant specifications and design concepts presented earlier, the estimated costs of treatment for three models having different production levels are shown in Tables 11-29, 11-30 and 11-31. The cost of Level 2 (BAT) is incremental over Level 1 (BPT) costs and provides for higher effluent quality with respect to toxic pollutants.

Table 11-32 presents a summary of the unit cost distribution between amortization and operation and maintenance components.

Basis For Regulations

Basis for BPT Limitations

BPT regulations are currently in effect for the diaphragm cell chlorine subcategory, 40 CFR 815.62(b). The Agency is revising the limitations, however, based on an increased unit flow rate.

A. Technology Basis

For BPT, the Agency is setting limitations based on equalization, alkaline precipitation and settling of lead and asbestos-bearing wastes and neutralization and settling of all wastewaters before discharge. All diaphragm cell chlorine plants are known to be using this technology (Level 1) or its equivalent.

B. Flow Basis

As described in Section 11, wastewater streams at diaphragm cell plants are separated into two types, those that require treatment for asbestos and metals removal and those that do not require such treatment. From data presented in Table 11-19, the unit flow rate of $1.2 \text{ m}^3/\text{kg}$ of cell room and cell wash wastes from one graphite anode plant was selected as the flow basis for wastes to be treated. Graphite anode plant data were used in this instance because the flows were higher than those of other plants and thus represent a conservative estimate of flow for other plants in the industry. Using available flow data the remaining waste streams total $7.6 \text{ m}^3/\text{kg}$ as shown in Table 11-33. Thus the total unit flow discharge used in the development of effluent limitations is $8.8 \text{ m}^3/\text{kg}$.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are being established is based on an evaluation of raw waste data from screening and verification sampling and on the treatability of toxic pollutants.

Table 11-34 presents the achievable concentrations of toxic metal pollutants (found at detectable levels in raw waste streams)

using the available treatment technology options. Based on literature treatability data presented in Section 8 and summarized in Table 8-11, the concentrations reflect the lowest level achievable by these technologies. Also presented in the table are the maximum three-day average raw waste concentrations observed during the sampling program.

Based on the occurrence of treatable levels of specific toxic metals, arsenic, cadmium, chromium, copper, lead, nickel and zinc are selected as candidate toxic pollutants for BPT regulations. Antimony, mercury, and silver were detected but at less than treatable levels.

Consideration of (1) the raw waste concentrations in Table 11-34 and (2) Section 8 on the control parameters for hydroxide precipitation, leads to the selection of copper, lead and nickel as toxic pollutants to be regulated. The operation of an hydroxide precipitation system at a pH of about 9.5 should be suitable for the removal of the metals that are present at treatable levels. Arsenic, cadmium, chromium and zinc are included for guidance but no limits are set because control of copper, lead and nickel will adequately control these other metals.

D. Basis of BPT Pollutant Limitations

Limitations are presented as both concentrations (mg/l) and loads (kg/kgg), and the relationship between the two is based on the unit flow rate (8.8 m³/kgg). The concentration basis therefore represents the concentration of the total plant discharge including both treated and untreated wastewaters. Guidance is presented as concentrations (mg/l) only.

BPT limitations, which apply at the combined process wastewater discharge for TSS and toxic metals and at the plant effluent for pH, are presented in Table 11-35.

1. Conventional Pollutants

a. pH

The treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS

The BPT limitations for TSS are based on a summary of monitoring data from Plant #207 (3). The long-term average discharge load of 0.30 kg/kgg is used to develop discharge limitations. Because variability

TABLE 11-29. MODEL PLANT TREATMENT COSTS

Subcategory		Chlorine - Diaphragm cell Production 19,100 metric tons per year	
		(\$)	
A. INVESTMENT COST		BPT	BAT ^a
Site development		30,000	0
Equipment		136,000	43,000
Monitoring equipment		20,000	0
Subtotal		186,000	43,000
Contractor's O & P ^b		27,900	6,450
Subtotal		213,900	49,450
Engineering		42,780	9,890
Subtotal		256,680	59,340
Contingencies		25,668	5,934
Subtotal		282,348	65,274
Land		27,000	0
TOTAL INVESTMENT COST		309,348	65,274
B. OPERATION AND MAINTENANCE COST			
Labor and supervision		112,000	14,000
Energy		2,200	800
Chemicals		1,500	1,500
Maintenance		28,235	6,527
Taxes and insurance		9,280	1,958
Residual waste disposal		5,800	0
Monitoring, analysis and reporting		15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST		174,015	32,286
C. AMORTIZATION OF INVESTMENT COST		45,938	10,620
TOTAL ANNUAL COST		219,953	42,906

^a Represents the incremental cost above that for BPT treatment^b Overhead and Profit

TABLE 11-30. MODEL PLANT TREATMENT COSTS

Subcategory Production	Chlorine - Diaphragm cell 95,500 metric tons per year		
		($\text{\$}$)	
A. INVESTMENT COST	BPT		BAT ^a
Site development	85,000		0
Equipment	261,000		70,000
Monitoring equipment	20,000		0
Subtotal	366,000		70,000
Contractor's O & P ^b	54,900		10,500
Subtotal	420,900		80,500
Engineering	84,180		16,100
Subtotal	505,080		96,600
Contingencies	50,508		9,660
Subtotal	555,588		106,260
Land	69,000		0
TOTAL INVESTMENT COST	624,588		106,260
B. OPERATION AND MAINTENANCE COST			
Labor and supervision	112,000		28,000
Energy	4,900		1,300
Chemicals	7,500		7,500
Maintenance	55,559		10,626
Taxes and insurance	18,738		3,188
Residual waste disposal	29,000		0
Monitoring, analysis and reporting	15,000		7,500
TOTAL OPERATION AND MAINTENANCE COST	242,696		58,115
C. AMORTIZATION OF INVESTMENT COST	90,394		17,289
TOTAL ANNUAL COST	333,091		75,404

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 11-31. MODEL PLANT TREATMENT COSTS

Subcategory Chlorine - Diaphragm cell Production 191,000 metric tons per year			
		(\$)	
A. INVESTMENT COST		BPT	BAT ^a
Site development	140,700		0
Equipment	353,000		108,500
Monitoring equipment	20,000		0
Subtotal	513,700		108,500
Contractor's O & P ^b	77,055		16,275
Subtotal	590,755		124,775
Engineering	118,151		24,955
Subtotal	708,906		149,730
Contingencies	70,891		14,973
Subtotal	779,797		164,703
Land	129,000		0
TOTAL INVESTMENT COST	908,797		164,703
B. OPERATION AND MAINTENANCE COST			
Labor and supervision	112,000		28,000
Energy	8,000		1,800
Chemicals	15,000		15,000
Maintenance	77,980		16,470
Taxes and insurance	27,264		4,941
Residual waste disposal	58,000		0
Monitoring, analysis and reporting	15,000		7,500
TOTAL OPERATION AND MAINTENANCE COST	313,244		73,711
C. AMORTIZATION OF INVESTMENT COST	126,873		26,797
TOTAL ANNUAL COST	440,116		100,509

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 11-32.MODEL PLANT UNIT TREATMENT COSTS

Subcategory Chlorine - Diaphragm cell

		Annual Treatment Costs (\$/kgg)	
		LEVEL OF TREATMENT	
COST ITEM	PRODUCTION (kgg/yr)	BPT	BAT*
Annual Operation and Maintenance	19,100	9.11	1.69
	95,500	2.54	0.61
	191,000	1.64	0.39
Annual Amortization	19,100	2.41	0.56
	95,500	0.95	0.18
	191,000	0.66	0.14
Total Annual Cost	19,100	11.52	2.25
	95,500	3.49	0.79
	191,000	2.30	0.53

*Represents the incremental cost above BPT

factors for TSS were not available for this plant, factors obtained from the hydrofluoric acid subcategory are used. In that subcategory, where the same technology of alkaline precipitation and settling is used, the average variability factor for daily measurements of TSS is 3.5 and the average factor for 30-day averages is 1.7. Thus, utilizing the long-term average discharge load of 0.30 kg/kg one obtains a maximum 30-day average load limit of:

$$(0.30 \text{ kg/kg}) (1.7) = 0.51 \text{ kg/kg}$$

and a 24-hour maximum limitation of:

$$(0.30 \text{ kg/kg}) (3.5) = 1.1 \text{ kg/kg}$$

The concentration bases then are derived by applying the model plant flow rate of 8.8 mg³/kg to obtain a maximum 30-day average concentration of 58 mg/l derived as follows:

$$\frac{0.51 \text{ kg/kg}}{8.8 \text{ m}^3/\text{kg}} \times \frac{1000 \text{ mg/l}}{\text{kg/m}^3} = 58 \text{ mg/l}$$

A 24-hour maximum concentration of 120 mg/l is derived from the variability factor ratio (VFR: 3.5/1.7 = 2.1) as follows:

$$(2.1) (58 \text{ mg/l}) = 120 \text{ mg/l (carrying two significant figures)}$$

From the above data, the implicit long-term average concentration is:

$$\frac{120 \text{ mg/l}}{3.5} = 34 \text{ mg/l}$$

The average concentration of TSS after lime addition and decantation in the Treatability Studies document (61) was 99 mg/l. This average was calculated from a limited number of experiments on a nonoptimized system. Despite these shortcomings, the average falls in between the maximum 30-day average and the 24-hour maximum concentration limit for TSS.

2. Toxic Pollutants

a. Lead

The BPT limitations for lead are based on long-term monitoring data from one graphite anode plant as presented in Appendix A. The plant is achieving a long-term average lead discharge of 0.0064 kg/kg.

TABLE 11-33. SUMMARY OF UNIT FLOWS AT DIAPHRAGM CELL PLANTS

SUBCATEGORY CHLORINE DIAPHRAGM CELL		
Stream Description	Unit Flow (m ³ /kkg)	Data Source
Cell room and cell wash wastes	1.2	Graphite anode plant
Chlorine condensate	0.78	Graphite anode plant
Tail gas scrubber waste	0.11	Graphite anode plant
Caustic filter wash	5.4	Graphite anode plant
Brine filter wash	0.45	Graphite anode plant
Caustic cooling blowdown	0.86	Metal anode plants average
Spent sulfuric acid	0.010	Metal anode plants average
Total Unit Flow Discharge 8.8 m ³ /kkg		

TABLE 11-34. COMPARISON OF RAW WASTE CONCENTRATIONS
OF TOXIC POLLUTANTS WITH TREATABILITY

SUBCATEGORY		CHLORINE (DIAPHRAGM CELL)	
Pollutant	Literature-based Treatability ⁽¹⁾ (mg/l)		Maximum Plant Raw Waste Average (mg/l)
	BPT	BAT	
Arsenic	0.50	0.50	0.30
Antimony	0.80	0.40	0.011
Cadmium	0.10	0.050	0.037
Chromium	0.10	0.050	1.9
Copper	0.50	0.40	17
Lead	0.30	0.050	21
Mercury	— ⁽²⁾	— ⁽²⁾	0.0030
Nickel	0.20	0.10	22
Silver	0.40	0.20	0.018
Zinc	0.50	0.40	3.0

(1) Literature-based treatability estimates from Table 8-11.

(2) Treatability with this technology not available.

Statistical analysis of monitoring data from the plant established a 30-day average variability factor of 1.6 and a 24-hour variability factor of 4.1. The ratio of the two variability factors, VFR, is 2.6. The maximum 30-day average limitation for lead is then obtained by multiplying the variability factor for 30-day averages by the long-term average load; i.e., $1.6 \times 0.0064 \text{ kg/kg} = 0.010 \text{ kg/kg}$. Similarly the 24-hour maximum limitation is obtained by multiplying the daily maximum variability factor by the long-term average load; i.e., $4.1 \times 0.0064 \text{ kg/kg} = 0.026 \text{ kg/kg}$.

The concentration basis for lead is derived from the relationship between concentration (C), unit load (L), and unit flow (Q).

$$C \text{ (mg/l)} = \frac{L \text{ (kg/kg)} \times 1000 \text{ mg/l}}{Q \text{ (m}^3\text{/kg)} \text{ kg/m}^3}$$

Thus the concentration basis for the maximum 30-day average for lead is:

$$\frac{0.010 \text{ kg/kg} \times 1000 \text{ mg/l}}{8.8 \text{ m}^3\text{/kg}} = 1.1 \text{ mg/l}$$

The concentration basis for the 24-hour maximum limitation is obtained by applying the variability factor ratio (VFR) of 2.6 to the maximum 30-day average concentration:

$$(1.1 \text{ mg/l}) (2.6) = 2.9 \text{ mg/l}$$

From the above data, the implicit long-term average concentration is:

$$\frac{2.9 \text{ mg/l}}{4.1} = 0.70 \text{ mg/l}$$

The average concentration of lead after lime addition and decantation in the Treatability Studies document (61) was 28 mg/l. This value is much higher than the values calculated above from the long-term monitoring data in Appendix A. The conclusion in the Treatability Studies document, that there was extremely poor settling of the metal hydroxide sludge, seems justified.

Monitoring data from six diaphragm cell plants presented in Table 11-36 indicate that plants using metal anodes are meeting the BPT lead limitations. One of two graphite anode plants is meeting the limitations.

TABLE 11-35. EFFLUENT LIMITATIONS
Chlorine - Diaphragm Cell
Best Practicable Control Technology Currently Available
Waste Water Flow: 8.8 m³/kkg

Pollutant	Subcategory Performance (mg/l)	Daily Variability Factor	Concentration (mg/l)		Effluent Limit (kg/kkg)	
		30-day avg. Variability Factor	Max. 30-day avg.	24-hr max.	Max. 30-day avg.	24-hr max.
<u>Conventional Pollutants:</u>						
TSS	34 ⁽¹⁾	3.5/1.7	58	120	0.51	1.1
<u>Toxic Pollutants:</u>						
Arsenic	0.50 ⁽²⁾	4.1/1.6	0.80	2.1	-- ⁽⁴⁾	-- ⁽⁴⁾
Cadmium	0.10 ⁽³⁾	4.1/1.6	0.16	0.41	-- ⁽⁴⁾	-- ⁽⁴⁾
Chromium	0.32 ⁽³⁾	2.2/1.1	0.35	0.70	-- ⁽⁴⁾	-- ⁽⁴⁾
Copper ⁽⁵⁾	0.50 ⁽²⁾	4.1/1.6	0.80	2.1	0.0070	0.018
Lead ⁽⁵⁾	0.70 ⁽¹⁾	4.1/1.6	1.1	2.9	0.010	0.026
Nickel ⁽⁵⁾	0.40 ⁽³⁾	4.1/1.6	0.64	1.6	0.0056	0.014
Zinc	0.80 ⁽³⁾	4.1/1.6	1.3	3.3	-- ⁽⁴⁾	-- ⁽⁴⁾

(1) Calculated from long-term monitoring load data.

(2) Lower limit of literature treatability for lime/clarification technology from Table 8-11.

(3) Estimated achievable long-term average concentration from Table 8-13.

(4) No load limits; concentration limits are provided for guidance purposes.

(5) Also applicable for PSES limitations.

The limitations and guidelines for the additional toxic pollutants are derived from two sources--industrial wastewater treatment system performance data (Tables 8-12 and 8-13) and literature-based treatability estimates (Table 8-11). A comparison of these values, along with effluent data from the sampling of two diaphragm cell plants, is presented in Table 11-37. The concentration bases are derived from the industrial wastewater treatment system performance data unless the observed concentrations are below literature-based treatability estimates. In such cases, the lower limit of the applicable treatability level is used.

b. Copper

The estimated achievable long-term average concentration for copper (0.40 mg/l from Table 8-13) is lower than the literature-based treatability estimate (0.50 mg/l from Table 8-11). Therefore, the latter value is used in place of the long-term average. Because no long-term monitoring data is available for copper in this industry, the variability factors used for lead are employed to obtain the concentration limits.

The 24-hour maximum concentration is:

$$(0.50 \text{ mg/l}) (4.1) = 2.1 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.50 \text{ mg/l}) (1.6) = 0.80 \text{ mg/l}$$

The load limitations for copper (kg/kkg) are calculated based on the unit flow rate of 8.8 m³/kkg, thus:

$$(2.1 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.018 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.80 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0070 \text{ kg/kkg}$$

c. Nickel

The nickel limits are based on the estimated achievable long-term average concentration of 0.40 mg/l which is obtained from Table 8-13. Because no long-term monitoring data is available for nickel in this industry, the variability factors used for lead are employed again.

The 24-hour maximum concentration is:

$$(0.40 \text{ mg/l}) (4.1) = 1.6 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.40 \text{ mg/l}) (1.6) = 0.64 \text{ mg/l}$$

The load limitations for nickel (kg/kkg) are calculated based on the unit flow rate of $8.8 \text{ m}^3/\text{kkg}$, thus:

$$(1.6 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.014 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.64 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0056 \text{ kg/kkg}$$

The average concentration of nickel after lime addition and decantation in the Treatability Studies document (61) was 0.41 mg/l . This is essentially equal to the estimated achievable long-term average concentration which was the basis of the nickel limits.

d. Arsenic

The industrial wastewater treatment system performance for arsenic (0.080 mg/l from Table 8-12) is lower than the literature-based treatability estimate (0.50 mg/l from Table 8-11). Therefore, the latter value is used in place of a long-term average to arrive at the arsenic guidance. Because no long-term monitoring data is available for arsenic in this industry, the variability factors used for lead are employed again.

The 24-hour maximum concentration is:

$$(0.50 \text{ mg/l}) (4.1) = 2.1 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.50 \text{ mg/l}) (1.6) = 0.80 \text{ mg/l}$$

e. Cadmium

The cadmium guidance is based on the estimated achievable long-term average concentration of 0.10 mg/l which is obtained from Table 8-13. Because no long-term monitoring data is available for cadmium in

TABLE 11-36. LEAD AND TSS DISCHARGES FROM SELECTED DIAPHRAGM CELL
CHLORINE PLANTS⁽¹⁾

SUBCATEGORY		CHLORINE - DIAPHRAGM CELL	
Plant	Lead Discharge (kg/kg)		Maximum
	Average		
#589*	0.0020		0.030
#738*	0.0010		0.015
#261*	0.0025(2)		0.019
#014*	0.0060(2), (4)		NA
#967(3)	0.0064		0.026
#207	0.021(2)		0.054
Plant	TSS Discharge (kg/kg)		Maximum
	Average		
#207	0.30(2)		0.57
#014*	2.8(2), (4)		NA

(1) From Reference 3

(2) Plant has "once-through" barometric condenser water.

(3) Long Term Data Appendix A.

(4) Total plant discharge including other products. Recent information from plant indicates current discharge levels much diminished from data given in Reference 3.

* Plants with metal Anodes

NA: Not available

TABLE 11-37. COMPARISON OF TOXIC POLLUTANTS IN
DIAPHRAGM CELL PLANT EFFLUENTS
WITH TREATABILITY

Pollutant	Literature-based Treatability ⁽¹⁾ (mg/l)		Industrial Waste Water Treatment System Performance (mg/l)		Metal Anode Plant #261 Effluent ⁽²⁾ (mg/l)	Graphite Anode Plant #967 Effluent ⁽³⁾ (mg/l)
	BPT	BAT	BPT	BAT		
Arsenic	0.50	0.50	0.080 ⁽⁴⁾	0.17 ⁽⁴⁾	0.12	0.30
Cadmium	0.10	0.050	0.10 ⁽⁵⁾	0.076 ⁽⁴⁾	0.0040	< 0.015
Chromium	0.10	0.050	0.32 ⁽⁵⁾	0.16 ⁽⁵⁾	< 0.050	< 0.050
Copper	0.50	0.40	0.40 ⁽⁵⁾	0.30 ⁽⁵⁾	< 0.025	0.031
Lead	0.30	0.050	0.15 ⁽⁵⁾	0.19 ⁽⁴⁾	NA	NA
Nickel	0.20	0.10	0.40 ⁽⁵⁾	0.30 ⁽⁵⁾	< 0.050	< 0.050
Zinc	0.50	0.40	0.80 ⁽⁵⁾	0.20 ⁽⁵⁾	< 0.025	0.15

(1) Literature-based treatability estimates from Table 8-11.

(2) Cell wash waste filtered with coagulant to remove asbestos.

(3) Flow-proportioned average discharge, consisting of lead treatment discharge and untreated filter backwashes, condensates, and scrubber wastes.

(4) Data from Table 8-12 (value presented or average of values presented).

(5) Estimated achievable long-term average concentrations from Table 8-13.

NA = Not available

this industry, the variability factors used for lead are employed again.

The 24-hour maximum concentration is:

$$(0.10 \text{ mg/l}) (4.1) = 0.41 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.10 \text{ mg/l}) (1.6) = 0.16 \text{ mg/l}$$

f. Chromium

The chromium guidance is based on the estimated achievable long-term average concentration of 0.32 mg/l which is obtained from Table 8-13. A daily variability factor of 2.2 and a 30-day variability factor of 1.1 are obtained from the Treatability Studies document (61).

The 24-hour maximum concentration is:

$$(0.32 \text{ mg/l}) (2.2) = 0.70 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.32 \text{ mg/l}) (1.1) = 0.35 \text{ mg/l}$$

The average concentration of chromium after lime addition and decantation in the Treatability Studies document (61) was 0.071 mg/l. This value is much lower than the estimated achievable long-term average concentration used above. The large difference is attributable to the very low average chromium concentration of raw waste in the Treatability Studies document (0.089 mg/l).

g. Zinc

The zinc guidance is based on the estimated achievable long-term average concentration of 0.80 mg/l which is obtained from Table 8-13. Because no long-term monitoring data is available for zinc in this industry, the variability factors used for lead are employed again.

The 24-hour maximum concentration is:

$$(0.80) (4.1) = 3.3 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.80) (1.6) = 1.3 \text{ mg/l}$$

Basis for BAT Effluent Limitations

Previous BAT regulations called for no discharge of process wastewater pollutants. The regulations were remanded. The newly promulgated BAT regulations provide for the discharge of pollutants following appropriate treatment of process wastes.

A. Technology Basis

Utilizing the cost estimates presented in this report the Agency has analyzed the cost effectiveness of the base level system (BPT) and an advanced level option (Level 2) for conventional and toxic pollutant removal. The economic impact on the diaphragm cell chlorine subcategory has been evaluated in consideration of the technology basis for the BAT limitations.

For BAT the Agency is promulgating limitations based on BPT technology with the addition of dual-media filtration (Level 2) and dechlorination of all process wastewaters. Filtration will remove additional toxic metals and has been used successfully in the mercury-cell chlorine subcategory. Dechlorination is being included in BAT because the toxicity of chlorine to aquatic life is well documented and it is a pollutant of concern to the Agency (59). Two chlorine plants are known to be practicing dechlorination. The Agency considered the addition of sulfide precipitation (Level 3) to the treatment of cell room wastes but rejected it because further reduction of toxic pollutants in this stream only would not substantially improve total discharge quality.

B. Flow Basis

The flow basis for BAT limitations is the model plant total discharge of 8.8 m³/kkg. (See Table 11-33).

C. Selection of Pollutants to be Regulated

For BAT regulations, the Agency has selected the same three toxic metals identified in the BPT regulations (copper, lead, and nickel) and total residual chlorine. The other four toxic metals (arsenic, cadmium, chromium, and zinc) are again included for guidance.

D. Basis of Pollutant Limitations

For BAT regulations, the Agency is promulgating more stringent controls on the discharge of the first three toxic metals on the basis of physical removal by filtration. Alkaline precipitation converts most dissolved metals into less toxic insoluble forms and excess alkalinity exists in most of the process wastes generated in this subcategory. Plants whose raw waste has toxic

metal concentrations below literature treatability levels, perhaps as a consequence of installing metal anodes, would only have to sample periodically to show they are meeting the regulations. Final BAT limitations, which apply at the combined process wastewater discharge for toxic metals and at the plant effluent for residual chlorine, are presented in Table 11-38.

1. Nonconventional Pollutant

Chlorine: Total residual chlorine limits are based on the data from Appendix A that were used to calculate BAT limits for the chlorine mercury cell subcategory. The chlorine containing waste streams from both technologies are similar and the methods for chlorine removal are identical. The long-term average concentration is 0.64 mg/l. The variability factor for daily measurements is 2.3 and the variability factor for 30-day averages is 1.4.

The 24-hour maximum concentration is:

$$(0.64 \text{ mg/l}) (2.3) = 1.5 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.64 \text{ mg/l}) (1.4) = 0.90 \text{ mg/l}$$

The load limitations for total residual chlorine (kg/kkg) are calculated based on the unit flow rate of 8.8 m³/kkg, thus:

$$(1.5 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.13 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.90 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0079 \text{ kg/kkg}$$

2. Toxic Pollutants

Dual-media filtration of BPT effluent will significantly reduce suspended metal precipitates. BAT limitations and guidelines are derived from two sources--industrial wastewater treatment system performance data (Tables 8-12 and 8-13) and literature-based treatability estimates (Table 8-11). A comparison of these values is presented in Table 11-37. The concentration bases are derived from the industrial wastewater treatment system performance data unless the observed concentrations are below literature-based treatability estimates. In such cases, the lower limit of the applicable treatability level is used.

There are insufficient data to calculate daily and 30-day variability factors for any of the toxic pollutants in this industry. A daily variability factor of 3.5 and a 30-day average variability factor of 1.4 will be used to determine BAT toxic pollutant limitations and guidelines. These variability factors are the result of evaluating the Treatability Studies document (61) data from other industries involving the removal of toxic metals via the lime/filter method.

a. Copper

The copper limits are based on the literature treatability level of 0.40 mg/l (Table 8-11) which is larger than the estimated achievable long-term average concentration of 0.30 mg/l (Table 8-13).

The 24-hour maximum concentration is:

$$(0.40 \text{ mg/l}) (3.5) = 1.4 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.40 \text{ mg/l}) (1.4) = 0.56 \text{ mg/l}$$

The load limitations for copper (kg/kkg) are calculated based on the unit flow rate of 8.8 m³/kkg, thus:

$$(1.4 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.012 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.56 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0049 \text{ kg/kkg}$$

b. Lead

The lead limits are based on the data in Table 8-12. The average of the lead values in Table 8-12, 0.19 mg/l, is used in place of a long-term average.

The 24-hour maximum concentration is:

$$(0.19 \text{ mg/l}) (3.5) = 0.67 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.19 \text{ mg/l}) (1.4) = 0.27 \text{ mg/l}$$

TABLE 11-38. EFFLUENT LIMITATIONS

Chlorine Diaphragm Cell

Best Available Technology

Waste Water Flow: $8.8 \text{ m}^3/\text{kg}$

Pollutant	Treatability (mg/l)	Daily Variability Factor <hr/> 30-day avg. Variability Factor	Concentration Basis (mg/l) <hr/> Max. 24-hr. 30-day max. avg.		Effluent Limit (kg/kg) <hr/> Max. 24-hr. 30-day max. avg.	
<u>Nonconventional Pollutant</u>						
Total Residual Chlorine	0.64(1)	2.3/1.4	0.90	1.5	0.0079	0.013
<u>Toxic Pollutants</u>						
Arsenic	0.50(2)	4.1/1.6	0.80	2.1	-(5)	-(5)
Cadmium	0.076(3)	3.5/1.4	0.11	0.27	-(5)	-(5)
Chromium	0.16(4)	3.5/1.4	0.22	0.56	-(5)	-(5)
Copper	0.40(2)	3.5/1.4	0.56	1.4	0.0049	0.012
Lead	0.19(3)	3.5/1.4	0.27	0.67	0.0024	0.0059
Nickel	0.30(4)	3.5/1.4	0.42	1.1	0.0037	0.0097
Zinc	0.40(2)	3.5/1.4	0.56	1.4	-(5)	-(5)

(1) Long-term average concentration from Appendix A.

(2) Lower limit of literature treatability for lime/filter technology from Table 8-11.

(3) Industrial waste water treatment system performance data from Table 8-12.

(4) Estimated achievable long-term average concentration from Table 8-13.

(5) No load limits; concentration limits are provided for guidance purposes.

The load limitations for lead (kg/kkg) are calculated based on the unit flow rate of 8.8 m³/kkg, thus:

$$(0.67 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0059 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.27 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0024 \text{ kg/kkg}$$

c. Nickel

The nickel limits are based on the estimated achievable long-term average concentration of 0.30 mg/l which is obtained from Table 8-13.

The 24-hour maximum concentration is:

$$(0.30 \text{ mg/l}) (3.5) = 1.1 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.30) (1.4) = 0.42 \text{ mg/l}$$

The load limitations for nickel (kg/kkg) are calculated based on the unit flow rate of 8.8 m³/kkg, thus:

$$(1.1 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0097 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average limit is calculated similarly, i.e.,

$$(0.42 \text{ mg/l}) (8.8 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0037 \text{ kg/kkg}$$

d. Arsenic

Because the BPT and BAT literature treatability levels for arsenic are identical, the BAT guidance for arsenic is set equal to the BPT guidance.

e. Cadmium

The cadmium guidance is based on the data in Table 8-12. The cadmium value in Table 8-12, 0.076 mg/l, is used in place of a long-term average.

The 24-hour maximum concentration is:

$$(0.076 \text{ mg/l}) (3.5) = 0.27 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.076 \text{ mg/l}) (1.4) = 0.11 \text{ mg/l}$$

f. Chromium

The chromium guidance is based on the estimated achievable long-term average concentration of 0.16 mg/l which is obtained from Table 8-13.

The 24-hour maximum concentration is:

$$(0.16 \text{ mg/l}) (3.5) = 0.56 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.16 \text{ mg/l}) (1.4) = 0.22 \text{ mg/l}$$

g. Zinc

The zinc guidance is based on the literature treatability level of 0.40 mg/l (Table 8-11) which is larger than the estimated achievable long-term average concentration of 0.20 mg/l (Table 8-13).

The 24-hour maximum concentration is:

$$(0.40 \text{ mg/l}) (3.5) = 1.4 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.40 \text{ mg/l}) (1.4) = 0.56 \text{ mg/l}$$

BCT Limitations

EPA has determined that the BAT technology for this subcategory is capable of removing significant amounts of conventional pollutants. However, EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned earlier. Thus, it is not now possible to apply the BCT cost test to this technology option. Accordingly, EPA is deferring a decision on the appropriate BCT limitations until EPA proposes the revised BCT methodology. However, the Agency has calculated the expected TSS effluent quality after application of dual-media filtration and the cost of the additional TSS removal. As described in Section 3, this cost was calculated to be \$0.53 per lb TSS removed.

Basis for New Source Performance Standards

A. Technology Basis

The Agency is basing NSPS limitations on the BAT technology of alkaline precipitation, filtration, and dechlorination and on the performance achieved at plants which exclude the use of lead in cell construction. The conversion to metal anodes has largely eliminated the source of lead in wastewaters, but residual lead contamination at a converted plant may exist for as long as a year or more. New metal anode plants should have relatively low lead concentrations in their wastewaters.

B. Flow Basis

The flow basis of 8.8 m³/kkg used for BPT and BAT limitations is conservatively being used for new sources.

C. Selection of Pollutants to be Regulated

For NSPS regulations, the Agency initially considered the same BAT pollutants (seven toxic metals and total residual chlorine), pH and TSS. Table 11-39 presents the results of verification sampling of raw wastes at a new chlorine plant using metal anodes. The total raw waste concentrations of toxic metals are, with the exceptions of chromium and lead, substantially below the estimated treatability of these metals using BAT technology, as shown in the table. Application of the information in Section 8 on the control parameters for hydroxide precipitation leads to the selection of lead as the toxic pollutant to be regulated. Control of this pollutant within the limitations being set will assure that other toxic metals are being controlled. Other metals are presented on a concentration basis for guidance purposes only.

D. Basis of Pollutant Limitations

For NSPS regulations the Agency is promulgating more stringent controls on the discharge of lead on the basis of lower raw waste loads generated at plants using metal anodes. New plants that have raw waste lead concentrations below estimated industry long-term averages would only have to sample periodically to show they are meeting the regulations. The NSPS regulations, which apply at the combined process wastewater discharge for TSS and lead and at the plant effluent for residual chlorine and pH, are shown in Table 11-40.

1. Conventional and Nonconventional Parameters

a. pH

The treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the

data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS

Limitations for TSS are the same as BPT regulations.

c. Total Residual Chlorine

Limitations for total residual chlorine are the same as in BAT regulations.

2. Toxic Pollutants

a. Lead

The concentration bases for lead is based on the estimated achievable long-term average of 0.15 mg/l (Table 11-39). Variability factors used to obtain BAT limits for lead are used for the NSPS limits. The concentration bases for lead are determined as follows:

The 24-hour maximum concentration is:

$$(0.15 \text{ mg/l}) (3.5) = 0.53 \text{ mg/l}$$

and the corresponding effluent limit is:

$$(0.53 \text{ mg/l}) (8.8 \text{ m}^3/\text{kg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0047 \text{ kg/kg}$$

The maximum 30-day average is:

$$(0.15 \text{ mg/l}) (1.4) = 0.21 \text{ mg/l}$$

and the corresponding effluent limit is

$$(0.21 \text{ mg/l}) (8.8 \text{ m}^3/\text{kg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.0018 \text{ kg/kg}$$

b. Other Toxic Pollutants

Guidance for the other toxic metals are the same as in BAT regulations.

Basis for Pretreatment Standards

A. Existing Sources

For Pretreatment Standards for Existing Sources (PSES), the Agency is promulgating the same limitations as for BPT (excluding

TABLE 11-39. COMPARISON OF RAW WASTE CHARACTERISTICS AT A NEW METAL ANODE PLANT WITH TREATABILITY OF TOXIC METALS

SUBCATEGORY CHLORINE DIAPHRAGM CELL		
Pollutant	Treatability	Concentration(mg/l)
		Plant #738B ⁽²⁾ Raw Waste
Arsenic	0.50 ⁽¹⁾	0.011
Cadmium	0.050 ⁽¹⁾	<0.025
Chromium	0.16 ⁽³⁾	0.066
Copper	0.30 ⁽³⁾	0.12
Lead	0.15 ⁽³⁾	0.11
Nickel	0.30 ⁽³⁾	0.067
Zinc	0.20 ⁽³⁾	0.093

(1)- Literature-based treatability estimates using BAT technology of dual media filtration following alkaline precipitation of metals (Table 8-11)

(2)- Verification sampling at new metal anode facility

(3)- Estimated achievable long-term average from Table 8-13.

TSS and pH) based on the identical treatment technology (see Table 11-35). The pollutants to be limited are copper, lead and nickel. Pretreatment is necessary because BPT provides better removal of toxic metals than is achieved by a well-operated POTW with secondary treatment installed. PSES are being set equal to BPT, because the POTW achieves equal or greater removal of the toxic metals remaining after application of BPT (PSES) technology than is achieved by the filtration required by BAT. Thus, a filter is not required for PSES because there is no pass-through.

B. New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is promulgating the same limitations as for NSPS based on the identical treatment technology without dechlorination being used for indirect dischargers (see Table 11-40). Dechlorination is unnecessary because influent to publicly-owned treatment works is often chlorinated. The pollutant to be limited is lead. The other pollutants (copper and nickel) are not being limited based on the assumption that all new plants will have effluent levels equal to the levels of a new metal anode plant. Pretreatment is necessary because NSPS provides better removal of toxic metals (when present at treatable levels) than is achieved by a POTW and hence these pollutants would pass through a POTW in the absence of pretreatment.

TABLE 11-40. EFFLUENT LIMITATIONS

Chlorine Diaphragm Cell

New Source Performance Standards

Waste Water Flow: $8.8 \text{ m}^3/\text{kg}$

Pollutant	Treatability (mg/l)	Daily Variability Factor	Concentration Basis (mg/l)		Effluent Limit (kg/kg)	
		30-day avg. Variability Factor	Max. 24-hr. 30-day max. avg.	Max. 24-hr. 30-day max. avg.		
<u>Conventional and Nonconventional</u>						
TSS	34	3.5/1.7	58	120	0.51	1.1
Total Residual Chlorine	0.64	2.3/1.4	0.90	1.5	0.0079	0.013
<u>Toxic Pollutants</u>						
Arsenic	0.50	4.1/1.6	0.80	2.1	-(2)	-(2)
Cadmium	0.076	3.5/1.4	0.11	0.27	-(2)	-(2)
Chromium	0.16	3.5/1.4	0.22	0.56	-(2)	-(2)
Copper	0.40	3.5/1.4	0.56	1.4	-(2)	-(2)
Lead (I)	0.15	3.5/1.4	0.21	0.53	0.0018	0.0047
Nickel	0.30	3.5/1.4	0.42	1.1	-(2)	-(2)
Zinc	0.20	3.5/1.4	0.28	0.70	-(2)	-(2)

(1) Also applicable to PSNS limitations.

(2) No load limits; concentration limits are provided for guidance purposes.

SECTION 12

HYDROFLUORIC ACID INDUSTRY

Industry Profile

General Description

Hydrofluoric acid (hydrogen fluoride or HF) is produced both as anhydrous and aqueous products. It is used in the manufacture of fluorocarbons which are used as refrigerating fluids and plastics, for pressurized packing, and as dispersants in aerosol sprays. HF is used in the production of aluminum, in the refining and enriching of uranium fuel, in pickling of stainless steel, in petroleum alkylation, and for the manufacture of fluoride salts. The industry data profile is given in Table 12-1. The status of regulations prior to promulgation of these new regulations is given in Table 12-2.

Subcategorization

Hydrogen fluoride is usually used in the production of aluminum fluoride (AlF_3) by reacting with hydrated alumina ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). Two aluminum fluoride plants are integrated with hydrofluoric acid production.

For both products (HF and AlF_3), process wastewaters are generated by the various gas scrubbers and by leaks and spills. In both cases, air pollution control scrubber effluents contain mainly fluoride, acidity and sulfate. The fluoride is present as the free ion as well as various complex fluoro anions. Calcium fluoride (CaF_2), generated as a solid waste, is a disposal problem for both subcategories because of its moderate toxicity.

However, combining hydrofluoric acid and aluminum fluoride into a single subcategory does not appear to offer any regulatory advantages when the two products are manufactured at the same plant location.

The wastewaters generated from both industries do not have a common production basis. In addition, the combined manufacture of these products does not create a unique or unusual situation, either with regard to the wastewater treatment requirements or compliance with discharge regulations.

Due to process differences and the variations in the pollutant loadings for the two industries, different variability factor ratios were used in obtaining the effluent limitations of the toxic pollutants. In the case of the hydrofluoric acid subcategory, nickel and zinc are chosen as the control toxic pollutants for the effluent limitations. On the other hand, chromium and nickel are the toxic metals controlled in the aluminum fluoride subcategory. These

TABLE 12-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	HYDROFLUORIC ACID
Total subcategory capacity rate	363,000 kkg/year
Total subcategory production rate	261,800 kkg/year
Number of plants in this subcategory	9
308 Data on file for	8
With total capacity of	*
With total production of	177,000 kkg/year
Representing capacity	*
Representing production	68 percent
Plant production range:	
Minimum	7,300 kkg/year
Maximum	62,000 kkg/year
Average production	22,100 kkg/year
Median production	15,800 kkg/year
Average capacity utilization	83 percent
Plant age range:	
Minimum	7 years
Maximum	58 years
Waste water flow range:	
Minimum	0 cubic meters/day
Maximum	4,700 cubic meters/day
Volume per unit product:	
Minimum	0 cubic meters/kkg
Maximum	86 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; and Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

* Data incomplete because certain plants did not respond to this question.

TABLE 12-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY HYDROFLUORIC ACID

SUBPART H (40 CFR 415.80, 3/12/74)

STANDARDS

Product Process	Parameters	BPCTCA*		BATEA*		NSPS*	
		Max. ¹ (mg/l)	Avg. ² (mg/l)	Max. ¹ (mg/l)	Avg. ² (mg/l)	Max. ¹ (mg/l)	Avg. ² (mg/l)
Hydrofluoric Acid	Fluoride	(30)	(15)	No discharge of pwwp ³		No discharge of pwwp	
	TSS	(50)	(25)	No discharge of pwwp		No discharge of pwwp	

* Section 415.82, 415.83, and 415.85 were remanded and reserved (41 FR 51601, November 23, 1976).

¹ Max. = Maximum of any one day.

² Avg. = Average of daily values for thirty consecutive days.

³ pwwp = Process wastewater pollutants.

differences are due to the different relative concentrations for chromium and zinc in the raw waste loads from the two products.

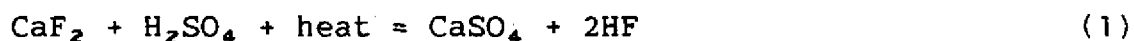
Furthermore, the opportunities for drip acid recycle (or the hydrolysis of complex fluoride prior to treatment) and scrubber water recycle are a function of plant design and age, rather than product mix.

An additional solid waste, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is generated from the hydrofluoric acid manufacture and supplies enough calcium for adequate fluoride removal from neutralized scrubber wastewaters generated by both HF and AlF_3 production. However, the applied treatment technology is essentially the same as that applied by manufacturers of either product alone.

In view of these considerations, hydrofluoric acid and aluminum fluoride remain separated as two distinct subcategories.

General Process Description and Raw Materials

HF is the most important manufactured compound of the fluoride family in volume of production. Fluorspar (mainly CaF_2) and sulfuric acid are the raw materials used for its manufacture. Fluorspar and sulfuric acid react endothermically at 200-250 degrees C and the reaction time is 20-60 minutes. The reaction is given as:

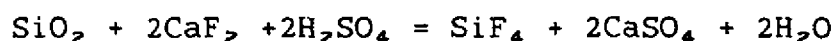


The reaction kinetics and the yield of product depends on the purity and fineness of the fluorspar. The concentration of sulfuric acid, the temperature of the reaction, and the ratio of sulfuric acid to fluorspar are among important variables.

Crude fluorspar, as mined, varies in CaF_2 content from 35 to 90 percent. The ore is upgraded by flotation which results in 98 percent CaF_2 being available for the production of HF. The analysis of a typical upgraded fluorspar is given as:

CaF_2	Minimum 97.5-98%
SiO_2	Maximum 1.0%
S	Maximum 0.05%
H_2O	Maximum 0.1%
CaCO_3	Principal remainder

Silica is a highly objectionable contaminant, since each pound consumes 2.0 pounds of fluorspar and 3.3 pounds of sulfuric acid by the following reaction:



Sulfuric acid having a concentration as low as 93 percent or as high as 99 percent is generally used. Dilute sulfuric acid enhances better mixing and liberation of fluoride but has two disadvantages; viz., the dilute acid is very corrosive and the water present in the acid evaporates and distills off with the HF gas, thus reducing product concentration. Concentrated sulfuric acid (greater than 98 percent) offsets these disadvantages but creates new problems. The vapor pressure of concentrated sulfuric acid is sufficiently high to cause large amounts of sulfuric acid to be carried away by the HF. Excess sulfuric acid, when used, will leave with the gypsum as part of the residue.

HF generators are, in the majority of cases, externally fired rotary kilns in which acid and fluorspar are fed continuously through a screw conveyor at the forward end and gypsum is removed from the other end through an air lock. The product HF may discharge from either end. The theoretical amount of gypsum produced is 3.4 kg/kg of HF produced, but because of the impurities in the fluorspar the actual amount of gypsum produced is higher and varies from 3.6 to 4.8 kg/kg of HF.

One manufacturer uses a patented process to supply internal heat to the reactor. The heat is supplied by introducing sulfur trioxide (SO_3) and water (as steam). The exothermic heat liberated by the reaction of SO_3 and water to produce sulfuric acid is used for the heat required for HF generation. Thus a part of the sulfuric acid is supplied as SO_3 .

The HF gas leaving the reactor is cooled in a precooler to condense high boiling compounds. The condensables are known as drip acid and largely consist of fluorosulfonic acid (HSO_3F) and unreacted sulfuric acid. In 1978, nine plants out of a total of eleven returned the drip acid to the reactor, while the remaining two sent the drip acid to the waste treatment plant. The HF gas from the precooler is cooled further and condensed in a cooler/refrigeration unit. The uncondensed gas containing the HF is scrubbed with sulfuric acid and refrigerated to recover the product. The scrubbed acid liquor is returned to the kiln, and residual vent gases are scrubbed further with water to remove HF and other fluoride compounds before they are vented to the atmosphere. The scrubber water is sent to the wastewater treatment plant. Figure 12-1 is a block flow diagram of the manufacturing process.

The crude HF is then distilled to remove the residual impurities, and the condensate, which is anhydrous HF, is stored in tanks. If aqueous HF is desired, the crude product is then diluted with water to form a 70 percent HF solution as the final product.

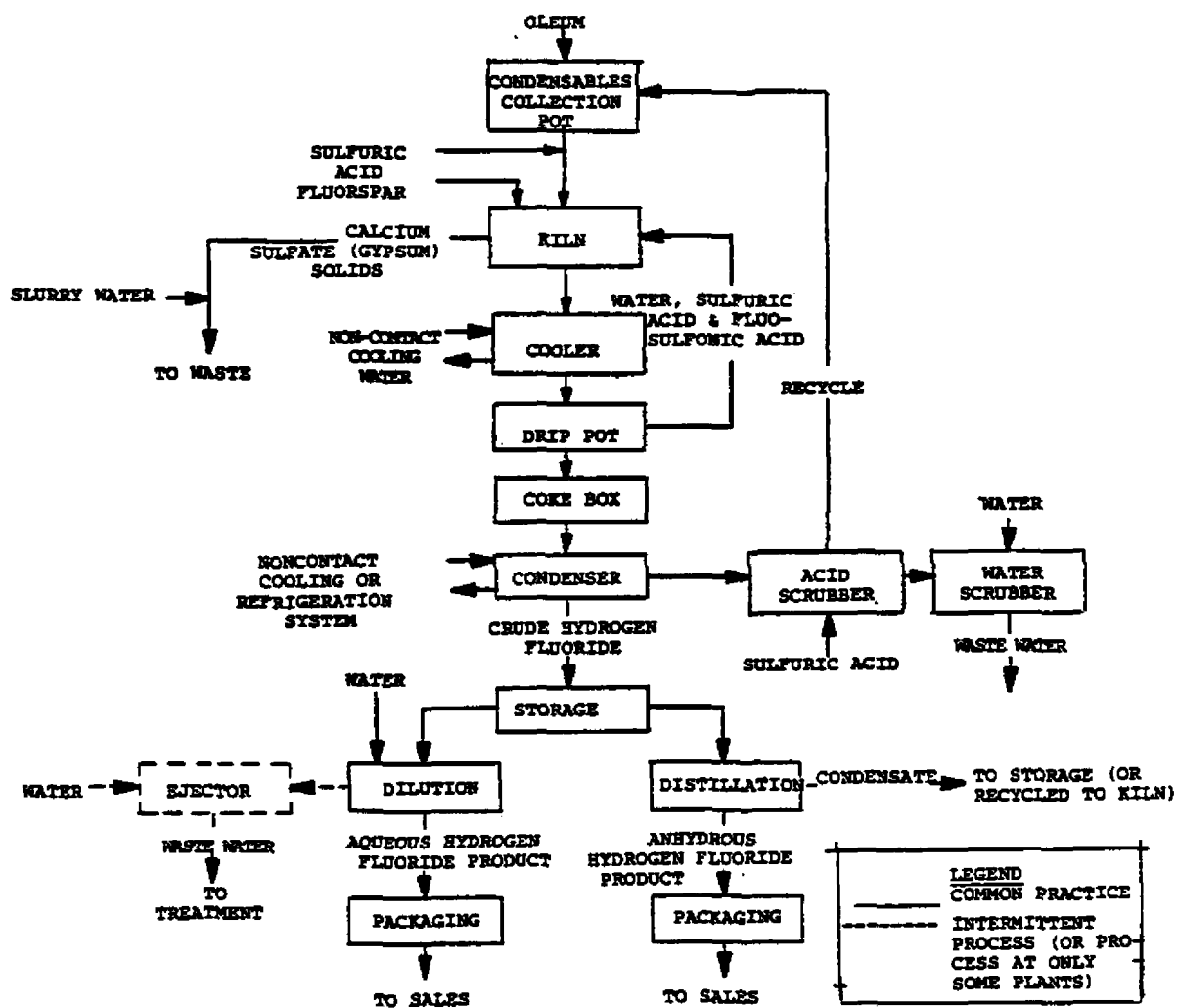


Figure 12-1. General process flow diagram for production of hydrofluoric acid.

Water Use and Waste Source Characteristics

Water Use

Water is used in HF production in noncontact cooling, air pollution control, product dilution, seals on pumps and kilns, and for equipment and area washdown. Although noncontact cooling constitutes the major use of water, water is also used, in a majority of cases, in the transport of gypsum as a slurry to the wastewater treatment facility. The water for gypsum transport is provided by either reusing the water from the treatment facility or by using once-through cooling water. Table 12-3 summarizes the water usage found in this study.

Waste Sources

A. Gypsum Solids

Gypsum solids are generated as a by-product. The amount produced is in the range of 3.6 to 4.8 kg/kg of HF produced. The gypsum also contains small amounts of sulfuric acid, HF, and calcium fluoride. Minor amounts of other impurities present in fluorspar are also removed with the gypsum. In five out of eleven plants producing HF, gypsum is slurried with treated wastewater, neutralized with lime or soda ash, and pumped to a gypsum storage pond. In one plant the gypsum slurry is pumped to the storage pond without treatment and in another plant partial neutralization is employed. Three plants transport the gypsum as a dry solid and dispose of it as a solid waste after mixing with lime for neutralization. The disposal method of one plant is not known. It should be noted that two of the eleven plants have recently discontinued HF production, one of which is in the group of five.

When gypsum solids from the kiln are slurried with water for treatment, the resulting stream constitutes the major source of wastewater. When kiln residue is disposed of as a solid waste, scrubber wastewater is the major source of waste. Table 12-4 gives the data for the direct and indirect process contact wastewater going to treatment facilities. Noncontact cooling water has not been included in the figures given in Table 12-4. Figure 12-2 is a graphical representation of production versus wastewater flow to inplant treatment facilities for plants whose wastewater includes the gypsum slurry and for those practicing disposal of kiln residue as a solid waste.

B.. Drip Acid

This is formed in the first stage of the cooling (i.e., in the precooler) of the gases emitted from the kiln. Drip acid mostly contains high boiling compounds consisting of complex fluorides, especially fluorosulfonic acid, and small amounts of hydrofluoric acid, sulfuric acid, and water. Fluorosulfonic acid is formed by

TABLE 12-3. WATER USAGE IN THE HYDROFLUORIC ACID SUBCATEGORY

Source	Water Usage at Plants (m ³ /kgg of HF)							(1) #705
	(1) #987	(1) #251	#753	#426	#120	#722	#167	
Non-contact Cooling	154	NA	63.5	110	NA	13.6	116	30.0
Gypsum Slurry Transport	NA	64.0	NA	*	NA	22.5	41.6	30.0
Maintenance, Equipment and Area Washdown	NA	2.40	2.11	NA	0.1	12.2	5.00	16.9
Air Pollution Control	7.90	14.4	4.23	NA	0.586	14.5	40.0	11.3

NA = Not Available

* = Not Applicable

(1) Discontinued HF production.

TABLE 12-4. WASTE WATER FLOW AND REUSE DATA FOR THE
HYDROFLUORIC ACID SUBCATEGORY

Plant	Kiln Residue Handling ⁽¹⁾	Reuse for Kiln Residue Slurry ⁽²⁾ (Percent)	Influent to Treatment Facility (m ³ /kkg) HF	Treated Effluent Discharged (m ³ /kkg) HF
#120	D	— ⁽⁴⁾	9.10	9.10
#426	D	— ⁽⁴⁾	0	Not available
#987 ⁽³⁾	D	— ⁽⁴⁾	13.6	13.6
#837	S	0	120	120
#967	S	0	125	125
#251 ⁽³⁾	S	0	84.7	84.7
#705 ⁽³⁾	S	30.0-35.0	58.2	39.3
#167	S	47.0	166	98.2
#753	S	65.0	31.4	11.1
#928	S	83.0	55.5	9.40
#664	S	94.0	96.6	5.80
#722	S	92.0-100	120	7.20
Averages: (S only)		42.8 percent	95.4 m ³ /kkg	54.6 m ³ /kkg

(1) D = Dry disposal S = Slurried to treatment

(2) Percent of waste water flow reused for residue slurry after treatment.

(3) Discontinued HF production.

(4) Not Applicable.

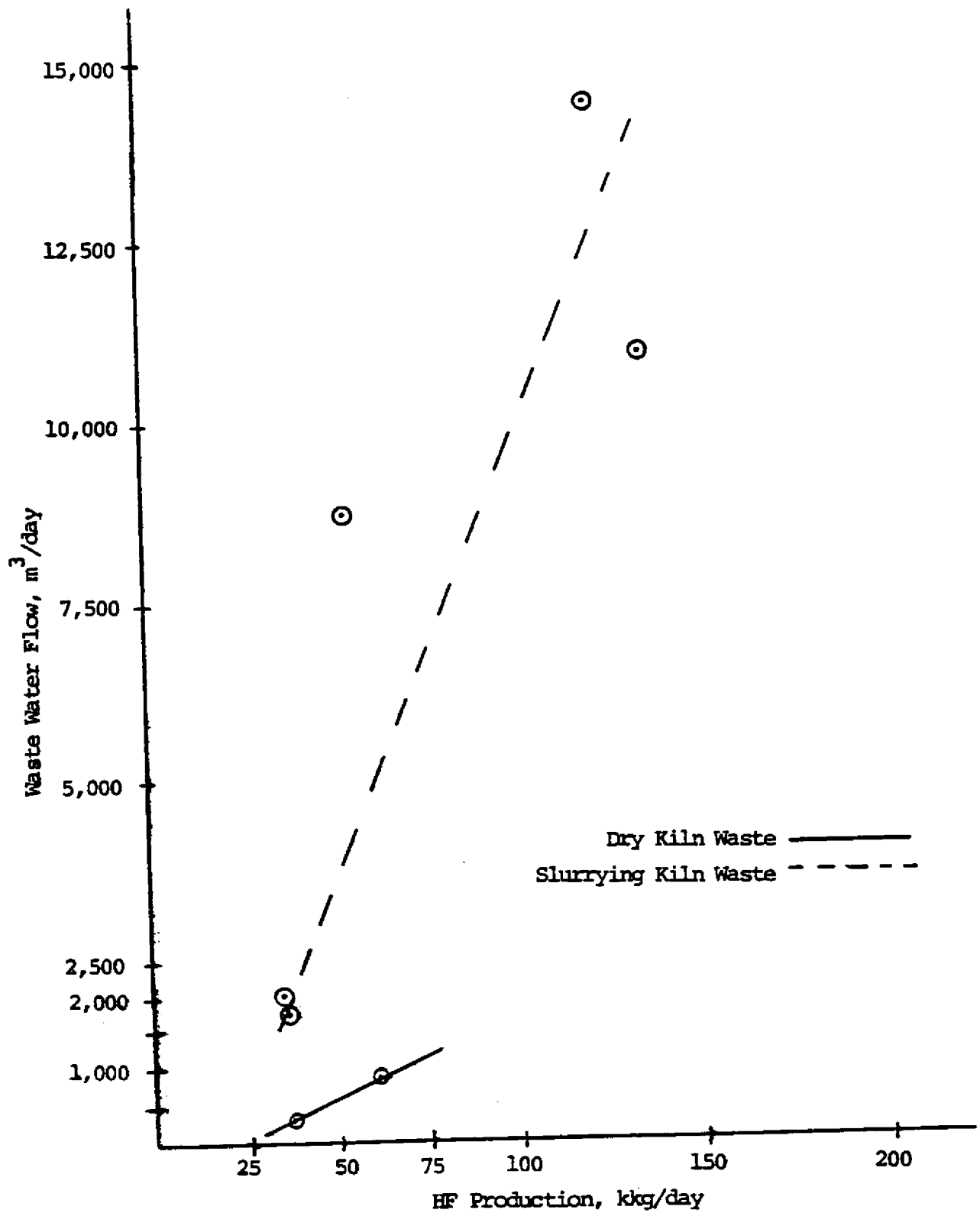


Figure 12- 2. Production versus waste flow data for HF plants.

reaction between hydrofluoric acid and sulfuric acid in the absence of water. The quantity of drip acid produced is relatively small. In the plants which recycle the drip acid back to the reactor, it is mixed with the sulfuric acid feed stream before it enters the kiln where it is hydrolyzed to form sulfuric acid and hydrofluoric acid. The critical factors for hydrolysis are temperature and retention time and enough water is normally present in the kiln for the reaction.

C. Noncontact Cooling Water

Noncontact cooling water is used for precooling the product gases emitted from the kiln. The possibility of product or other process compounds leaking into the cooling water is very small; however, in the event that the cooling water does become contaminated, the proposed limitations for fluoride may be exceeded. Depending on the merits of the situation, the upset and bypass provisions may apply. In some plants, the cooling water is used to transport the waste gypsum.

D. Scrubber Wastewater

Scrubber water is another wastewater source, and in plants which practice dry disposal of gypsum, scrubber water constitutes the predominant and major source of wastewater. It contains fluoride, sulfate, and acidity. The fluoride is present as HF, silicon tetrafluoride (SiF_4), and hexafluorosilicic acid H_2SiF_6 . Silica present in the ore as an impurity reacts with HF forming silicon tetrafluoride as shown in Equation 3.



In the scrubber, the silicon tetrafluoride is converted to hexafluorosilicic acid according to the following equations:



E. Distillation Wastes

The distillation waste generally contains HF and water. In some cases the vent gases from the distillation column are scrubbed before they are emitted to the atmosphere, and the resulting scrubber water requires treatment.

The range of wastewater quality of the different streams generated from the production of HF is summarized in Table 12-5. The data are taken from the prior development documents, 308 Questionnaire responses, and industry visits.

F. Spar Drying Wastewater

Wet fluorspar is first processed through a dryer to remove essentially all of the water. The steam and dust generated is passed through a scrubber from which the wastewater is sent to the gypsum neutralization tank. As shown in Table 12-6, the contribution of the spar drying wastewater is insignificant compared to the total amount of process wastewater and hence can be neglected. The data is taken from 308-Questionnaire responses.

G. Other Solid Wastes

The total solids generated from the process and the treatment system consist of gypsum and the fluoride precipitated as calcium fluoride. Table 12-7 gives the amount of suspended solids generated from the process and the quantity of total suspended solids generated at the wastewater treatment plant for the HF plants visited in screening and verification. The data indicate that the gypsum waste constitutes more than 95 percent of the total solids produced. Table 12-8 gives the amount of gypsum solids produced at different HF manufacturing facilities. The data shows that 3.8 to 4.7 kg gypsum solids are produced per kg of product.

Description of Plants Visited and Sampled

Screening

Plant #705 was visited and process wastewater samples were collected and analyzed for conventional, nonconventional and toxic pollutants. The process used at this site is similar to the conventional HF manufacturing process described earlier. The drip acid is sent to the wastewater treatment facility and the gypsum produced from the reactor is slurried with water and also sent to the treatment facility. The wastewaters from the HF production facility are combined with aluminum fluoride plant wastewaters. The combined raw wastewater is treated with lime and sent to settling ponds before discharge. Figure 12-3 shows the general process and the locations of the sampling points. Table 12-9 gives the flow data and the total suspended solids (TSS) and fluoride emissions.

Verification

The same streams at Plant #705 were sampled again in the verification phase. The variation in the flow of the streams in the two sampling phases was negligible. Table 12-10 gives the TSS and fluoride load summary of the sampled streams.

Two more HF plants (Plant #251 and #167) were sampled in the verification phase. The drip acid at both facilities is also sent to the waste treatment plant and the hydrofluoric acid wastewaters are

TABLE 12-5. WASTE FLOW FROM HYDROFLUORIC ACID MANUFACTURING PLANTS

Source of Waste Water	Flow in m ³ /kg of Hydrofluoric Acid Plants								
	#251 ⁽¹⁾	#987 ⁽¹⁾	#753	#426	#120	#722	#167	#705 ⁽¹⁾	#837
Gypsum Slurry	64.0	Dry disposal	NA	Dry disposal	Dry disposal	(Total Recycle)	122	(Total Recycle)	6.50
Drip Acid	0.0490	0	0	0	0	0	NA	0.0180	0
Scrubber Waste Water	14.4	8.30	2.30	NA	0.624	(Total Recycle)	40.0	11.3	1.12
Other *	0.530	0.530	8.40	NA	5.55	NA	5.20	22.5	NA

(1) Discontinued HF production

NA = Not Available

* Other does not include wasteflows from storm water runoff.

TABLE 12-6. FLOW AND POLLUTION CONCENTRATION DATA OF SPAR DRYING AND TOTAL PROCESS WASTE WATER FOR PLANTS #251 AND #837 PRODUCING HYDROFLUORIC ACID

Plant	Stream Description	Flow (m ³ /kgg of HF)	Total Suspended Solids (kg/kgg of HF)
# 251	Spar drying waste water	1.20 (1.8%) ⁽¹⁾	70.8 (1.8%) ⁽¹⁾
	Total process waste water	66.9	4000
# 837	Spar drying waste water	1.11 (1%) ⁽¹⁾	16.7 (0.5%) ⁽¹⁾
	Total process waste water	114	3140

(1) Number in parentheses is the percentage contribution of a pollutant parameter of the spar drying waste water to that of the total process waste water.

TABLE 12-7. SOLID WASTE GENERATED AT THE HYDROFLUORIC ACID PLANTS SAMPLED

Plant	Gypsum Solids Going To Treatment Facility (kg/kgg of HF)	Total Solids Produced (kg/kgg of HF)
#705 ⁽¹⁾	4.73	4.78
#251 ⁽¹⁾	3.81	NA
#167	3.94	NA

(1) Discontinued HF production.

NA = Not Available

TABLE 12-8. GYPSUM SOLIDS PRODUCTION IN THE HYDROFLUORIC ACID SUBCATEGORY

Plant	Kiln Residue Produced (kg/kg of HF)	Kiln Residue Disposal/Treatment Method
#837	3.86	S
#705 ⁽¹⁾	4.73	S
#167	3.94	S
#722	NA	S
#120	NA	D
#426	4.00	D
#987 ⁽¹⁾	4.13	D
#251 ⁽¹⁾	3.81	S
#753	NA	S
#967	NA	S
#928	NA	S

S = Slurried with water and sent to waste water treatment facility.

D = Dry disposal.

NA = Not Available.

(1) = Discontinued HF production.

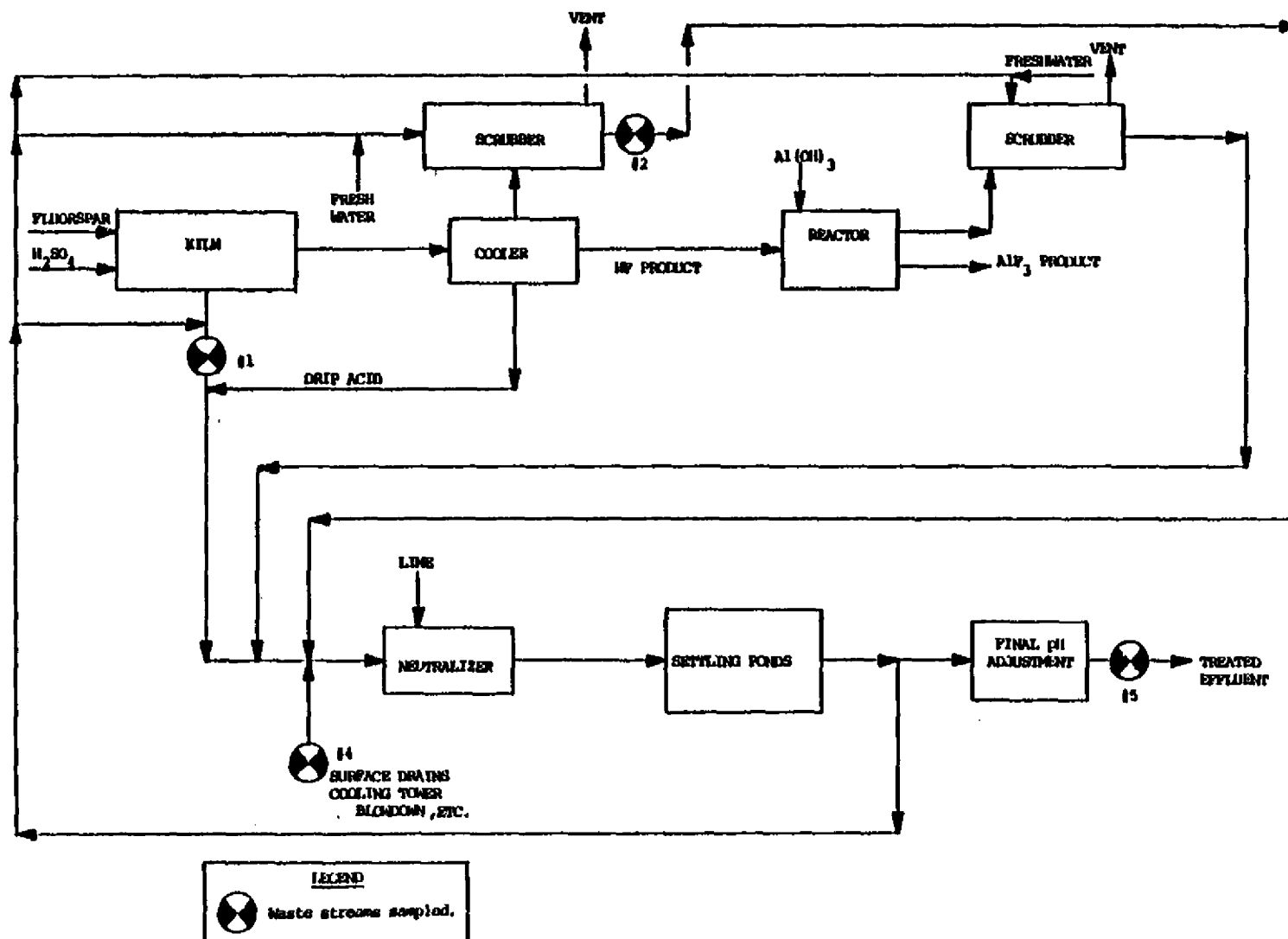


Figure 12-3. General process flow diagram at plant #705 showing the sampling points.
Hydrofluoric acid manufacture.

TABLE 12-9. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS OF PLANT #705 PRODUCING HYDROFLUORIC ACID⁽¹⁾

Stream No.	Sampled Stream Description	Screening Data ⁽²⁾		Total Suspended Solids (kg/kkg of HF)
		Flow (m ³ /kkg of HF)	Fluoride (kg/kkg of HF)	
1	Kiln Slurry	26.6	15	4700
2	Scrubber Waste Water	10.0	9.6	0.070
3	Surface Drains Cooling Tower Blowdown	20.0	6.9	3.9
4	Treated Effluent	23.3 ⁽³⁾	1.6	1.9

(1) This plant has discontinued the production of HF since the time of sampling.

(2) One 72-hour composite sample of each waste water stream.

(3) The discharged effluent consists of the treated waste waters from hydrofluoric acid and aluminum fluoride plants.

combined with aluminum fluoride plant waste for treatment. In addition to drip acid, Plant #251 wastewater consists of scrubber water, gypsum slurry, and plant area hose down. The treatment consists of gypsum ponds where the suspended solids are removed. The overflow from the last gypsum pond is neutralized and the pH adjusted with wastes from other product lines. Figure 12-4 is a block diagram of the process showing the sampling locations at Plant #251.

At Plant #167, the major raw waste sources are the kiln waste slurry, the absorber tails from the condensate (drip acid) recycle system, and the ejector water which is used to quench the off-gases from the absorber. All three of these waste streams are collected in a common neutralization pit where lime slurry is added. The waste then flows into a series of three lagoons for solids removal and final pH adjustment prior to discharge. Most of the gypsum settles out in the first lagoon and the overflow enters the second lagoon where commingling with wastes from other processes takes place. Verification sampling data from this plant were obtained from four sampling points. These are: 1) the kiln waste slurry, 2) the absorber tails, 3) the ejector water, and 4) the effluent from the first lagoon. The fourth sampling point is the last point at which all wastewater originating in the HF plant can be intercepted.

Summary of the Toxic Pollutant Data

Eleven toxic pollutants were found in the raw waste samples from HF Plant #705. They were also verified at three other typical HF plants practicing BPT treatment. No organic toxic pollutants were found at detectable levels. The results were:

Maximum Raw Waste Concentrations Observed ($\mu\text{g/l}$)

Pollutant	Screening Plant #705	Verification
		Plants #705, #251, #167
Copper	770	600
Lead	5200	200
Selenium	25	230
Zinc	8100	11000
Antimony	70	2800
Arsenic	10	160
Cadmium	2.0	60
Chromium	73	1200
Mercury	2.0	43
Nickel	150	2000
Thallium	5.5	63

Section 5 of this report describes the methodology of the screening and verification sampling program. In the Hydrofluoric Acid industry, a total of 12 days of sampling were conducted at Plants # 705, #251,

TABLE 12-10. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANTS #705, #251, AND #167 PRODUCING HYDROFLUORIC ACID

Plant	Stream No.	Sampled Stream Description	Verification Data ⁽¹⁾		
			Flow (m ³ /kgg of HF)	Fluoride (kg/kgg of HF)	Total Suspended Solids (kg/kgg of HF)
#705 ⁽²⁾	1	Kiln Slurry	26.6	3.8	4700
	2	Scrubber Waste Water	10.0	1.5	0.019
	4	Surface Drains Cooling Tower Blowdown	20.0	3.4	4.0
#251 ⁽²⁾	5	Treated Effluent	23.3 ⁽³⁾	0.54	0.040
	5	AHF Plant Hosedown	1.20	1.9	0.26
	6	SO ₂ Scrubber Waste	14.4	0.31	0.10
	2	Gypsum Pond Inlet	84.7	58	3800
	3	Gypsum Pond Outlet	84.7	27	0.80
#167	1	Kiln Slurry	122	4.9	170
	2	Ejector & Absorber Unit Wastes from Kilns #1, #2, and #4	25.0	14	0.36
	3	Ejector & Absorber Unit Wastes from Kilns #5 and #6	14.6	20	0.41
	4	Effluent from First Lagoon	162	11	22

(1) Three 24-hour composite samples of each waste water stream.

(2) These plants have now discontinued their HF production.

(3) Consists of the combined flow from hydrofluoric acid and aluminum fluoride plants.

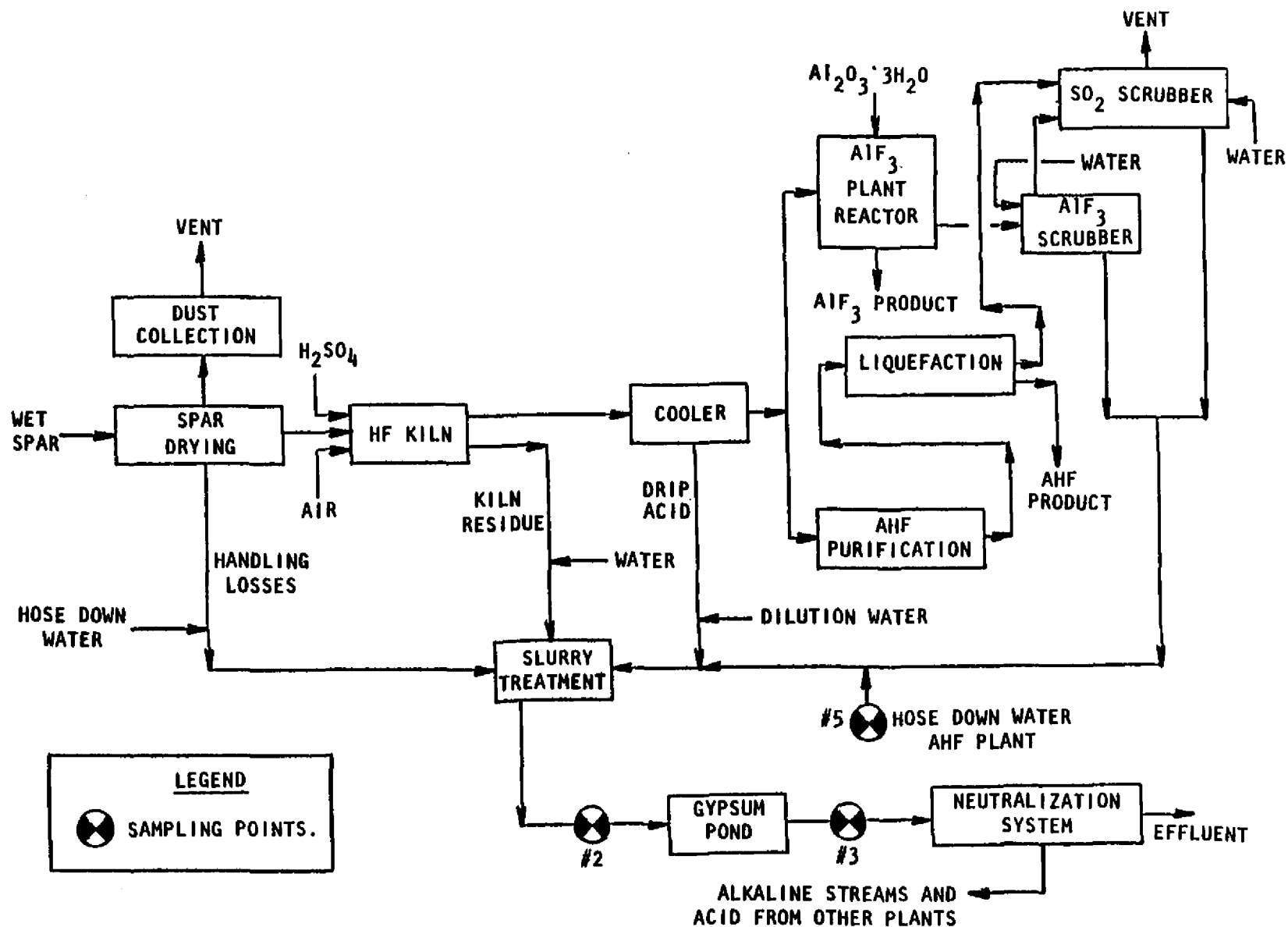


Figure 12-4. General process flow diagram at Plant #251 showing the sampling points. Hydrofluoric acid manufacture.

and #167. Sixteen different sampling points were involved covering the raw waste source, the various raw waste streams, and the treated effluents at these plants. The evaluation of toxic metal content of these process related waste streams was based on 572 analytical data points. The screening for toxic organic pollutants at Plant #705 generated an additional 635 analytical data points. The daily raw waste loads were calculated from the waste stream flow rates measured or estimated at the time of sampling and the measured pollutant concentration.

That is,

$$\text{Daily loading (as kg of pollutant per day)} = \frac{(C)(Q)}{1000}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: $\text{kg/m}^3 = 1000 \text{ mg/l}$), and

Q is the waste stream flow rate expressed in unit of m^3/day . (m^3 , a cubic meter, is equal to 264.2 U.S. gallons)

Similarly, the unit loadings were calculated from the reported hydrofluoric acid production rate, the waste stream flow rate, and the measured pollutant concentration.

$$\text{Unit loading (as kg of pollutant per kkg of hydrofluoric acid)} = \frac{(C)(Q)}{1000 (P)}$$

where C and Q are the same as described above, and P is the hydrofluoric acid production rate expressed in units of kkg/day. (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs.)

The minimum, average, and maximum values are based on data from those plants where the particular pollutant was found at concentrations greater than the analytical detection limits and significant in that it could conceivably be treated by an available treatment technology regardless of economic considerations.

In Table 12-11, the toxic pollutant raw waste data are presented as the average daily concentrations and the unit loading found at the individual plants. The overall averages are also shown and were subsequently used in the calculations of the average daily loadings and the average unit loadings shown in Table 12-12 along with the corresponding minimum and maximum values.

Based on the total annual production of this subcategory and the average waste load generated per unit product, the estimated total toxic pollutant raw waste loads generated each year for this subcategory are as follows:

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Copper	6600
Lead	10000
Selenium	260
Zinc	110000
Antimony	8900
Arsenic	1400
Cadmium	79
Chromium	4700
Mercury	130
Nickel	10000
Thallium	840

Pollution Abatement Options

Toxic Pollutants of Concern

Toxic pollutants in raw wastewaters and slurries typical of the HF industry include the heavy metals often found as impurities in fluorspar. These metals are zinc, lead, nickel, antimony, chromium, arsenic, copper, and selenium. Raw wastewaters from plants practicing dry disposal of kiln wastes may include some of the same heavy metals in scrubber and area washdown wastes, but in considerably smaller amounts, since the spent ore is hauled as a solid waste and bypasses the wastewater treatment facilities. Although the fluorosulfonate anion is found in HF wastes containing drip acid, organic compounds are not anticipated in wastewaters from this industry. No toxic organic pollutants were found at significant levels.

Process Modifications and Technology Transfer Options

- A. Gypsum produced in the kiln can be disposed of as a solid waste instead of being slurried with water and sent to the wastewater treatment facility. The solids in this case are mixed with lime and stored in piles on the land surface until alternative disposal methods are found or the site abandoned. Although the dry disposal method is labor intensive (involving transportation and landfill operating cost), it has been found to be less expensive due to the reduced initial capital requirement and operating costs relative to the wet slurry method which requires a more extensive system of pipes, pumps, and on-site impoundments.
- B. The use of soda ash in place of lime for neutralization has some advantages. It eliminates or reduces the problem of scale formation in the pipelines and scrubbers when the treated wastewater is recycled. It offers a faster reaction time and better control of pH than lime. Even though the cost of soda ash is higher than lime, soda ash has been found overall to be a less expensive alternative at some plants. One plant reported that a combination of brine and soda ash has been found to present the

TABLE 12-11. TOXIC POLLUTANT RAW WASTE DATA

SUBCATEGORY: HYDROFLUORIC ACID

(1)

Average Daily Pollutant Concentrations and Loadings at Plants Sampled
(mg/l)

(kg/kkg of Anhydrous HF)

	#705(S)	#705(V)	#251(V)	#167(V)	Overall Average
Antimony	0.018 0.0010	0.010 0.00057	0.12 0.010	0.74 0.12	0.22 0.033
Arsenic	0.051 0.0029	* *	0.11 0.0091	0.028 0.0046	0.062 0.0055
Cadmium	0.0014 0.000080	0.0060 0.00034	* *	0.0030 0.00047	0.0035 0.00030
Chromium	0.062 0.0035	0.26 0.015	0.47 0.040	0.074 0.012	0.22 0.018
Copper	0.41 0.023	0.26 0.015	0.12 0.010	0.32 0.051	0.28 0.025
Lead	2.47 0.14	0.044 0.0025	0.059 0.0050	0.062 0.010	0.66 0.039
Mercury	0.00090 0.000050	0.0053 0.00030	0.018 0.0015	0.0010 0.00016	0.0060 0.00050
Nickel	0.062 0.0035	0.48 0.027	1.18 0.10	0.15 0.025	0.47 0.039
Selenium	0.0070 0.00040	* *	0.017 0.0014	0.0074 0.0012	0.011 0.0010
Thallium	* *	* *	0.039 0.0033	0.019 0.0030	0.029 0.0032
Zinc	4.0 0.23	0.21 0.012	0.28 0.024	8.2 1.3	3.2 0.41

S - Screening data from one 72-hour composite sample of individual or combined raw waste streams.

V - Verification data from three 24-hour composite samples, averaged, from each raw waste sampling point.

* - Concentration below significant level.

(1) The methodology of the sampling program is described in Section 5.1.2, and Section 12.3.3 presents the scope of sampling in the Hydrofluoric Acid industry.

TABLE 12-12. SUMMARY OF RAW WASTE LOADINGS FOUND IN
SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY: HYDROFLUORIC ACID							
Pollutant	Daily Loadings (kg/day)			Unit Loadings (kg/kg)			No. Of Plants Averaged*
	Minimum	Average	Maximum	Minimum	Average	Maximum	
<u>Toxic</u>							
Antimony	0.023	2.0	6.4	0.00057	0.034	0.12	4
Arsenic	0.012	0.50	1.2	0.00030	0.0055	0.0090	3
Cadmium	0.0031	0.014	0.025	0.000077	0.00030	0.00047	3
Chromium	0.15	1.7	5.4	0.0035	0.018	0.040	4
Copper	0.60	1.4	2.80	0.0096	0.025	0.051	4
Lead	0.10	1.8	5.4	0.0025	0.039	0.14	4
Mercury	0.0021	0.057	0.21	0.000050	0.00050	0.0015	4
Nickel	0.14	4.1	14	0.00035	0.039	0.10	4
Selenium	0.016	0.093	0.20	0.00040	0.0010	0.0014	3
Thallium	0.16	0.31	0.45	0.0030	0.0032	0.0033	2
Zinc	0.49	21	72	0.012	0.41	1.3	4
<u>Conventional & Nonconventional</u>							
TSS	190000	310000	520000	3800	4200	4800	3
Fluoride	13	2900	7900	8.8	34	58	4

* Only those plants where the pollutant was observed at treatable levels were included.

best alternative for operation of the recycle system at a minimum cost. After the use of soda ash, the treated effluent water can be totally recycled, either to the scrubber or to the kiln for transportation water for the gypsum.

As the pH approaches 6, sodium in soda ash replaces calcium present in the gypsum waste. This frees enough calcium ion to precipitate fluoride as calcium fluoride. Where the scrubber water is the predominant source of wastewater, the water has to be treated first with enough lime to precipitate fluoride as calcium fluoride. Soda ash can then be added to the supernatant to precipitate calcium followed by neutralization with HCl to reduce scaling problems.

- C. Two out of a total of 11 plants manufacturing hydrofluoric acid send the drip acid to the wastewater treatment facility. The rest of the plants recycle it to the reactor. When discharged to the waste treatment system, the fluorosulfonic acid does not hydrolyze and leaves with the treated effluent as a complex fluoride in soluble form. The total fluoride concentration of the effluent will be higher for the plants discharging drip acid compared to those which do not, after the same neutralization treatment. The two plants discharging drip acid to waste looked into the feasibility of returning it to the kiln, but because of the unique design of the kilns, they found it to be economically unattractive. Bench scale studies have shown that the drip acid can be hydrolyzed to free the HF.



The two plants not returning the drip acid to the kiln should be able to hydrolyze the material in a separate unit before commingling it with other wastes, thus avoiding the treatability problem associated with complex fluorides.

Best Management Practices

- A. Runoff can be collected from raw material and product storage, process, and impoundment areas. It should be treated with other process waste at the wastewater treatment facility. Leachate and permeate control needs to be practiced on the solid waste stored in many plant premises as gypsum piles. There is a risk that uncontrolled stockpiling may contaminate the local ground water.
- B. Ponds designed for solids removal must be deep enough to have a minimum of disturbance from wind and rain. In those areas where the rainfall rate exceeds yearly evaporation, the collection of runoff from raw material, product storage, process, and impoundment areas may lead to serious water balance problems. Recycle ponds would have to be designed to handle this excess loading.

Prevailing Control and Treatment Practices

Plant #705 combines the hydrofluoric acid wastes, including the gypsum slurry, with aluminum fluoride waste. The combined wastewater, after neutralization, is sent to settling lagoons before discharge. This plant was visited in both the screening and verification phases of the project and a fuller description of waste treatment practice is given above.

Plant #837 combines the gypsum slurry and plant area hosedown wastewater with the equipment washings, leaks, and spills etc. from the aluminum fluoride plant and neutralizes them with lime. The solids are removed in settling ponds before discharge. The wastewater from scrubbers of both hydrofluoric acid and aluminum fluoride plants is sent to an adjoining facility for use.

Plant #251 also combines the hydrofluoric acid and aluminum fluoride wastewater. The suspended solids in the combined wastewater are removed in the gypsum ponds. The overflow from the gypsum ponds is neutralized and the pH adjusted with the wastewater from other products which are manufactured on the site. The plant is in the process of installing a new proprietary treatment process to further reduce the fluoride in its wastewaters.

Two plants, #120 and #987, dispose of the kiln residue as a solid waste after lime addition. The wastewater in both cases is treated with lime and the solids are separated; in one case in a clarifier followed by a filtration, and in the other by lagooning.

At Plant #167, the combined wastewater (including the gypsum) is neutralized with lime and then settled in lagoons before discharge.

Plant #722 practices complete recycle. The gypsum slurry, scrubber water, and other wastewaters are combined and treated with soda ash for neutralization. The neutralized solution is settled in lagoons and then is recycled to the scrubbers and to the kiln to slurry the gypsum.

Plant #426 disposes of the gypsum solids from the kiln as a solid waste after lime addition. The scrubber water is used to make another product. The noncontact cooling water is neutralized when required with caustic soda and settled before discharge.

Advanced Treatment Technologies

Although alkaline precipitation, sulfide precipitation, the xanthate process, and ion exchange might be applied to clarified solutions for control of metal ions, only alkaline precipitation can be readily used for slurried kiln wastes from HF production. Sulfide precipitation from cleared solutions could be used to provide additional removal of zinc, lead, nickel, and copper and to a lesser extent, antimony.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT and BAT)

Neutralization with lime, used widely in the HF industry, is shown as the BPT treatment, principally to control pH and the nonconventional pollutant fluoride - which is precipitated as calcium fluoride. Sufficient settled effluent may be reused (0-35 percent) to transport kiln waste to the treatment facility as a slurry, and the remainder is adjusted to a pH between 6 and 9 before discharge. The flow diagram is shown in Figure 12-5. For BAT, 65 percent effluent reuse is incorporated into the Level 1 treatment system.

B. Level 2

Treatment is alkaline precipitation using additional lime and close control of pH in second-stage neutralization, followed by lagoon settling. Sufficient lagoon effluent is reused to transport kiln waste to the treatment facility as a slurry and the remainder is filtered to remove finely divided metal hydroxides. The flow diagram is shown in Figure 12-6.

C. Level 3

It is assumed that 65 percent of the Level 2 effluent is reused for transporting spent kiln waste to the treatment facility. For the remaining 35 percent, pH adjustment and sulfide precipitation are used ahead of the Level 2 dual-media filter, to react with residual lead, copper, nickel, zinc, and antimony which may not have reached their optimum pH levels for alkaline precipitation. The flow diagram for this treatment is shown in Figure 12-7.

D. Level 4

As an alternative to Level 2, Level 4 employs soda ash instead of lime for neutralization, depending on the spent ore to contain enough calcium to precipitate calcium fluoride. Use of soda ash permits increased effluent recycling without the scaling problems associated with calcium sulfate. To control salinity and sodium alkalinity, a final effluent blowdown of at least 10 percent of the influent rate is maintained. The common heavy metals will be precipitated as carbonates and hydroxides with varying degrees of effectiveness at pH levels attainable with soda ash. The effluent is filtered and adjusted to a pH between 6 and 9 before discharge or process recycling. (Figure 12-8.)

E. Level 5

Level 5 treatment is dry handling and off-site chemical landfill for the kiln waste and two-stage alkaline precipitation with

clarification and filtration for the liquid process wastes. Heavy metal precipitation with soda ash permits partial recycling for uses other than slurry transport. (Figure 12-9.)

Incremental cost and performance estimates for the alternative levels of treatment and control were evaluated in detail as part of the rule-making process which lead to the proposed regulations (45 FR 49450, July 24, 1980). This material is presented in the proposed Development Document (60).

Equipment for Different Treatment Levels

A. Equipment Functions

Level 1, typical of existing treatment facilities, utilizes very little equipment, but depends on lime neutralization in settling lagoons, with final pH adjustment.

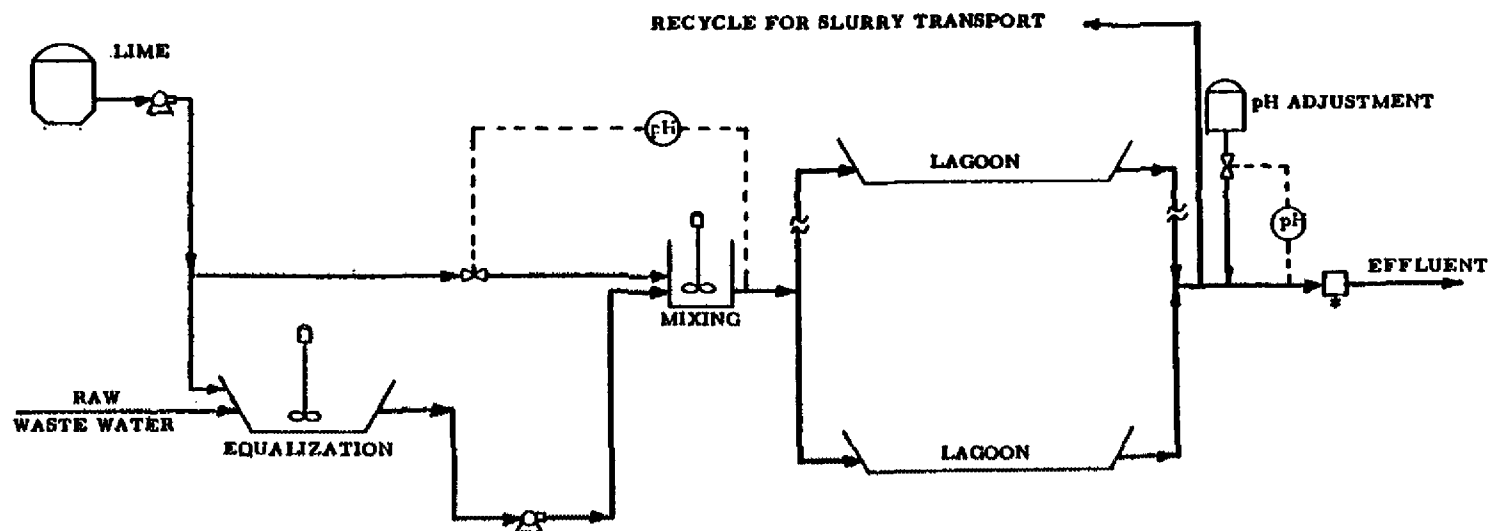
In Level 2, conventional dual-media filtration is added to the Level 1 system. In Level 3, standard reagent mixing and solution feeding units are added to the Level 2 system. In Level 4, which is an alternate to Level 2, the same type of chemical feed equipment is used for soda ash as was used for lime in Level 2. Conventional lagoons and dual-media filters are used in Level 4, but special attention to selection of materials is required because of the high salinity of recycled effluent. In Level 5, dry kiln waste disposal is recommended with conventional dry solids handling equipment. Lagoons, clarifiers, and filters are used for scrubber, noncontact cooling, and other miscellaneous liquid wastes. In this case, equipment for storing and handling the dry kiln waste is not considered to be wastewater treatment, and the cost is not included in the cost estimates.

B. Chemical Handling

Lime (as CaO) is the major chemical used in Levels 1 and 2, along with minor amounts of hydrochloric acid for final pH adjustment. With normal precautions, these chemicals pose no special hazards. In Level 3, ferrous sulfide is prepared on-site by mixing sodium bisulfide and ferrous sulfate. Although sodium bisulfide can release toxic H_2S at pH levels below 7, the hazard can be mitigated by avoiding acid conditions and by providing adequate ventilation. After mixing its components, the ferrous sulfide solution is stable at the pH levels employed in the process. In Level 4, only sodium carbonate and hydrochloric acid are used, with no unusual safety hazards or special handling problems. In Level 5, only lime, soda ash and hydrochloric acid are used, introducing no special problems of safety or handling.

C. Separation and Removal of Solids

Solids are accumulated in unlined settling lagoons. In Level 4, calcium fluoride will still precipitate in the lagoons but the



* Includes flow monitoring, pH monitoring and sampler

Figure 12-5. Level 1 waste water treatment for hydrofluoric acid subcategory.

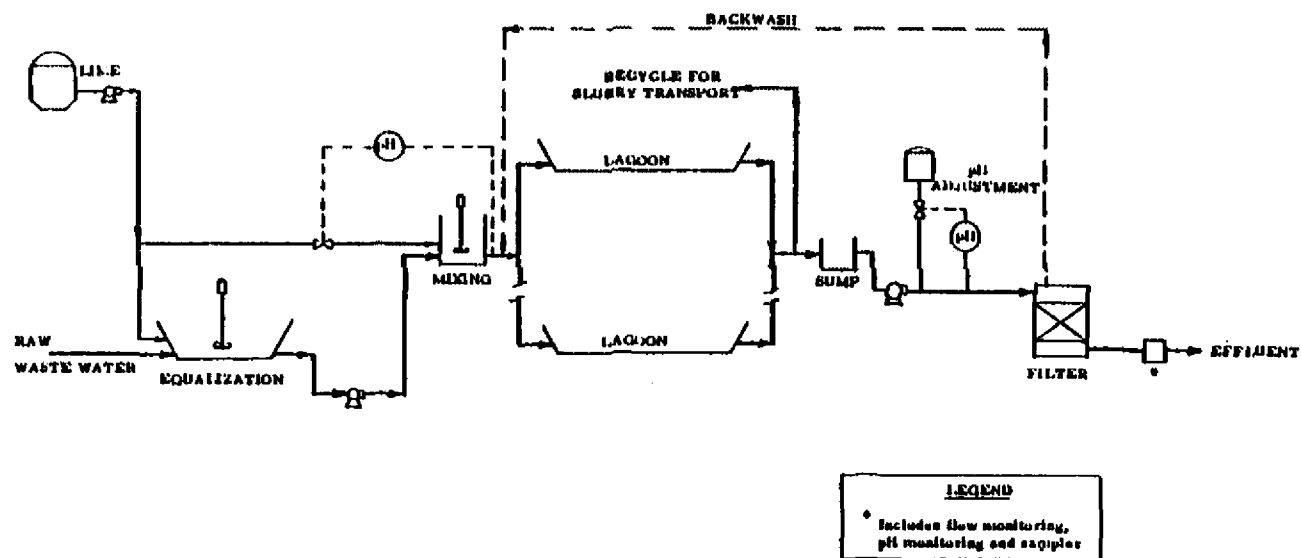
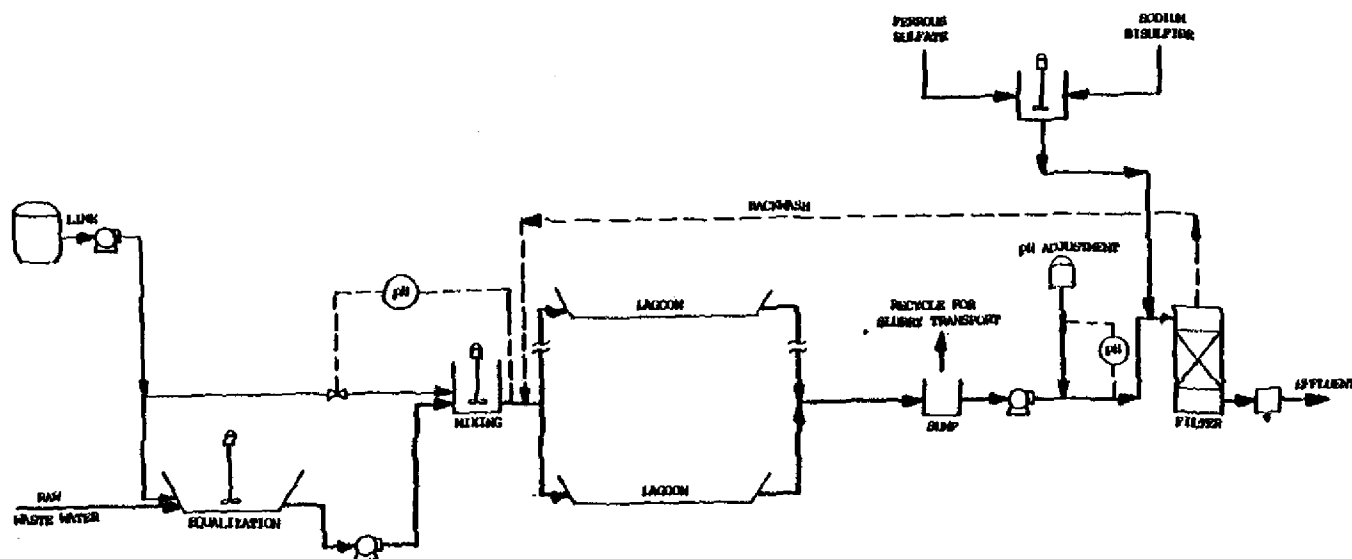


Figure 12-6. Level 2 waste water treatment for hydrofluoric acid subcategory.



*Includes flow monitoring, pH monitoring and sampler

Figure 12-7. Level 3 waste water treatment for hydrofluoric acid subcategory.

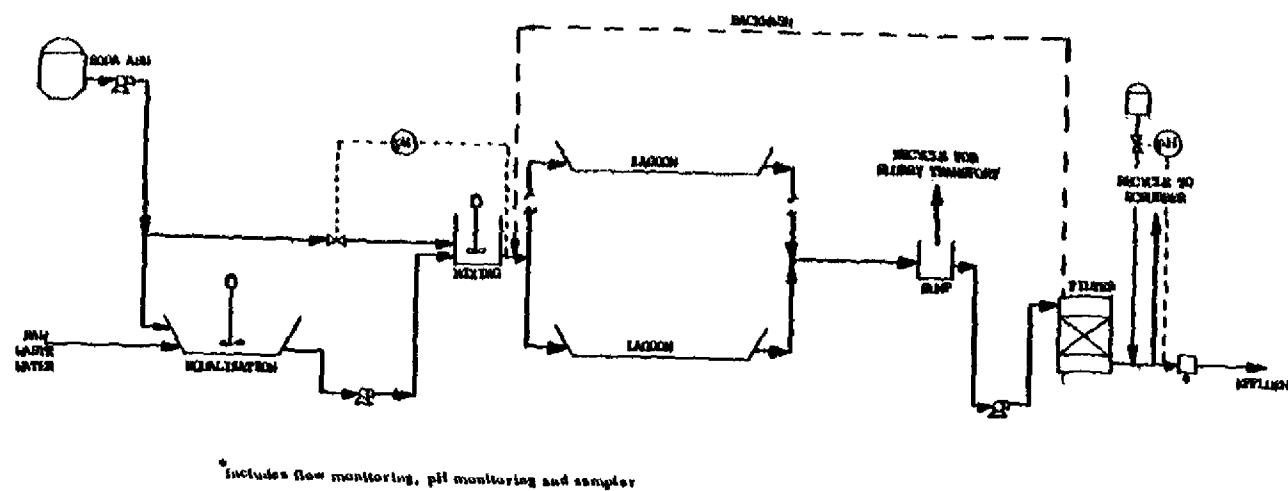


Figure 12-8. Level 4 waste water treatment for hydrofluoric acid subcategory.

total sludge quantities will be less than in Levels 1, 2, and 3 where lime is used. Solids from Level 4 treatment will be alkaline, very saline, and difficult to consolidate. Dry solids from the Level 5 model are not subjected to treatment, except for nominal application of lime before hauling in dry form to an approved chemical landfill.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed. The BPT model treatment consists of:

- A. Slurry transportation of kiln solids to an equalization basin.
- B. Application of lime to precipitate fluoride and toxic metals, followed by lagoon settling.
- C. pH adjustment before final discharge.
- D. Scrubber, cooling, and distillation wastes enter the equalization basin.

It is assumed that drip acid is recycled to the process reactor and does not appear directly in the waste stream.

In the BAT treatment, 65 percent of the BPT treated effluent is reused to transport kiln wash to the treatment facility as a slurry.

Wastewater Flow

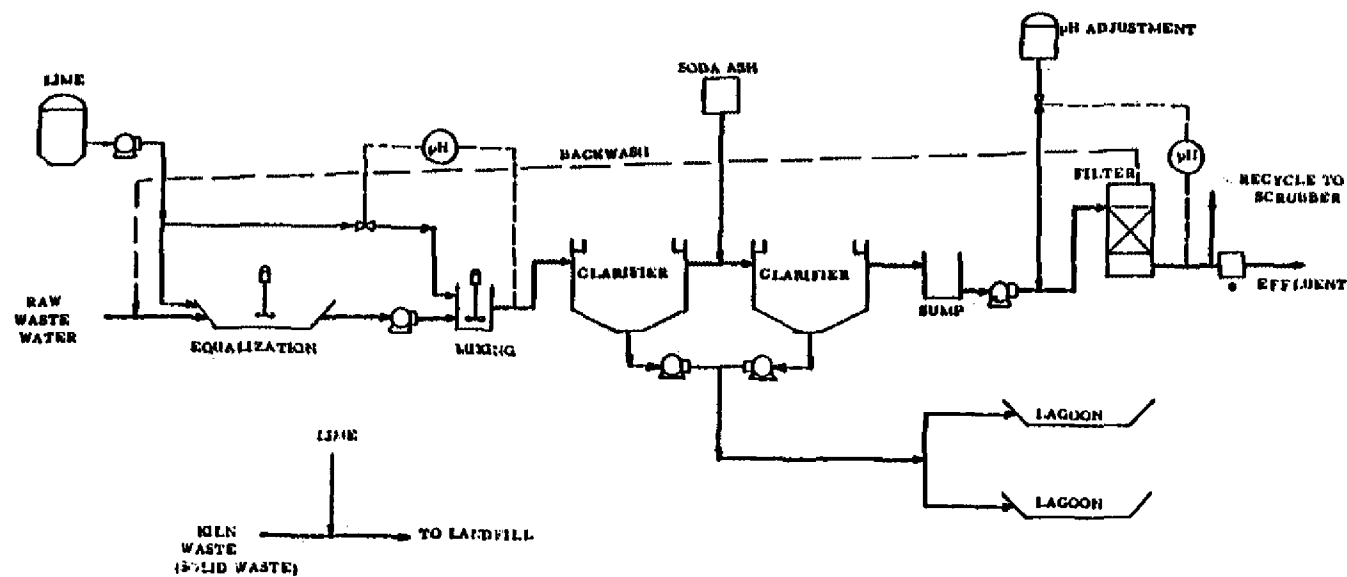
The data in Table 12-4 for plants sending the gypsum solids to the treatment facility indicate that the unit flow varies from approximately 31.0 m³/kgg of HF to 166 m³/kgg of HF. For the model plants, a constant unit flow of 95.4 m³/kgg of HF is assumed.

HF Production

In the HF subcategory, production ranges from a minimum of 7,300 kkg/year to a maximum of 62,000 kkg/year with a mean of 22,100 kkg/year and a median of 15,800 kkg/year. For wastewater treatment cost estimates, three production levels were selected as model plants. These are 19,100 kkg/year, 38,200 kkg/year, and 57,300 kkg/year.

Wastewater Pollutant Load

The amount of kiln residue varies from 3.8 to 4.1 kg/kg of HF produced. The wastewater going to treatment model plants is assumed to contain 3.8 kg of solid kiln residue per kg of HF. Fluoride emissions in wastewater have been shown to vary as indicated below:



* Includes flow monitoring, pH monitoring and sampler.

Figure 12-9. Level 5 waste water treatment for hydrofluoric acid subcategory.

<u>Source of Data</u>	<u>Fluoride, (kg/kkg)</u>
Reference 3	20
Reference 3	37
Screening and Verification	3.8 to 58
Phase Sampling (Tables 12-9 and 12-10)	

For the model plants, the average fluoride loading from kiln wastes of 31 kg/kkg HF produced was used to establish treatment requirements and related costs.

The costs shown at each level of treatment correspond to the model plant BPT system (Level 1) and the BAT system which may add to or modify the existing BPT system to meet more stringent pollutant removal requirements.

Treatment costs at Levels 2, 3, 4, and 5 are given in the proposed Development Document (60).

The estimated costs for three models having different production levels are given in Tables 12-13, 12-14, and 12-15. For these models, both the hydraulic and the pollution loads per unit of production are held constant over the entire range of production.

Table 12-16 presents a summary of the unit cost distribution between amortization and operation and maintenance cost components at various production rates and levels of treatment.

At the second level of treatment, the cost estimate is based on 65 percent of the wastewater flow being recirculated.

Model Plant Control Costs for Existing Sources

For the model plant control costs for existing sources at the BPT and BAT levels of treatment, the disposal of the sludge is on-site and hence the land requirements are fairly large. Chemicals, sludge hauling, and disposal costs have a significant impact on the total annual costs.

Basis for Regulations

Evaluation of BPT Treatment Practices

Control and treatment practices for eleven plants producing HF are presented in Table 12-17. Also indicated are other product-related wastewater sources and pollutant loads discharged.

It is clear from the table that a wide variation in effluent quality exists within this subcategory. The factors believed to cause these variations are the following:

A. Dry Residue Handling

The disposal of kiln waste by dry handling rather than slurring is practiced currently at three plants. This process eliminates the major source of wastewater generated at most plants, greatly reducing the raw waste loads to be treated. The only sources of wastewater remaining are from air pollution control and washdown.

B. Effluent Reuse

Reuse of treated wastewater for slurry transport of kiln wastes is commonly practiced to varying degrees and clearly has a major effect on pollutant loads discharged. Although four plants do not practice reuse, the fact that five plants do practice reuse demonstrates that the practice is both technologically and economically feasible.

C. Recycle of Condensables

Recycling of drip acid or condensable cooler bottoms reduces the loading of fluoride in the treated effluent since the fluoride species (fluorosulfonic acid) in this material is not removed by conventional lime treatment. Only two plants do not recycle drip acid.

D. Other Related Products

Most hydrofluoric acid plants also discharge wastes from related products such as aluminum fluoride, fluorocarbons, hexafluorosilicic and tetrafluoroboric acids to treatment. These other product wastes can account for higher raw waste loadings and increase the potential for complex fluorides formation and can also impact treatment efficiency by diluting the raw waste. In addition, commingling of other product wastes will limit the percentage of reuse of the total plant treated effluent.

In addition to the above factors, the design and operation of the treatment facilities affect the effluent quality. Solids removal depends on retention time and surge capacity. Precipitation of fluoride requires careful pH control and in areas of heavy rainfall or winds, adequate freeboard or multiple ponds are necessary to limit the discharge of high pollutant loads due to unfavorable climatic conditions.

E. Pollutant Removal with BPT Treatment

Treatment level 1 is BPT in the Hydrofluoric Acid industry. Table 12-18 presents a summary of long term effluent monitoring

TABLE 12-13. MODEL PLANT TREATMENT COSTS

Subcategory	Hydrofluoric acid 19,100 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT^a
Site development	410,000	0
Equipment	429,500	45,000
Monitoring equipment	20,000	0
Subtotal	859,500	45,000
Contractor's O & P ^b	128,925	6,750
Subtotal	988,425	51,750
Engineering	197,685	10,350
Subtotal	1,186,110	62,100
Contingencies	118,611	6,210
Subtotal	1,304,721	68,310
Land	1,020,000	0
TOTAL INVESTMENT COST	2,324,721	68,310
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	14,000
Energy	14,000	1,500
Chemicals	534,800	0
Maintenance	130,472	6,831
Taxes and insurance	69,742	2,049
Residual waste disposal	350,000	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	1,170,014	31,880
C. AMORTIZATION OF INVESTMENT COST	212,278	11,114
TOTAL ANNUAL COST	1,382,292	42,994

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 12-14. MODEL PLANT TREATMENT COSTS

Subcategory	Hydrofluoric acid	
Production	38,200 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT^a
Site development	735,000	0
Equipment	551,500	70,000
Monitoring equipment	20,000	0
Subtotal	1,306,500	70,000
Contractor's O & P ^b	195,975	10,500
Subtotal	1,502,475	80,500
Engineering	300,495	16,100
Subtotal	1,802,970	96,600
Contingencies	180,297	9,660
Subtotal	1,983,267	106,260
Land	1,940,000	0
TOTAL INVESTMENT COST	3,923,267	106,260
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	14,000
Energy	19,500	3,100
Chemicals	1,069,000	0
Maintenance	193,327	10,626
Taxes and insurance	117,698	3,193
Residual waste disposal	700,000	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	2,175,525	38,414
C. AMORTIZATION OF INVESTMENT COST	322,678	17,289
TOTAL ANNUAL COST	2,498,202	55,702

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 12-15. MODEL PLANT TREATMENT COSTS

Subcategory	Hydrofluoric acid Production 57,300 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT^a
Site development	1,050,000	0
Equipment	928,000	100,000
Monitoring equipment	20,000	0
Subtotal	1,998,000	100,000
Contractor's O & P ^b	299,700	15,000
Subtotal	2,297,700	115,000
Engineering	459,540	23,000
Subtotal	2,757,240	138,000
Contingencies	275,724	13,800
Subtotal	3,032,964	151,800
Land	2,890,000	0
TOTAL INVESTMENT COST	5,922,964	151,800
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	14,000
Energy	28,000	4,600
Chemicals	1,604,000	0
Maintenance	303,296	15,180
Taxes and insurance	177,689	4,554
Residual waste disposal	1,050,000	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	3,233,985	45,834
C. AMORTIZATION OF INVESTMENT COST	493,463	24,698
TOTAL ANNUAL COST	3,727,449	70,532

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 12-16. MODEL PLANT UNIT TREATMENT COSTS

Subcategory Hydrofluoric acid			
Annual Treatment Costs (\$/kkg)			
COST ITEM	PRODUCTION (kkg/yr)	LEVEL OF TREATMENT	
		BPT	BAT*
Annual Operation and Maintenance	19,100	61.26	1.67
	38,200	56.95	1.01
	57,300	56.44	0.80
Annual Amortization	19,100	11.11	0.58
	38,200	8.45	0.45
	57,300	8.61	0.43
Total Annual Cost	19,100	72.37	2.25
	38,200	65.40	1.46
	57,300	65.05	1.23

*Represents the incremental cost above BPT

data on total suspended solids (TSS) and fluoride from four plants. Means, standard deviations, and variability factors are given where sufficient data are available. These performance characteristics are later utilized for the development of the regulations on TSS and fluoride.

The ability of BPT treatment to remove toxic pollutants can be estimated by comparing the raw waste data presented in Table 12-11 with the corresponding treated effluent data presented in Table 12-19. The latter expresses the removal efficiency as the calculated average percent removal observed at these plants. The BPT removal efficiency for some of the toxic metals is undoubtedly augmented to some degree by the fact that the raw waste may carry insoluble forms of the metals that were never completely leached out of the ore. Removal of these forms would take place simply by settling out; however, the effluent concentrations of some metals such as chromium, nickel, and zinc remain at concentrations higher than should be achievable by alkaline precipitation. This suggests that these metals are largely in solution coming into the treatment system and that the optimum conditions for metal hydroxide formation were not being attained at the time of sampling.

The original BPT limitations for this subcategory shown in Table 12-2 required zero pollutant discharge except during periods of excess rainfall. Objections to the zero-discharge limitations concerned the feasibility of using gypsum-saturated water for reuse in the air pollution control scrubbers.

The BPT wastewater control and treatment technology allows for the discharge of process wastewater after appropriate treatment. This technology is practiced widely in the industry and should pose no technical problems. Implementation of BPT at all sites in the industry will achieve the indicated pollutant discharge levels.

The nine plants presently producing hydrofluoric acid all have installed BPT treatment or the equivalent. At the time of sampling, seven of the 11 plants operating were meeting the proposed fluoride limitations and eight were meeting the proposed TSS limitations according to the data available (60). Although there was practically no long term monitoring data available to support the additional proposed limitations on toxic metals, the screening and verification data indicated that all three plants sampled were meeting the proposed limitations on antimony, copper, and lead, while two of the plants were meeting the proposed zinc limitation and one plant was meeting the proposed chromium and nickel limitations. With the limited amount of toxic metal data, it was not possible to estimate compliance or noncompliance on a statistical basis. The Agency has conducted additional treatability studies (61) and has utilized the results of this work in formulating the final regulations as described in the following sections.

TABLE 12-17. SUMMARY OF WASTE WATER CONTROL AND TREATMENT TECHNOLOGY EMPLOYED AT HYDROFLUORIC ACID PLANTS⁽¹⁾

Plant	Product-Related Waste Water Sources	Control and Treatment Technology Employed	Amount of Treated Waste Water Reused	Cooler Bottoms (Condensables) Recycled?	Effluent Volume in m ³ /metric ton (gal/short ton) of Actual Production	Long Term Average Pollutant Wasteload Discharged (kg/metric ton) (lb/1000 lb)	
						Fluoride	TSS
426	Hydrofluoric acid fluosillicic acids production	Dry residue hauling and dumping; neutralization with caustic of noncontact cooling water and floor drainage	0	Yes	465 (111,397) includes noncontact cooling water	1.2	ND
664	Hydrofluoric acid production	Residue slurry, neutralization with sodium carbonate, settling, recycle	94%	Yes	5.78 (1,360)	0.10	0.27
167	Hydrofluoric acid, fluorocarbon, chlorine/sodium hydroxide, and hydrochloric acid production	Residue slurry, lime treatment, settling, recycle	47%	Yes	103 (24,200)	18	0.45 (Net) ⁽³⁾
120	Hydrofluoric acid production	Planned dry residue handling, lime treatment, clarification	0	Yes	ND	ND	ND
967	Hydrofluoric acid, fluorocarbon, and sulfuric acid production	Residue slurry, settling (Recycle and pH polishing facilities under construction.)	Present: 0 Planned: 70% to 75%	Yes	125 (30,000)	Present: 24 Expected with additional facilities: 1.8	16 2.1
928	Hydrofluoric acid and aluminum fluoride production	Residue slurry, settling, recycle (Flocculation, lime treatment, and clarification facilities under construction.)	83%	Yes	9.44 (2,260)	Present: 1 Expected with additional facilities: 0.65	1.7 0.75
837	All hydrofluoric acid generated as used captively for aluminum fluoride production	Residue slurry, lime treatment, settling	0	Yes	134 (32,200)	1.8	3.1
753	Hydrofluoric acid production	Residue slurry, lime treatment, settling, recycle, pH polishing	65%	Yes	11.0 (2,650)	0.64	0.38
251 ⁽²⁾	HF, AlF ₃ , chlorine/sodium hydroxide, aluminum oxide, and fluorocarbon production	Residue slurry, settling, neutralization	0	1 Kiln: Yes 3 Kilns: No	22.2 x 10 ³ (553 x 10 ⁶)	46	530
705 ⁽²⁾	Hydrofluoric acid and aluminum fluoride production	Residue slurry, lime treatment, settling, recycle, pH polishing	30% to 35%	No	25.9 (6,204)	3.2	0.64
722	Hydrofluoric and, in recent past, fluoboric, acid production	Residue slurry, lime treatment, settling, recycle, pH polishing	92% to 100%	Yes	0-10.3 (0-2,460)	0-0.81	0 to 0.54
987 ⁽²⁾	Hydrofluoric Acid	Dry residue hauling	0	Yes	8.8	ND	ND

(1) Adapted from Calspan (Reference 3).

(2) Hydrofluoric Acid production has been discontinued at these plants since the time of sampling.

(3) Effluent loading less the influent loading.

ND = Not determined.

Basis for BPT Effluent Limitations

A. Technology Basis

For BPT, the Agency is promulgating limitations for which the technology basis is, or is equivalent to, equalization, lime neutralization/alkaline precipitation, solids removal by settling or thickening, final pH adjustment, and discharge of clarified effluent. The in-house process recycling of the reactor condensables (drip acid) is necessary to meet the fluoride limitations.

B. Flow Basis

The reuse of treated wastewater to slurry kiln residues to the treatment system is not required for meeting the BPT limitations. BPT or its equivalent is practiced by all plants in this industry including six which reuse, for slurrying residues, proportions of their treated wastewater ranging from 30 to 100 percent of the plant flow as shown in Tables 12-4 and 12-17.

The practice of reusing wastewater in this manner has two opposing effects on the plant effluent:

1. A decrease in the net discharge unit flow rate (m^3/kg), and
2. An increase in the fluoride concentrations (mg/l).

As a result, the fluoride unit loading (kg/kg) in the effluent does not decrease as a direct proportion to the decrease in the flow rate, but is partially offset due to the increase in fluoride concentration as a function of percent reuse. The relationship of percent water reuse to fluoride concentrations and unit loadings is shown in Figure 12-10. The apparent reason for the increase in fluoride concentration with reuse is a calcium deficiency which may result from the buildup of sulfate at plants where reuse is practiced. Other pollutants such as TSS and metals would not be expected to exhibit similar concentration offset effects in these systems.

It should be noted that while the practice of reusing wastewater for kiln residue slurrying may be advantageous in some locations with respect to alternative water supply costs, there is no associated reduction in the hydraulic load, size, or cost of the BPT treatment system itself.

The net result of water reuse is a moderate decrease in the effluent fluoride loadings which is achieved at a small additional annual cost of less than one percent of the estimated BPT treatment systems cost (Tables 12-13, 12-14, and 12-15).

The model plant BPT treatment system is based on an inflow rate of $95.4 \text{ m}^3/\text{kg}$ derived from the average of nine plants which

TABLE 12-18. SUMMARY OF LONG TERM MONITORING DATA FROM FOUR
(1)
HYDROFLUORIC ACID PLANTS

Plant No.	Parameter	Treated Waste Load (kg/kg) or (lb/1000lb)						
		Daily Data				30-Day Average Data		
		Long Term Average (X)	St.Dev. (S)	St.Dev. (S')	(2) VF	(2) Long Term Average (X)	St.Dev. (S)	(2) VF
#664	Fluoride	0.10	0.090	0.77	4.5	0.10	0.040	1.7
	TSS	0.29	—	—	—	0.27	—	—
#753	Fluoride	0.72	0.27	0.36	2.2	0.64	0.15	1.4
	TSS	0.38	—	—	—	—	—	—
#722	Fluoride	0.81	0.52	0.59	3.3	—	—	—
	TSS	0.54	0.37	0.62	3.5	—	—	—
(3) #705	Fluoride	—	—	—	—	0.49	0.22	1.7
	TSS	—	—	—	—	0.84	0.37	1.7

(1)
Based on Reference 3 data.

(2)
In the case of daily measurements, the variability factor, VF, for a lognormal distribution is found by the expression $\ln(VF) = S'(Z - 0.5S')$, where S' is the estimated standard deviation of the logarithm derived from the arithmetic mean, X , and the arithmetic standard deviation, S , according to the relationship, $(S')^2 = \ln \left[1.0 + \left(\frac{S}{X} \right)^2 \right]$. When the value of Z is 2.33, the variability factor for the 99 percentile is obtained. For 30-day average measurements, a normal distribution is obtained and the variability factor is found by the expression, $VF = 1.0 + Z \left(\frac{S}{X} \right)$. When the value of Z is 1.64, the variability factor is for the 95 percentile. Please refer to Section 9.2 for a more detailed discussion of the statistical analysis of long term data.

(3)
Although Plant #705 does not recycle the drip acid, the TSS data is not adversely affected and is used as the basis for the 30-day average VF.

— Not Available.

TABLE 12-19. TOXIC POLLUTANT TREATED EFFLUENT DATA

SUBCATEGORY: HYDROFLUORIC ACID

(1) Average Daily Pollutant Concentrations and Loadings at Plants Sampled (mg/l) (kg/kkg of Anhydrous HF)					
	#705 (S)	#705 (V)	#251 (V)	#167 (V)	(2) Overall Average Average % Removal
Antimony	<0.010 <0.00021	<0.0020 <0.000042	<0.17 <0.017	0.047 0.012	<0.057 <0.0073 74
Arsenic	<0.0030 <0.000063	<0.010 <0.00021	<0.020 <0.0020	0.016 0.0040	<0.012 <0.0016 81
Cadmium	0.00030 0.0000060	<0.0017 <0.000035	<0.0020 <0.00020	0.0087 0.0022	<0.0032 <0.00060 9 9
Chromium	0.014 0.00029	<0.046 <0.00096	0.22 0.022	0.050 0.013	<0.093 <0.0091 62
Copper	0.10 0.0021	<0.020 <0.00042	0.070 0.0069	0.060 0.015	<0.063 <0.0061 77
Lead	0.0060 0.00012	<0.022 <0.00046	<0.031 <0.0031	0.010 0.0026	<0.017 <0.0015 97
Mercury	<0.00040 <0.0000080	<0.00050 <0.000010	<0.0010 <0.00010	0.0065 0.0017	<0.0020 <0.00044 67
Nickel	0.050 0.0010	<0.010 <0.00021	0.52 0.052	0.090 0.023	<0.17 <0.019 64
Selenium	0.033 0.00069	<0.0050 <0.00010	<0.071 <0.0070	0.010 0.0026	<0.030 <0.0025 Effluent >Influent
Thallium	0.0070 0.00015	<0.0012 <0.000025	<0.0070 <0.00069	0.0030 0.00069	<0.0045 <0.00039 85
Zinc	0.071 0.0015	0.053 0.0011	0.16 0.015	1.9 0.49	0.55 0.13 83

(S) Screening data from one 72-hour composite sample of treated effluent.

(V) Verification data from three 24-hour composite samples.

(1) The effluent data presented here corresponds to the raw waste data shown in Table 12-11. The methodology of the sampling program is described in Section 5.1.2, and the scope of sampling in the Hydrofluoric Acid industry is described in Section 12.3.3.

(2) When averaging values indicated as "less than" (<), the absolute value was used and the resulting average was indicated as a "less than" value.

handle the kiln residues in a slurry system as shown in Table 12-4. The treated effluent flow rate is 54.6 m³/kkg which is the average effluent flow rate for the same nine plants and corresponds to the reuse of about 43 percent of the flow for residue slurrying and other uses.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific numerical effluent limitations are promulgated is based on an evaluation of raw waste data from the screening and verification sampling program. The following two major factors were considered:

Raw waste pollutant concentrations - A tabular summary of maximum raw waste concentrations is presented in Section 12. Data from the one plant sampled for screening were used to determine the need for verification sampling. The maximum concentrations found during verification are also shown for comparison. For each pollutant, the maximum concentration observed gave a preliminary indication of its potential significance in the subcategory. On this basis, the preliminary selection of candidates for regulation included zinc, lead, antimony, nickel, chromium, and copper in decreasing order of their apparent pollution potential. These pollutants were observed at least once during the sampling program at concentrations considered treatable in this industry using one of the available technology options. The other metals, chromium, thallium, and mercury exhibited maximum concentrations that were considerably lower.

Total subcategory raw waste pollutant loadings - Pollutant raw waste loading data were used to evaluate the overall magnitude of the pollution potential for the subcategory. Data from the plants sampled are presented in Table 12-11 and the daily and unit loadings are summarized in Table 12-12. This information, coupled with the estimated total hydrofluoric acid production rate of 261,800 kkg/year, yielded the approximate total annual pollutant loading rates for the subcategory shown in Section 12. This method of ranking the pollution potential of the observed toxic metals confirmed the maximum concentration based ranking and indicated that zinc, nickel, lead, antimony, copper, and chromium were the six dominant toxic metals in terms of both total mass loadings and treatable raw waste concentrations.

In view of the treatment technology already implemented in this industry, the added BPT regulation of any one of these pollutants may provide assurance that all of the observed toxic metals would receive adequate treatment and control. This includes taking credit for incidental removal of metals which are either below practical treatability limits or are not particularly amenable to removal by alkaline precipitation methods. The latter includes cadmium, selenium, thallium, and mercury. Based on the argument provided in Section 8, the control of zinc and nickel, having the highest loadings and concentrations in the wastewater, would

effectively control the other toxic metals in the treatment system. Thus, zinc and nickel were selected as the control parameters of toxic pollutants for BPT regulations.

D. Basis of Pollutant Limitations

1. Conventional and nonconventional parameters

a. pH: The treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS and Fluoride: The data presented in Tables 12-12 and 12-18 were used for the development of TSS and fluoride limitations. However, because of the wide range of product mixes, significant differences in residue handling, wastewater treatment, reuse practices, and dilution with other product waste streams, it was necessary to select only those plants where the effect of BPT technology could be clearly observed. The plants excluded are:

#426 and #120 because kiln residues are handled as a dry solid,

#167, #967, and #251 because the combined treatment of HF wastes along with the wastewaters from other major products generated high fluoride loadings in the large volume discharges with fluoride at its minimum treatability concentration,

#705 because cooler bottom condensables (drip acids) are not recycled back to the process but are added to the raw waste contributing complex fluorides which tend to remain in solution after lime treatment. TSS data are not affected.

Data from the remaining five plants are presented in Table 12-20 which summarizes the development of the regulations for total suspended solids and fluoride. Since the BPT level of treatment does not require the reuse of treated wastewater for slurring kiln residues, the performance of Plant #837 was used as the long term average unit loading basis for the TSS and fluoride limitations. The variability factors used for fluoride are based on the long term data from Plants #664 and #753 and those used for TSS are derived from Plant #722 for daily measurements and Plant #705 for 30-day average measurements as indicated in Table 12-20.

The maximum 30-day average TSS limitation was obtained by multiplying the variability factor for 30-day averages from Table 12-20 by the long term average waste load; i.e., $1.7 \times 3.1 \text{ kg/kkg} = 5.3 \text{ kg/kkg}$. Similarly, the 24-hour maximum TSS limitation was obtained by multiplying the variability

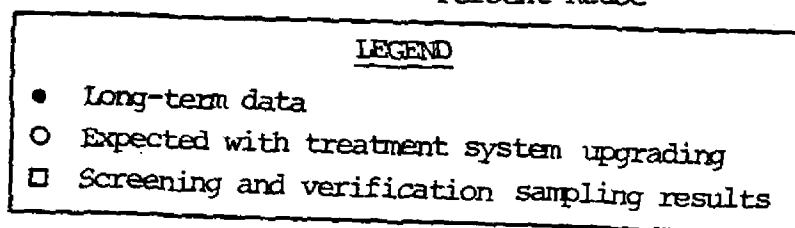
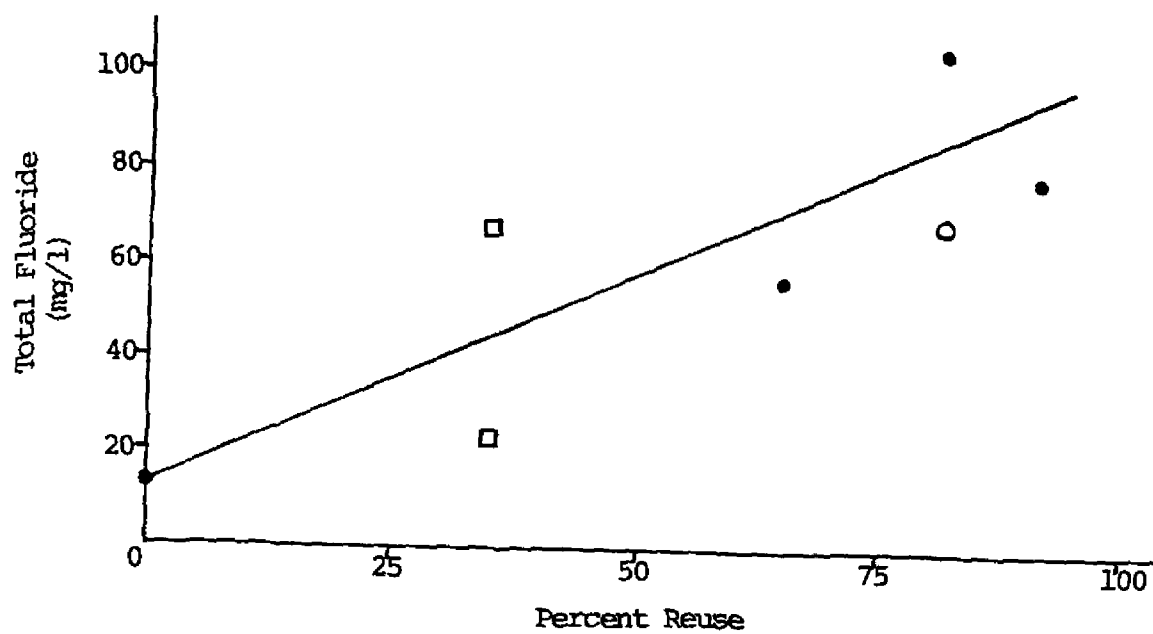
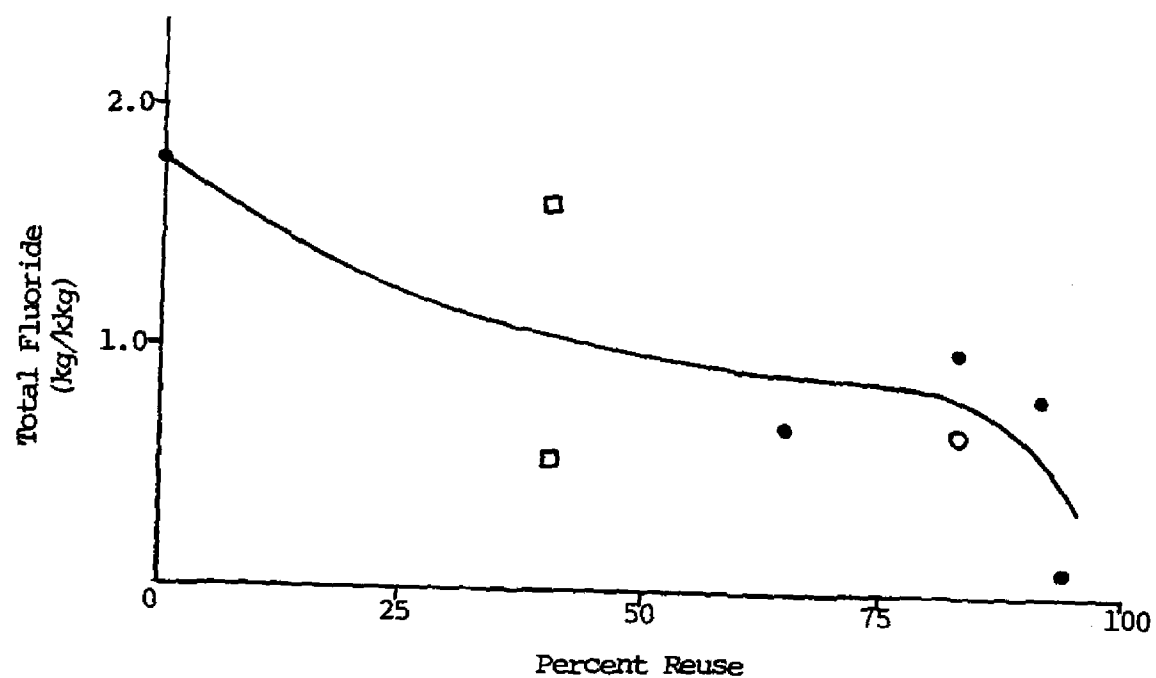


Figure 12-10. Fluoride loads and concentrations discharged at selected hydrofluoric acid plants.

factor for daily measurements by the long term average; i.e., $3.5 \times 3.1 \text{ kg/kg} = 11 \text{ kg/kg}$. The same approach was taken to obtain the fluoride limitations; i.e., $1.6 \times 1.8 \text{ kg/kg} = 2.9 \text{ kg/kg}$ for the maximum 30-day average, and $3.4 \times 1.8 \text{ kg/kg} = 6.1 \text{ kg/kg}$ for the 24-hour maximum limitation. These computations are shown on Table 12-20 and the BPT limitations are presented in Table 12-21.

The concentration basis (C) for each effluent is derived from the relationship between concentration (C), flow (Q), and unit loading,

$$C \text{ (as mg/l)} = 1000 \frac{(L)}{(Q)}$$

where L is the effluent limitation expressed as a unit loading in kg of pollutant per kg of product (kg/kg), and Q is the flow rate expressed as cubic meters per kg of product (m^3/kg). (Note: $\text{kg}/\text{m}^3 = 1000 \text{ mg/l}$.)

Thus, the concentration basis for the maximum 30-day average TSS limitation is:

$$\frac{(5.3 \text{ kg/kg})}{(54.6 \text{ m}^3/\text{kg})} \times \frac{(1000 \text{ mg/l})}{(\text{kg}/\text{m}^3)} = 97 \text{ mg/l}$$

and the concentrations basis for the 24-hour maximum limitation is obtained by a similar calculation or simply by applying the variability factor ratio, VFR, from Table 12-21 to the maximum 30-day average concentration; that is:

$$(\text{VFR}) (\text{max. 30-day average concentration or loading})$$

$$= 24\text{-hour maximum concentration or loading}$$

In the same manner, the concentration basis for the maximum 30-day average fluoride limitation is:

$$\frac{(2.9 \text{ kg/kg})}{(54.6 \text{ m}^3/\text{kg})} \times \frac{(1000 \text{ mg/l})}{(\text{kg}/\text{m}^3)} = 53 \text{ mg/l}$$

and the 24-hour maximum fluoride concentration is $2.1 \times 53 \text{ mg/l} = 111 \text{ mg/l}$. (Note: due to rounding off, this value differs just slightly from the value that appears in Table 12-21 which was obtained by calculating the concentration directly from the 24-hour maximum limitation; i.e.,

$$\frac{(6.1 \text{ kg/kg})}{(54.6 \text{ m}^3/\text{kg})} \times \frac{(1000 \text{ mg/l})}{(\text{kg}/\text{m}^3)} = 112 \text{ mg/l}$$

In either case, only two significant figures should be taken.)

Performance evaluation and review of discharge quality has been complicated by problems associated with chemical analysis. Prior to July 1976, the methods generally used for the analysis of fluoride in industry were specific ion electrode or colorimetry. These methods did not detect the soluble complex fluoride species present in the wastewater. The best method of total fluoride detection (free as well as complex) is distillation followed by analysis using the specific ion electrode. Using the distillation method, the complex fluorides are hydrolyzed and the resulting HF is carried over with the distillate along with any free HF in the sample. Thus, the method of total fluoride analysis used for effluent monitoring is capable of measuring free fluoride and the fluoride present in the form of complex ions which are not removed by lime treatment. Monitoring data on effluent fluoride levels using the revised method are likely to be higher than the levels previously reported under the same treatment conditions.

2. Toxic pollutants

The effluent limitations set for the selected toxic pollutant control parameters are derived from three sources of information. These are 1) screening and verification sampling data, 2) literature based treatability estimates (Section 8), and 3) a limited amount of long-term monitoring data from Plant #251.

The sampling results represent plant performance observed during three days of sampling at each of the plants. The treated effluent data on the toxic pollutants found at significant levels are summarized in Table 12-19. The average values shown for each pollutant are interpreted as being approximately equal to a long-term average unless there is some reason to believe that abnormal conditions existed either in the process operation or in the treatment system at the time of sampling. Abnormal conditions would dictate that high values should either be excluded or regarded as daily maxima rather than monthly averages. For this subcategory, the screening and verification data are believed to represent normal influent and effluent values at the plants sampled.

For a number of metal pollutants, the sampling data demonstrate that the effluent quality and percent removal with full scale BPT systems are considerably better than the literature treatability data in Section 8 would indicate for that particular technology. For example, even though arsenic, cadmium, mercury, and thallium average influent concentrations are well below the accepted treatability limits for lime/settling shown in Table 8-11, greater than 60 percent removals were observed for all but cadmium as is shown in Table 12-19. This high degree of incidental

TABLE 12-20. DEVELOPMENT OF TSS AND FLUORIDE LIMITATIONS

Plant	Reuse (percent)	Long Term Average Waste Load Discharged	
		Fluoride (kg/kkg of HF)	TSS (kg/kkg of HF)
#837	0	1.8	3.1
#753	65	0.72	0.38
#928	83	1.0	1.7
#722	92	0.81	0.54
#664	94	0.10	0.29

Variability Factor for Daily Measurements $3.4^{(1)}$ $3.5^{(5)}$

Variability Factor for 30-Day Averages $1.6^{(1)}$ $1.7^{(6)}$

Variability Factor Ratio (VFR) $3.4/1.6 = 2.1^{(2)}$ $3.5/1.7 = 2.1^{(2)}$

Effluent Limitations for BPT
(from Plant #837)

a. Daily Max $3.4 \times 1.8 \text{ kg/kkg} = 6.1^{(3)}$ $3.5 \times 3.1 \text{ kg/kkg} = 11^{(3)}$
b. Max 30-Day Avg $1.6 \times 1.8 \text{ kg/kkg} = 2.9^{(4)}$ $1.7 \times 3.1 \text{ kg/kkg} = 5.3^{(4)}$

Effluent Limitations for BAT
(from Plant #928)

a. Daily Max $3.4 \times 1.0 \text{ kg/kkg} = 3.4^{(3)}$ NA
b. Max 30-Day Avg $1.6 \times 1.0 \text{ kg/kkg} = 1.6^{(4)}$ NA

NA - Not Applicable

- (1) Variability factor average of Plants #664, #722 and #753 from Table 12-18.
- (2) Ratio of the daily (24-hr) variability factor to the 30-day average variability factor. This value appears on the Proposed Limitations tables.
- (3) The long term average loading in kg/kkg multiplied by the variability factor for daily measurements as shown.
- (4) The long term average loading in kg/kkg multiplied by the variability factor for 30-day measurements as shown.
- (5) Variability factor from Plant #722, Table 12-18.
- (6) Variability factor from Plant #705, Table 12-18.

Table 12-21. Effluent Limitations
Hydrofluoric Acid
Best Practicable Control Technology Currently Available
Waste Water Flow: 54.6 m³/kgg of HF (43% Reuse)*

Pollutant	Subcategory Performance (mg/l)	Concentration Basis VFR ⁽¹⁾ (mg/l)	Effluent Limit (kg/kgg of HF)			
			Max		Max	
			30-day Avg	24-hr Max	30-day Avg	24-hr Max
<u>Conventional and Nonconventional Pollutants:</u>						
Total Suspended Solids	57 ⁽²⁾	3.5/1.7	97	200	5.3	11
Fluoride	33 ⁽²⁾	3.4/1.6	53	110	2.9	6.1
<u>Toxic Pollutants:</u>						
Antimony	0.80 ⁽³⁾	3.9/1.2	0.96	3.1	— ⁽⁵⁾	— ⁽⁵⁾
Arsenic	0.50 ⁽³⁾	3.9/1.2	0.60	2.0	— ⁽⁵⁾	— ⁽⁵⁾
Chromium	0.32 ⁽³⁾	3.9/1.2	0.38	1.3	— ⁽⁵⁾	— ⁽⁵⁾
Copper	0.32 ⁽³⁾	3.9/1.2	0.38	1.3	— ⁽⁵⁾	— ⁽⁵⁾
Lead	0.13 ⁽³⁾	3.9/1.2	0.16	0.51	— ⁽⁵⁾	— ⁽⁵⁾
Nickel	0.17 ⁽⁴⁾	3.9/1.2	0.20	0.66	0.011	0.036
Selenium	0.20 ⁽³⁾	3.9/1.2	0.24	0.78	— ⁽⁵⁾	— ⁽⁵⁾
Zinc	0.55 ⁽⁴⁾	3.9/1.2	0.66	2.2	0.036	0.12

(1) - VFR: ratio of the 24-hour variability factor to the 30-day variability factor.

(2) - Long term average based on loading data and variability factors selected from Table 12-18.

(3) - The lower limit of the literature treatability estimate (Table 8-11) and industrial waste water treatment system performance (Table 8-12) are used as the basis for the long term average when the observed average of the sampling data is below this level.

(4) - Average effluent concentration from screening and verification sampling data.

(5) - No effluent limitation required.

* - From Table 12-4.

removal supports the contention that by applying effluent limitations just to the dominant metal pollutant(s), effective control of the other metals will also be assured.

In Table 12-21, the concentration bases for the BPT limitations are derived from the averaged effluent sampling data unless the observed pollutant concentration is actually below the literature treatability level. In some cases, the lowest applicable treatability level from Table 8-11 is used. This approach results in the setting of achievable effluent limitations for all of the pollutants of concern and provides for the possibility of wider variations in the influent quality. Such variations may be associated with different fluorspar impurity levels or other process variables not fully taken into account by the limited data obtained.

The basis for the BPT limitations on the control metals, zinc and nickel is given below. For the other toxic metals, the concentration bases are derived below and are intended to serve as guidance in cases where these pollutants are found to be of serious concern.

a. Zinc

The raw waste concentrations of zinc ranged as high as 11.3 mg/l (Section 12, Table of Maximum Concentrations Observed) and averaged about 3.2 mg/l (Table 12-11) for the plants sampled. BPT treatment achieved an average removal of better than 80 percent with an average performance concentration of about 0.55 mg/l in the treated effluent shown in Table 12-19. This level of performance approximately equals that obtained from the literature treatability data in Table 8-11. The average performance value is used as the concentration basis for the proposed maximum 30-day average effluent limitation of 0.036 kg/kg using the model plant flow of 54.6 m³/kgg (Table 12-4). This limitation was achieved by all but one of the plants sampled. Using the model plant flow of 54.6 m³/kgg from Table 12-15, the limitation was calculated as follows:

$$(0.66 \text{ mg/l})(54.6 \text{ m}^3/\text{kgg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.036 \text{ kg/kg}$$

where 0.66 is the maximum 30-day average concentration calculated by multiplying the average concentration (0.55) by the 30-day variability factor, 1.2:

$$(0.55 \text{ mg/l})(1.2) = 0.66 \text{ mg/l}$$

Since the long term monitoring data on zinc are not available from the HF industry, the variability factor ratio (VFR) of 3.3 was derived from the nickel sulfate industry data. The same VFR was used for the other toxic metals in the HF effluent. This is supported by the fact that nickel is a dominant toxic metal in the HF process wastewater, and is assumed to have equal or better performance characteristics compared with the wastewater from the nickel sulfate industry. Thus,

$$\text{VFR} = \frac{\text{VF of daily measurements}}{\text{VF of 30-day averages}} = \frac{3.9}{1.2} = 3.3$$

and the 24-hour maximum limitation for zinc is:

$$(3.3) (0.036 \text{ kg/kg}) = 0.12 \text{ kg/kg}.$$

The effluent limitations on zinc and the other metals of concern are given in Table 12-21.

b. Nickel

The sampling data indicate better than 60 percent BPT removal of nickel resulting in an average effluent quality of about 0.17 mg/l. Using a monthly variability factor of 1.2, a value of 0.20 mg/l is used as the concentration basis for the maximum 30-day average effluent limitation of 0.011 kg/kg. A VFR of 3.3 was used following the same rationale described for zinc. Thus, the maximum 30-day average limitation is:

$$(0.20 \text{ mg/l})(54.6 \text{ m}^3/\text{kg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.011 \text{ kg/kg}$$

and the 24-hour maximum limitation is:

$$(3.3) (0.011 \text{ kg/kg}) = 0.036 \text{ kg/kg}.$$

c. Lead

The observed average raw waste concentration of lead (0.66 mg/l) was not far above the 0.13 mg/l estimated long term average treatability according to industry's performance data in Table 8-12. Using a monthly variability factor of 1.2, the concentration basis for the maximum 30-day average is:

$$(1.2) (0.13 \text{ mg/l}) = 0.16 \text{ mg/l}$$

Based on a 24-hour variability factor of 3.9, the concentration basis for the 24-hour maximum is:

$$(3.9) (0.13 \text{ mg/l}) = 0.51 \text{ mg/l}$$

No effluent limitation is set for lead.

d. Antimony

According to literature treatability data (Table 8-11), the lower limit of treatability for antimony is 0.80 mg/l as a long term average. Based on VFR of 3.9/1.2, the concentration basis for the maximum 30-day average is:

$$(1.2) (0.80 \text{ mg/l}) = 0.96 \text{ mg/l}$$

and the concentration basis for the 24-hour maximum is:

$$(3.9) (0.80 \text{ mg/l}) = 3.1 \text{ mg/l}$$

No effluent limitation is set for antimony.

e. Copper: With 0.32 mg/l as the average treatability for copper (Table 8-12), the concentration basis for the maximum 30-day average is:

$$(1.2) (0.32 \text{ mg/l}) = 0.38 \text{ mg/l}$$

and the concentration basis for the 24-hour maximum is:

$$(3.9) (0.32 \text{ mg/l}) = 1.25 \text{ mg/l}$$

No effluent limitation is set for copper.

f. Chromium: Similar to copper, an average treatability of 0.32 mg/l is used for chromium. The concentration for the maximum 30-day average is:

$$(1.2) (0.32 \text{ mg/l}) = 0.38 \text{ mg/l}$$

and the concentration basis for the 24-hour maximum is:

$$(3.9) (0.32 \text{ mg/l}) = 1.3 \text{ mg/l}$$

No effluent limitation is set for chromium.

g. Other Metals

The concentration bases for arsenic and selenium are also presented in Table 12-21.

Basis for BCT Effluent Limitation

EPA has determined that the BAT technology for this subcategory is capable of removing significant amounts of conventional pollutants. However, EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned earlier. Thus, it is not now possible to apply the BCT cost test to this technology option. Accordingly, EPA is deferring a decision on the appropriate BCT limitations until EPA proposes the revised BCT methodology. However, the Agency has calculated the TSS loading based on the estimated performance of BAT treatment, and the cost of the additional TSS removal. As described in Section 3, this cost was calculated to be \$0.32 per pound of TSS removed.

By adjusting the loading to account for the decrease in effluent flow rate from BPT (54.6 m³/kkg) to BAT (33.4 m³/kkg), the TSS maximum 30-day average effluent loading becomes:

$$(5.3 \text{ kg/kkg}) \times \frac{(33.4 \text{ m}^3/\text{kkg})}{(54.6 \text{ m}^3/\text{kkg})} = 3.2 \text{ kg/kkg}$$

The corresponding 24-hour maximum effluent loading is then obtained by applying the VFR value of 2.1 (Table 12-21). That is:

$$(2.1)(3.2 \text{ kg/kkg}) = 6.7 \text{ kg/kkg}$$

Basis for BAT Effluent Limitations

A. The Application of Advanced Level Treatment

Utilizing the cost estimates presented in this report, the Agency has analyzed the cost effectiveness of the base level systems (BPT) and the various advanced level options for conventional, nonconventional and toxic pollutant removal. The economic impacts on the Hydrofluoric Acid industry have been evaluated in detail (53) and taken into consideration in the selection of the technology basis for the BAT regulations.

For BAT, the Agency is promulgating limitations based on treatment consisting of Level 1 technology. The Agency considered the use of treatment Level 2 (addition of a dual-media filter) but did not adopt it because the installation of the filter is not cost effective in the removal of TSS, fluorides and toxic metals. In addition, the use of treatment Level 3 (addition of sulfide precipitation) was considered but rejected due to lack of performance data. EPA also considered Level 4, a variation of Level 2, that would substitute soda ash in the lime precipitation step and allow 90 percent recycle of effluent. This option was rejected due to being prohibitively expensive. Pollutants limited by the final BAT regulation are fluoride, nickel, and zinc.

B. Technology Basis

For BAT, the Agency is setting the effluent limitations on fluoride and the toxic metals based on the BPT treatment system, coupled with the requirement of at least 65 percent effluent reuse for kiln residue slurring.

In Section 7.0 "Hydrofluoric Acid Subcategory" of EPA's Treatability Studies for the Inorganic Chemicals Manufacturing Point Source Subcategory (EPA 440/1-80/103) (61), the conclusion states:

"A major conclusion that can be drawn from this study is that the addition of dual-media filtration after alkaline precipitation and settling is not particularly effective for the reduction of final TSS and total fluoride concentrations. Further, dual-media filtration does not appear to be justified on the basis of additional toxic metal removal judging by the results presented in Table 7-3."

A summary of the filter removal efficiencies for the pollutants selected for the treatability study is given in Table 12-22.

The minimum reuse rate of 65 percent was selected because it is typical of the five plants (Plants #167, #753, #928, # 664, and # 722) which presently practice reuse as is shown in Table 12-4.

C. Flow Basis

With the model plant inflow rate of $95.4 \text{ m}^3/\text{kgg}$ and the reuse of 65 percent of the treated effluent, the quantity discharged is $33.4 \text{ m}^3/\text{kgg}$; i.e., $(1.00 - 0.65)(95.4 \text{ m}^3/\text{kgg}) = 33.4 \text{ m}^3/\text{kgg}$.

D. Selection of Pollutants to be Regulated

For the BAT regulations, the Agency has selected fluoride and the same two toxic metals identified in the BPT regulations. The rationale for their selection is discussed above.

E. Basis of Pollutant Limitations

1. Nonconventional pollutants

The only nonconventional pollutant found in the wastewater in this subcategory is fluoride. The limitation for BAT is based on the performance of the four plants shown in Table 12-20 that presently reuse at least 65 percent of their treated effluent. The long term average effluent loading taken from Table 12-22 is $1.0 \text{ kg}/\text{kgg}$ for Plant #928, since the percent reuse for this plant is intermediate in range for the three plants considered for BAT (Plants #753, # 928, and #722). Plant #664 is excluded from consideration for BAT because the high degree of recycle practiced requires

the extensive use of soda ash. The use of this performance in conjunction with the 30-day average variability factor of 1.6 and the model plant net discharge rate of 33.4 m³/kkg results in a calculated maximum 30-day average concentration of 50 mg/l total fluoride. Thus, the maximum 30-day average limitation is:

$$(1.6)(1.0 \text{ kg/kkg}) = 1.6 \text{ kg/kkg}$$

and its concentration basis is:

$$\frac{(1.6 \text{ kg/kkg})}{(33.4 \text{ m}^3/\text{kkg})} \times \frac{1000 \text{ mg/l}}{(\text{kg/m}^3)} = 50 \text{ mg/l}$$

This represents a six percent reduction in fluoride concentration in going from BPT (43 percent reuse) to BAT (65 percent reuse). The use of a fixed loading limitation allows the permissible concentration to increase as a function of percent reuse. The 24-hour maximum limitation on fluoride is obtained by utilizing the long term average and variability factor for daily measurements,

$$(3.4)(1.0 \text{ kg/kkg}) = 3.4 \text{ kg/kkg}$$

and the concentration basis is:

$$\frac{(3.4 \text{ kg/kkg})}{(33.4 \text{ m}^3/\text{kkg})} \times \frac{(1000 \text{ mg/l})}{(\text{kg/m}^3)} = 100 \text{ mg/l}$$

The variability factors used for the BAT limitations on fluoride are the same as for BPT shown in Table 12-20. The BAT limitations for the Hydrofluoric Acid Subcategory are presented in Table 12-23.

2. Toxic pollutants

For BAT regulations, the EPA is proposing more stringent controls on the discharge of the two toxic metals of concern on the basis of a reduced volume of discharge. Alkaline precipitation converts most of the dissolved metals into less toxic, insoluble forms such as hydroxides and hydrated oxides. Other mechanisms of removal including coprecipitation and flocculation are undoubtedly involved during the treatment process and probably account for a substantial portion of the removal of certain toxic metals.

The bases for the BAT limitation on the two control metals, zinc and nickel, are given below. The concentration bases of other metals are derived below and are intended to serve as guidance in cases where these pollutants are found to be of serious concern.

a. Zinc

TABLE 12-22. SUMMARY OF CONCENTRATIONS AND FILTER REMOVAL EFFICIENCIES OF POLLUTANTS SELECTED FOR STUDY IN THE HYDROFLUORIC ACID SUBCATEGORY

	Total Chromium	Total Zinc	Total Nickel	Free Fluoride	Total Fluoride	TSS
Average raw waste concentration (mg/l)	0.30	1.09	1.23	219.8	--	3315
Average supernatant concentration (mg/l)	0.073	0.10	0.46	45.9	116	333
Average filter effluent concentra- tion (mg/l)	0.067	0.05	0.41	42.2	91	134
Average filter removal efficiency (%)	6	36	17	6	20	53

The same value of 0.55 mg/l used for BPT is used as the treatability limit for zinc. As in the BPT regulations, a variability factor ratio (VFR) of 3.9/1.2 was used for zinc and the other metals in setting the BAT limitations and concentration bases. Thus, the concentration basis for the maximum 30-day average effluent limitation is:

$$(1.2) (0.55 \text{ mg/l}) = 0.66 \text{ mg/l}$$

and the maximum 30-day average effluent limitation is:

$$(0.66 \text{ mg/l}) (33.4 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.022 \text{ kg/kg}$$

The concentration basis for the 24-hour maximum limitation is:

$$(3.9) (0.55 \text{ mg/l}) = 2.2 \text{ mg/l}$$

and the 24-hour maximum limitation is:

$$(2.15 \text{ mg/l}) (33.4 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.022 \text{ kg/kg}$$

This represents an overall reduction of 40 percent from the BPT loading limitation. The BAT limitations on zinc and nickel are included in Table 12-23.

b. Nickel

The same value of 0.17 mg/l used for BPT is used as the treatability limit for nickel. The concentration basis for the maximum 30-day average effluent limitation is:

$$(1.2) (0.17 \text{ mg/l}) = 0.20 \text{ mg/l}$$

and the maximum 30-day average effluent limitation is:

$$(0.20 \text{ mg/l}) (33.4 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0060 \text{ kg/kg}$$

The concentration basis for the 24-hour maximum limitation is:

$$(3.9) (0.17 \text{ mg/l}) = 0.66 \text{ mg/l}$$

and the 24-hour maximum effluent limitation is:

$$(0.66 \text{ mg/l}) (33.4 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.20 \text{ kg/kg}$$

TABLE 12-23. EFFLUENT LIMITATIONS
HYDROFLUORIC ACID
Best Available Technology
Wastewater Flow: 33.4 m³/kkq of HF (65% Reuse)*

Pollutant	Treatability (mg/l)	VFR ⁽¹⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kkg of HF)	
			Max.	24-hr.	Max	24-hr.
			30-day Avg.	Max.	30-day Avg.	Max.
<u>Nonconventional Pollutants:</u>						
Fluoride, F	31 ⁽²⁾	3.4/1.6	50	100	1.6	3.4
<u>Toxic Pollutants:</u>						
Antimony	0.80	3.9/1.2	0.96	3.1	--(3)	--(3)
Arsenic	0.50	3.9/1.2	0.60	2.0	--(3)	--(3)
Chromium	0.32	3.9/1.2	0.38	1.3	--(3)	--(3)
Copper	0.32	3.9/1.2	0.38	1.3	--(3)	--(3)
Lead	0.13	3.9/1.2	0.16	0.51	--(3)	--(3)
Nickel	0.17	3.9/1.2	0.20	0.66	0.0060	0.020
Selenium	0.20	3.9/1.2	0.24	0.78	--(3)	--(3)
Zinc	0.55	3.9/1.2	0.66	2.2	0.022	0.072

(1) VFR: ratio of the 24-hour variability factor to the 30-day variability factor.

(2) 30-day average calculated for the model plant based on data in Table 12-20.

(3) No effluent limitations.

* The effluent flow rate is 35 percent of the average influent shown in Table 12-4 (i.e., 0.35 X 95.4 m³/kkq = 33.4 m³/kkq).

This represents an overall 44 percent decrease from the corresponding BPT level.

c. Lead

Using a treatability limit of 0.13 mg/l for lead, the maximum 30-day average concentration basis is:

$$(1.2) (0.13 \text{ mg/l}) = 0.16 \text{ mg/l}$$

The 24-hour maximum concentration basis is:

$$(3.9) (0.13 \text{ mg/l}) = 0.51 \text{ mg/l}$$

No effluent limitation is set for lead.

d. Antimony

Using a treatability limit of 0.80 mg/l for antimony, the maximum 30-day average concentration basis is:

$$(1.2) (0.8 \text{ mg/l}) = 0.96 \text{ mg/l}$$

The 24-hour maximum concentration basis is:

$$(3.9) (0.8 \text{ mg/l}) = 3.1 \text{ mg/l}$$

No effluent limitation is set for antimony.

e. Copper

Using a treatability limit of 0.32 mg/l for copper, the maximum 30-day average concentration basis is:

$$(1.2) (0.32 \text{ mg/l}) = 0.38 \text{ mg/l}$$

The 24-hour maximum concentration basis is:

$$(3.9) (0.32 \text{ mg/l}) = 1.3 \text{ mg/l}$$

No effluent limitation is set for copper

f. Chromium.

Using a treatability limit of 0.32 mg/l for chromium, the maximum 30-day average concentration basis is:

$$(1.2) (0.32 \text{ mg/l}) = 0.38 \text{ mg/l}$$

The 24-hour maximum concentration basis is:

$$(3.9) (0.32 \text{ mg/l}) = 1.3 \text{ mg/l}$$

No effluent limitation is set for chromium.

g. Other Metals

The concentration bases for arsenic and selenium are also given in Table 12-23.

Basis for the New Source Performance Standards

BAT was selected as the basis for NSPS limitations. The pollutants to be controlled for NSPS are pH, total suspended solids, fluorides, nickel and zinc. The NSPS limitations are given in Table 12-24.

In addition to the toxic pollutants controlled by the BAT, a total suspended solids limitation was developed for NSPS. Based on the data in Table 12-20, a long term average of 1.7 kg/kkg (Plant #928) was used for the TSS. The variability factor ratio (VFR) used is 2.1,

$$\frac{3.5}{1.7} = 2.1$$

Thus, the 24-hour maximum effluent limitation for TSS is:

$$(3.5) (1.7 \text{ kg/kkg}) = 6.0 \text{ kg/kkg HF}$$

The maximum 30-day average limitation for TSS is:

$$(1.7) (1.7 \text{ kg/kkg}) = 3.0 \text{ kg/kkg HF}$$

Basis for the Pretreatment Standards

A. Existing Sources

The Agency is not promulgating PSES because there are no indirect dischargers in the subcategory. Instead, we are excluding the subcategory from categorical PSES under the provisions of paragraph 8(b) of the Settlement Agreement.

B. New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is setting limitations equal to NSPS because NSPS provides better removal of nickel and zinc than is achieved by a well-operated POTW with secondary treatment installed and therefore these pollutants would pass through a POTW in the absence of pretreatment. The pollutants to be regulated are fluoride, nickel, and zinc as indicated in Table 12-24.

Table 12-24. Effluent Limitations
Hydrofluoric Acid
New Source Performance Standards [†]
Waste Water Flow: 33.4 m³/kkg of HF (65% Reuse) *

Pollutant	Treatability (mg/l)	VFR ⁽¹⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kkg of HF)	
			Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
<u>Conventional and Nonconventional Pollutants:</u>						
Total Suspended Solids, TSS	53	3.5/1.7	90	180	3.0	6.0
Fluoride, F ⁽²⁾	31 ⁽³⁾	3.4/1.6	50	100	1.6	3.4
<u>Toxic Pollutants:</u>						
Antimony	0.80	3.9/1.2	0.96	3.1	— ⁽⁴⁾	— ⁽⁴⁾
Arsenic	0.50	3.9/1.2	0.60	2.0	— ⁽⁴⁾	— ⁽⁴⁾
Chromium	0.32	3.9/1.2	0.38	1.3	— ⁽⁴⁾	— ⁽⁴⁾
Copper	0.32	3.9/1.2	0.38	1.3	— ⁽⁴⁾	— ⁽⁴⁾
Lead	0.13	3.9/1.2	0.16	0.51	— ⁽⁴⁾	— ⁽⁴⁾
Nickel ⁽²⁾	0.17	3.9/1.2	0.20	0.66	0.0060	0.020
Selenium	0.20	3.9/1.2	0.24	0.78	— ⁽⁴⁾	— ⁽⁴⁾
Zinc ⁽²⁾	0.55	3.9/1.2	0.66	2.2	0.022	0.072

(1) - VFR: ratio of the 24-hour variability factor to the 30-day variability factor.

(2) - Also applicable for PSES limitations.

(3) - 30-day average calculated for the model plant based on the data in Table 12-20.

(4) - No effluent limitation.

* - The effluent flow rate is 35 percent of the average influent shown in Table 12-4 (i.e., $0.35 \times 95.4 \text{ m}^3/\text{kkg} = 33.4 \text{ m}^3/\text{kkg}$).

† - This table is also applicable to the PSNS effluent limitations except for the TSS limitation.

SECTION 13

HYDROGEN PEROXIDE INDUSTRY

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT, NSPS, or pretreatment regulations for the Hydrogen Peroxide Subcategory using either the electrolytic process or the organic process.

The bases for this exclusion are: 1) only one plant exists that manufactures hydrogen peroxide using the electrolytic process and 2) no toxic pollutants were found in the wastes using the organic process. Therefore, this subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Assessment of the Water Pollution Potential

Production Processes and Effluents

In the electrolytic process, ammonium (or other) bisulfate solution is electrolyzed, yielding ammonium persulfate at the anode and hydrogen gas at the cathode. The persulfate is then reacted with water to yield hydrogen peroxide and original bisulfate. Hydrogen peroxide is separated from bisulfate by fractionation, after which it is concentrated and filtered. The only waste is a stream of condensate from the fractionation condenser.

The organic process involves the reduction of alkylanthraquinone by hydrogen over a supported metal catalyst to produce the corresponding alkylhydroanthraquinone. The reacted mixture is oxidized to form hydrogen peroxide and original alkylanthraquinone. The peroxide is extracted with water and the organic material in the solvent is recycled to the process. Since the manufacture of hydrogen peroxide by the organic process consists of a series of exothermic chemical reactions, the bulk of the water usage is for process cooling (contact and noncontact). Noncontact cooling accounts for over 90 percent of the total water usage in this subcategory. The wastewater sources include contact cooling (barometric-condenser) water, purification washing of the organic working solutions, regeneration waste from the deionizers, and leaks and spills.

Plants

Only one plant exists in the United States that manufactures hydrogen peroxide using the electrolytic process. The hydrogen peroxide subcategory profile data received in response to Section 308 letters is given in Table 13-1.

TABLE 13-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	HYDROGEN PEROXIDE
<hr/>	
Total subcategory capacity rate	
Total subcategory production rate	85,700 kkg/year
Number of plants in this subcategory	4
308 Data on file for	4
With total capacity of	102,200 kkg/year
With total production of	57,000 kkg/year
Representing capacity	
Representing production	66 percent
Plant production range:	
Minimum	5,560 kkg/year
Maximum	28,730 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	15 years
Maximum	27 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

NA = Not Available.

Three plants product hydrogen peroxide by the organic process.

Toxic Pollutants

Data has been received on 100 percent of the industry as a result of Section 308 letters. A sampling survey for toxic pollutants was made for three plants. At one plant, pentachlorophenol was found in significant concentrations. However, it was determined that its presence was due to its use as a weed killer at the plant site and this use was discontinued. Two more plants were sampled in the verification phase, and the survey indicated that no toxic pollutants were being discharged in significant quantities.

Toxic pollutants found during sampling were as follows:

<u>Pollutant</u>	<u>Maximum Concentration Observed (μg/l)</u>
Zinc	256
Pentachlorophenol	4850
Bis(2-ethylhexyl)phthalate	20
Chloroform	11
Naphthalene	11

Status of Regulations

Since no toxic pollutants were found in significant concentrations, the subcategory is excluded under Paragraph 8 of the Settlement Agreement.

SECTION 14

TITANIUM DIOXIDE INDUSTRY

INDUSTRY PROFILE

General Description

Titanium dioxide (TiO_2) is manufactured by a chloride process, a sulfate process, and a chloride-ilmenite process. This subcategory is subdivided into three segments, one for each process because of the difference in raw materials used, wastewater flows, and raw waste characteristics. TiO_2 is a high volume chemical, ranking within the first fifty of all U.S. chemicals production. Over fifty percent of the titanium dioxide produced is used in paints, varnishes, and lacquers. About one third is used in the paper and plastics industries. Other uses are found in ceramics, ink, and rubber manufacturing.

The industrial profile data for the chloride segment are presented in Table 14-1, while the status of regulations prior to promulgation of this new regulation is given in Table 14-2.

Subcategorization

The Titanium Dioxide Subcategory is divided into three different processes requiring separate consideration. Two processing techniques including sulfate and the chloride process using two major ores including rutile and ilmenite dictate a division into the sulfate process, chloride process/rutile ore, and chloride process/ilmenite ore (one step) based on current practice. Details concerning subcategorization are discussed in Section 4.

General Process Description and Raw Materials

In the chloride process, the raw materials used are rutile or upgraded ilmenite ore, which are relatively pure materials with a high titanium and a low iron content. For upgrading ilmenite (FeTiO_3), a beneficiation process removes part or all of the iron. Several patented processes exist for the beneficiation step and two or three are in current operation on a commercial scale. The wastes from the chloride process using a one step beneficiation of ilmenite in titanium dioxide production are different from those produced using high grade titanium ore (rutile or upgraded ilmenite).

In the chloride process, the ore and coke are dried and then reacted with chlorine to form titanium tetrachloride. The chemical reaction taking place in the reaction is given as:

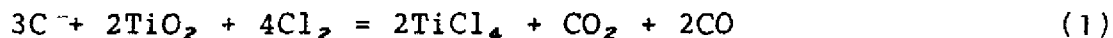


TABLE 14-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY TITANIUM DIOXIDE (CHLORIDE PROCESS)

Total subcategory capacity rate	610,000 kkg/year
Total subcategory production rate	389,000 kkg/year
Number of plants in this subcategory	5
308 Data on file for	5
With total capacity of	184,600 kkg/year
With total production of	142,000 kkg/year
Representing capacity	30 percent
Representing production	37 percent
Plant production range:	
Minimum	16,900 kkg/year
Maximum	45,200 kkg/year
Average production	28,400 kkg/year
Median production	25,600 kkg/year
Average capacity utilization	77 percent
Plant age range:	
Minimum	6 years
Maximum	15 years
Waste water flow range:	
Minimum	1,140 cubic meters/day
Maximum	4,770 cubic meters/day
Volume per unit product:	
Minimum	29.3 cubic meters/kkg
Maximum	110 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978, and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

TABLE 14-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY		TITANIUM DIOXIDE					
SUBPART		V (40 CFR 415.220, 3/13/74)					
STANDARDS							
		BPCTCA*		BATEA*		NSPS*	
		Max. ¹	Avg. ²	Max.	Avg.	Max.	Avg.
Product		kg/kkg	kg/kkg	kg/kkg	kg/kkg	kg/kkg	kg/kkg
Process	Parameters	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Chloride							
Process	TSS	4.6	2.3	2.6	1.3	2.6	1.3
	Iron	0.72	0.36	0.36	0.18	0.36	0.18
Sulfate							
Process	TSS	21.0 (100.0)**	10.5 (50.0)	10.6	5.3	10.6	5.3
	Iron	1.7 (8.1)	0.84 (4.0)	0.84	0.42	0.84	0.42

* Sections 415.220, 415.222, 415.223 and 415.225 were remanded and reserved (41 FR 51601, November 23, 1976).

¹ Max. = Maximum of any one day.

² Avg. = Average of daily values for thirty consecutive days.

** = Flow basis 210,000 l/kg.

The reaction takes place at a temperature of 800-1000 degrees C and a fluidized bed reactor is generally used. The product gases leaving the reactor consist of titanium tetrachloride, unreacted chlorine, carbon dioxide, carbon monoxide, and minor amounts of heavy metal chlorides. The gases are initially cooled to 250 degrees C to remove the impurities, although in some cases purification is accomplished by washing the gases with liquified titanium tetrachloride. Iron chloride and small amounts of vanadium, zirconium, and other trace metal chlorides are removed by centrifugation and the liquid recycled to the absorber. Titanium tetrachloride is liquefied from the gases after the first stage of cooling by further cooling to ambient temperature. Copper, hydrogen sulfide, and, in some cases, proprietary organic complexing agents are added for purification to the condensed solution. Copper acts as a catalyst to decompose the phosgene formed in the TiCl_4 stream. Organic complexing agents aid in separation of the TiCl_4 from other chlorides such as cupric chloride and silicon tetrachloride.

The residual uncondensed gases generally consist of hydrochloric acid, chlorine, carbon monoxide, carbon dioxide, nitrogen, and some titanium tetrachloride. They are treated to remove acidic materials before being vented to the atmosphere.

The liquefied titanium tetrachloride contains impurities such as aluminum chloride, silicon tetrachloride, etc., which are removed by distillation. The distillate is the purified titanium tetrachloride and the impurities remain as a residual which becomes waste. The tail gases from the distillation column are scrubbed to remove acidic materials. The titanium tetrachloride product is then reacted with oxygen, as air, forming titanium dioxide and chlorine:



The rate of reaction is negligible below 600 degrees C but increases rapidly above this temperature, and is generally maintained between 1200-1400 degrees C for efficient reaction and conversion. The needed heat is supplied by passing the reactants through heat exchangers, by electric discharges, or by use of fluidized beds. After the oxidation reaction, the titanium dioxide forms a solid and is separated from the gases either in cyclones, baghouse filters, or Cottrell precipitators. The residual chlorine is refrigerated and liquefied. The tail gases are scrubbed with caustic soda to remove chlorine before being vented to the atmosphere. When air is used for oxidation, chlorine recovery is achieved by absorption in trichloroethylene, followed by distillation to remove chlorine. The titanium dioxide is then sent to the finishing operation where it is vacuum degassed and then treated with alkali, using a minimum amount of water to remove traces of absorbed chlorine and hydrochloric acid. The pigment is then milled, surface treated for end-use application, dried, and packaged for sale. A generalized process flow diagram, including the waste streams, is shown in Figure 14-1.

Water Use and Waste Source Characteristics

Water Use

Water is used in noncontact cooling, for scrubbing the tail gases from the purification and oxidation reactors to remove contaminants, and in the finishing operation of the product. The total amount of water usage varies from 45.3 to 555 m³/kkg of TiO₂ produced, as shown in Table 14-3. The table also shows that cooling water constitutes the major use of water and varies from 10.7 to 426 m³/kkg of TiO₂ produced.

Waste Sources

A. Wastes from Cooling Chlorinator Gas

The waste consists of solid particles of unreacted ore, coke, iron, and small amounts of vanadium, zirconium, chromium, and other heavy metal chlorides. They are either dissolved in water and sent to the wastewater treatment facility or disposed of in landfills as a solid waste.

B. Chlorinator Process Tail Gas Scrubber Waste

The uncondensed gases, after the liquefaction of titanium tetrachloride, are initially wet scrubbed to remove hydrogen chloride, chlorine, phosgene, and titanium tetrachloride. In a second stage, they are scrubbed with caustic soda to remove chlorine as hypochlorite.

C. Distillation Bottom Wastes

These contain copper, sulfide, and organic complexing agents added during purification in addition to aluminum, silicon, and zirconium chlorides. These are removed as waterborne wastes and reaction with water converts silicon and anhydrous aluminum chlorides to their respective oxides.

D. Oxidation Tail Gas Scrubber Wastes

The gases from the oxidation unit are cooled by refrigeration to liquefy and recover chlorine. The uncondensed off-gasses are scrubbed with water or caustic soda to remove residual chlorine. When caustic soda is used as the scrubbing solution, the resulting solution of sodium hypochlorite is either sold, decomposed, sent to the wastewater treatment facility, or discharged without treatment. The scrubber waste stream also contains titanium dioxide particulates.

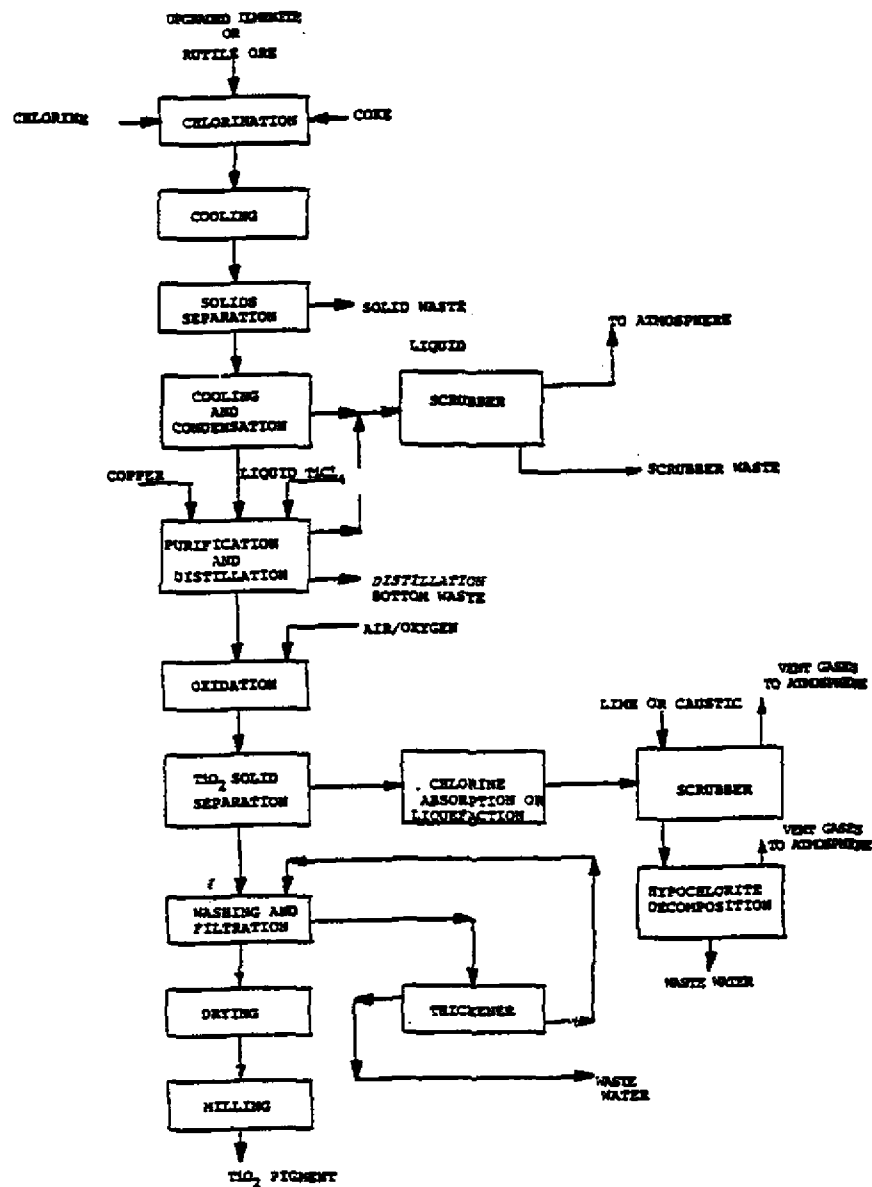


Figure 14-1. General process diagram for production of titanium dioxide (chloride process) from high grade ores.

TABLE 14-3. WATER USAGE IN TITANIUM DIOXIDE-CHLORIDE PROCESS/HIGH GRADE ORES SUBCATEGORY

Water Use	Water Usage at Plants (m ³ /kg of TiO ₂)		
	Water Use		
	Plant #102	Plant #172	Plant #199
Noncontact cooling	182	10.7	426
Direct process contact	10.5	15.5	73.2
Indirect process contact	NA	0.72	26.5
Maintenance, equipment cleaning and work area washdown	6.65	0.52	2.80
Air pollution control	0.25	7.14	11.3
Noncontact ancillary uses	11.6	10.4	9.5
Sanitary & portable water	0.23	0.31	5.6
Total	211	45.3	555

NA = Not available

E. Finishing Operations Waste

The liquid wastes from the finishing operation contain titanium dioxide as suspended solid and dissolved sodium chloride formed by the neutralization of residual HCl with caustic soda.

The range of wastewater flows requiring treatment is summarized in Table 14-4. The wide range of flow occurs because some plants use additional water to wash solid process residues to the waste treatment system.

Description Of Plants Visited And Sampled

Screening

Plant #559 was visited and the waste effluents were sampled in the screening phase of the program. Plant # 559 makes titanium dioxide using both the sulfate and the chloride processes. The wastewaters from both processes are mixed and undergo combined treatment.

The solids from the chloride process, called pit solids, (mainly unreacted ore, coke, iron, and trace metal chlorides including $TiCl_4$) are separated from the first stage cooling of the chlorinated gases and are slurried with water. The slurried pit solids and the distillation column bottom residue effluents from the chloride process are sent to a large settling pond (called the weak acid pond) where they are mixed with the weak acid from the sulfate process. The overflow from the settling pond is neutralized with ground calcium carbonate in a reactor. The reactor effluent is filtered, aerated to remove iron, and combined with neutralized strong-acid waste effluent from the sulfate process. The combined scrubber and contact cooling wastewaters from both the sulfate and chloride processes are also combined at this point. The combined wastewater is neutralized and solids settled out in a pond prior to final discharge. A flow diagram of the treatment facility, including the sampling locations, is shown in Figure 14-2.

Problems were encountered during the sampling of the pit solids and distillation bottoms. The pipes carrying the wastes from the process discharged at the bottom of the settling pond and it was not possible to take the samples right at the outlet of the pipe. The combined sample of the two streams was taken at the surface of the discharge. It is probable that some solids settled before the stream reached the surface. Table 14-5 gives the waste flows and pollutant loadings for the streams sampled at Plant #559. Because of the intermixing of the waste effluents from both chloride and sulfate processes, the pollutant loadings in Table 14-5 were calculated by proportioning according to the relative hydraulic loadings.

Verification Plant #172 was sampled in the verification phase. Titanium dioxide is made at this facility by the chloride process only. The strong acid wastes and the spent coke and ore residues are hauled to a secure chemical landfill for disposal. The wastewater

TABLE 14-4. WASTE WATER FLOW FOR TITANIUM DIOXIDE-CHLORIDE PROCESS
SUBCATEGORY

SUBCATEGORY	TITANIUM DIOXIDE (Chloride Process)
Plant	Unit Waste Water Flow Going to Treatment Plant (m ³ /kg of TiO ₂)
#102	29.3 ⁽¹⁾
#172	34.7 ⁽¹⁾
#559	91.0 ⁽²⁾
#199	110.0 ⁽²⁾

(1) Off-site disposal of process solid residues.

(2) Process solid residues are slurried to waste treatment. The average flow of Plants #559 and #199 was used as the model plant flow for cost estimating and regulation development.

from the process, mainly the scrubber water, is collected in trenches and sent to a central reactor basin. Other discharges, including a part of the total rain runoff, are also collected in ditches and sent to the reactor basin. In the reactor basin sodium hydroxide is used for neutralization and the resulting effluent is mixed with the remaining rain runoff and sent to the first of two retention basins arranged in series. The overflow from the second retention basin is pH adjusted with sulfuric acid before discharge. A simplified diagram of the treatment system, including the sampling points, is shown in Figure 14-3. Table 14-6 gives the waste flow and pollutant loadings for the streams sampled.

Toxic Pollutant Concentrations

Chromium was identified in the raw wastewater for Plant #172 at a concentration considered treatable based on information summarized in Section 8. Four toxic metal pollutants were identified above treatable levels at Plant #559, although it is likely that the levels observed included some contributions from the sulfate process, since the two raw waste effluents are intermixed before treatment. No toxic organic pollutants were identified above treatable levels in the raw wastes at either plant. The maximum concentration of toxic metal pollutants observed during screening and verification are presented as follows:

Maximum Raw Waste Concentrations Observed (ug/l)

Pollutant	Screening Plant #559	Verification Plant #172
Chromium	152,000	1800
Lead	5,150	14
Nickel	6,320	85
Zinc	3,300	660

The screening and verification sampling program and the methodology used have been described in Section 5 of this report. A total of six days of sampling was conducted at Plants #559 and #172. Five effluent waste streams were sampled at Plant #559 and three streams were sampled at Plant #172. At each sampling point, three 24-hour composite samples were collected for analysis. The evaluation of toxic metal content of these process related waste streams was based 550 analytical data points. The average unit loadings and concentrations for conventional, nonconventional, and toxic pollutants found in the raw waste effluents for Plants #559 and #172 are given in Table 14-7.

The total quantities of toxic pollutants generated each year for this Subcategory (calculated as total subcategory production times average unit toxic pollutant load from Table 14-7) are as follows:

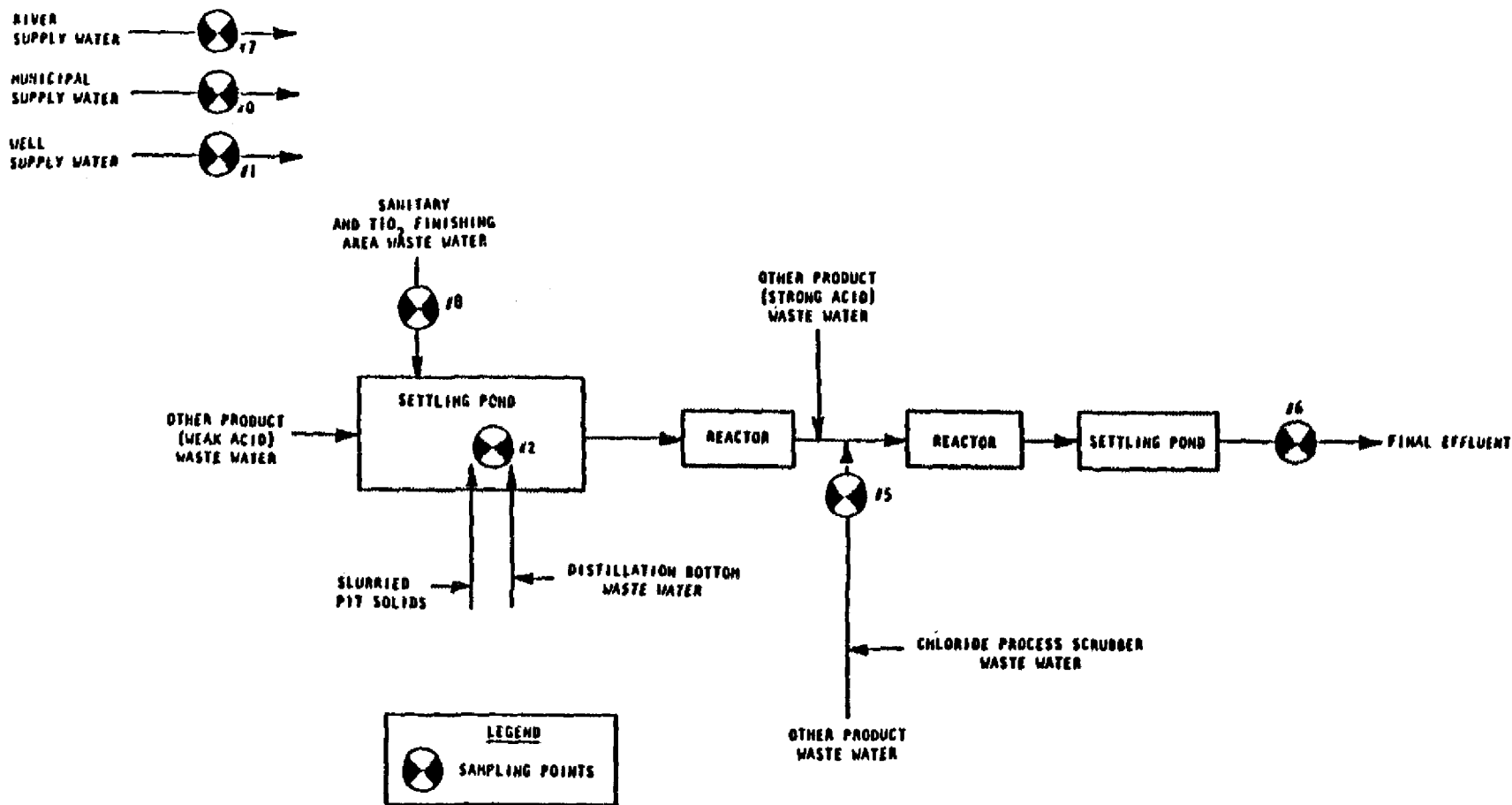


Figure 14-2. General flow diagram at Plant #559 showing the sampling points.
(Titanium dioxide -- chloride process manufacture.)

TABLE 14-5. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE⁽¹⁾
STREAMS OF PLANT #559 PRODUCING TITANIUM DIOXIDE BY
CHLORIDE-RUTILE PROCESS

Pollutant	STREAM #2			STREAM #5			CALCULATED ESTIMATE			STREAM #6		
	Pit Solids and Distillation Bottoms			Scrubber and Contact Cooling Water			Total Raw Waste			Treated Effluent		
	Unit Flow (m ³ /kkg)	Conc., (mg/l)	Unit Load (kg/kkg)	Unit Flow (m ³ /kkg)	Conc., (mg/l)	Unit Load (kg/kkg)	Unit Flow (m ³ /kkg)	Conc., (mg/l)	Unit Load (kg/kkg)	Unit Flow (m ³ /kkg)	Conc., (mg/l)	Unit Load (kg/kkg)
	10.9			80.1			91			91		
TSS		6903	75.2		314	25.2		1103	100.4		23	2.1
Iron		1348	14.7		143	11.5		288	26.2		4.4	0.4
Chromium		112	1.2		0.11	0.01		13.3	1.21		0.03	0.003
Lead		3.53	0.04		0.009	0.001		0.5	0.041		0.002	0.0002
Nickel		3.46	0.04		0.016	0.001		0.5	0.041		0.005	0.0004
Zinc		2.12	0.02		0.13	0.01		0.3	0.03		0.06	0.005

(1) See Figure 14-2 for location of sampling points.

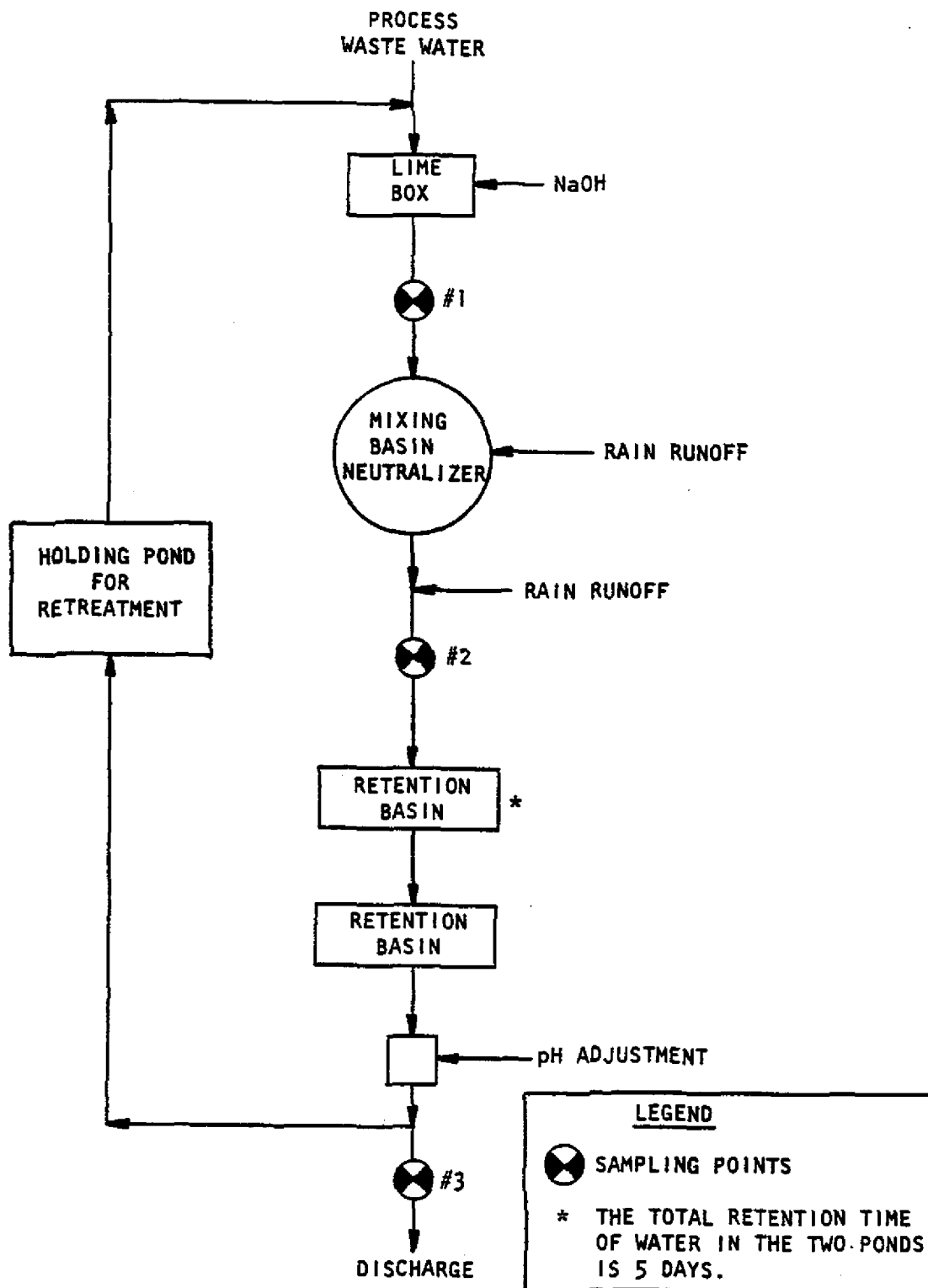


Figure 14-3. General flow diagram at Plant #172 showing the sampling points. Titanium dioxide (chloride process) manufacture.

TABLE 14-6. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #172 PRODUCING TITANIUM DIOXIDE (CHLORIDE PROCESS)

Pollutant	STREAM #1		STREAM #3	
	(Raw Waste Influent) ⁽¹⁾		(Treated Effluent) ⁽¹⁾	
	Avg. Conc. (mg/l)	Unit Load ⁽²⁾ (kg/kg)	Avg. Conc. (mg/l)	Unit Load (kg/kg)
TSS	171	5.93	6.7	0.23
Iron	2.9	0.10	0.33	0.01
Chromium	0.72	0.03	0.02	0.0007
Lead	0.005	0.0002	0.002	0.00007
Nickel	0.08	0.003	0.01	0.0003
Zinc	0.3	0.01	0.09	0.003

(1) Unit flow is $34.7 \text{ m}^3/\text{kg}$.

(2) Unit load equals the product of the pollutant concentration in mg/l and the unit flow in m^3/kg divided by a conversion factor of 1000.

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Chromium	241,000
Lead	8,200
Nickel	8,500
Zinc	7,800

Pollution Abatement Options

Toxic Pollutants of Concern

The dominant toxic pollutant observed in the raw waste effluents for the Titanium Dioxide (Chloride Process) Subcategory is chromium. Chromium was found at treatable concentrations at both plants sampled in the screening and verification phase. Lead, nickel, and zinc were found in the raw waste of Plant #559 at treatable levels, but were not present in the Plant #172 raw waste. At Plant #559, the chloride process waste effluents are mixed with the sulfate process waste effluents before treatment. It is likely that the three major toxic pollutants found were contributed by the sulfate process wastes since it uses a low purity ore (ilmenite). At Plant #172, the solids generated from the chloride process (which consist of solid particles of unreacted ore, coke, iron, and other heavy metals) are hauled to a landfill for disposal. It is probable that most of the toxic metal pollutants are present in this solid waste and hence do not appear in the wastewaters.

Process Modification and Technology Transfer Options

- A. Research to develop economical techniques to recover the vanadium and other metal values from the solid wastes generated from the process waste treatment system would appear to be a fruitful area of investment.
- B. New plants can utilize refrigeration and high pressures for chlorine liquefaction. This would reduce or eliminate the chlorine residual problem in the tail gases. The capital cost to modernize old plants is high, but these plants should have a caustic soda or lime scrubber instead of a water scrubber to remove residual chlorine from the tail gases. Caustic or lime scrubbing removes a significant portion of the chlorine from the tail gases in view of analagous data from the chlorine subcategory presented in Section 11.
- C. Best Management Practices

Provision should be made at all plants to collect storm water runoff from the plant site and send it to the treatment facility. Three out of a total of six existing plants are presently treating storm water runoff.

TABLE 14-7. RAW WASTE POLLUTANT DATA SUMMARY OF THE SAMPLED STREAMS

SUBCATEGORY: TITANIUM DIOXIDE (CHLORIDE PROCESS)

Average Daily Pollutant Concentration and Loadings at Plants Sampled			
kg/kg of TiO ₂			
(mg/l)			
Pollutant	Plant #559	Plant #172	Overall Average
Iron	26.2 (288)	0.10 (2.9)	13.15
Chromium	1.21 (13.3)	0.03 (0.72)	0.62
Lead	0.041 (0.5)	0.0002 (0.005)	0.021
Nickel	0.041 (0.5)	0.003 (0.08)	0.022
Zinc	0.03 (0.3)	0.01 (0.3)	0.02
TSS	100.4 (1103)	5.93 (171)	53.17

D. Prevailing Control and Treatment Practices

At Plant #172, the solid wastes consisting of spent ore and coke are hauled to an off-site landfill. Process wastewaters consisting of scrubber and contact-cooling effluents and a part of the surface runoff are sent to a mixing basin where they are neutralized with caustic soda. The effluent from the basin is then sent to two retention ponds in series. Additional or residual rain water runoff is added to the ponds for clarification. The overflow from the last pond is monitored and discharged to a surface stream. At Plant #559, the wastewaters from both chloride and sulfate processes are combined with the weak acid effluent from the sulfate process in a pond. The overflow from the pond is neutralized with limestone and oxidized with air for the removal of iron. The wastewater is then mixed with the neutralized strong acid waste (from the sulfate process) and scrubber waters (from both the chloride and sulfate processes), and neutralized with lime in a reactor and sent to a final settling pond. The overflow from the pond is the final discharge.

At Plant #199, all the process wastewaters are combined, including storm water and sanitary wastewater. The combined wastewater is sent to a four-stage neutralization system, and the effluent from each of the four stages of neutralization is sent to a thickener. The thickener overflow is transferred to the first of three settling ponds, also in series. The underflow from the thickener is heated to improve its filtration characteristics and filtered in four rotary drum filters. The thickened solids from the filters are disposed of in a landfill and the filtrate is combined with wash water and vacuum pump seal water prior to being recycled to the fourth stage of the neutralization train. The overflow from the last settling pond is discharged.

The process wastewater streams at Plant #102 are received in two tanks, neutralized with lime, and then sent to a settling basin. The settled solids are retained in the settling lagoons. The plant has future plans for treating boiler blowdown, cooling tower blowdown, leaks, and spills with the process wastewater.

At Plant #605, the unreacted ore and coke are disposed of as a solid waste in the pit. The wastewater from the process is passed to two tanks for flow equalization and the water is then reacted with ground limestone slurried in water. The treated solution is centrifugally treated to remove coarse solids which are separated and landfilled. A flocculating agent is added to the centrate and the solution is sent to a clarifier. The clarifier overflow is degassed and the pH adjusted with caustic soda (if required) before discharge.

E. Advanced Treatment Technologies

Neutralization and settling are practiced for the treatment of chloride process raw waste effluents at all the five plants for which 308 data are available. Air oxidation, sulfide precipitation, xanthate precipitation, and ion exchange might be applied to the clarified solutions for control of metals. Sulfide precipitation or the xanthate process could be used to provide additional removal of zinc, lead, and nickel.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT/BAT)

The chloride process wastes are equalized, neutralized with lime to a pH range of 6 to 9, and settled in lagoons before discharge. Level 1 treatment is typical of industry practice and for this reason was selected as the technology basis for BPT regulations.

B. Level 2 (NSPS)

Alkaline precipitation as a second-stage lime treatment to an optimum pH (9 to 10) is added to Level 1 to precipitate metallic hydroxides, which are then filtered before discharge. Filtration removes traces of metallic hydroxides which do not separate in a gravity system. Level 2 technology was selected as the basis for the proposed BAT limitations because it provides an economical method for the removal of additional toxic metals. For the reasons discussed below under Basis for New Source Performance Standards, the Agency did not select this option for BAT in the promulgated regulation, but did select it for NSPS.

C. Level 3

Ferrous sulfide treatment is added ahead of the Level 2 filter to precipitate the heavy metals more effectively.

Alkaline precipitation was chosen as Level 2 because it readily supplements existing lime neutralization by the simple addition of filtration and increasing the Level 1 lime dosage. Sulfide precipitation was chosen at Level 3 because it provides a polishing treatment for most residual heavy metals beyond Level 2 treatment.

Figures 14-4, 14-5, and 14-6 show the model treatment systems adopted for the chloride process wastes.

Equipment for Different Treatment Levels

A. Equipment Functions

BPT treatment is essentially lagooning with lime neutralization, using no special equipment except a lime feeder and mixer.

In Level 2, second stage lime treatment is followed by gravity clarification and multi-media filtration, with necessary pH controls.

In Level 3, ferrous sulfide is added ahead of the Level 2 filter, to react with residual heavy metals more completely than in the alkaline precipitation step at Level 2.

B. Chemicals and Handling

Lime and hydrochloric acid are fed with conventional equipment at all levels, and ferrous sulfide is prepared on-site by mixing ferrous sulfate with sodium bisulfide. When normal dust control and good ventilation are used, there should be no adverse effects from handling these chemicals, although care should be taken that hydrogen sulfide gas is not generated.

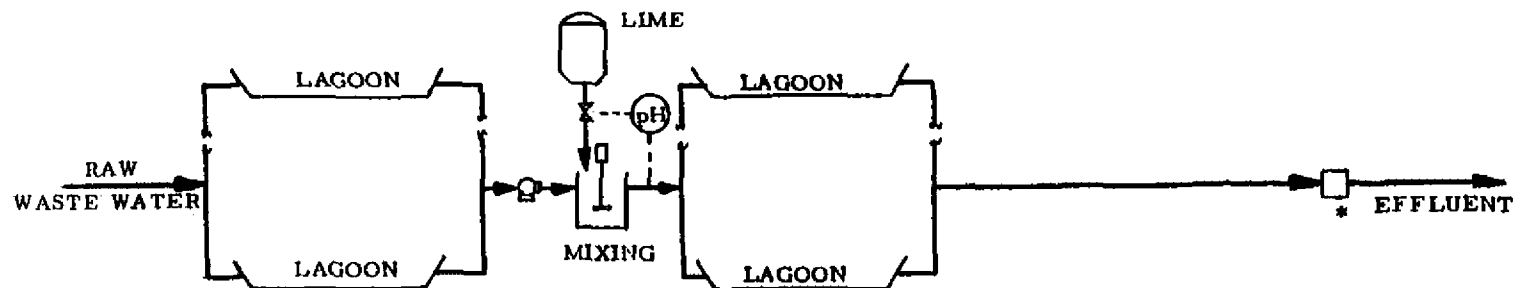
C. Separation and Removal of Solids

Inert ore fractions and precipitated solids are accumulated in clay-lined lagoons, which are alternately drained. Solids are mechanically removed to self-draining 18 ft. high storage piles on land provided at the site for a 10-year operating period. At Levels 2 and 3, small amounts of heavy metal precipitates in the clarifier underflow are filter pressed and hauled to a secure landfill.

Treatment Cost Estimates

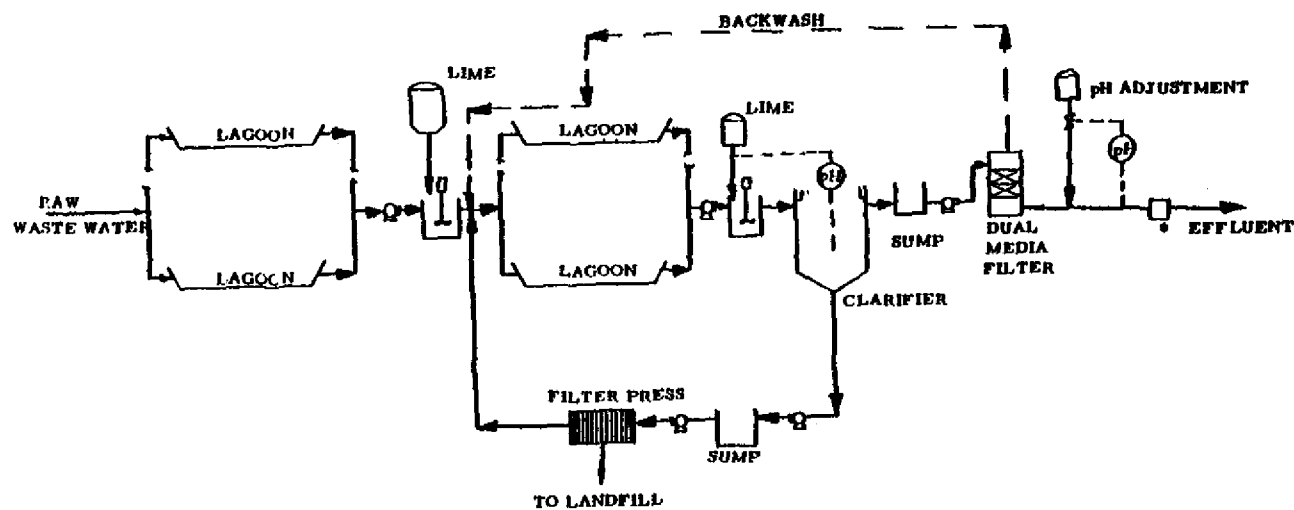
General Discussion

To determine the treatment cost, a model plant concept was developed. A raw waste unit flow was selected and pollutants to be treated were selected based on the treatment system data available for the five TiO_2 plants and the screening and verification sampling program. Three production levels were then selected to cover the entire subcategory range. Treatment costs for BPT and NSPS were calculated for each of the model plant production ranges using the unit flow and unit pollutant loads. The unit flow of $100 \text{ m}^3/\text{kg}$ used for the model plant in regulation development has been selected to be representative of the subcategory and it is assumed that the unreacted ore and coke are slurried and sent to the treatment system instead of being disposed of in a landfill as a solid waste.



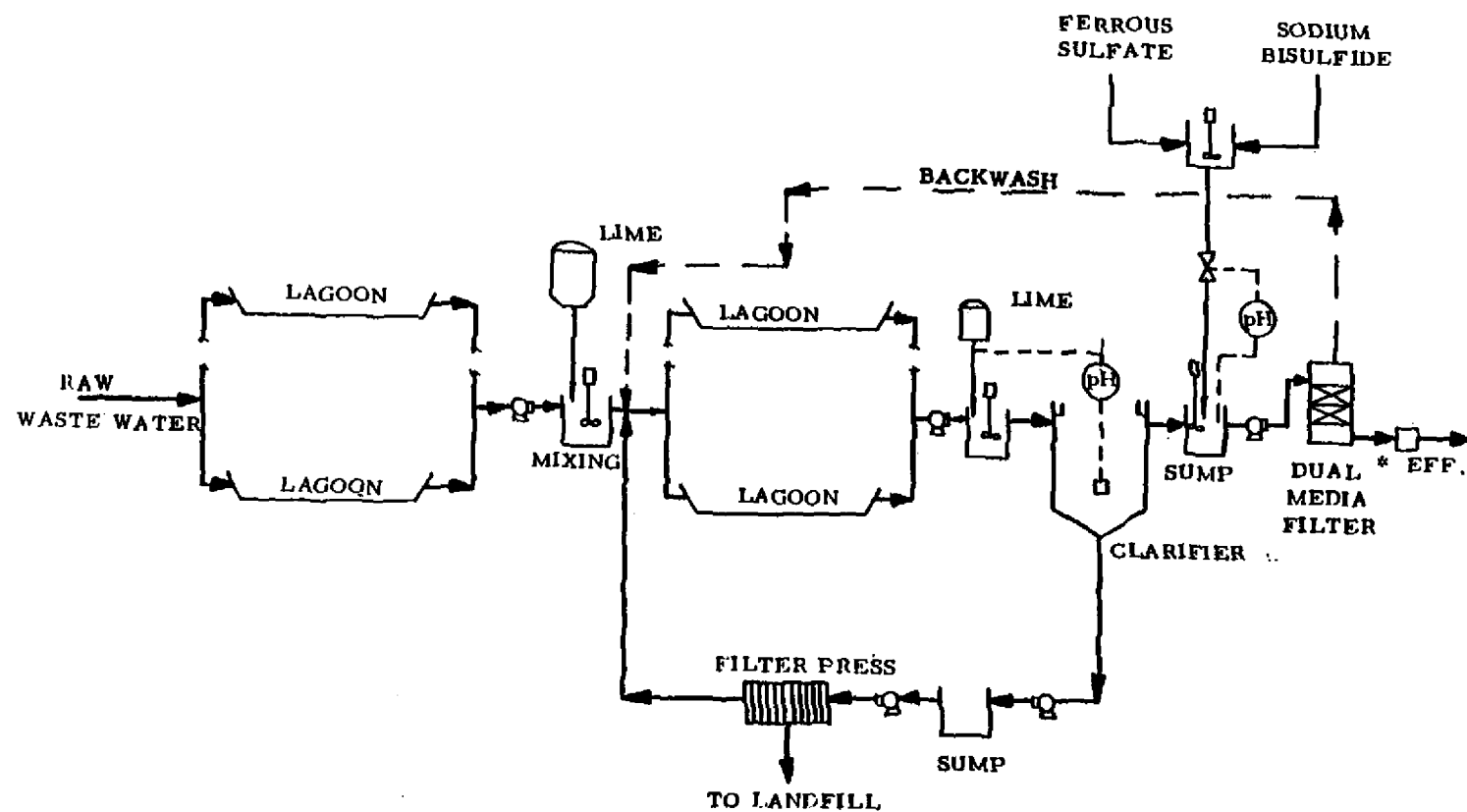
* Includes flow monitoring, pH monitoring and sampler.

Figure 14-4. Level 1 (BPT/BAT) waste water treatment for titanium dioxide -- chloride process.



* Includes flow monitoring, pH monitoring and sampler.

Figure 14-5. Level 2 (NSPS) waste water treatment for titanium dioxide -- chloride process.



* Includes flow monitoring, pH monitoring and sampler.

Figure 14-6. Level 3 waste water treatment for titanium dioxide -- chloride process.

A. Wastewater Flow

The unit waste effluent flow varies from 29.3 to 110.0 m³/kkg of TiO₂ for the four plants as shown in Table 14-4. The primary reason for the variation in the flow is that some plants slurry the spent ore and coke (solid waste from chloride process) and send it to the treatment system, and others haul the dry solids to a landfill. The flow variation is also dependent on the difference in chlorine recovery process from the tail gas and the amount of scrubbing liquid used. Small variations in flow also result from the finishing operation which is dependent on the type of titanium dioxide end product desired. Plants #559 (unit flow of 91 m³/kkg) and #199 (unit flow of 110 m³/kkg) send the solid waste from the manufacturing process to the treatment facility. It is assumed for treatment system cost estimation that the solids are included in the raw waste flow to the treatment system. A constant unit flow of 100 m³/kkg of TiO₂ has been used for the model plants, which is an average of the unit flows of Plants #559 and #199.

B. Pollutant Load

The primary pollutants occurring in the wastewater are suspended solids, acidity, and the chlorides of ferric iron, chromium, and other trace metals. The suspended solids (TSS) loading values for Plants #559 and #172 are 100.4 and 5.93 kg/kkg of TiO₂ (Table 14-7). The low value represents a plant that hauls ore and coke off-site, while the high value is believed to be too low due to nonrepresentative sampling. The amount of solids produced are higher than the values indicated for the sampled plants. Consequently, a higher suspended solids loading of 500 kg/kkg of TiO₂ (reported in the 308 data from Plant #199) is assumed for the model plant. To establish treatment chemical requirements and related costs, the toxic pollutant loadings for the model plant are taken as the average values of the unit pollutant loadings of the plants sampled in the screening and verification program (Table 14-6) and the selected pollutant values are:

<u>Pollutant</u>	<u>Unit Loading (kg/kkg of TiO₂)</u>
Chromium	0.63
Lead	0.021
Zinc	0.020
Iron	13.15
Nickel	0.022

C. Production Rates

Six plants produce titanium dioxide from rutile ore or upgraded ilmenite ore using the chloride process at a total production rate of 142,000 metric tons per year. Production ranges from a minimum of 16,900 kkg/year to a maximum of 45,200 kkg/year with a

mean of 28,400 kkg/year and a median of 25,600 kkg/year. For wastewater treatment cost estimates, three production levels were selected as model plants. These are 16,900 kkg/year, 25,500 kkg/year, and 45,200 kg/year. This range of production includes all United States plants.

Model Plant Control and Treatment Costs

The estimated costs for the three models having different production levels are given in Tables 14-8, 14-9, and 14-10. The costs shown at each level of treatment correspond to the model plant BPT (Level 1) system and higher level (NSPS) system which may add to or modify the existing BPT system to meet more stringent toxic pollutant removal requirements. The higher level (NSPS) also furnishes a better effluent quality with respect to the conventional and nonconventional parameters. Tables 14-11, 14-12, and 14-13 present the estimated NSPS treatment costs for the three models having different production levels. For model plants at the base level of treatment, amortization, chemicals, and the residual waste disposal costs have a significant impact on the total annual costs. At NSPS treatment level, amortization, chemicals, and labor constitute a major portion of the additional annual costs. Table 14-14 presents a summary of the unit cost distribution between amortization and the operation and maintenance cost components at various production rates and levels of treatment.

Basis For Regulations

Evaluations of BPT Treatment Practices

All the plants producing titanium dioxide by the chloride process using rutile ore or upgraded ilmenite ore practice neutralization and settling for control and treatment of the waste effluents. A variation in the effluent quality is expected because of the method of handling the unreacted ore and coke (generated as solid residue from the chloride process). Two of the six plants haul the residue to a secure landfill for disposal while the remainder slurry the residue with water and send it to the treatment system. No information is available about recycling the treated wastewater at any of the plants.

A. Pollutant Removal with BPT Treatment

Treatment Level 1 is equivalent to BPT in the TiO_2 subcategory (chloride process).

Plants #559 and #172 practice neutralization and settling of the raw waste. At Plant #559, the chloride process raw wastewater is mixed with the sulfate process wastewater for treatment. Also, at Plant #559 the spent ore and coke (solid residues from the chloride process) are slurried with water and sent to the treatment facility, whereas at Plant #172 the solid residues are hauled to a chemical landfill. Long-term treated effluent data have been submitted by both plants #559 and #172. The derivation

TABLE 14-8. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process	
Production	16,900 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	175,600	0
Equipment	205,000	0
Monitoring equipment	20,000	0
Subtotal	400,600	0
Contractor's O & P ^b	60,090	0
Subtotal	460,690	0
Engineering	92,138	0
Subtotal	552,828	0
Contingencies	55,283	0
Subtotal	608,111	0
Land	192,000	0
TOTAL INVESTMENT COST	800,111	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	0
Energy	5,900	0
Chemicals	140,000	0
Maintenance	60,811	0
Taxes and insurance	24,003	0
Residual waste disposal	108,000	0
Monitoring, analysis, and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	409,714	0
C. AMORTIZATION OF INVESTMENT COST	98,940	0
TOTAL ANNUAL COST	508,654	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-9. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process	
Production	25,500 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	244,100	0
Equipment	215,000	0
Monitoring equipment	20,000	0
Subtotal	479,100	0
Contractor's O & P ^b	71,865	0
Subtotal	550,965	0
Engineering	110,193	0
Subtotal	661,158	0
Contingencies	66,116	0
Subtotal	727,274	0
Land	276,000	0
TOTAL INVESTMENT COST	1,003,274	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	0
Energy	6,800	0
Chemicals	211,000	0
Maintenance	72,727	0
Taxes and insurance	30,098	0
Residual waste disposal	164,000	0
Monitoring, analysis, and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	555,626	0
C. AMORTIZATION OF INVESTMENT COST	118,327	0
TOTAL ANNUAL COST	673,953	0

^a Represents the incremental cost above that for BPT treatment^b Overhead and Profit

TABLE 14-10. MODEL PLANT TREATMENT COSTS

Subcategory		Titanium dioxide - Chloride process	
Production		45,200 metric tons per year	
		(\$)	
A. INVESTMENT COST		BPT	BAT ^a
Site development		395,000	0
Equipment		275,000	0
Monitoring equipment		20,000	0
Subtotal		690,000	0
Contractor's O & P ^b		103,500	0
Subtotal		793,500	0
Engineering		158,700	0
Subtotal		952,200	0
Contingencies		95,220	0
Subtotal		1,047,420	0
Land		504,000	0
TOTAL INVESTMENT COST		1,551,420	0
B. OPERATION AND MAINTENANCE COST			
Labor and supervision		56,000	0
Energy		86,000	0
Chemicals		374,000	0
Maintenance		104,742	0
Taxes and insurance		46,543	0
Residual waste disposal		294,999	0
Monitoring, analysis, and reporting		15,000	0
TOTAL OPERATION AND MAINTENANCE COST		977,284	0
C. AMORTIZATION OF INVESTMENT COST		170,415	0
TOTAL ANNUAL COST		1,147,699	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-11. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process	
Production	16,900 metric tons per year	
		(\$)
A. INVESTMENT COST		NSPS
Site development	175,600	
Equipment	724,000	
Monitoring equipment	20,000	
Subtotal	919,600	
Contractor's O & P ^a	137,940	
Subtotal	1,057,540	
Engineering	211,508	
Subtotal	1,269,048	
Contingencies	126,905	
Subtotal	1,395,953	
Land	192,000	
TOTAL INVESTMENT COST	1,587,953	
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	140,000	
Energy	11,500	
Chemicals	174,000	
Maintenance	139,595	
Taxes and insurance	47,639	
Residual waste disposal	117,000	
Monitoring, analysis, and reporting	15,000	
TOTAL OPERATION AND MAINTENANCE COST	644,734	
C. AMORTIZATION OF INVESTMENT COST	227,122	
TOTAL ANNUAL COST	871,855	

^a Overhead and Profit

TABLE 14-12. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process	
Production	25,500 metric tons per year	
	(\$)	
A. INVESTMENT COST		NSPS
Site development	244,100	
Equipment	853,000	
Monitoring equipment	20,000	
Subtotal	1,117,100	
Contractor's O & P ^a	167,565	
Subtotal	1,284,665	
Engineering	256,933	
Subtotal	1,541,598	
Contingencies	154,160	
Subtotal	1,695,758	
Land	276,000	
TOTAL INVESTMENT COST	1,971,758	
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	140,000	
Energy	13,500	
Chemicals	262,000	
Maintenance	169,576	
Taxes and insurance	59,153	
Residual waste disposal	175,000	
Monitoring, analysis, and reporting	15,000	
TOTAL OPERATION AND MAINTENANCE COST	834,229	
C. AMORTIZATION OF INVESTMENT COST	275,900	
TOTAL ANNUAL COST	1,110,128	

^a Overhead and Profit

TABLE 14-13. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process	
Production	45,200 metric tons per year	
		($\text{\$}$)
A. INVESTMENT COST		NSPS
Site development	395,000	
Equipment	1,215,000	
Monitoring equipment	20,000	
Subtotal	1,630,000	
Contractor's O & P ^a	244,500	
Subtotal	1,874,500	
Engineering	374,900	
Subtotal	2,249,400	
Contingencies	224,940	
Subtotal	2,474,340	
Land	276,000	
TOTAL INVESTMENT COST	2,750,340	
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	140,000	
Energy	19,000	
Chemicals	469,000	
Maintenance	247,434	
Taxes and insurance	82,510	
Residual waste disposal	314,000	
Monitoring, analysis, and reporting	15,000	
TOTAL OPERATION AND MAINTENANCE COST	1,286,944	
C. AMORTIZATION OF INVESTMENT COST	402,575	
TOTAL ANNUAL COST	1,689,519	

^a Overhead and Profit

of the variability factors for daily maximum and 30-day averages for both plants are given in Tables 14-15 and 14-16.

The concentration of the raw waste and treated effluent along with the percent removal of the pollutants by the treatment system for Plants #559 and #172 sampled in the screening and verification program are given in Table 14-17.

In the chloride process, most iron is in the ferric state and is readily removed by alkaline precipitation. Toxic metal removal is also improved, since ferrite coprecipitation will occur which tends to provide a better effluent quality than alkaline precipitation alone, as observed at Plant #559.

Basis for BPT Effluent Limitations

A. Technology Basis

For BPT, the Agency is basing limitations on equalization, neutralization, and settling or clarification. All plants in this segment of the industry have BPT technology installed.

B. Flow Basis

The flow going to the treatment system at different plants varies and is dependent on the method of disposal of the spent ore and coke (pit solids) and on the finishing operation. The spent ore and coke are either hauled to a landfill as solid residue or sent to the treatment system. For the model plant treatment system, the solid residues from the manufacturing process are assumed to be slurried with water and sent to the treatment system. Plant #559 and #199 do, in fact, send the solid residues to the treatment system. The model plant treatment system is based on an inflow rate of 100 m³/kg of TiO₂ which is an average value of the effluent flow of plants #559 and #199. The treated effluent flow is assumed to be the same as the influent flow. The water added or removed in the treatment system through chemical addition, precipitation, and evaporation have been neglected, as it varies from plant to plant and is dependent on the selection of treatment chemicals as well as climatic conditions and is insignificant in comparison to the total flow.

C. Selection of Pollutants to be Regulated

The selection of pollutants for regulation is based on an evaluation of the waste data from the screening and verification sampling program. The two major factors considered were the individual plants raw waste concentrations and the total subcategory pollutant loadings.

TABLE 14-14. MODEL PLANT UNIT TREATMENT COSTS

Subcategory Titanium dioxide - Chloride process

Annual Treatment Costs (\$/kg)

COST ITEM	PRODUCTION (kg/yr)	LEVEL OF TREATMENT		
		BPT	BAT*	NSPS
Annual Operation and Maintenance	16,900	24.24	NA	38.15
	25,500	21.79	NA	32.71
	45,200	21.62	NA	28.47
Annual Amortization	16,900	5.85	NA	13.44
	25,500	4.64	NA	10.82
	45,200	3.77	NA	8.91
Total Annual Cost	16,900	30.10	NA	51.59
	25,500	26.43	NA	43.53
	45,200	25.39	NA	37.38

*Represents the incremental cost above BPT

TABLE 14-15. HISTORICAL EFFLUENT MONITORING
DATA SUMMARY WITH VARIABILITY FACTOR
TREATMENT WITH IRON REMOVAL
Daily Measurements

Subcategory: Titanium Dioxide

Chloride Process (Rutile Ore)

Plant #559

April 76 through September 78

Statistic	Pollutant						
	TSS	Cadmium	Chromium	Iron	Lead	Nickel	Zinc
<u>Daily Data</u> ⁽¹⁾							
No. of Points	889	109	128	854	128	128	128
Average \bar{x} , ppm	21	0.058	0.072	0.620	0.068	0.080	0.15
Standard Deviation, S	65.9	0.044	0.054	3.46	0.041	0.07	0.20
Standard Deviation, S'	1.54	0.68	0.67	1.86	0.56	0.76	1.02
Variability Factor	11.0	3.85	3.81	13.7	3.2	4.4	6.4
<u>30-day</u> ⁽¹⁾ <u>Averages</u>							
No. of Points	30	26	30	28	30	30	30
Standard Deviation	21.8	0.042	0.038	0.94	0.04	0.05	0.16
Variability Factor	3.04	2.4	2.04	4.0	2.1	4.4	3.1
<u>Variability</u> ⁽²⁾ <u>Factor Ratio</u>							
VFR	3.6	1.6	1.9	3.4	1.5	1.0	2.1

(1) Section 8.2 presents a discussion of the approach and methodology employed in the statistical evaluation of data.

(2) VFR is the ratio of the variability factor for daily measurements to the variability factor for monthly averages.

TABLE 14- 16. HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY
FACTORS
DAILY MEASUREMENTS

SUBCATEGORY: TITANIUM DIOXIDE-Chloride Process -- Plant #172
(Rutile/Upgraded Ilmenite Ore)

Statistic	Pollutant			
	TSS	Chromium	Copper	Zinc
<u>Daily Data</u> ⁽¹⁾				
No. of Points	454	454	454	454
Average \bar{x} , ppm	5.39	0.0080	0.020	0.020
Standard deviation, S	9.13	0.016	0.030	0.027
Standard deviation, S'	1.16	1.27	1.08	1.02
Variability factor	7.6	8.6	6.9	6.4
<u>30-Day Averages</u> ⁽¹⁾				
No. of Points	15	15	15	15
Standard deviation, S	6.31	0.012	0.028	0.026
Variability factor	2.92	3.46	3.29	3.13
<u>Variability Factor Ratio</u> ⁽²⁾				
VFR	2.6	2.5	2.1	2.1

(1) Section 8.2 presents a discussion of the approach and methodology employed in the statistical evaluation of data.

(2) VFR is the ratio of the variability factor for daily measurements to the variability factor for monthly averages.

TABLE 14-17. TREATMENT PERFORMANCE DATA OF SAMPLED PLANTS #559 AND #172

SUBCATEGORY: TITANIUM DIOXIDE-Chloride Process

Pollutant	Plant #559			Plant #172		
	Pollutant Concentration (mg/l)		Percent Removal	Pollutant Concentration (mg/l)		Percent Removal
	Raw Waste	Treated Effluent		Raw Waste	Treated Effluent	
TSS	1103	23	97.9	171	6.7	96.1
Iron	288	4.4	98.5	2.9	0.33	88.6
Chromium	13.3	0.030	99.8	0.72	0.020	97.2
Lead	0.50	0.002	99.6	0.005	0.002	60.0
Nickel	0.50	0.005	99.0	0.08	0.010	87.5
Zinc	0.30	0.060	80.0	0.30	0.090	70.0

1. Raw Waste Concentration

Plant #559 was visited in the screening phase for sampling of the raw and treated wastewater. For each pollutant, the maximum concentration observed gave a preliminary indication of its pollution potential. Five pollutants were found above treatability levels in the raw waste of Plant #559 and they were: chromium, iron, nickel, lead, and zinc (see above). A second plant, #172, was sampled in the verification phase and chromium was the only pollutant found above treatability levels in the raw waste. At Plant #559, the wastewater from the chloride process is mixed with the sulfate process wastewater and the chloride process effluents were sampled at the point of mixing. It is highly probable that the sampled waste included the sulfate process effluent impurities since the sulfate process for the manufacture of TiO_2 uses an ore of lesser purity. In addition, control of chromium should also provide adequate removal of nickel, lead, and zinc which may coincidentally occur at treatable levels. For these reasons, nickel, lead, and zinc will not require effluent limitations. The discussion of wastewater treatment chemistry in Sections 7 and 8 presents the basis for selecting one toxic metal control parameter which effectively ensures the control of the other metals present. The conventional and toxic pollutants of concern include chromium and TSS. Iron, a nonconventional pollutant, is also present as a major impurity in the rutile or upgraded ilmenite ore and was found at treatable levels in Plants #559 and #172.

2. Total Subcategory Raw Waste Pollutant Loading

Chromium was the only toxic pollutant found in significant concentrations in the raw waste of both plants sampled in the screening and verification phase. The average unit raw waste chromium loading (Table 14-7) obtained from the plants sampled was multiplied by the total TiO_2 subcategory production by the chloride process to evaluate the overall magnitude of the pollutant potential for the subcategory. The value of 241,000 kg/year of chromium discharged by the subcategory in the effluent indicated the necessity of control of this pollutant.

The treatment technology practiced by the industry removes the chromium and iron to low levels as seen from the effluent quality of the plants sampled and as shown in Table 14-17.

D. Basis of Pollutant Limitations

1. Conventional and Nonconventional Parameters

a. pH

The treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

- b. TSS Long-term effluent data is available for TSS from Plants #559 and #172. At Plant #172, the solid residues from the manufacturing process are sent to a landfill. Although the amount of solids sent to the treatment system at Plant #559 is high compared with that selected for the model plant (because of intermixing of sulfate waste), the long-term average concentration of 21 mg/l (Table 14-15) calculated from the monitored data submitted by Plant #559 is selected as the treatment performance basis for the subcategory. The variability factors of the daily measurements and monthly averages (11 and 3.04) derived from the long-term data of plant #559 and given in Table 14-15 are used to calculate the concentration basis. The unit effluent limitations are calculated using the model plant unit flow of 100 m³/kkg. The calculations are given below:

The maximum 30-day average concentration is:

$$(21 \text{ mg/l}) (3.04) = 64 \text{ mg/l}$$

The 24-hour maximum concentration is:

$$(21 \text{ mg/l}) (11) = 230 \text{ mg/l}$$

The maximum 30-day average effluent limit is:

$$(64 \text{ mg/l}) (100 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 6.4 \text{ kg/kkg}$$

The 24-hour maximum effluent limit is:

$$(230 \text{ mg/l}) (100 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 23 \text{ kg/kkg}$$

c. Iron

The Agency has decided not to promulgate limitations on iron for existing sources because of the increased cost of treatment when iron is controlled and because two plants operate both the chloride process and the sulfate process and send wastewater from both processes to the same treatment facility. In order for these two plants to treat the chloride process wastewater to remove iron, they would either also have to treat the

sulfate process wastewater to remove iron or undertake a massive reconstruction of the treatment facility. Such a reconstruction or removal of iron in the sulfate process would wipe out the recycle benefits and treatment cost reduction associated with the final BPT/BAT limitations for the sulfate process, and would probably result in the closure of the two sulfate process lines, with attendant increase in unemployment. Control of toxic metal pollutants will be adequate at existing plants even without an iron removal step. We are providing guidance for use by permit writers in cases where control of iron is warranted by water-quality considerations.

The subcategory performance standard of 0.62 mg/l selected for iron is based on the long-term average of the effluent data submitted by Plant #559 (Table 14-15).

For the model plant, it is assumed that iron is present in the ferric state in the raw waste from the chlorination process. Using the variability factor of the daily measurement of 4.0 and the variability factor of the monthly averages of 13.7 estimated from the long-term monitored effluent data of Plant #559 for iron (Table 14-15), and the model plant unit flow of 100 m³/kkg, the concentration basis is determined. The limitations can be developed in the event that iron becomes a concern. The concentrations are developed as follows:

The maximum 30-day average concentration basis is:
 $(0.62 \text{ mg/l}) (4.0) = 2.5 \text{ mg/l}$

The 24-hour maximum concentration basis is:

$(0.62 \text{ mg/l}) (13.7) = 8.5 \text{ mg/l}$

The maximum 30-day average concentration of 2.5 mg/l is higher than the achievable effluent concentration of 1.6 mg/l reported in the literature (10). The latter concentration is based on the performance of lime neutralization followed by settling of acid mine drainage waste, and may not be appropriate for this subcategory.

2. Toxic Pollutants

Chromium is the only regulated toxic pollutant because of its presence at treatable levels in the raw waste of the plants surveyed.

a. Chromium:

The chromium limitation is based primarily on long-term monitoring data available for Plant #559. A waste treatment system influent concentration for chromium of 13.3 mg/l was observed at Plant #559 during screening. The long-term data summarized in Table 14-15 indicates a current treatment performance of 0.070 mg/l and a monthly average and daily measurement variability factor of 2.0 and 3.8, respectively. Review of long-term average treatment data for chromium in Tables 8-12 and 8-13 indicates that 0.070 mg/l shows excellent removal when compared to the same treatment technology for chromium removal in other industries. A long-term average of 0.15 mg/l for chromium is used as the basis for the final limitation. This value is in agreement with the observed performance data from other industries summarized in Tables 8-12 and 8-13. The monthly average and daily measurement variability factors of 2.0 and 3.8, respectively, are representative of BPT treatment performance and are used for the purpose of establishing the limitations.

The 30-day average concentration basis is:

$$(0.15 \text{ mg/l}) (2.0) = 0.30 \text{ mg/l}$$

The daily maximum concentration basis is:

$$(0.15 \text{ mg/l}) (3.8) = 0.57 \text{ mg/l}$$

The 30-day average effluent limit is:

$$(0.30 \text{ mg/l}) (100 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.030 \text{ kg/kg}$$

The daily maximum effluent limit is:

$$(0.57 \text{ mg/l}) (100 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.057 \text{ kg/kg}$$

b. Other metals

Lead, nickel, and zinc were found in the raw waste of Plant #559 in the treatability range. They were not found in the raw waste of Plant #172. The concentration limitations for the three pollutants are given and are intended to serve as guidance in cases where the pollutants are found to be of concern.

The long-term average and corresponding variability factors are based on long-term data from Plant #559 and data presented in Table 8-12 for lead, nickel, and zinc. In all

cases, the long-term average observed for Plant #559 was adjusted after evaluation of treatment performance for other industries summarized in Table 8-12. The long-term averages for lead, nickel, and zinc are 0.15 mg/l, 0.10 mg/l, and 0.20 mg/l, respectively, based on review of the table. Selection of variability factors was made directly from Table 14-15 for the appropriate pollutants. The variability factors corresponding to chromium (the primary pollutant of concern) were selected for nickel.

The concentration basis is determined as follows:

The 24-hour maximum concentration for lead is:

$$(0.15 \text{ mg/l}) (3.2) = 0.48 \text{ mg/l}$$

The maximum 30-day average concentration for lead is:

$$(0.15 \text{ mg/l}) (2.1) = 0.32 \text{ mg/l}$$

The 24-hour maximum concentration for nickel is:

$$(0.10 \text{ mg/l}) (3.8) = 0.38 \text{ mg/l}$$

The maximum 30-day average concentration for nickel is:

$$(0.10 \text{ mg/l}) (2.0) = 0.20 \text{ mg/l}$$

The 24-hour maximum concentration for zinc is:

$$(0.20 \text{ mg/l}) (6.4) = 1.28 \text{ mg/l}$$

The maximum 30-day average concentration for zinc is:

$$(0.20 \text{ mg/l}) (3.1) = 0.62 \text{ mg/l}$$

The limitations for BPT presented in Table 14-18.

Basis for BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned earlier, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT because the only technology option that removes significant amounts of conventional pollutants is not economically achievable. See the discussion of iron under BPT limitations above. Removal of significant additional amounts of conventional pollutants can be achieved in this subcategory only if iron is also removed.

As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated today. Accordingly, there is no need to

TABLE 14-18. EFFLUENT LIMITATIONS
 TITANIUM DIOXIDE - CHLORIDE PROCESS (RUTILE OR UPGRADED ILMENITE ORE)
 Best Practicable Control Technology Currently Available
 Waste Water Flow: 100 m³/kgg of TiO₂

Pollutant	Subcategory Performance (mg/l)	VFR ⁽¹⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kgg of TiO ₂)	
			Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
<u>Conventional and Nonconventional Pollutants:</u>						
Total Suspended Solids	21 ⁽²⁾	11.0/3.0	64	230	6.4	23
Iron	0.62 ⁽²⁾	13.7/4.0	2.5	8.5	— ⁽⁴⁾	— ⁽⁴⁾
<u>Toxic Pollutants:</u>						
Chromium	0.15 ⁽³⁾	3.8/2.0	0.30	0.57	0.030	0.057
Lead	0.15 ⁽³⁾	3.2/2.1	0.32	0.48	— ⁽⁴⁾	— ⁽⁴⁾
Nickel	0.10 ⁽³⁾	3.8/2.0	0.20	0.38	— ⁽⁴⁾	— ⁽⁴⁾
Zinc	0.20 ⁽³⁾	6.4/3.1	0.62	1.28	— ⁽⁴⁾	— ⁽⁴⁾

- (1) VFR: Ratio of the variability factor of the daily measurements to the variability factor of the monthly averages.
- (2) Long term average based on data and variability factors of plant #559 selected from Table 14-15.
- (3) Limitation based on long term data at plant #559 and review of Table 8-12.
- (4) No effluent limitation.

wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Effluent Limitations

The Application of Advanced Level Treatment

The advanced level technologies, viz., the use of sulfide and xanthate as a polishing step to the base level treatment system (BPT), were considered for BAT and NSPS but were rejected on the basis of cost. Level 1, used for BPT, is selected for BAT treatment technology.

A. Technology Basis

Alkaline precipitation followed by settling used for BPT (Level 1) is the same as for BAT.

B. Flow Basis

A unit wastewater flow rate of 100 m³/kgg of TiO₂ used for the BPT model plants has been selected for BAT.

C. Selection of Pollutants to be Regulated

Chromium is the pollutant identified for regulation.

1. Nonconventional Pollutants

The concentration basis was developed for iron which can be used for guidance in the event that iron becomes an environmental concern.

2. Toxic Pollutants

a. Chromium

The limitations for BAT are the same as selected for BPT.

b. Other Metals

Lead, nickel, and zinc are not limited. However, achievable concentration levels are contained in this document for use as guidance if these pollutants are found to be of concern. The values are the same as those selected for BPT.

Table 14-19 gives the limitations for BAT.

TABLE 14-19. EFFLUENT LIMITATIONS
TITANIUM DIOXIDE-CHLORIDE PROCESS (RUTILE/UPGRADED ILMENITE ORE)
Best Available Technology
Wastewater Flow: 100 m³/kgg of TiO₂

Pollutant	Subcategory Performance (1) (mg/l)	VFR(2)	Concentration Basis (mg/l)		Effluent Limit (kg/kgg of TiO ₂)	
			Max.	24-hr.	Max.	24-hr.
			30-day Avg.	Max.	30-day Avg.	Max.
<u>Nonconventional Pollutants:</u>						
Iron	0.62	13.7/4.0	2.5	8.5	--(3)	--(3)
<u>Toxic Pollutants:</u>						
Chromium	0.15	3.8/2.0	0.30	0.57	0.030	0.057
Lead	0.15	3.2/2.1	0.32	0.48	--(3)	--(3)
Nickel	0.10	3.8/2.0	0.20	0.38	--(3)	--(3)
Zinc	0.20	6.4/3.1	0.62	1.28	--(3)	--(3)

(1) See Table 14-17 for details.

(2) VFR: Ratio of the variability factor of the daily measurements to the variability factor of the monthly averages.

(3) No effluent limitation.

Basis for New Source Performance Standards

A. Application of Advanced Level Treatment

The concentration of conventional, nonconventional, and toxic pollutants can be reduced by filtering the clarified effluent from BPT in a dual-media filter.

B. Technology Basis

For new plants, the recommended wastewater treatment technology is lime neutralization and precipitation, settling, and dual-media filtration (equivalent to Level 2). All the existing chloride process plants using rutile/upgraded ilmenite ore currently practice neutralization and settling, but only published treatability data and the results of our treatability study are available on the performance of dual-media filters.

C. Flow Basis

The raw effluent flow rate is the same as that used for BAT, namely 100 m³/kg of TiO₂. It is assumed that the unreacted ore and coke are slurried with water and sent to the treatment system. The selected flow value is an average of the unit effluent flow rate of two plants (#559 and #199) practicing this method of solids disposal.

D. Selection of Pollutants to be Regulated

The pollutants regulated for BPT are also regulated for NSPS in addition to iron. The pollutant parameters of concern are pH, TSS, iron, and chromium. Concentration limits are provided for lead, nickel, and zinc in cases where these pollutants become a concern.

NSPS are based on the addition of an iron removal step to BPT/BAT treatment. New plants can achieve significant reductions in wastewater flow, thus reducing overall treatment costs, even with the inclusion of the iron-removal step. See also the discussion of NSPS for the Sulfate Process in this section.

I. Conventional Parameters

a. pH

For NSPS, the BPT limitation is retained. Control of the final effluent within the range of pH 6.0 to 9.0 is required on the basis of data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS

Since there is no in-plant performance data available on the addition of filtration to the treated wastewater effluent, treatability studies were performed on a chloride process raw wastewater to estimate the effectiveness of dual-media filtration for the removal of the selected pollutants (61). Results of these studies support the use of filters to achieve a 38 percent additional removal for TSS. This reduction is applied to the selected BPT maximum 30-day average of 64 mg/l. The maximum 30-day average concentration basis is then given by: $(64 \text{ mg/l}) (1.00-0.38) = 40 \text{ mg/l}$. Likewise, the 24-hour maximum concentrations and unit effluent limitations are obtained from the BPT limitations (Table 14-18) as shown below.

The maximum 30-day average concentration is:

$$(64 \text{ mg/l})(0.62) = 40 \text{ mg/l}$$

The 24-hour maximum concentration is:

$$(230 \text{ mg/l})(0.62) = 140 \text{ mg/l}$$

The maximum 30-day average effluent limit is:

$$(6.4 \text{ kg/kkg})(0.62) = 4.0 \text{ kg/kkg}$$

The 24-hour maximum effluent limit is:

$$(23 \text{ kg/kkg})(0.62) = 14 \text{ kg/kkg}$$

2. Nonconventional Pollutants

a. Iron

The Treatability Study (61) which tests the effectiveness of dual-media filtration on the removal of iron from the lime treated and clarified wastewater from BPT treatment support a removal efficiency of 38 percent. The concentration basis and effluent limitation for NSPS are obtained by multiplying the selected BAT (or BPT) limitations (Table 14-18) by 0.62 as follows:

The 30-day average concentration basis is:

$$(2.5 \text{ mg/l})(0.62) = 1.6 \text{ mg/l}$$

The 24-hour maximum concentration basis is:

$$(8.5 \text{ mg/l})(0.62) = 5.3 \text{ mg/l}$$

The 30-day average effluent limit is:
 $(0.25 \text{ kg/kg})(0.62) = 0.16 \text{ kg/kg}$

The 24-hour maximum effluent limit is:

$$(0.84 \text{ kg/kg})(0.62) = 0.52 \text{ kg/kg}$$

3. Toxic Pollutants

a. Chromium

Results of the Treatability Study (61) indicate that an additional 60 percent removal of chromium can be achieved using a dual-media filtration polishing step. Therefore, the limitation is developed by application of a 0.60 reduction factor to the BPT/BAT limitation in Table 14-16 as follows:

$$(\text{BPT/BAT limitation})(1.00-0.60) = 0.40 (\text{BPT/BAT limitation})$$

The maximum 30-day concentration basis is:

$$(0.30 \text{ mg/l})(0.40) = 0.12 \text{ mg/l}$$

The daily maximum concentration basis is:

$$(0.57 \text{ mg/l})(0.40) = 0.23 \text{ mg/l}$$

The maximum 30-day average effluent limit is:

$$(0.030 \text{ kg/kg})(0.40) = 0.012 \text{ kg/kg}$$

The maximum daily effluent limit is:

$$(0.57 \text{ kg/kg})(0.40) = 0.23 \text{ kg/kg}$$

b. Other Metals

Treatability studies have indicated that the following increased removals of lead, nickel, and zinc can be achieved by filtration (40,41,61).

Additional Removal by Filtration Using Settled Effluent

Lead	80%
Nickel	14%
Zinc	6%

The additional levels of removal are applied to the corresponding BAT (or BPT) concentration for the above metals to get the NSPS concentrations.

The maximum 30-day average lead concentration basis is:

$$(0.32 \text{ mg/l})(0.20) = 0.064 \text{ mg/l}$$

The 24-hour lead concentration basis is:

$$(0.48 \text{ mg/l})(0.20) = 0.096 \text{ mg/l}$$

The maximum 30-day average nickel concentration basis is:

$$(0.20 \text{ mg/l})(0.86) = 0.17 \text{ mg/l}$$

The maximum 24-hour concentration basis for nickel is:

$$(0.38 \text{ mg/l})(0.86) = 0.33 \text{ mg/l}$$

The maximum 30-day average concentration basis for zinc is:

$$(0.62 \text{ mg/l})(0.94) = 0.58 \text{ mg/l}$$

The 24-hour maximum concentration basis for zinc is:

$$(1.28 \text{ mg/l})(0.94) = 1.20 \text{ mg/l}$$

The conventional, nonconventional, and toxic pollutant limitations for NSPS are given in Table 14-20.

Basis for Pretreatment Standards

Existing Sources

Since there are no indirect dischargers in this subcategory, we are not promulgating PSES but are instead excluding this subcategory from categorical PSES under the provisions of paragraph 8(b) of the Settlement Agreement.

New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is basing limitations on NSPS. The pollutants to be regulated are iron and chromium (See Table 14-20). These pollutants are regulated because NSPS provides better removal of iron and chromium than is achieved by a well-operated POTW with secondary treatment installed and therefore iron and chromium would pass through the POTW in the absence of pretreatment.

Titanium Dioxide - Sulfate Process Industry Profile

TABLE 14-20. EFFLUENT LIMITATIONS
TITANIUM DIOXIDE - CHLORIDE PROCESS
New Source Performance Standards
Waste Water Flow: 100 m³/kkg of TiO₂

Pollutant	Treatability	VFR ⁽¹⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kkg of TiO ₂)	
			Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
<u>Conventional and Nonconventional Pollutants:</u>						
Total Suspended Solids	13	11.0/3.0	40	140	4.0	14
Iron ⁽²⁾	0.38	13.7/4.0	1.6	5.3	0.16	0.52
<u>Toxic Pollutants:</u>						
Chromium ⁽²⁾	0.060 ⁽⁴⁾	3.8/2.0	0.12	0.23	0.012	0.023
Lead	0.030 ⁽⁴⁾	3.2/2.1	0.064	0.096	— ⁽³⁾	— ⁽³⁾
Nickel	0.086 ⁽⁴⁾	3.8/2.0	0.17	0.33	— ⁽³⁾	— ⁽³⁾
Zinc	0.19 ⁽⁴⁾	6.4/3.1	0.58	1.2	— ⁽³⁾	— ⁽³⁾

(1) VFR: Ratio of variability factor of the daily measurements to the variability factor of the monthly averages.

(2) Also applicable for PSNS limitations.

(3) No effluent limitations.

(4) Long term average from Table 14-18 multiplied by the appropriate percent removal factor indicated in Section 14.7.5.

TABLE 14- 21. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	TITANIUM DIOXIDE	SULFATE PROCESS
Total subcategory capacity rate		401,000 kkg/year
Total subcategory production rate		259,000 kkg/year
Number of plants in this subcategory		4
308 Data on file for		5
With total capacity of		320,000 kkg/year
With total production of		246,000 kkg/year
Representing capacity		80 percent
Representing production		95 percent
Plant production range:		
Minimum		31,000 kkg/year
Maximum		74,500 kkg/year
Average production		49,000 kkg/year
Median production		43,000 kkg/year
Average capacity utilization		76 percent
Plant age range:		
Minimum		23 years
Maximum		54 years
Waste water flow range:		
Minimum		35,000 cubic meters/day
Maximum		125,000 cubic meters/day
Volume per unit product		
Minimum		300 cubic meters/kkg
Maximum		780 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

TABLE 14-22. ANALYSIS OF ILMENITE ORES¹

Chemical Constituent	UNITED STATES					CANADA		
	Virginia Piney River	Roseland	New York	Florida	California	Ivry	Bourget	Allard
TiO ₂	44.3	51.4	44.4	64.1	48.2	42.5	22.4	37.3
FeO	35.9	37.9	36.7	4.7	39.1	39.1	36.9	26.3
Fe ₂ O ₃	13.8	1.6	4.4	25.6	10.4	20.7	31.2	30.0
SiO ₂	2.0	4.6	3.2	0.3	1.4	0.88	1.0	NA
Al ₂ O ₃	1.21	0.55	0.19	1.5	0.2	1.05	6.01	NA
P ₂ O ₅	1.01	0.17	0.07	0.21	NA	NA	0.93	0.004
ZrO ₂	0.55	NA	0.006	NA	0.05	NA	NA	NA
MgO	0.07	2.35	0.80	0.35	0.6	2.0	1.50	NA
MnO	0.52	0.70	0.35	1.35	0.1	0.04	NA	0.10
CaO	0.15	0.59	1.0	0.13	0.1	0.1	0.55	NA
V ₂ O ₅	0.16	0.07	0.24	0.13	0.05	0.36	NA	0.39
Cr ₂ O ₃	0.27	NA	0.001	0.1	0.03	0.15	NA	NA

¹Constituents expressed as weight percent.

NA: Not Available

General Description

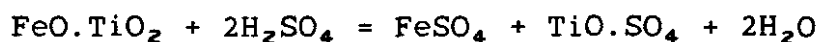
The industrial profile for the Sulfate Process Segment of the Titanium Dioxide Subcategory is presented in Table 14-21 and the status of regulations prior to promulgation of this regulation is shown in Table 14-2

General Process Description and Raw Materials

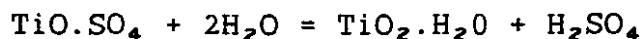
A. Sulfate Process - General Description

Among the various titanium ores, ilmenite is available in abundance. Ilmenite is a low-grade titanium ore with a TiO_2 content varying from 45 to 60 percent. Ilmenite ore and slag from iron production generally comprise the raw materials used for the preparation of titanium dioxide by the sulfate process. Large amounts of water and sulfuric acid are used in this process, and the majority of the plants are co-located with sulfuric acid plants. Table 14-22 gives the analysis of various ilmenite ores. The preparation of TiO_2 by the sulfate process utilizes three important steps:

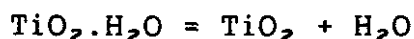
1. Digestion:



2. Precipitation:



3. Calcination:



The ore is dried, ground, and then reacted with sulfuric acid. The reaction takes place at 160° and the reacted mixture consists of titanyl, ferrous, and ferric sulfates. The product is dissolved in water. The total iron in the reacted product is kept in the ferrous state by the addition of scrap iron. After the reduction, the product is dissolved in water and clarified with the aid of flocculating agents to remove insoluble impurities such as silicon, zirconium, and unreacted ore. The iron is removed from the clear solution by cooling the solution to 10°C when hydrated ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) crystallizes. The ferrous sulfate crystals (commercial copperas) are mechanically separated from the solution by filtration or centrifugation. The concentrated titanyl sulfate solution is diluted with water and heated to form titanium dioxide hydrate. The solution is filtered, and the filtrate, known as strong acid, is separated and either discharged or recycled. The $\text{TiO}_2 \cdot \text{H}_2\text{O}$ filter residue is slurried with water and conditioning agents are added to control particle size, color, dispersibility, and photochemical stability. The conditioning agents include potassium, zinc, antimony, and calcium compounds, and phosphate salts. The solution is filtered and the filtrate is known as weak acid. The product is then rinsed to remove

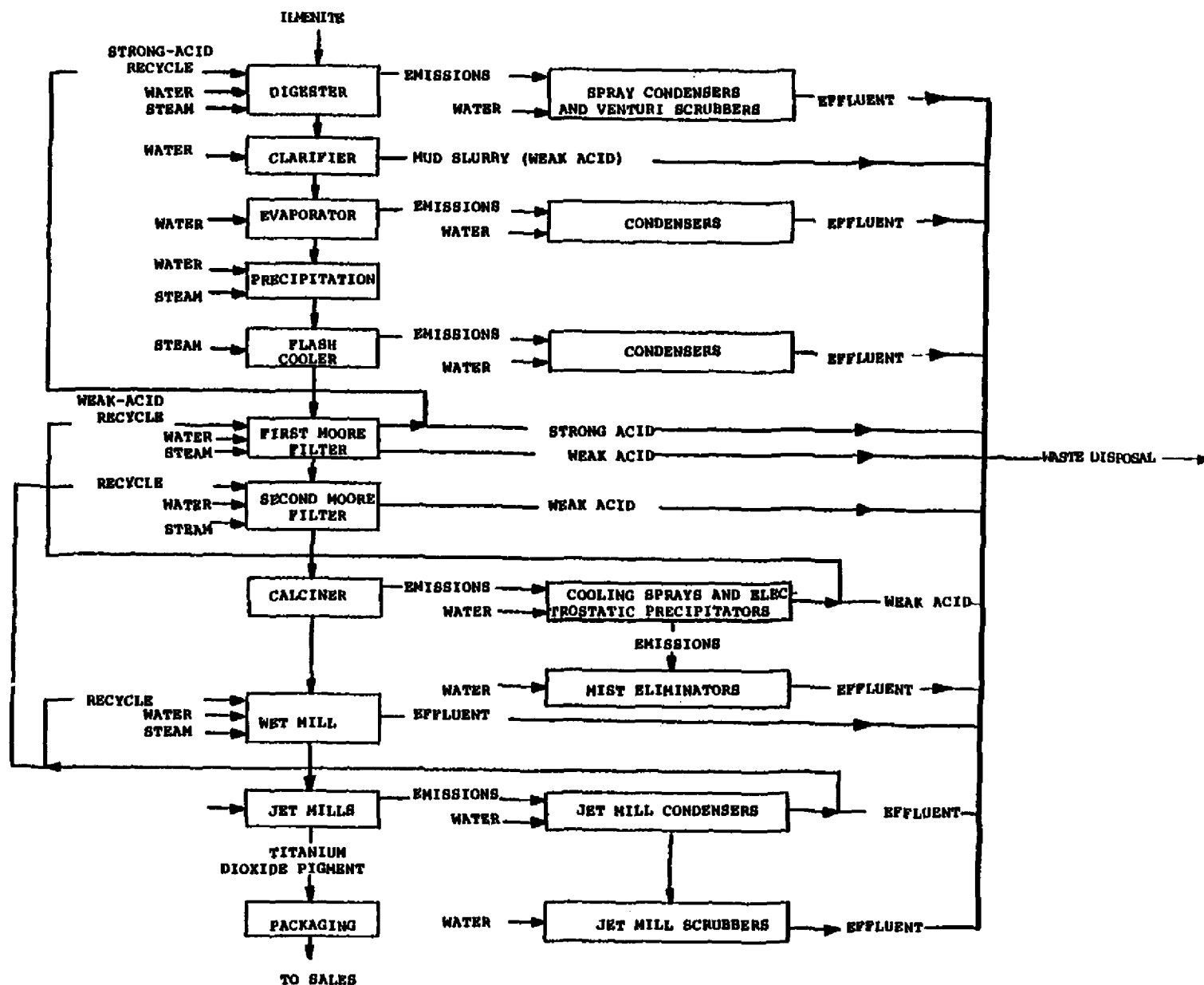


Figure 14-7. General process flow diagram for production of titanium dioxide by sulfate process.

TABLE 14-23. WATER USAGE IN TITANIUM DIOXIDE - SULFATE PROCESS SUBCATEGORY

Uses	Water Usage per Unit of Production (m ³ /kgg of TiO ₂)		
	Plant #555	Plant #694	Plant #696
Noncontact cooling	47.8	408	149
Direct process contact	390	588	297
Indirect process contact (pumps, seals, leaks, spills, etc.)	6	1.6	4
Maintenance, equipment cleaning and work area washdown	3	1.8	4
Air pollution control	258	78	81
Noncontact ancillary uses (boilers, utilities, etc.)	36	33	NA

NA: Not Available

iron and unreacted acid. Residual acids in the precipitate are removed along with the water of hydration by calcination. The resulting TiO_2 pigment is sent to finishing operations, which vary according to the end product requirement and application. The wet finishing operations may include some, or all, of the following steps: pulping, milling, surface treatment with proprietary agents in solution, washing, and drying. The alternative dry finishing operations may include one or more milling steps followed by packaging. A simplified block diagram of the sulfate process is shown in Figure 14-7.

Water Use and Waste Source Characteristics

Water Use

Water is used in the preparation of titanium dioxide by the sulfate process for noncontact cooling, air emission control, and for process reactions. In the process, water is used to leach the soluble sulfate salts from the reaction mass and to convert the titanyl sulfate to titanium dioxide hydrate. Water is also used to wash the titanium dioxide hydrate precipitate free from residual acid and iron. Water is used for air emission control during the drying of ore, on digester units, and for the cleaning of the kiln gases before they are vented to the atmosphere. In the digester unit, water seals are used to maintain a vacuum on the digester units. Large amounts of water are also used in the finishing operations. Table 14-23 is a summary of water usage in the titanium dioxide subcategory using the sulfate process.

Waste Sources

A. Digester Sludge

After the digestion of the ore in sulfuric acid, the resulting sulfates are dissolved in water and the insoluble impurities are removed in a clarifier or filter. These include silica, alumina, sulfuric acid, and unreacted iron. The quality of this waste varies and depends on the type and quality of ore used. Data on the quantity of this waste indicates that approximately 210 kg/kkg is produced.

B. Copperas

The recovered ferrous sulfate is marketed or disposed of as a solid waste. The amount of copperas generated is about 950 kg/kkg of TiO_2 . The copperas generally contains small amounts of adsorbed sulfuric acid.

C. Strong Acid Waste

When water is added to the titanyl sulfate solution after the removal of copperas, sulfuric acid and the hydrate of

titanium dioxide are formed. The acid contained in solution is removed by filtration and the filtrate is known as strong acid solution. The concentration of sulfuric acid varies from 15 to 30 percent as H_2SO_4 . In addition to sulfuric acid, the waste stream contains ferrous sulfate, titania, antimony, and other heavy metal salts. A part of the acid is returned to the process and the rest sent to the treatment facility.

D. Weak Acid Waste Stream

The waste generated from washing the titanium dioxide hydrate precipitate is known as weak acid. The concentration of sulfuric acid in this waste varies from two to four percent as H_2SO_4 and contains various impurities, including iron sulfate, titania, antimony, and other heavy metal salts. It also includes, in some cases, the conditioning agents added to the precipitate prior to washing, to control and improve the quality of the final product. The weak acid may also include the kiln exhaust scrubber waste.

E. Scrubber Wastes

Scrubber wastewater results from the scrubbing of vapors emitted during the drying of the ore, during digestion, and during kiln drying. The amount of wastewater generated depends on the amount of water used and type of emission controls practiced. The scrubber water contains titanium dioxide particulates, acid mist, sulfur trioxide and sulfur dioxide. Of all the waste produced from titanium dioxide-sulfate process manufacture subcategory, the scrubber wastewater constitutes the major portion.

F. Wet Milling Waste

These wastes are generated during wet finishing of the titanium dioxide pigment. Wet milling is used to produce pigment particles of the desired size and surface character and requires steam and water for repulping the pigment. Caustic soda is also used to remove any residual acidity from the titanium dioxide pigment during the finishing operation. The wastewater from wet finishing operation, therefore, contains titania, sodium sulfate, and other agents added to improve or achieve desired properties in the final product.

Description of Plants

Screening

Plant #555 was visited and its waste streams sampled in the screening phase by an EPA Region II team. The pigment manufacturing operation

TABLE 14-24. RAW WASTE CHARACTERISTICS (INDUSTRY DATA) (1) FOR PLANT #555
(PRODUCTION OF TiO_2 BY SULFATE PROCESS)

Waste Source	Unit Flow (m^3/kg of TiO_2)	pH*	Pollutant Waste Loads, (kg/kg of TiO_2)				
			Acidity (as H_2SO_4)	NH_3 (as N)	Fe	TSS	TDS
Digestion	115	3.0	20.8	NA	0.042	9.3	35.7
Clarification	3.58	2.5	26.7	NA	8.42	175	40.8
Evaporation	113	4.0	18.7	NA	1.14	3.2	20.2
Cooling	20	6.1	2.49	NA	0.099	0.46	3.09
Strong Acid from first Moore Filtration	8.49	< 0.5	2.360	NA	139	0.959	2.815
Weak Acid from first Moore Filtration	12.2	2.0	88.3	NA	3.8	0.23	98.8
Weak Acid from second Moore Filtration	10.4	1.7	148	NA	0.29	0.13	151
Weak Acid from first stage Calcination	12.0	2.0	20.8	NA	0.22	2.0	7.50
Weak Acid from second stage Calcination	40.0	2.2	19.2	NA	0.64	4.92	33.1
Calcination Mist Eliminators	38.7	3.0	7.50	NA	0.02	0.21	27.9
Wet Milling Washing and Drying	11.1	8.0	NA	8.6	0.01	2.13	11.0
Jet-Mill Condenser	27.0	6.5	NA	NA	0.01	1.1	2.7
Jet-Mill Scrubbers	18.0	7.4	NA	NA	0.13	1.7	3.58
Boiler and Water Plants	16.6	9.0	NA	NA	0.66	5.25	8.92

NA: Not Available

* Value in pH units

(1) - Response to 308 Questionnaire, 1976

utilizes a titania slag for the production of TiO_2 by the sulfate process. After digestion of the slag in sulfuric acid the residual gangue material is filtered out and the clear liquor is concentrated by evaporation. The crude pigment is formed by hydrolysis with water and steam and processed to form both anatase and rutile type pigment products. Table 14-24 presents raw waste flows and pollutant characteristics for Plant #555.

Wastewater samples were collected at five points and analyzed for the conventional, nonconventional, and toxic pollutants. These sampling points were designated as 1) the contact air scrubbers on the digesters, 2) the black end flume containing wastes from major cuttings, filter sludges, acid filtrates, and evaporator and condenser waters, 3) the white end flume carrying finishing process filtrates, noncontact cooling water, and sanitary wastes, 4) northside jet air scrubbers, and 5) southside jet air scrubbers.

At present, all of the process waste streams are collected in a settling basin which is open to tidal fluctuations that provide diurnal flushing of the effluent into the receiving waters.

Verification

Plant #559 was surveyed in both the screening phase and verification phase of the study. At this plant the strong acid is sent to a lined holding pond for equalization. Effluent from the pond is neutralized with ground calcium carbonate limestone in a reactor. A minimum amount is added to raise the pH to a level such that calcium sulfate, but not ferrous hydroxide, is precipitated. The CO_2 formed during the reaction is vented to the atmosphere and the calcium sulfate slurry goes to a clarifier. The underflow from the clarifier is filtered to produce pure gypsum crystals at a concentration of 70 to 80 percent.

The weak acid is sent to a settling pond, where it is combined with a small quantity of other wastes. The effluent from the weak acid pond is mixed with the calcium sulfate clarifier overflow and neutralized with ground calcium carbonate in a three-stage reactor. Pebble and slaked lime are also added to raise the pH and precipitate more calcium sulfate. Air is also introduced to convert the ferrous iron to ferric iron. The effluent from the reactor goes to another clarifier, and the clarifier underflow is filtered to concentrate the solids to 70 percent. The overflow from the second clarifier is mixed with the other process wastewaters. These include the scrubber, finishing, and cooling wastewaters. The combined water is neutralized with slaked lime before it is sent to a final settling pond, the effluent from which is discharged. Figure 14-8 gives the flow diagram of the treatment process and shows the sampling locations for both screening and verification. Table 14-25 gives the flow data for the waste streams and conventional and nonconventional pollutant emissions.

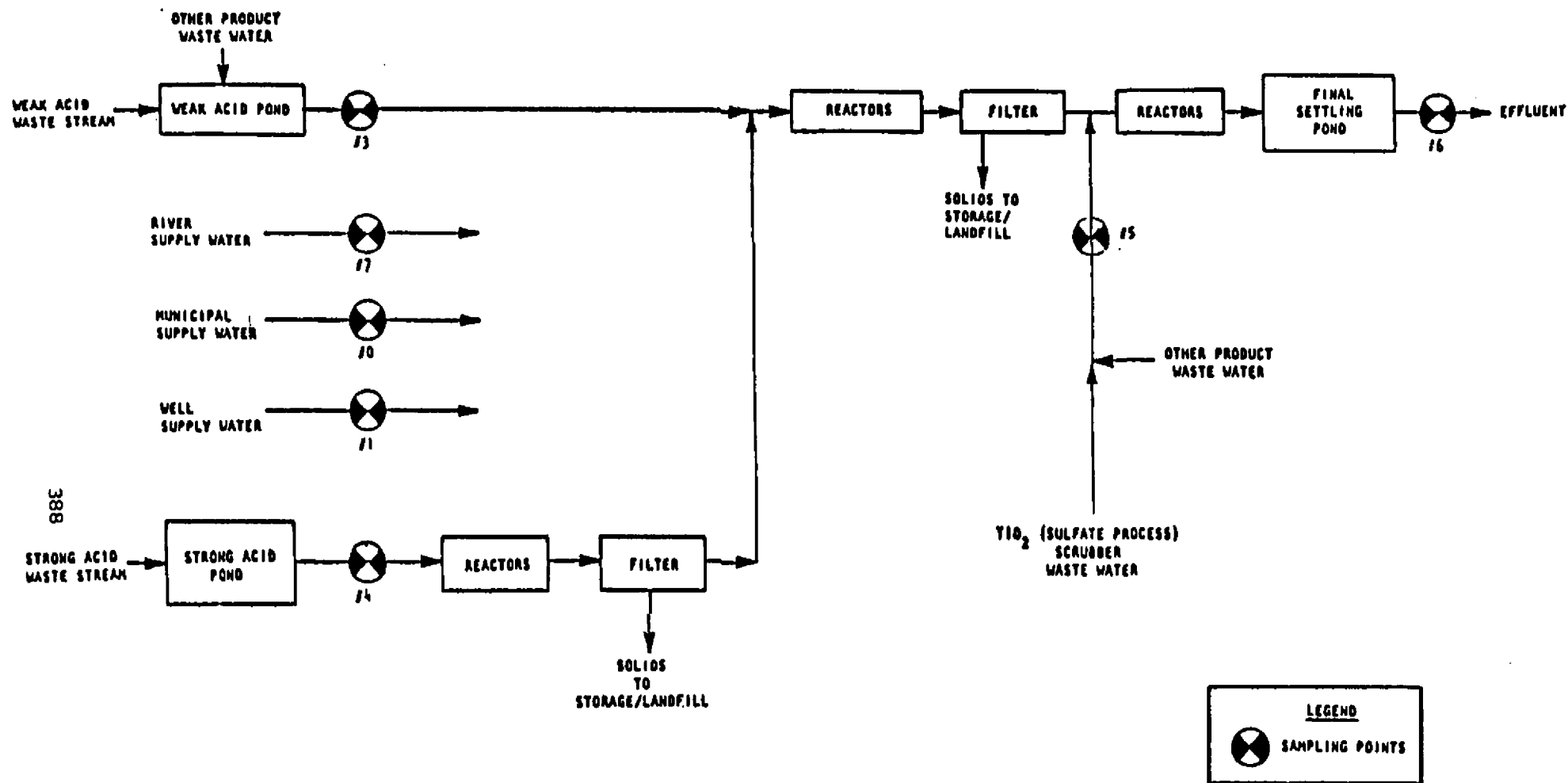


TABLE 14-25. FLOWS AND POLLUTANT CONCENTRATIONS FOR THE WASTE STREAMS
SAMPLED FOR PLANT #559 PRODUCING TITANIUM DIOXIDE

Stream No (4)	Sampled Stream Description	Unit Flow (m ³ /kkg)	TSS Load (kg/kkg of TiO ₂)	Iron Load (kg/kkg of TiO ₂)
3	Weak Acid Pond Overflow	6.8(1)(2)	1.23	1.23
4	Strong Acid Pond Overflow	6.1	205.9	106.3
5	Scrubber and Contact Cooling Water	361.4(1)(2)	113.5	51.68
6	Final Treatment Effluent	436(1)(2)(3)	10.0	1.92

(1) The flow is contributed by the sulfate process stream.

(2) The pollutant load was calculated by multiplying the flow contributed by the sulfate process stream times the concentration of pollutant. Pollutant Load = (total stream flow) x (fraction contributed by sulfate process waste) x stream pollutant concentration.

(3) While calculating the unit flow the contributions to the treatment process from precipitation, the water in the treatment chemicals, losses from evaporation and from solids leaving the process have not been considered.

(4) See Figure 14-8 for sampling point location.

Other Plant Descriptions

At Plant #694, the clarification sludge which contains the unreacted ore is sent to waste disposal. The weak acid effluent from the plant is neutralized with slaked lime and the grit is settled out for landfill disposal. After the separation of grit, the aqueous stream is discharged to a municipal treatment system. The other wastes, together with runoff from the plant site, are collected, and sent to a lagoon for solids removal, and the overflow discharges to a river.

At Plant #696, the raw wastes were sent to thickeners to remove the suspended solids and the overflow was discharged. Depending on the titanium content, the underflow from the thickeners was either recycled or disposed of in a landfill. This plant has discontinued operations.

At Plant #605, the process raw waste streams are combined and sent to a reactor for neutralization with a water slurry of finely ground calcium carbonate. The effluent from the reactor is hydrocycloned into three fractions. The first fraction, which is the coarse gypsum slurry, is separated from the reactor effluent at a concentration of 85 to 90 percent, and placed in a self-draining dewatering system. The "dry" solids are finally trucked to a landfill. The second fraction separated in the hydrocyclone is a fine gypsum slurry which is recycled to the neutralization reactor. The residual gel slurry forms the third fraction, and this is sent to a thickener after CO_2 degassing. A flocculating agent is added to the flow to the thickener to promote solids separation and thickening. The underflow from the thickener is centrifuged and the solids landfilled. The filtrate from the centrifuge is recycled to the thickener, and the thickener overflow is discharged.

The volume and characteristics of wastewater streams from different sulfate process titanium dioxide plants do not differ greatly. Some variations, however, are noted as a result of differences in ore qualities, in location and in process details. The majority of the dissolved pollutants in wastewater from this segment of the TiO_2 industry consist of acidity and iron. Segregation of the wastewater is important for control and treatment practices and aids in developing economically feasible treatment systems. Generally, weak and strong acid streams are segregated from each other as well as from the less contaminated wastewaters which include contact cooling, scrubbing, and some finishing operation wastes. The unit flows for the segregated raw waste streams at different facilities are shown in Table 14-26.

The average total effluent flow rate is $475 \text{ m}^3/\text{kgg}$ (Table 14-16) for Plants #555, #694, and #559. Complete flow data is not available for Plants #696 and #605.

TABLE 14-26. PROCESS WASTE WATER FLOW AT PLANTS # 555, #694 and #559
TITANIUM DIOXIDE (SULFATE PROCESS)

Plant	Flow in (m ³ /kkg of TiO ₂)			
	Strong acid	Weak acid	Scrubber and contact cooling water	Total Effluent
#555	8.5	78.2	362	449
#694	16	67	457	540
#559	6.1	69	361	436
Average	10	72	393	475

Toxic Pollutant Concentrations

Section 5 of this report describes the scope and methodology of the sampling program. In the Sulfate Process segment of the Titanium Dioxide Subcategory, 18 different sampling points were selected for studying the toxic pollutant characteristics of the water supplies, the raw process wastewaters, and the plant effluent at two major manufacturing facilities. For the inorganic constituents 575 analytical data points were generated and an additional 1,824 data points were obtained for the organic toxic pollutants excluding blanks and duplicates for quality control.

The only organic toxic pollutant found during the screening program was phenol which was observed at only one of the two plants sampled. The maximum raw waste concentration of phenol was 0.020 mg/l, however the raw water source for the plant contained as much as 0.0070 mg/l. This is well below the treatability level for phenol, therefore, phenol is not considered a significant or process related pollutant.

Daily raw waste loads were calculated from the flow rates measured or estimated at the time of sampling and the measured pollutant concentrations. That is,

$$\text{daily loading (as kg of pollutant per day)} = \frac{(C)(Q)}{1000}$$

where the concentration (C) of the pollutant is expressed in units of mg/l (Note: 1 kg/m³ = 1000 mg/l), and the flow rate (Q) expressed in units of m³/day (a cubic meter, m³, is equal to 264 U.S. gallons).

Similarly, the unit loadings were calculated from the reported TiO₂ production rate (P), the waste stream flow rate (Q), and the measured pollutant concentration (C).

$$\text{Unit loading (as kg of pollutant per day kkg of TiO}_2\text{)} = \frac{(C)(Q)}{1000(P)}$$

where C and Q are expressed in the same units described above, and the production (P) is expressed in units of kkg/day (kkg is 1000 kg, a metric ton, which is equal to 2205 lb).

The maximum concentration of toxic pollutants found in the raw waste at concentrations above the treatability level in the screening and verification program were:

TABLE 14-27. SUMMARY OF RAW WASTE LOADINGS FOUND IN SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY TITANIUM DIOXIDE - SULFATE PROCESS						
Pollutant	Loading Range, (kg/day)		Unit Loading, (kg/kg)			No. of Plants (1)
	Minimum	Maximum	Minimum	Average	Maximum	
<u>Toxic</u>						
Antimony	5.0	28	0.032	0.11	0.22	3
Arsenic	1.9	4.0	0.012	0.19	0.032	3
Cadmium	.068	7.2	0.00044	0.019	0.057	3
Chromium	140	530	1.1	2.0	3.4	3
Copper	8.2	19	0.065	0.085	0.12	3
Lead	3.0	65	0.024	0.18	0.42	3
Nickel	3.7	23	0.029	0.080	0.15	3
Selenium	7.0	9.5	0.0020	0.031	0.060	2
Thallium	0.47	1.2	0.0030	0.0055	0.0080	2
Zinc	1.8	85	0.014	0.34	0.55	3
<u>Conventional and Nonconventional</u>						
TSS				320		1
Iron, Fe				600		1

(1) - Data are taken only from those plants where pollutants were found above detection limits, or, in the case of TSS and Iron, where data are available.

TABLE 14-28. TOXIC POLLUTANTS: AVERAGE RAW WASTE LOADS AND CONCENTRATIONS

SUBCATEGORY

TITANIUM DIOXIDE - SULFATE PROCESS

	Screening				Verification		Average
	Plant #555		Plant #559		Plant #559		
	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)	
Antimony	0.77	0.22	0.16	0.080	0.074	0.032	0.34
Arsenic	0.11	0.032	0.029	0.014	0.028	0.012	0.06
Cadmium	0.29	0.057	0.0020	0.0009	0.0010	0.00044	0.10
Chromium	3.8	1.1	7.0	3.4	3.1	1.4	4.63
Copper	0.20	0.065	0.25	NA	NA	0.070	0.20
Lead	0.075	0.024	0.20	0.10	0.96	0.42	0.41
Nickel	0.091	0.029	0.31	0.15	0.14	0.061	0.18
Selenium	NA	< 0.06	NA	NA	0.0050	0.0020	0.005
Thallium	NA	NA	0.020	0.0080	0.0070	0.0030	0.014
Zinc	0.088	0.014	1.1	0.55	1.04	0.45	0.74

NA = Not Available

Maximum Concentration Observed ($\mu\text{g/l}$)

<u>Pollutant</u>	<u>Screening</u> <u>(Plants #555 & #559)</u>	<u>Verification</u> <u>(Plant #559)</u>
Cadmium	340	12
Chromium	124,000	31,000
Copper	1,500	1,000
Lead	3,700	5,200
Nickel	6,400	1,300
Zinc	3,800	1,700

A summary of daily and unit (per unit of production) raw waste loads for all plants sampled can be found in Table 14-27. Individual plant raw waste loads and concentrations found in sampling are given in Table 14-28.

Based on the total annual production of this industry and the average waste load generated per unit product, the estimated total toxic pollutant raw waste loads generated each year for this subcategory are as follows:

<u>Pollutant</u>	<u>Total Annual Raw</u> <u>Waste Load (Kg/year)</u>
Cadmium	5,000
Chromium	510,000
Copper	22,000
Lead	47,000
Nickel	21,000
Zinc	88,000
Antimony	29,000
Arsenic	49,000
Selenium	8,000
Thallium	1,400

Pollution Abatement Options

Toxic Pollutants of Concern

The toxic pollutants found above treatability levels in this industry were evaluated on the basis of the maximum concentration observed in the process raw wastewaters. These values are shown above. Using cadmium as an example of a borderline case, its maximum observed concentration of 0.34 mg/l (340 $\mu\text{g/l}$) is considered significant because removal efficiencies ranging from 70 to 97 percent could possibly be achieved on the basis of the lower limits of treatability shown in Table 8-11 for lime/settling, lime/filter, and sulfide/filter technologies. The BAT ultimately selected as a basis for regulations may not be as effective as the most advanced technology considered at this stage of the evaluation of alternatives.

The sampling data from this industry indicate that the toxic pollutants of concern are chromium, zinc, nickel, lead, copper, antimony, arsenic, and cadmium in decreasing order of the maximum amounts found. Selenium and thallium were detected at levels too low to be treated effectively. The relative pollutant concentrations and loadings in the raw waste largely reflect the amounts of impurities in the ilmenite ore or titania slag being processed. The major impurity found in the various grades of raw material is ferrous iron as indicated in Table 14-22. The toxic metal impurities would also be expected to occur in a wide range of concentrations in the raw materials.

The advanced treatment technology options evaluated for the sulfate process segment of the industry were selected for their ability to remove toxic metals of concern with greater efficiency than the prevailing (BPT) practice which also removes TSS, iron, and sulfate from the wastewaters.

Process Modifications and Technology Transfer Options

Specific process modification recommendations are not made. However, several areas for further investigation suggest themselves. They are:

- A. One of the water borne wastes, the strong sulfuric acid produced from the TiO_2 sulfate process, has a sulfuric acid concentration that varies from 15 to 30 percent as H_2SO_4 . Currently, only a small portion of it is recycled. Research is needed to find cost-effective ways to concentrate the acid to 90 percent and to eliminate the impurities (especially iron) so that it can be reused in the digester. This will eliminate much of the alkali requirements for neutralization and relieve disposal problems associated with solid waste gypsum.
- B. Economical methods need to be developed for the recovery of iron oxide, aluminum, and vanadium from the waste to the extent that markets are available for these materials.
- C. If markets could be developed for the sale of ferrous sulfate (copperas), solid waste disposal problems would be reduced. Currently, a portion is sold and the rest disposed of as a solid waste.

Best Management Practices

Storm water runoff from the plant site should be collected and sent to the treatment facility for the removal of suspended solids.

Prevailing Control and Treatment Practices

The treatment practices of the plants producing TiO_2 by the sulfate process are given above.

Advanced Treatment Technologies

Although sulfide precipitation, the xanthate process, and ion-exchange might be applied to the clarified solution obtained by alkaline precipitation, oxidation and settling the costs incurred are high because of the large quantity of water (more than 400 m³/kg of TiO₂) that must be treated. The sulfate process is one of two subcategories (the other being the Soda Ash Solvay Process) in the Inorganic Chemicals Industry studied in this report that generates the largest quantities of waste effluent.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT/BAT)

In the Level 1 treatment, the strong and weak acid streams are independently equalized in lined lagoons and neutralized in a reactor with ground limestone to a pH range of 5 to 5.5, precipitating calcium sulfate and forming carbon dioxide, which remains in solution, along with large quantities of ferrous iron. Solids are generated in a thickener at the unit rate of 3 kkg per kkg of products. The thickener overflow joins the large but relatively unpolluted flow of "other wastes", and the combined wastewaters are treated to pH 6 to 9 and passed through a polishing lagoon prior to discharge. Level 1 treatment allows recovery of gypsum solids without contamination by iron and toxic metal pollutants. The flow schematic for Level 1 is presented in Figure 14-9a.

B. Level 2 (NSPS)

In the Level 2 treatment, the blended strong and weak acid streams are neutralized with calcium carbonate. Most of the toxic metal pollutants are precipitated and separated along with gypsum in first stage thickeners. Aeration then oxidizes any ferrous iron present and removes CO₂ before mixing with miscellaneous plant waste containing minor amounts of toxic metal pollutants. The combined stream is then given lime treatment to pH 9 and settled in polishing lagoons before discharge. This three-step system is patterned after an existing system which separates the acid streams from miscellaneous wastes in order to make possible the recovery of pure and impure gypsum from the relatively consistent acid streams. Alkaline precipitation of more toxic metals and significant removal of arsenic occur during the last two stages of lime neutralization, and settling of precipitated toxic pollutants occurs in the final polishing lagoons. Because waste flow rates are unusually high in the sulfate process, long-term lagoon settling is more cost effective than dual-media filtration. The mechanical aeration step used for oxidizing ferrous iron may contribute an important mechanism for the simultaneous removal of additional heavy metals present, very similar to the ferrite coprecipitation method described in the Treatment Technology

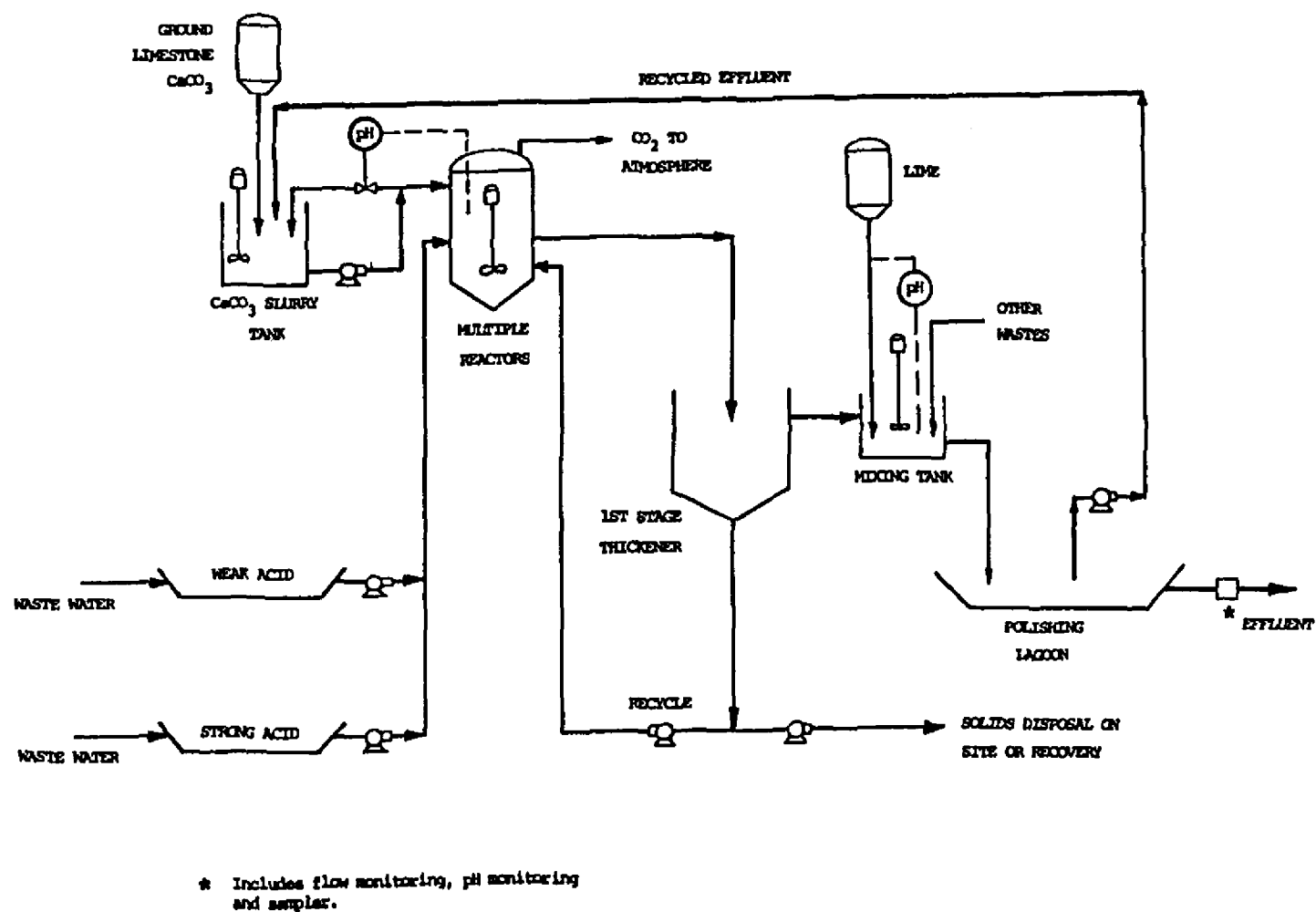
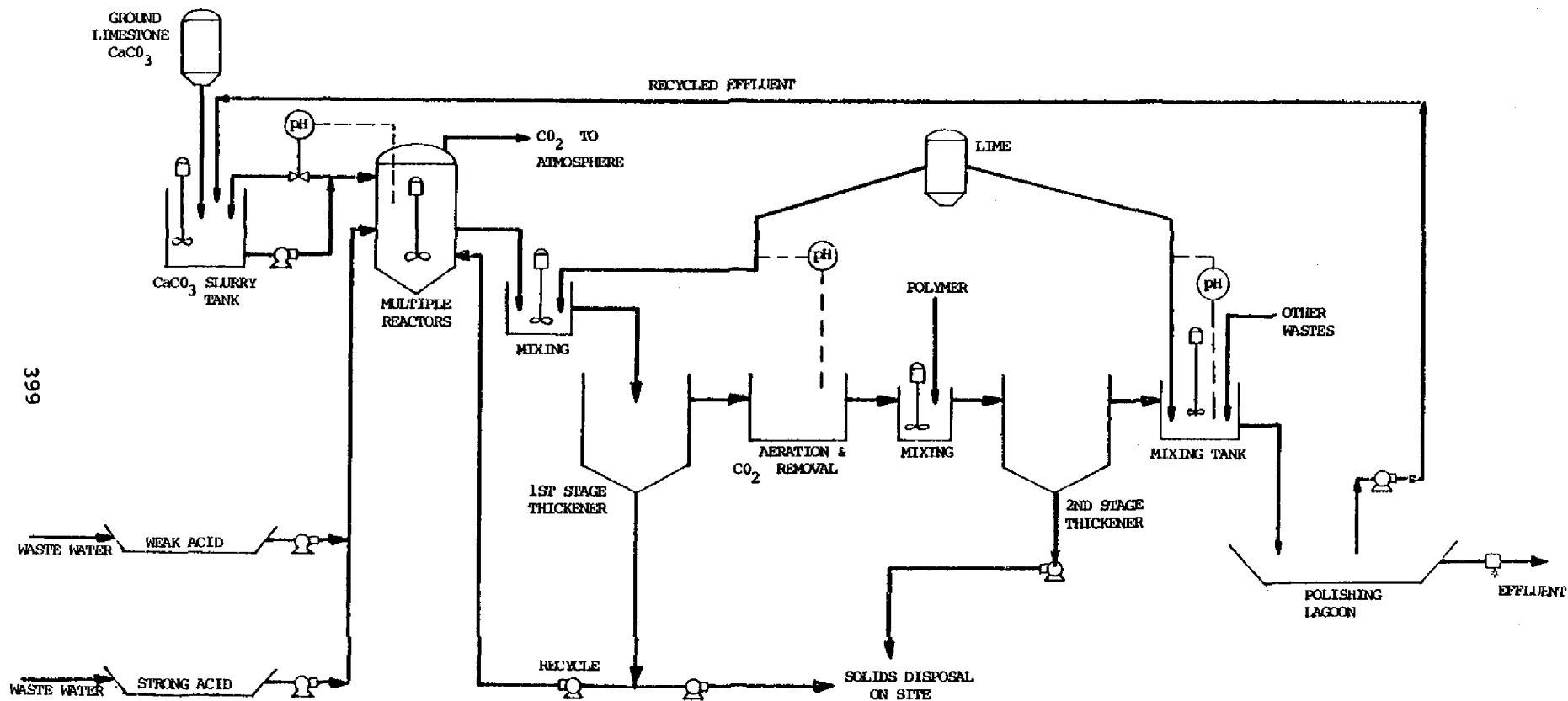


Figure 14-9a. Level 1 waste water treatment for titanium dioxide - sulfate process.



* Includes flow monitoring, pH monitoring and sampler

Figure 14-9b. Level 2 waste water treatment for titanium dioxide - sulfate process.

Assessment section. The flow diagram of the treatment system is shown in Figure 14-9b.

Although the Model Plant does not include equipment for gypsum recovery, it is based on separation of waste streams, making pure or impure gypsum recovery possible by intercepting thickener underflow(s).

C. Level 3

Level 3 for the sulfate process employs the described NSPS treatment for strong acid, weak acid, and 55 percent of the "other wastes". The remaining other wastes receive soda ash treatment and settling, to permit recycling a nonscaling effluent for scrubbers and miscellaneous uses. Toxic metal pollutants in the separated recycle stream are settled as hydroxides or carbonates, plus any calcium arsenate formed, and periodically removed to secure landfill. The flow diagram of this treatment is shown in Figure 14-10.

Equipment for Different Treatment Levels

A. Equipment Functions

Treatment of wastewater from the sulfate process involves the mechanized handling of large quantities of chemicals and reaction products, primarily gypsum.

The BPT model includes rail car deliveries of ground limestone and lime, bucket elevators, storage bins, multiple feeders, mechanical feeders and one stage thickening to recover gypsum. Calcium saturated thickener overflow and miscellaneous other wastes are subjected to pH adjustment and one-day settling in a polishing pond prior to discharge.

In Level 2 or NSPS, wastewater treatment requires the use of mechanical aerators, lime addition, and second stage thickening equipment in addition to equipment specified for BPT treatment to remove additional toxic metals and iron.

In Level 3, to reduce the raw waste load of toxic metals, only 55 percent of the NSPS "other waste" flow joins the treated acid waste stream, for Level 2 treatment as described above. However, the remaining 45 percent of "other waste" is given separate treatment with soda ash and settled in a lagoon, for recycle to miscellaneous scrubber and noncontact cooling purposes. Treatment of the strong and weak acid streams, including oxidation and settling of ferrous iron, remains the same as in the NSPS model.

B. Chemicals and Handling

First stage neutralization employs ground limestone, while lime is used in cases where second stage and final alkaline

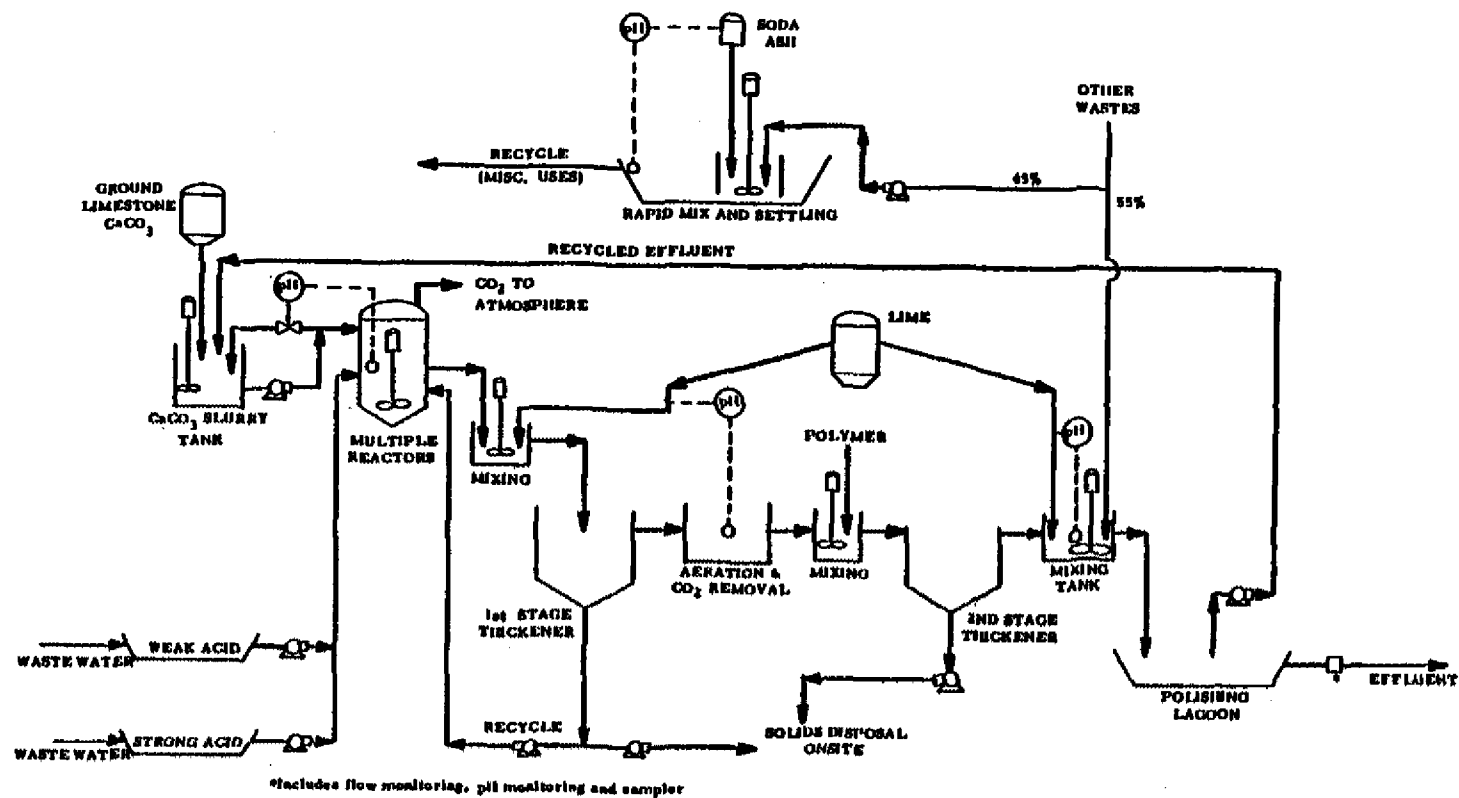


Figure 14-10. Level 3 waste water treatment for titanium dioxide - sulfate process.

precipitation are employed. Oxygen is supplied from atmospheric air, and polymer is added to assist in the second stage settling of iron hydroxide when required. Aside from the bulk handling of large amounts of these common chemicals, there are no special hazards involved in their use.

C. Separation and Removal of Solids

Large quantities of thickener underflow are pumped to spreading areas for consolidation of the solids, which are later pushed to 18 foot high piles on land provided for 10 years of operation. Solids from occasional draining of the polishing lagoon and the Level 3 recycling lagoon are returned to the aeration step of the waste acid streams, after which they will be settled out in the second stage thickener, being handled as part of the thickener underflow. Although no dewatering equipment is provided, the first and second stage thickeners are sources of pure and impure gypsum for future byproduct recovery.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed. For conceptual design a representative unit waste flow was selected, together with three different TiO_2 production rates. The latter were chosen to cover most of the rates typical for the TiO_2 (Sulfate Process) subcategory. The selected daily TiO_2 production for the model plant was multiplied by the selected unit flow to obtain the volume of influent to the treatment system. The selected unit raw waste pollutant loads were also multiplied by the model plant production rate to determine the pollutant load on the treatment system. Capital and equipment costs were then calculated based on developed conceptual design parameters for each model plant production rate. The rationale used for the model plant selection is given below.

A. Wastewater Flow

Waste effluent data is available for three plants and is given in Table 14-26. For the model the average value of the three plants data has been used. The unit flow data for strong acid ranges from 6.1 to 15 m^3/kg of TiO_2 . (Table 14-26). For the model plant the average value of 10 m^3/kg has been used. Unit flows for the weak acid stream range from 67 to 78 m^3/kg . For the model plant, a unit flow of 72 m^3/kg of TiO_2 is used. The third segregated stream includes contact cooling water, scrubber water, and finishing operation wastewater. The unit flow for this stream varies from plant to plant and depends largely on the type and quality of the TiO_2 pigment end product desired. For model plants a total flow which consists of strong acid, weak acid, scrubber effluents, and product finishing wastewaters of 475 m^3/kg of TiO_2 was used.

B. Production

Four plants produce titanium dioxide by the sulfate process at a total production rate of 259,000 metric tons per year. Production ranges from a minimum of 31,000 kkg/yr to a maximum of 74,500 kkg/yr with an average of 49,000 kkg/yr and a median of 43,000 kkg/yr. For treatment cost estimates, three production levels were selected. These were 31,800 kkg/yr, 47,700 kg/yr, and 74,500 kkg/yr.

C. Wastewater Pollutant Load

As stated before, the principal pollutants occur in the strong and weak acid streams and include high acidity (sulfuric acid), suspended solids, iron and other heavy metal sulfates. The other wastewaters contain titanium dioxide and small amounts of other heavy metals on suspended solids. Iron concentrations vary depending on the grade of ilmenite ore used.

Model Plant Control and Treatment Costs

The average raw waste pollutant loadings given in Table 14-27 were used for the model plant. For the model plants, a total iron loading of 600 kg/kkg was used with the assumption that two-thirds was spent ferric hydroxide and one-third (200 kg/kkg of TiO_2) was soluble ferrous iron. The unit sulfate and suspended solid loadings for the different wastewater streams for the model plant were:

Stream	Sulfate Loading (kg/kkg of TiO_2)	TSS Loading (kg/kkg of TiO_2)
Weak Acid	2,300	300
Strong Acid	1,800	200
Other Wastewater	Negligible	113

E. Chemical Usage

In the model BPT system, powdered limestone is used for first stage neutralization of mixed strong and weak acids, at the unit rate of 3,000 kg/kkg of TiO_2 . For iron removal (NSPS), pebble lime (CaO) is used for second stage neutralization of the mixed acid streams and for the final neutralization of the total combined flow, including the other miscellaneous wastes. The unit application of CaO for all purposes is 0.235 kg/kkg of TiO_2 .

F. Solids Produced

Existing plants have attempted to produce two grades of saleable gypsum from the strong and weak acid streams. At present, one plant has successfully identified a market that will partly offset the cost of solids handling and disposal. The plant currently employs BPT treatment which generates gypsum solids of sufficient purity to be sold. NSPS treatment generates iron oxide laden gypsum which is, at

present, unsuitable for sale. The total solids produced in the model plant are assumed to be 5,200 kg/kg of TiO_2 for BPT and 5,500 kg/kg of TiO_2 for NSPS.

Treatment Costs

The estimated costs for three models having different production levels are given in Tables 14-29, 14-30, and 14-31. The costs represent the total cost required for treatment system implementation and assume that the plant has no treatment system in place.

Table 14-32 presents a summary of the unit cost distribution between amortization and operation and maintenance cost components at different production levels and at the BPT and NSPS levels of treatment.

For existing sources at the first level of treatment, the costs reflect disposal of sludge on-site, hence land requirements are fairly large. However, this cost can be offset by a revenue on the sale of gypsum, currently practiced at one plant. These off-setting revenues are not included in the costs presented in Tables 14-29, 14-30, 14-31, and 14-32. These off-setting revenues are included in the Economic Impact Analysis of Pollution Control Technologies for Segments of the Inorganic Chemicals Manufacturing Industry, EPA 440/2-81-023. Amortization, chemicals, labor, and residual waste disposal costs have significant impact on the annual costs.

The total annual costs presented in Table 14-32 would increase by 20 to 40 percent if the sludge dewatering equipment is to be installed for gypsum recovery.

Basis For Regulations

Evaluation of BPT Practices

Out of a total of four TiO_2 plants (sulfate process) that are currently in operation, only one plant (#559) has a BPT treatment system. The other three plants practice partial neutralization and settling. The BPT limitations are based on available long-term data from Plant #559 and treatment performance information in Section 8.

A. Pollutant Removal with BPT Treatment

Treatment Level 1 is equivalent to the BPT in the Titanium Dioxide (Sulfate Process) industry. Means, standard deviations, and variability factors were calculated from data submitted by Plant #559 for final effluent quality, and the results are given in Tables 14-33a and 14-33b. The performance characteristics are utilized for the development of the BPT regulations.

The ability of the treatment system to remove conventional and toxic pollutants was estimated by comparing the treated effluent

TABLE 14-29. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Sulfate process		
Production	31,800 metric tons per year		
A. INVESTMENT COST	BPT	BAT ^a	NSPS
Site development	232,500	0	316,500
Equipment	958,600	0	2,551,000
Monitoring equipment	7,800	0	20,000
Subtotal..... ^b	1,198,900	0	2,887,500
Contractor's O & P.....	179,835	0	433,125
Subtotal	1,378,735	0	3,320,625
Engineering	275,800	0	664,125
Subtotal	1,654,535	0	3,984,750
Contingencies	275,800	0	398,475
Subtotal	1,930,335	0	4,383,225
Land	636,000	0	1,372,000
TOTAL INVESTMENT COST....	2,566,335	0	5,755,225
B. OPERATION AND MAINTENANCE COST			
Labor and supervision....	252,000	0	504,000
Energy.....	34,000	0	96,000
Chemicals.....	1,760,000	0	1,589,000
Maintenance	193,032	0	438,323
Taxes and insurance.....	76,989	0	172,657
Residual waste disposal..	141,000	0	210,000
Monitoring, analysis, and reporting.....	15,000	0	15,000
TOTAL OPERATION AND MAINTENANCE COST.....	2,472,021	0	3,024,979
C. AMORTIZATION OF INVESTMENT COST	314,063	0	713,151
TOTAL ANNUAL COST.....	2,786,084	0	3,738,130

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-30. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Sulfate process		
Production	47,700 metric tons per year		
A. INVESTMENT COST	BPT	BAT ^a	NSPS
Site development	316,200	0	439,000
Equipment	1,213,200	0	3,288,500
Monitoring equipment	7,800	0	20,000
Subtotal..... ^b	1,537,200	0	3,747,500
Contractor's O & P.....	230,580	0	562,125
Subtotal	1,767,780	0	4,309,625
Engineering	353,560	0	861,925
Subtotal	2,121,340	0	5,171,550
Contingencies	353,560	0	517,155
Subtotal	2,474,900	0	5,688,705
Land	960,000	0	1,920,000
TOTAL INVESTMENT COST....	3,434,900	0	7,608,705
B. OPERATION AND MAINTENANCE COST			
Labor and supervision....	336,000	0	672,000
Energy.....	51,000	0	138,000
Chemicals.....	2,640,000	0	2,384,000
Maintenance	247,492	0	568,871
Taxes and insurance.....	103,047	0	228,261
Residual waste disposal..	209,000	0	315,000
Monitoring, analysis, and reporting.....	15,000	0	15,000
TOTAL OPERATION AND MAINTENANCE COST.....	3,601,539	0	4,321,132
C. AMORTIZATION OF INVESTMENT COST	402,669	0	925,552
TOTAL ANNUAL COST.....	4,004,208	0	5,246,684

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-31. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Sulfate process		
Production	74,500 metric tons per year		
A. INVESTMENT COST	BPT	BAT ^a	NSPS
Site development	418,300	0	631,000
Equipment	1,622,700	0	4,352,000
Monitoring equipment	7,800	0	20,000
Subtotal..... ^b	2,048,800	0	5,003,000
Contractor's O & P.....	307,320	0	750,450
Subtotal	2,356,120	0	5,753,450
Engineering	471,200	0	1,150,690
Subtotal	2,827,320	0	6,904,140
Contingencies	471,200	0	690,414
Subtotal	3,298,520	0	7,594,554
Land	1,470,000	0	2,940,000
TOTAL INVESTMENT COST....	4,768,520	0	10,534,554
B. OPERATION AND MAINTENANCE COST			
Labor and supervision....	336,000	0	672,000
Energy.....	71,000	0	199,000
Chemicals.....	4,100,000	0	3,719,000
Maintenance	329,854	0	759,455
Taxes and insurance.....	143,056	0	316,037
Residual waste disposal..	283,000	0	420,000
Monitoring, analysis, and reporting.....	15,000	0	15,000
TOTAL OPERATION AND MAINTENANCE COST.....	5,277,910	0	6,100,492
C. AMORTIZATION OF INVESTMENT COST	536,672	0	1,235,634
TOTAL ANNUAL COST.....	5,814,582	0	7,336,126

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-32 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Titanium dioxide - Sulfate process

COST ITEM	PRODUCTION (kg/yr)	Annual Treatment Costs (\$/kg)		
		LEVEL OF TREATMENT		
		BPT	BAT*	NSPS
Annual Operation and Maintenance	31,800	77.74	NA	95.13
	47,700	75.50	NA	90.59
	74,500	70.84	NA	81.89
Annual Amortization	31,800	9.88	NA	22.43
	47,700	8.44	NA	19.40
	74,500	7.20	NA	16.59
Total Annual Cost	31,800	87.61	NA	117.55
	47,700	83.95	NA	109.99
	74,500	78.05	NA	98.47

*Represents the incremental cost above BPT

qualities with the raw waste qualities of the sampled waste streams.

Basis for BPT Effluent Limitations

A. Technology Basis

For BPT, the Agency is basing limitations on equalization, limestone neutralization and clarification, followed by pH adjustment before final polish and discharge of the effluent. This technology is chosen because it has been installed and operated successfully by a plant in the industry.

B. Flow Basis

Waste flow data is available for three plants and the average value of 475 m³/kkg of TiO₂ (Table 14-26) is taken as the inflow for the model plant treatment system. The treatment plant effluent flow is taken to be the same as the influent flow and the loss or addition of water through chemicals, evaporation, precipitation, and through solids removal have been neglected.

C. Selection of Pollutants to be Regulated

Selection of pollutants for limitation was based on a number of criteria including raw waste pollutant concentrations during sampling, total subcategory raw waste pollutant loading, and experience related to the control of pollutant removal by alkaline treatment technology presented in Section 8. The Agency decided not to regulate the nonconventional pollutant iron under BPT and BAT because of increased cost of the treatment when iron is controlled and because the gypsum solids produced by the treatment with iron removal can be reused only if dissolved iron is not controlled. One plant has developed a market for reuse of the gypsum. The Agency estimates that requiring iron removal at existing plants would increase treatment costs by up to 40 percent and generate large quantities of waste solids for disposal. Based on our economic impact analysis (63), the Agency believes that two of the four existing TiO₂ sulfate process plants would close, with the attendant increase in unemployment, if the plants were required to control iron. Control of toxic metal pollutants will be adequate at existing plants even without an iron removal step.

Review of Tables 14-27, 14-28, and 14-34 indicates that six pollutants were consistently identified at treatable concentrations. Total suspended solids, iron, chromium, lead, nickel, and zinc were all identified at treatable levels on the average during sampling.

The toxic pollutants can be divided into two groups exhibiting similar behavior depending on the treatment pH. Review of alkaline treatment in Section 8 shows that chromium, lead, and

TABLE 14-33a. HISTORICAL EFFLUENT MONITORING DATA SUMMARY
 SUBCATEGORY - TITANIUM DIOXIDE
 SULFATE PROCESS PLANT #559 - TREATMENT WITHOUT
 IRON REMOVAL ⁽¹⁾

Parameter ⁽²⁾	Pollutant (mg/l)				
	TSS	Iron	Chromium	Nickel	Zinc
<u>Daily Data</u>					
No. of Points	30 ⁽³⁾	84	81	82	54
Average, \bar{x}	50	330	0.23	0.14	0.50
Standard Deviation, S	59	73	0.20	0.12	0.60
Standard Deviation, S' (of logs)	0.95	0.20	0.75	0.74	0.95
Variability Factor	5.8	1.5	4.4	4.3	5.8
<u>Monthly Averages</u>					
No. of Points	20	20	20	20	13
Standard Deviation, S _m	44	42	0.11	0.099	0.21
Variability Factor	1.6	1.2	1.9	2.1	1.7
Variability Factor Ratio	3.6	1.3	2.3	2.0	3.4

- (1) Lead and cadmium concentrations were less than 0.10 mg/l for the 20 months.
- (2) Refer to Table 14-33b for explanation of statistical parameters.
- (3) Based on one month of data for April 1981.

TABLE 14-33b. HISTORICAL EFFLUENT MONITORING DATA SUMMARY
SUBCATEGORY - TITANIUM DIOXIDE
SULFATE PROCESS PLANT #559 - TREATMENT WITH IRON REMOVAL

	Pollutant						
	TSS	Cadmium	Chromium	Iron	Lead	Nickel	Zinc
<u>Daily Data</u>							
No. of Points	299	109	128	854	128	128	128
Average, \bar{x}	21.0	0.060	0.070	0.62	0.068	0.08	0.151
Standard Deviation, $S^{(1)}$	65.93	0.044	0.054	3.46	0.041	0.071	0.204
Standard Deviation, $S^{(2)}$	1.54	0.68	0.67	1.86	0.56	0.76	1.02
Variability ⁽³⁾ Factor	11.0	3.85	3.81	13.65	3.16	4.39	6.41
<u>Monthly Averages</u>							
No. of Points	30	26	30	28	30	30	30
Standard ⁽¹⁾ Deviation	21.84	0.042	0.038	0.94	0.04	0.048	0.16
Variability ⁽⁴⁾ Factor	3.04	2.43	2.04	4.00	2.14	4.39	3.05
Variability Factor Ratio							
VFR ⁽⁵⁾	3.62	1.58	1.87	3.38	1.48	1.00	2.10

- (1) S is the arithmetic standard deviation and is given by

$$S = \sqrt{\frac{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}{n-1}}$$

where x_i is the data value for point i

\bar{x} is the mean value

n is the number of data points

- (2) S' is the estimated standard deviation of the logarithms

$$S' = \sqrt{\ln\left(1 + \left(\frac{S}{\bar{x}}\right)^2\right)}$$

where S is the arithmetic standard deviation

\bar{x} is the mean value

- (3) The variability factor (VF) of daily measurements for lognormal distribution is found by the expression

$$\ln(VF) = S' (2 - 0.5 S')$$

where S' is defined in Note 2 above.

$$z = 2.33 \text{ for 99th percentile}$$

- (4) The variability factor (VF) for 30-day average measurements is found by the expression

$$VF = 1.0 + z \left(\frac{S_m}{\bar{x}_m} \right)$$

where \bar{x}_m is the mean value of the monthly averages

S_m is the arithmetic standard deviation of the monthly averages

$$z = 1.64 \text{ for 95th percentile}$$

- (5) VFR: Ratio of the 24-hour variability factor to the 30-day variability factor

TABLE 14-34. VERIFICATION RESULTS FROM - SULFATE PROCESS
TITANIUM DIOXIDE PLANT #559

Pollutant	Waste Stream				
	Raw Waste		Treated Effluent		Removal Efficiency (%)
	Unit Load	Concentration	Unit Load	Concentration	
	(kg/kg)	(mg/l)	(kg/kg)	(mg/l)	
Total Suspended Solids	116	266	10.0	23	91
Iron	364	835	1.92	4.4	99
Cadmium	0.00045	0.0010	0.000040	0.00010	90
Chromium	1.3	3.1	0.011	0.025	99
Copper	0.070	0.16	0.002	0.0050	97
Lead	0.040	0.96	0.00090	0.0020	99
Nickel	0.060	0.14	0.0020	0.0050	96
Zinc	0.45	1.0	0.030	0.062	94
Arsenic	0.012	0.028	0.0040	0.010	64
Antimony	0.030	0.074	0.0060	0.015	80
Selenium	0.0020	0.0050	0.0020	0.0050	0
Thallium	0.0030	0.0070	0.0010	0.0030	60

zinc can be removed together at pH 8.0-9.5, while nickel requires a higher pH. Therefore, chromium and nickel were selected based on their relative significance in the raw waste and due to their representative nature regarding overall toxic metal removal. Lead, zinc, cadmium, copper, arsenic, and antimony are of lower significance on the basis of sampling results. No toxic organic pollutants were identified at significant concentrations.

D. Basis of Pollutant Limitations

1. Conventional and Nonconventional Parameters

a. pH

The treated effluent is to be controlled within the range of pH 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS and Iron

The long-term average values of 50 mg/l for TSS and 330 mg/l for iron derived from the monitoring data of Plant #559 (Table 14-33a) was used as the subcategory performance values. The variability factors for daily measurements and monthly averages estimated from Plant #559 long-term data (Table 14-33a) were used in calculating the concentration basis and effluent limitations as described below.

Total Suspended Solids

The TSS maximum 30-day average concentration is:

$$(50 \text{ mg/l})(1.6) = 80 \text{ mg/l}$$

The 24-hour maximum TSS is:

$$(50 \text{ mg/l})(5.8) = 290 \text{ mg/l}$$

The TSS maximum 30-day average effluent limit was obtained by using the model plant unit flow of 475 m³/kkg as follows:

$$(80 \text{ mg/l})(475 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 38 \text{ kg/kkg}$$

The 24-hour maximum TSS effluent limit is:

$$(290 \text{ mg/l})(475 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 140 \text{ kg/kkg}$$

Iron

The maximum 30-day average iron concentration is determined similarly from Table 14-33a as follows:

$$(330 \text{ mg/l})(1.2) = 400 \text{ mg/l}$$

The 24-hour maximum iron concentration is:

$$(330 \text{ mg/l})(1.5) = 500 \text{ mg/l}$$

The concentrations are presented in Table 14-35 as guidance.

2. Toxic Pollutants

The effluent limitations for chromium and nickel were established on the basis of long-term monitoring data for Plant #559 which are presented in Table 14-33a.

a. Chromium

The chromium limitation is based primarily on long-term monitoring data available for Plant #559. A treatment system raw waste influent concentration for chromium of 3.1 mg/l was observed at Plant #559 during sampling. The long-term data summarized in Table 14-33a indicates a current treatment performance of 0.23 mg/l and a monthly average and daily measurement variability factor of 1.9 and 4.4, respectively.

The chromium maximum 30-day average concentration is given by:

$$(0.23 \text{ mg/l})(1.9) = 0.44 \text{ mg/l}$$

The chromium 24-hour maximum concentration is given by:

$$(0.23 \text{ mg/l})(4.4) = 1.0 \text{ mg/l}$$

The chromium maximum 30-day average effluent limit is developed using the model plant flow of 475 m³/kkg and concentration limit above as follows:

$$(0.44 \text{ mg/l}) (475 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.21 \text{ kg/kkg}$$

The chromium 24-hour maximum effluent limit is given by:

$$(1.0 \text{ mg/l}) (457 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.48 \text{ kg/kkg}$$

TABLE 14-35. EFFLUENT LIMITATIONS
TITANIUM DIOXIDE SULFATE PROCESS

Best Practicable Control Technology Currently Available
Waste Water Flow: 475 m³/kkg of TiO₂

Pollutant	Subcategory Performance (mg/l)	VFR ⁽¹⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kg of TiO ₂)	
			Max. 30-day Avg.	24-hr Max.	Max. 30-day Avg.	24-hr Max
<u>Conventional and Nonconventional Pollutants</u>						
Total Suspended Solids	50 ⁽²⁾	$\frac{5.8}{1.6}$	80	290	38	140
Iron	330 ⁽²⁾	$\frac{1.5}{1.2}$	400	500	— ⁽⁴⁾	— ⁽⁴⁾
<u>Toxic Pollutants</u>						
Chromium	0.23 ⁽²⁾	$\frac{4.4}{1.9}$	0.44	1.0	0.21	0.48
Lead	0.15 ⁽³⁾	$\frac{3.2}{2.1}$	0.32	0.48	— ⁽⁴⁾	— ⁽⁴⁾
Nickel	0.14 ⁽²⁾	$\frac{4.3}{2.1}$	0.29	0.60	0.14	0.29
Zinc	0.50 ⁽²⁾	$\frac{5.8}{1.7}$	0.85	2.9	— ⁽⁴⁾	— ⁽⁴⁾
Cadmium	0.10 ⁽³⁾	$\frac{3.9}{2.4}$	0.24	0.39	— ⁽⁴⁾	— ⁽⁴⁾
Copper	0.40 ⁽³⁾	$\frac{3.8}{2.0}$	0.80	1.5	— ⁽⁴⁾	— ⁽⁴⁾
Antimony	0.80 ⁽⁵⁾	$\frac{3.8}{2.0}$	1.6	3.0	— ⁽⁴⁾	— ⁽⁴⁾
Arsenic	0.50 ⁽⁵⁾	$\frac{3.8}{2.0}$	1.0	1.9	— ⁽⁴⁾	— ⁽⁴⁾

- (1) VFR: Ratio of the variability factor of the daily measurements to the variability factor of the monthly averages.
 (2) Long-term average based on loading data and variability factors of Plant #559 selected from Table 14-33a.
 (3) Limitation based on long-term data at Plant #559 and review of Table 8-12.
 (4) No effluent limitation.
 (5) The lower limit of the literature treatability estimate (Table 8-11) is used as the basis for the long-term average limitation.

b. Nickel

The long-term average concentration for nickel at Plant #559 is 0.14 mg/l from Table 14-33a for the treated effluent. The average nickel concentration observed during sampling was 0.18 mg/l for Plant #555 and #559 (Table 14-28). The long-term average and variability factors observed for Plant #559 were used to develop the limitations as follows:

The maximum 30-day concentration for nickel is:

$$(0.14 \text{ mg/l}) (2.1) = 0.29 \text{ mg/l}$$

The 24-hour maximum concentration is:

$$(0.14 \text{ mg/l}) (4.3) = 0.60 \text{ mg/l}$$

The nickel maximum 30-day average effluent limit is:

$$(0.29 \text{ mg/l}) (475 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.14 \text{ kg/kg}$$

The nickel 24-hour maximum effluent limit is:

$$(0.60 \text{ mg/l}) (475 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.29 \text{ kg/kg}$$

c. Other Metals

Lead, zinc, cadmium, copper, arsenic, and antimony were also present in the raw wastewater. A concentration level is developed for these toxic pollutants which can be used to develop a limitation in the event that they become a concern. Development of the concentration level is primarily made on a similar basis as established previously for the primary pollutants. Information used to establish the concentration level for each pollutant is summarized as follows:

<u>Summary</u> <u>Pollutant</u>	<u>Long-term</u> <u>Average</u>	<u>Variability(1)</u> <u>Factor of the</u> <u>Monthly Average</u>	<u>Variability(1)</u> <u>Factor of the</u> <u>Daily</u> <u>Measurements</u>
Zinc	0.50 mg/l(5)	1.7	5.8
Cadmium	0.10 mg/l(1,2)	2.4	3.9
Copper	0.40 mg/l(3)	2.0	3.8
Arsenic	0.50 mg/l(4)	2.0	3.8
Antimony	0.80 mg/l(4)	2.0	3.8
Lead	0.15 mg/l(1,2)	2.1	3.2
(1) Table 14-33b			
(2) Table 8-12			
(3) Table 8-13			
(4) Table 8-11			
(5) Table 14-33a			

The concentration levels are developed for all the pollutants as follows:

The maximum 30-day = (Long-term average X (Monthly average
concentration concentration) variability factor)

The 24-hour maximum = (Long-term average X (Daily measurement
concentration) variability factor)

Summaries of the conventional and toxic pollutant limitations for BPT are presented in Table 14-35.

Basis for BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned earlier, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT because the only technology option that removes significant amounts of conventional pollutants is not economically achievable. See the discussion of iron under BPT above. Removal of significant additional amounts of conventional pollutants can be achieved in this subcategory only if iron is also removed.

As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated today. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

TABLE 14-36. EFFLUENT LIMITATIONS
TITANIUM DIOXIDE SULFATE PROCESS
Best Available Technology
Wastewater Flow: 475 m³/kgg of TiO₂

Pollutant	Subcategory (1) Performance	VFR (2)	Concentration Basis (mg/l)		Effluent Limit (kg/kgg of TiO ₂)	
			Max.		Max.	
			30-day Avg.	24-hr. Max.	30-day Avg.	24-hr. Max.
<u>Nonconventional Pollutants:</u>						
Iron	330	1.5/1.2	400	500	--(3)	--(3)
<u>Toxic Pollutants:</u>						
Chromium	0.23	4.4/1.9	0.44	1.0	0.21	0.48
Lead	0.15	3.2/2.1	0.32	0.48	--(3)	--(3)
Nickel	0.14	4.3/2.1	0.29	0.60	0.14	0.29
Zinc	0.50	5.8/1.7	0.85	2.9	--(3)	--(3)
Cadmium	0.10	3.9/2.4	0.24	0.39	--(3)	--(3)
Copper	0.40	3.8/2.0	0.80	1.5	--(3)	--(3)
Antimony	0.80 (4)	3.8/2.0	1.6	3.0	--(3)	--(3)
Arsenic	0.50 (4)	3.8/2.0	1.0	1.9	--(3)	--(3)

(1) Limitations for BPT Table 14-35.

(2) VFR: Ratio of the variability factor of the daily measurements to the variability factor of the monthly averages.

(3) No effluent limitation.

(4) The lower limit of the literature treatability estimate (Table 8-11) is used as the basis for the long-term average limitation.

Basis for BAT Effluent Limitations

For BAT, the Agency is basing limitations on treatment consisting of Level 1 technology, and is the same as BPT. Treatments requiring aeration for iron removal (Level 2) and 55 percent recycle through use of soda ash precipitation (Level 3) were considered but rejected because of costs. The limitations for BAT are given in Table 14-36.

Basis for New Source Performance Standards

For NSPS, the Agency is basing limitations on equalization, limestone neutralization, clarification, aeration, alkaline precipitation and settling, followed by pH adjustment before final polish in a lagoon and discharge of the effluent (Level 2). This technology is chosen because it has been installed and operated successfully by Plant #559.

A. Flow Basis

Waste flow data is available for three plants and the average value of 475 m³/kkg of TiO₂ (Table 14-26) is taken as the influent to the model treatment system.

B. Selection of Pollutants to be Regulated

The same pollutants considered for BPT are also considered for the NSPS regulations. These pollutants include total suspended solids (TSS), iron, chromium, lead, nickel, and zinc which were identified at treatable levels on the average during sampling. Iron was selected in addition to TSS, chromium, and nickel for regulation on the basis of additional removal of large quantities of iron and additional TSS and toxic metal removal beyond the BPT/BAT level with the application of aeration and alkaline precipitation to BPT treatment.

An iron removal step added to BPT/BAT technology is used for NSPS/PSNS because the additional treatment provides better removal of toxic metals, and the more stringent standards are unlikely to pose a significant barrier to entry. New sulfate process plants are unlikely because the two alternate processes are more economical. However, if a company did want to construct a new sulfate process plant, a process change involving the recycle and reuse of the strong acid wastewater would likely be adopted. This process change would reduce production costs, and would also reduce the amount of strong acid wastewater treated and discharged by 70 to 90 percent. Reducing the flow of the strong acid wastewater reduces treatment costs substantially and also substantially reduces the amount of gypsum solids produced by treatment. With the smaller amount of gypsum solids produced, disposal of the solids as waste is competitive with sale of the solids for reuse, when cost of sales is considered. At least one company using the sulfate process is actively developing the recycle/reuse technology. One other company using the chloride

TABLE 14-37. EFFLUENT LIMITATIONS
TITANIUM DIOXIDE SULFATE PROCESS
New Source Performance Standards
Wastewater Flow: 475 m³/kkg of TiO₂

Pollutant	Subcategory Performance (mg/l)	VFR (1)	Concentration Basis (mg/l)		Effluent Limit (kg/kkg of TiO ₂)	
			Max.		Max.	
			30-day Avg.	24-hr. Max.	30-day Avg.	24-hr. Max.
<u>Conventional and Nonconventional Pollutants</u>						
Total Suspended Solids	21(2)	11.0/3.0	64	230	30	110
Iron(6)	0.62(2)	13.7/4.0	2.5	8.5	1.2	4.1
<u>Toxic Pollutants</u>						
Chromium(6)	0.15(3)	3.8/2.0	0.30	0.57	0.14	0.27
Lead	0.15(3)	3.2/2.1	0.32	0.48	--(4)	--(4)
Nickel(6)	0.10(3)	3.8/2.0	0.20	0.38	0.095	0.18
Zinc	0.20(3)	6.4/3.1	0.62	1.3	--(4)	--(4)
Cadmium	0.10(3)	3.9/2.4	0.24	0.39	--(4)	--(4)
Copper	0.40(3)	3.8/2.0	0.80	1.5	--(4)	--(4)
Antimony	0.80(5)	3.8/2.0	1.6	3.0	--(4)	--(4)
Arsenic	0.50(5)	3.8/2.0	1.0	1.9	--(4)	--(4)

(1) VFR: Ratio of the variability factor of the daily measurements to the variability factor of the monthly averages.

(2) Long-term average based on loading data and variability factors of Plant #559 selected from Table 14-33b.

(3) Limitation based on long-term data at plant #559 and review of Table 8-12.

(4) No effluent limitation.

(5) The lower limit of the literature treatability estimate (Table 8-11) is used as the basis for the long-term average limitation.

(6) Applicable to PSNS regulations.

ilmenite process has recently built a new plant that discharges 50 percent less total wastewater than comparable plants.

C. Basis of Pollutant Limitations

1. Conventional and Nonconventional Parameters

a. pH

The treated effluent is to be controlled within the range of pH 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS and Iron

The long-term average values of 21 mg/l for TSS and 0.62 mg/l for iron derived from the monitoring data of Plant #559 (Table 14-33b) were used as the subcategory performance values. The variability factors for daily measurements and monthly averages estimated from Plant #559 long-term data (Table 14-33b) were used in calculating the concentration basis and effluent limitations as determined below

Total Suspended Solids

The TSS maximum 30-day average concentration is:

$$(21 \text{ mg/l}) (3.04) = 64 \text{ mg/l}$$

The 24-hour maximum TSS is:

$$(21 \text{ mg/l}) (11.0) = 230 \text{ mg/l}$$

The TSS maximum 30-day average effluent limit was obtained by using the model plant unit flow of 475 m³/kkg as follows:

$$(64 \text{ mg/l}) (475 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 30 \text{ kg/kkg}$$

The 24-hour maximum TSS effluent limit is:

$$(230 \text{ mg/l}) (475 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 110 \text{ kg/kkg}$$

Iron

The maximum 30-day average iron concentration is determined similarly from Table 14-33b as follows:

$$(0.62 \text{ mg/l}) (4.0) = 2.5 \text{ mg/l}$$

The 24-hour maximum iron concentration is:

$$(0.62 \text{ mg/l}) (13.7) = 8.5 \text{ mg/l}$$

The maximum 30-day average iron effluent limit is:

$$(2.5 \text{ mg/l}) (475 \text{ m}^3/\text{kg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 1.2 \text{ kg/kg}$$

The 24 hour maximum iron effluent limit is:

$$(8.5 \text{ mg/l}) (475 \text{ m}^3/\text{kg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 4.1 \text{ kg/kg}$$

The conventional and nonconventional pollutants limitations are presented in Table 14-37 for treatment with iron removal.

2. Toxic Pollutants

The effluent limitations for chromium with iron removal is based primarily on long-term monitoring data for Plant #559 and review of treatment performance information in Tables 8-12 and 8-13 for other industries utilizing the same treatment technology for removal of the pollutant.

a. Chromium

The chromium limitation with iron removal is based primarily on long-term monitoring data available for Plant #559. A treatment system raw waste influent concentration for chromium of 3.2 mg/l was observed at Plant #559 during sampling. The long-term data summarized in Table 14-33b indicates a current treatment performance of 0.070 mg/l and a monthly average and daily measurement variability factor of 2.0 and 3.8, respectively.

Review of long-term average treatment data for chromium in Tables 8-12 and 8-13 indicates that 0.070 mg/l shows excellent removal when compared to the same treatment technology for chromium removal in other industries. A long-term average of 0.15 mg/l for chromium is used as the basis for the final limitation based on observed performance data from other industries summarized on the tables in Section 8. The final limitations are developed below for chromium.

The chromium maximum 30-day average concentration is given by:

Basis for Pretreatment Standards

A. Existing Sources

The only wastewater discharged to the POTW from the one existing indirect discharger is a small portion of the weak acid stream. Based on data provided in response to Section 308 request, it is unlikely that this wastewater contains any toxic metals at treatable levels. Therefore, we are excluding this subcategory from categorical PSES under the provisions of Paragraph 8(b) of the Settlement Agreement.

B. New Sources

For pretreatment standards for New Sources (PSNS), the Agency is basing limitations on NSPS. The pollutants to be regulated are iron, chromium, and nickel as indicated in Table 14-37. Pretreatment is required because NSPS provides better removal of iron and toxic metals than does a well-operated POTW with secondary treatment installed and therefore chromium, nickel, and iron would pass through the POTW in the absence of pretreatment.

Titanium Dioxide - Chloride - Ilmenite Process Industry Profile

General Description

Total subcategory production capacity is given in Table 14-38 Profile Data Summary. The 308 data available for the TiO_2 Subcategory does not adequately cover the one-step chloride-ilmenite process; however, supplementary information has been submitted by industry (55). The status of regulations prior to promulgation of this regulation is presented in Table 14-2. Additional information on the chloride-ilmenite process industry is given in this section.

General Process Description and Raw Materials

For the manufacture of titanium dioxide by the combined ore beneficiation-chloride process, a generalized process flow diagram including the waste streams is shown in Figure 14-11.

The direct use of ilmenite ore for the manufacture of titanium dioxide pigments requires the application of either the sulfate process or the one-step ore beneficiation/chlorination process which is referred to in this document as the chloride-ilmenite process. Processes which involve a separate ore beneficiation step (either at the plant or at the ore source) resulting in an upgraded or a synthetic rutile product to be used as feed material for a chloride process would not be classified as a chloride-ilmenite process. A separate ore beneficiation process would fall within the Ore Mining and Dressing Category for regulatory purposes, and the manufacture of TiO_2 from an upgraded ilmenite or synthetic rutile would be in the same classification as a chloride process using natural rutile ore.

TABLE 14-39. AVERAGE WATER USAGE FOR TiO_2 PRODUCTION
BY THE CHLORIDE -ILMENITE PROCESS

Use	Plant #237	Plant #550 (m^3/kg of TiO_2)	Plant #713
Noncontact Cooling	73-140	330-390	15-16
Process Contact and Cleanup	100-140 ⁽¹⁾	47- 59	60 ⁽²⁾
Noncontact Ancillary Uses (Boilers, Sanitary, etc.)	9- 11	6- 7	5- 6

Source of data, (55).

(1) The average total flow of $120 \text{ m}^3/\text{kg}$ is used as the basis for BPT.

(2) The average flow of $60 \text{ m}^3/\text{kg}$ is used as the basis for NSPS.

TABLE 14-41. SUMMARY OF RAW WASTE LOADINGS FOUND IN SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY TITANIUM DIOXIDE - SULFATE PROCESS (Applied to Chloride Ilmenite Process)						
Pollutant	Loading Range (kg/day)		Unit Loading (kg/kg)			No. of Plants (1)
	Minimum	Maximum	Minimum	Average	Maximum	
<u>Priority</u>						
Antimony	5.0	28	0.032	0.11	0.22	3
Arsenic	1.9	4.0	0.012	0.19	0.032	3
Cadmium	0.068	7.2	0.00044	0.019	0.057	3
Chromium	140	530	1.1	2.0	3.4	3
Copper	8.2	19	0.065	0.085	0.12	3
Lead	3.0	65	0.024	0.18	0.42	3
Nickel	3.7	23	0.029	0.080	0.15	3
Selenium	7.0	9.5	0.0020	0.031	0.06	2
Thallium	0.47	1.2	0.0030	0.0055	0.0080	2
Zinc	1.8	85	0.014	0.34	0.55	3
<u>Conventional</u>						
TSS				320		1
Iron				600		1

(1) - Data are taken only from those plants where pollutants were found above detection limits, or in the case of TSS and Iron, where data are available.

TABLE 14-42. TOXIC POLLUTANT AVERAGE RAW WASTE LOADS AND CONCENTRATIONS

SUBCATEGORY TITANIUM DIOXIDE - Sulfate Process (Applied to Chloride Ilmenite Process)							
	Screening				Verification		Average (mg/l)
	Plant #555 (mg/l)	Plant #555 (kg/kg)	Plant #559 (mg/l)	Plant #559 (kg/kg)	Plant #559 (mg/l)	Plant #559 (kg/kg)	
Antimony	0.77	0.22	0.16	0.080	0.074	0.032	0.34
Arsenic	0.11	0.032	0.029	0.014	0.028	0.012	0.06
Cadmium	0.29	0.057	0.002	0.0009	0.0010	0.00044	0.10
Chromium	3.8	1.1	7.0	3.4	3.1	1.4	4.63
Copper	0.20	0.065	0.25	0.12	0.16	0.070	0.20
Lead	0.075	0.024	0.20	0.10	0.96	0.42	0.41
Nickel	0.091	0.029	0.31	0.15	0.14	0.061	0.18
Selenium	NA	< 0.06	NA	NA	0.005	0.002	0.005
Thallium	NA	NA	0.02	0.008	0.007	0.003	0.014
Zinc	0.088	0.014	1.1	0.55	1.04	0.45	0.74

NA = Not Available

Daily raw waste loads were calculated from the flow rates measured or estimated at the time of sampling and the measured pollutant concentrations. That is,

$$\text{Daily loading (as kg of pollutant per day)} = \frac{(C)(Q)}{1000}$$

where the concentration (C) of the pollutant is expressed in units of mg/l, (Note: 1 kg/m³ = 1000 mg/l), and the flow rate (Q) is expressed in units of m³/day (m³, a cubic meter, is equal to 264 U.S. gallons).

Similarly, the unit loading were calculated from the reported TiO₂ production rate (P), the waste stream flow rate (Q), and the measured pollutant concentration (C).

$$\text{Unit loading (as kg of pollutant per kkg of TiO}_2\text{)} = \frac{(C)(Q)}{1000(P)}$$

where C and Q are expressed in the same units described above, and the production (P) is expressed in units of kkg/day (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs).

A summary of daily and unit per unit of production raw waste loads for the plants sampled is presented in Table 14-41 and the individual plant averages are given in Table 14-42.

The estimated total annual raw wastewater load of toxic pollutants generated by the Chloride-Ilmenite Process is given below.

Pollutant	Total Annual Raw Wastewater Load (kg/year)
Chromium	1,050,000
Nickel	42,000
Zinc	178,000
Lead	94,000
Copper	44,000
Cadmium	9,900
Antimony	58,000
Thallium	2,900
Arsenic	99,000
Selenium	16,000

Section 5 of this report described the scope and methodology of the sampling program and this section indicates the size of the analytical data base on toxic pollutants for the sulfate process segment. This is the basis for selecting pollutants of concern in the chloride-ilmenite segment of the TiO₂ subcategory.

Pollution Abatement Option

Toxic Pollutants of Concern

Rationale for selection of the toxic pollutants of concern are presented in this section for the sulfate process industry. The sampling data evaluations resulted in the selection of chromium, zinc, nickel, lead, copper, antimony, arsenic, and cadmium on the basis of raw waste maximum concentrations and total annual industry loads.

The major impurity found in the various grades of raw material is ferrous iron as shown in Table 14-22. In the sulfate process the unwanted iron remains largely in the ferrous state and may be crystallized out of the acid waste streams and sold as copperas (ferrous sulfate). In the chloride-ilmenite process, the same ore impurity is oxidized to some extent to the ferric state during the chlorination step. This appears in the acid waste streams as ferric chloride (FeCl_3) in the amounts indicated in Table 14-41.

Iron, in either the ferrous or ferric state, is classified as a nonconventional pollutant. However, when present in large amounts, such as it is in the TiO_2 industry, it can be a considerable aid to toxic metal removal in treatment systems designed to take advantage of coprecipitation processes.

Process Modifications and Technology Transfer Options

The comments made in regard to the Titanium Dioxide-Chloride Process for rutile and upgraded ores in this section are generally applicable to the Chloride-Ilmenite Process.

Best Management Practices

Storm water runoff from the plant site should be collected and sent to the treatment facility for the removal of suspended solids.

Prevailing Control and Treatment Practices

The three chloride-ilmenite plants from which the water use and waste source information was obtained all handle the disposal of the concentrated process waste stream separately by either ocean dumping or deep well injection. The availability of either of these methods of disposal for a particular plant is a matter handled on a case-by-case basis by the appropriate regulatory agencies from which various approvals and permits are required under the Marine Protection, Research and Sanctuaries Act of 1972 for ocean disposal or by state and local authorities for deep well injection. For the purpose of developing the model plant concept and specifying a generally applicable waste treatment technology for the chloride-ilmenite industry, the assumption has been made that neither the ocean dumping nor the deep well injection disposal options are generally available, and that the concentrated process waste is,

therefore, included in the raw waste influent to the model plant wastewater treatment system.

In practice, one plant disposes of the entire metal chloride, HCl, and TSS waste by ocean dumping. The remainder of the plants dispose of the concentrated waste by deep well injection after use of surface lagoons for removal of settleable solids.

The dilute process waste streams are segregated to the extent possible from noncontact sources and treated in conventional in-plant systems utilizing equalization and spill diversion facilities followed by lime neutralization/coagulation, solid separation in a settling pond, and final discharge of the treated effluent. Chemical coagulating agents such as ferric chloride and alum may be used either before or after pH control as an aid in the removal of metal hydroxides and other suspended solids.

Advanced Treatment Technology

Advanced treatment technology options for the in-plant treatment of process wastes have been evaluated as possible polishing step additions to a conventional system for equalization, neutralization, and clarification in ponds prior to discharge. Such options include:

- A. Aeration for a) decarbonization if limestone is used for neutralization, and b) ferrite coprecipitation, assuming that sufficient ferrous iron is already present or is added to the system as needed (the latter may also be accomplished by adding scrap iron to the acid wastes).
- B. An alkaline precipitation step under optimum conditions for metal hydroxide precipitation, i.e., pH 9-10.
- C. Dual-media filtration for additional removal of suspended solids including toxic metal hydroxides.
- D. Sulfide precipitation for additional toxic metal removal followed by filtration.
- E. Other metal removal technologies including xanthate precipitation, ion exchange, and membrane applications, all of which were regarded as inappropriate from a practical and economic point of view.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT)

Figure 14-12 shows the model treatment system for treatment with and without iron removal. Calcium carbonate (limestone) is used to neutralize the concentrated acid waste stream. Aeration is

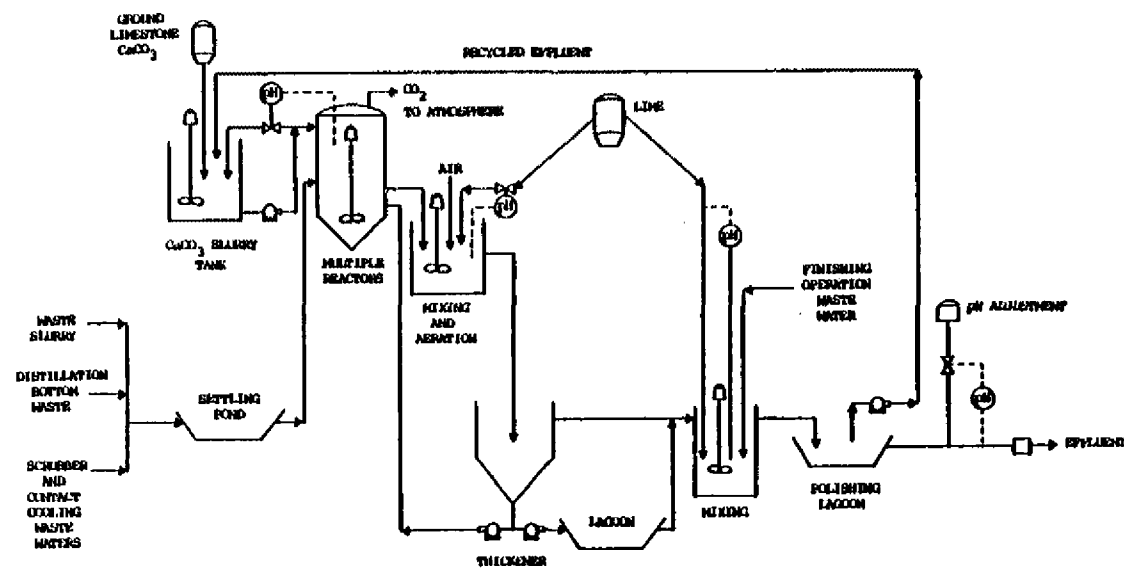


Figure 14-12. Level 1 waste water treatment for titanium dioxide - chloride (ilmenite ore) process.

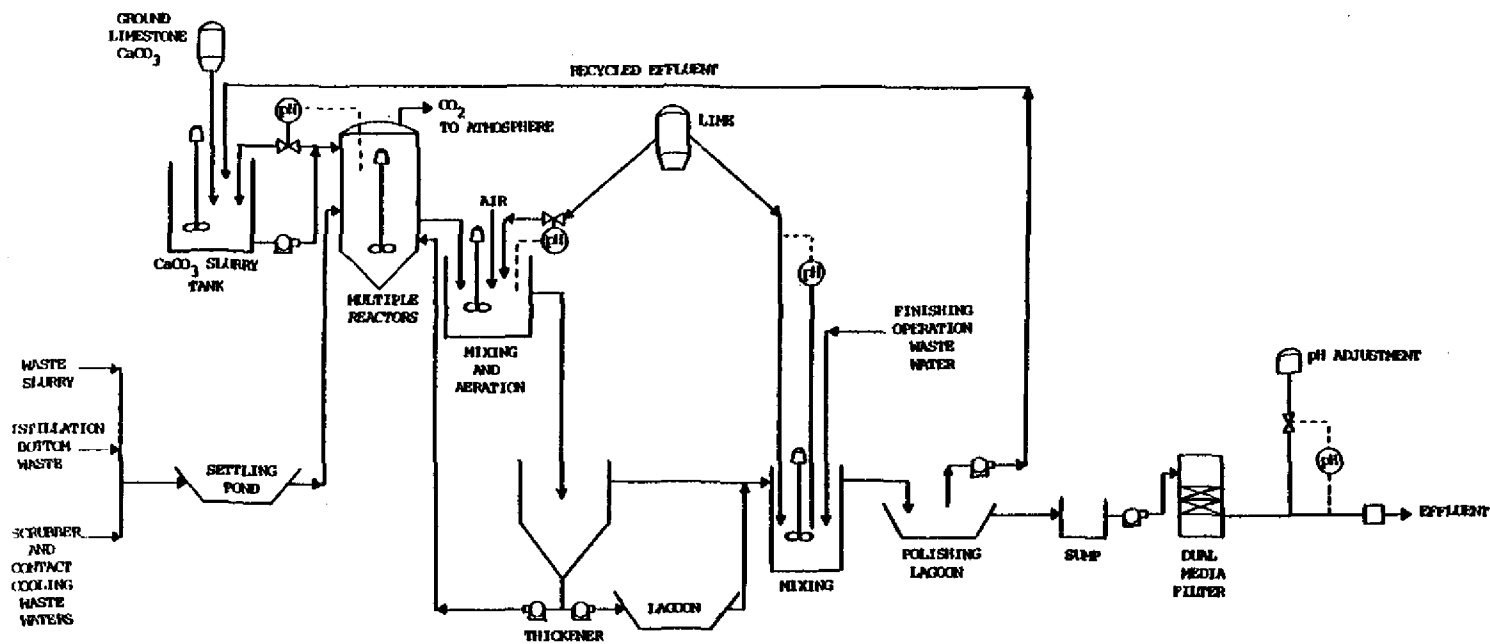


Figure 14-13. Level 2 waste water treatment for titanium dioxide - chloride (ilmenite ore) process.

then used to primarily remove CO_2 prior to pH adjustment to reduce demand for treatment chemicals, and mixing with dilute and miscellaneous plant wastes. The combined stream is given lime treatment to pH 9-10 for iron and toxic pollutant removal or 6-9 during treatment without iron and toxic metal removal. All wastewater passes through a clarifier and final polishing lagoon prior to discharge.

This technology was used as the treatment model for BPT regulations because of the similarity of wastes to those in the TiO_2 -Sulfate Process Industry. This technology is available and, to some degree, already employed in the TiO_2 -Chloride-Ilmenite Industry. The proposed BPT treatment can remove greater than 95 percent of the major pollutants of concern including toxic metals according to preliminary treatability estimates. No iron removal is required for BPT.

B. Level 2 (NSPS)

Level 2 treatment adds iron removal as described in Level 1 and dual-media filtration to the Level 1 technology for additional removal of iron, suspended solids, and toxic metal hydroxides following the alkaline precipitation and settling steps. The flow diagram for Level 2 is shown in Figure 14-13. This level of treatment was selected as the basis for NSPS because it provides a relatively economical method for removing additional toxic metals.

Equipment for Different Treatment Levels

A. Equipment Functions

Unlike treatment of the wastewaters from the TiO_2 Sulfate Process, limestone neutralization of the Chloride-Ilmenite Process wastewaters does not generate large quantities of solids (e.g., gypsum) which require mechanized separation and transfer to sizable on-site or off-site disposal areas. The solids that are generated from TSS and metal precipitate separation can be collected in moderate-sized lagoons and periodically transferred to appropriate chemical landfill disposal sites in accordance with the Resource Conservation and Recovery Act (RCRA) (as amended, 42 USC 6901, et seq.). The Level 1 treatment model includes rail car deliveries of ground limestone and lime, bucket elevators, storage bins, multiple reactors and chemical feeders, mechanical aerators and thickeners for solids removal. The clarified overflow is treated with lime for additional toxic metals removal and settled in a one-day polishing pond prior to final pH adjustment, monitoring and discharge.

B. Chemicals and Chemical Handling

First stage neutralization utilizes ground limestone while lime is used for second stage neutralization and final alkaline

precipitation. Oxygen is supplied as air to oxidize any ferrous iron remaining in addition to CO₂ removal, and treatment chemicals may be added as required for removal of precipitated metals and other suspended solids. Aside from the large scale bulk chemical handling requirements for limestone and lime, there are no particular hazards involved.

C. Disposal of Solids

Periodic removal of solids from settling impoundments will require compliance with RCRA regulations as applicable to on-site or off-site chemical disposal site operation. However, this subcategory has not been listed under RCRA-ISS for hazardous pollutants.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed. Cost estimates have been prepared for Level 1 (BPT) treatment, and for Level 2 (NSPS). The model plant specifications given below were utilized for cost estimating and for development of the regulations.

A. Production

There are three plants at different locations producing (or capable of producing) titanium dioxide by the combined ilmenite ore beneficiation - chlorination process. Annual capacity of these plants varies from 136,000 metric tons to 207,000 metric tons. For treatment cost estimates, four production levels were selected. These were 35,000 kg/year, 70,000 kkg/year, 113,7570 kkg/year, and 157,500 kkg/year.

B. Wastewater Flows

Wastewater is typically segregated into two streams; strong acidic wastewater flow from beneficiation-chlorination of ilmenite ore and air emission scrubbing facilities, and the other wastewater from process reactions, washings, product transport, cooling tower blowdown, water treatment blowdown, and other operations. For the model plants, a unit flow of 6 m³/kkg of product for the concentrated acidic wastewater and 114 m³/kkg of product for the dilute wastes is used. The treatment system is designed to handle a total flow of 120 m³/kkg of product (Table 14-39).

For the NSPS model plant, a unit flow of 6 m³/kkg of product for the concentrated acidic wastewater is used. Because of improved design which allows for recycle systems and more efficient process water utilization, dilute wastewater is considerably reduced (62). The total combined wastewater flow of 60 m³/kkg of

product is used (Table 14-39). The treatment system for Level 2 (NSPS) is BPT plus dual-media filtration.

C. Pollutant Load

The principal pollutants occurring in the wastewaters are TSS, iron, chromium, nickel, zinc, and hydrochloric acid. For the model plants, the following unit pollutant loads have been considered:

TSS	175 kg/kkg of TiO_2
HCl	230 kg/kkg of TiO_2
Iron	375 kg/kkg of TiO_2
Chromium	1.4 kg/kkg of TiO_2
Nickel	0.1 kg/kkg of TiO_2
Zinc	0.5 kg/kkg of TiO_2

The loading values for TSS, HCl, and iron are based on data submitted by industry on the chloride-ilmenite process. The chromium loading is an estimated average derived from a wide range of ilmenite ore qualities and the nickel and zinc loadings are taken from the screening and verification data on the TiO_2 sulfate process.

D. Chemical Usage

In the model BPT system, powdered limestone is used for first stage neutralization of strong acidic waste flow at the unit rate of 302 kg/kkg of TiO_2 . Pebble lime (CaO) is used for second stage neutralization of the total combined flows. Lime is used at the unit rate of 42 kg/kkg of TiO_2 .

E. Solid Waste

The solids produced in the treatment facility consist of iron hydroxides, the original suspended solids introduced in the influent and solids derived from the treatment chemicals added for neutralization. The total solids produced in the model plant are assumed to be 890 kg/kkg of TiO_2 . Assuming an average production rate and 50 percent moisture content, the volume of sludge generated is 1.8 m^3/kkg .

Model Plant Control and Treatment costs

The estimated costs for four models having different production levels are given in Tables 14-43, 14-44, 14-45, and 14-46.

For existing sources at the first level of treatment, the disposal of sludges is on-site, hence land requirements are fairly large. Amortization, chemicals, labor, and residual waste disposal costs have significant impact on the annual costs.

TABLE 14-43. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process (Ilmenite ore) Production 35,000 metric tons per year	
		(\$)
A. INVESTMENT COST	BPT	BAT^a
Site development	292,200	0
Equipment	851,500	0
Monitoring equipment	20,000	0
Subtotal	1,163,700	0
Contractor's O & P ^b	174,555	0
Subtotal	1,338,255	0
Engineering	267,651	0
Subtotal	1,605,906	0
Contingencies	160,591	0
Subtotal	1,766,497	0
Land	252,000	0
TOTAL INVESTMENT COST	2,018,497	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	336,000	0
Energy	31,000	0
Chemicals	260,000	0
Maintenance	176,650	0
Taxes and insurance	60,555	0
Residual waste disposal	105,000	0
Monitoring, analysis, and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	984,205	0
C. AMORTIZATION OF INVESTMENT COST	287,409	0
TOTAL ANNUAL COST	1,271,614	0

^a Represents the incremental cost above that for BPT treatment^b Overhead and Profit

TABLE 14-44. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process (Ilmenite ore) Production 70,000 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	520,000	0
Equipment	1,023,500	0
Monitoring equipment	20,000	0
Subtotal	1,563,500	0
Contractor's O & P ^b	234,525	0
Subtotal	1,798,025	0
Engineering	359,605	0
Subtotal	2,157,630	0
Contingencies	215,763	0
Subtotal	2,373,393	0
Land	492,000	0
TOTAL INVESTMENT COST	2,865,393	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	504,000	0
Energy	43,000	0
Chemicals	510,000	0
Maintenance	237,339	0
Taxes and insurance	85,962	0
Residual waste disposal	105,000	0
Monitoring, analysis, and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	1,500,301	0
C. AMORTIZATION OF INVESTMENT COST	386,151	0
TOTAL ANNUAL COST	1,886,452	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-45. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process (Ilmenite ore)	
Production	113,750 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	784,000	0
Equipment	1,377,000	0
Monitoring equipment	20,000	0
Subtotal	2,181,000	0
Contractor's O & P ^b	327,150	0
Subtotal	2,508,150	0
Engineering	501,630	0
Subtotal	3,009,780	0
Contingencies	300,978	0
Subtotal	3,310,758	0
Land.....	780,000	0
TOTAL INVESTMENT COST	4,090,758	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	588,000	0
Energy	62,000	0
Chemicals	823,000	0
Maintenance	331,076	0
Taxes and insurance	122,723	0
Residual waste disposal	210,000	0
Monitoring, analysis, and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	2,151,799	0
C. AMORTIZATION OF INVESTMENT COST	538,660	0
TOTAL ANNUAL COST	2,690,459	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-46. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride process (Ilmenite ore)	
Production	157,500 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	1,053,600	0
Equipment	1,590,000	0
Monitoring equipment	20,000	0
Subtotal	2,663,600	0
Contractor's O & P ^b	399,540	0
Subtotal	3,063,140	0
Engineering	612,628	0
Subtotal	3,675,768	0
Contingencies	367,577	0
Subtotal	4,043,345	0
Land	1,080,000	0
TOTAL INVESTMENT COST	5,123,345	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	588,000	0
Energy	71,000	0
Chemicals	1,141,000	0
Maintenance	404,334	0
Taxes and insurance	153,700	0
Residual waste disposal	210,000	0
Monitoring, analysis, and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	2,583,035	0
C. AMORTIZATION OF INVESTMENT COST	657,852	0
TOTAL ANNUAL COST	3,240,887	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 14-47. MODEL PLANT TREATMENT COSTS

Subcategory Production	Titanium dioxide - Chloride (Ilmenite ore) 35,000 metric tons per year	
		($\text{\$}$)
A. INVESTMENT COST		NSPS
Site development		280,000
Equipment		1,046,500
Monitoring equipment		20,000
Subtotal		1,346,500
Contractor's O & P ^a		201,975
Subtotal		1,548,475
Engineering		309,695
Subtotal		1,858,170
Contingencies		185,817
Subtotal		2,043,987
Land		252,000
TOTAL INVESTMENT COST		2,295,987
B. OPERATION AND MAINTENANCE COST		
Labor and supervision		350,000
Energy		34,200
Chemicals		260,000
Maintenance		204,399
Taxes and insurance		68,880
Residual waste disposal		105,000
Monitoring, analysis and reporting		15,000
TOTAL OPERATION AND MAINTENANCE COST		1,037,478
C. AMORTIZATION OF INVESTMENT COST		332,557
TOTAL ANNUAL COST		1,370,035

^a Overhead and Profit

TABLE 14-48. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride (Ilmenite ore)	
Production	70,000 metric tons per year	
		(\$)
A. INVESTMENT COST		NSPS
Site development	496,500	
Equipment	1,323,500	
Monitoring equipment	20,000	
Subtotal	1,840,000	
Contractor's O & P ^a	276,000	
Subtotal	2,116,000	
Engineering	423,200	
Subtotal	2,539,200	
Contingencies	253,920	
Subtotal	2,793,120	
Land	492,000	
TOTAL INVESTMENT COST	3,285,120	
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	518,000	
Energy	49,500	
Chemicals	510,000	
Maintenance	279,312	
Taxes and insurance	98,554	
Residual waste disposal	105,000	
Monitoring, analysis and reporting	15,000	
TOTAL OPERATION AND MAINTENANCE COST	1,575,366	
C. AMORTIZATION OF INVESTMENT COST	454,441	
TOTAL ANNUAL COST	2,029,806	

^a Overhead and Profit

TABLE 14-49. MODEL PLANT TREATMENT COSTS

Subcategory Production	Titanium dioxide - Chloride (Ilmenite ore) 113,750 metric tons per year	
		($\$$)
A. INVESTMENT COST		NSPS
Site development	752,000	
Equipment	1,822,000	
Monitoring equipment	20,000	
Subtotal	2,594,000	
Contractor's O & P ^a	389,100	
Subtotal	2,983,100	
Engineering	596,620	
Subtotal	3,579,720	
Contingencies	357,972	
Subtotal	3,937,692	
Land	780,000	
TOTAL INVESTMENT COST	4,717,692	
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	602,000	
Energy	71,700	
Chemicals	823,000	
Maintenance	393,769	
Taxes and insurance	141,531	
Residual waste disposal	210,000	
Monitoring, analysis and reporting	15,000	
TOTAL OPERATION AND MAINTENANCE COST	2,257,000	
C. AMORTIZATION OF INVESTMENT COST	640,662	
TOTAL ANNUAL COST	2,897,662	

^a Overhead and Profit

TABLE 14-50. MODEL PLANT TREATMENT COSTS

Subcategory	Titanium dioxide - Chloride (Ilmenite ore)	
Production	157,500 metric tons per year	
		(\$)
A. INVESTMENT COST		NSPS
Site development	1,015,000	
Equipment	2,175,000	
Monitoring equipment	20,000	
Subtotal	3,210,000	
Contractor's O & P ^a	481,500	
Subtotal	3,691,500	
Engineering	738,300	
Subtotal	4,429,800	
Contingencies	442,980	
Subtotal	4,872,780	
Land	1,080,000	
TOTAL INVESTMENT COST	5,952,780	
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	602,000	
Energy	85,000	
Chemicals	1,141,000	
Maintenance	487,278	
Taxes and insurance	178,583	
Residual waste disposal	210,000	
Monitoring, analysis and reporting	15,000	
TOTAL OPERATION AND MAINTENANCE COST	2,718,861	
C. AMORTIZATION OF INVESTMENT COST	792,801	
TOTAL ANNUAL COST	3,511,663	

^a Overhead and Profit

TABLE 14-51. MODEL PLANT UNIT TREATMENT COSTS

Subcategory Titanium dioxide - Chloride (Ilmenite ore)

Annual Treatment Costs (\$/kg)

LEVEL OF TREATMENT

COST ITEM	PRODUCTION (kg/yr)	BPT	BAT*	NSPS
Annual Operation and Maintenance	35,000	28.12	NA	29.64
	70,000	21.43	NA	22.51
	113,750	18.92	NA	19.84
	157,500	16.40	NA	17.26
Annual Amortization	35,000	8.21	NA	9.50
	70,000	5.52	NA	6.49
	113,750	4.74	NA	5.63
	157,500	4.18	NA	5.03
Total Annual Cost	35,000	36.33	NA	39.14
	70,000	26.95	NA	29.00
	113,750	23.65	NA	25.47
	157,500	20.58	NA	22.30

*Represents the incremental cost above BPT

The unit waste flow of 6 m³/kgg of product for the concentrated acidic wastewater stream is the same for BPT and NSPS systems. The NSPS treatment technology is the same as BPT, but the total combined acidic and dilute wastewater flow for the NSPS system is much less than for the BPT model; however, the reduced flow has negligible impact on costs because the unit waste loads are the same. Table 14-47, 14-48, 14-49, and 14-50 present the estimated NSPS treatment costs for four models having different production levels. There is insignificant difference in the estimated total annual costs per kkg of product between BPT and NSPS levels of treatment for the model plant designs.

Table 14-51 presents a summary of the unit cost distribution between amortization and operation and maintenance cost components at different productions at the BPT and NSPS level of treatment.

Basis for Regulations

Evaluation of BPT Treatment Practices

The prevailing control and treatment practices in the TiO₂ Chloride-Ilmenite industry have been reviewed in this section. For the purpose of regulations development, it has been assumed that neither ocean dumping nor deep well injection methods are generally available as disposal options for all or any portion of the process-related wastes.

Basis for BPT Effluent Limitation

A. Technology Basis

The BPT limitations are based on technology involving equalization, limestone neutralization, clarification, aeration, alkaline precipitation, and settling followed by final pH adjustment and discharge. The rationale for the selection of Level 1 technology is given above.

B. Flow Basis

The BPT model plant flow rate is based on the reported average process contact and clean up wastewater flow at Plant #237 of 120 m³/kgg as indicated in Table 14-39.

C. Selection of Pollutants to be Regulated

Specific information concerning the characteristics of the combined strong and dilute acid waste streams in the Chloride-Ilmenite process is not available. In view of the lack of such information which would indicate the concentration of pollutants in this industry, it is necessary to use data from the Sulfate Process as a guide in the selection of pollutants to be limited. Considering the many similarities in the chloride and sulfate processes, including use of the same ore with known impurities, treatment technology, and generation of strong and

dilute acid waste streams, it is extremely likely that TSS, chromium, and nickel are present at treatable concentrations, and are, therefore, limited for this industry. It is also likely that iron, lead, zinc, cadmium, copper, antimony, and arsenic may also be present on occasion at treatable levels and are, therefore, considered as potential candidates for limitation. Details on the selection of these pollutants for limitation are presented in this section for the Titanium Dioxide-Sulfate Process.

1. Conventional and Nonconventional Parameters

a. TSS and Iron

The removal characteristics of total suspended solids (TSS) is influenced by the removal of iron. For BAT, the long-term average concentration of 50 mg/l for TSS and 330 mg/l for iron were achieved (Table 14-33a) and were used as the performance values. The variability factors for daily measurements and monthly averages estimated from Plant #559 (Table 4-33a) were used in determining the concentration basis and effluent limitations for TSS as follows:

The maximum monthly average TSS concentration is:

$$(50 \text{ mg/l}) (1.6) = 80 \text{ mg/l}$$

The 24-hour maximum TSS concentration is:

$$(50 \text{ mg/l}) (5.8) = 290 \text{ mg/l}$$

The maximum monthly average limitation is:

$$(80 \text{ mg/l}) (120 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 9.6 \text{ kg/kkg}$$

The 24-hour maximum limitation is:

$$(290 \text{ mg/l}) (120 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 35 \text{ kg/kkg}$$

For iron, the concentration basis is determined from data in Table 14-33a as follows:

The maximum 30-day average concentration is:

$$(330 \text{ mg/l}) (1.2) = 400 \text{ mg/l}$$

The maximum 24-hour concentration is:

$$(330 \text{ mg/l}) (1.5) = 500 \text{ mg/l}$$

TABLE 14-52. EFFLUENT LIMITATIONS
TITANIUM DIOXIDE CHLORIDE PROCESS USING ILMENITE
Best Practicable Control Technology Currently Available
Wastewater Flow: 120 m³/kgg

Pollutant	Estimated Treatability	VFR(1)	Concentration Basis (mg/l)		Effluent Limit (kg/kgg)	
			Max.	24-hr.	Max.	24-hr.
			30-day Avg.	Max.	30-day Avg.	Max.
<u>Conventional/ Nonconventional Pollutants</u>						
Total Suspended Solids	50(2)	5.8/1.6	80	290	9.6	35
Iron	330(2)	1.5/1.2	400	500	--(4)	--(4)
<u>Toxic Pollutants</u>						
Chromium(5)	0.23	4.4/1.9	0.44	1.0	0.053	0.12
Lead	0.15	3.2/2.1	0.32	0.48	--(4)	--(4)
Nickel(5)	0.14	4.3/2.1	0.29	0.60	0.035	0.072
Zinc	0.50	5.8/1.7	0.85	2.9	--(4)	--(4)
Cadmium	0.10	3.9/2.4	0.24	0.39	--(4)	--(4)
Copper	0.40	3.8/2.0	0.80	1.5	--(4)	--(4)
Antimony	0.80	3.8/2.0	1.6	3.0	--(4)	--(4)
Arsenic	0.50	3.8/2.0	1.0	1.9	--(4)	--(4)

(1) VFR: The ratio of the variability factor for daily measurements to the variability factor for monthly averages.

(2) Long-term average from plant #559 monitoring data (Table 14-33a)

(3) Long-term average and variability factors are based on the same rationale as the TiO₂ Sulfate Process Table 14-35.

(4) No effluent limitation.

(5) Applicable to BAT limitations.

The concentration basis and appropriate limitations are summarized in Table 14-52.

2. Toxic Pollutants

The toxic pollutants that are limited include chromium and nickel. Lead, zinc, cadmium, copper, antimony, and arsenic are considered as potential candidates for limitation. Details concerning the selection and treatment performance of these pollutants for the purpose of setting numerical limitations is identical to discussions in this section for the Titanium Dioxide-Sulfate Process. Only those factors considered specific to the Chloride-Ilmenite Process for the purpose of setting the limitations are considered. The BPT effluent limitations are presented in Table 14-52.

a. Chromium

Chromium limitations for BPT treatment were based on Table 14-35. The maximum 30-day average concentration of 0.44 mg/l and daily maximum concentration of 1.0 mg/l were used to determine the limitations as follows:

The maximum 30-day average limitation is:

$$(0.44 \text{ mg/l}) (120 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.053 \text{ kg/kg}$$

The 24-hour maximum limitation is:

$$(1.0 \text{ mg/l}) (120 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.12 \text{ kg/kg}$$

The limitations are presented in Table 14-52 for BPT treatment.

b. Nickel

Nickel limitations for BPT treatment were based on Table 14-35. The maximum 30-day average concentration of 0.29 mg/l and daily maximum concentration of 0.60 mg/l were used to determine the limitations as follows:

The maximum 30-day average limitation is:

$$(0.29 \text{ mg/l}) (120 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.033 \text{ kg/kg}$$

The maximum 24-hour limitations is:

$$(0.60 \text{ mg/l}) (120 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.72 \text{ kg/kg}$$

The limitations are presented in Table 14-52 for BPT treatment

c. Other Metals

Potential candidates for limitation include lead, zinc, cadmium, copper, antimony, and arsenic which are included in the limitations on a concentration basis in the event they are identified as a concern. The concentration basis values are presented in Table 14-52 for BPT and are identical to values developed in Table 14-35 for the Titanium Dioxide -Sulfate Process.

Basis for BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned earlier, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT because the only technology option that removes significant amounts of conventional pollutants is not economically achievable. See the discussion of iron under BPT in the Sulfate Process above. Removal of significant additional amounts of conventional pollutants can be achieved in this subcategory only if iron is also removed.

As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated today. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Effluent Limitations

For BAT, the Agency is basing limitations on the application of Level 1 technology which is equivalent to BPT. The model plant flow basis of 120 m³/kkg used for BPT is also used for BAT. The BAT limitations are presented in Table 14-52. A more advanced technology using soda ash precipitation and recycle of wastewater was considered for the similar sulfate process but was rejected on the basis of cost and because its performance has not been demonstrated.

Basis for the New Source Performance Standards

A. Technology Basis

For NSPS the Agency is basing limitations on the application of Level 2 treatment technology which adds dual-media filtration and iron removal steps to the BPT system for greater efficiency in the removal of toxic metals, iron, and suspended solids. This treatment greatly increases the coprecipitation of toxic metals and prevents large quantities of dissolved and suspended iron from entering receiving water bodies and interfering with other water uses.

B. Flow Basis

The reported data on process contact and clean-up wastewater flow at Plant #173 is selected as the basis of a model plant for new sources. Process modifications resulting in a greatly increased efficiency of water use reduce the average flow rate to 60 m³/kkg as shown in Table 14-39.

C. Basis for Pollutant Limitations

1. Conventional Parameters

a. pH

The treated effluent is to be controlled within the range of pH 6.0 to 9.0. This limitation is based on data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS

The concentration basis for the TSS maximum 30-day average limitation is obtained by applying an average filtration efficiency of 38 percent removal (41,60) to the corresponding concentration of 64 mg/l with iron removal (Table 14-37). That is:

$$(1.00-0.38) (64 \text{ mg/l}) = 40 \text{ mg/l}$$

The maximum 30-day average limitation is obtained by applying the NSPS model plant flow rate of 60 m³/kkg:

$$(40 \text{ mg/l}) (60 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 2.4 \text{ kg/kkg}$$

The TSS daily maximum limitation is determined as follows:

$$(1.00-0.38) (230 \text{ mg/l}) = 140 \text{ mg/l}$$

The daily maximum limitation is:

$$(140 \text{ mg/l}) (60 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 8.4 \text{ kg/kkg}$$

The NSPS limitations are presented in Table 14-53.

2. Nonconventional Pollutants

The only nonconventional pollutant of concern is iron. For NSPS, the Agency is basing a maximum 30-day average limitation on an average filtration efficiency of 38 percent removal (41,60). Thus the appropriate concentration basis

TABLE 14-53. EFFLUENT LIMITATIONS
Titanium Dioxide - Chloride Process Using Ilmenite
New Source Performance Standards*
Waste Water Flow: 60 m³/kg

Pollutant	Estimated Treatability (mg/l)	VFR (1)	Concentration Basis (mg/l)		Effluent Limit (kg/kg)	
			Max.	24-hr.	Max.	24-hr.
			30-day Avg.	Max.	30-day Avg.	Max.
<u>Conventional and Nonconventional Pollutants</u>						
Total suspended Solids	13	11.0/3.0	40	140	2.4	8.4
Iron	0.38	13.7/4.0	1.6	5.3	0.096	0.32
<u>Toxic Pollutants</u>						
Chromium (3)	0.060	3.8/2.0	0.12	0.23	0.0072	0.014
Lead (3)	0.030	3.2/2.1	0.064	0.096	— (4)	— (4)
Nickel (3)	0.086	3.8/2.0	0.17	0.33	0.010	0.020
Zinc (3)	0.19	6.4/3.1	0.58	1.2	— (4)	— (4)
Cadmium (3)	0.075	3.9/2.4	0.18	0.29	— (4)	— (4)
Copper (3)	0.23	3.8/2.0	0.46	0.87	— (4)	— (4)
Antimony (3)	0.80	3.8/2.0	1.6	3.0	— (4)	— (4)
Arsenic (3)	0.50	3.8/2.0	1.0	1.9	— (4)	— (4)

- (1) VFR: Ratio of the variability factor for the daily measurements to the variability factor of the monthly averages.
- (2) Based on the application of pollutant - specific removal efficiencies for dual-media filtration to adjust the BPT performance on treatability estimates shown in Table 14-52.
- * Including pretreatment standards for new sources (PSNS) covering iron and toxic metals which are expressed as concentrations.
- (3) Applicable to PSNS limitations.
- (4) No effluent limitations.

is derived from the corresponding concentration basis of 2.5 mg/l of iron used for the maximum 30-day average (Table 14-37). That is:

$$(1.00-0.38) (2.5 \text{ mg/l}) = 1.6 \text{ mg/l}$$

The limitation for NSPS is:

$$(1.6 \text{ mg/l}) (60 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 0.096 \text{ kg/kkg}$$

Similarly the 24-hour maximum iron concentration is:

$$(1.00-0.38) (8.5 \text{ mg/l}) = 5.3 \text{ mg/l},$$

and the limitation is:

$$(5.3 \text{ mg/l}) (60 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{(1000 \text{ mg/l})} \right) = 0.32 \text{ kg/kkg}$$

3. Toxic Pollutants

Addition of iron removal and a dual-media filtration system as a polishing step in NSPS is expected to remove additional toxic pollutants. This removal is estimated based on literature treatability (41) and the treatability study (61). The following removal efficiencies for the toxic pollutants are used for the limitations after careful consideration of available information:

Toxic Pollutant	Percent Removed	Percent Remaining
Chromium	60	40
Lead(1)	80	20
Nickel	14	86
Zinc(1)	6	94
Cadmium(1)	25	75
Copper (1)	42	58
Antimony(1)	0	100
Arsenic(1)	0	100

(1) No limitation given; concentration basis presented in Table 14-53.

a. Chromium

The long-term average concentration is determined for chromium by application of a 60 percent removal to 0.15 mg/l in Table 14-37 as follows:

$$(0.15 \text{ mg/l}) (1.00-0.60) = 0.060 \text{ mg/l}$$

The maximum 30-day concentration for chromium is:

$$(0.060 \text{ mg/l}) (2.0) = 0.12 \text{ mg/l},$$

and the 24-hour maximum concentration is:

$$(0.060 \text{ mg/l}) (3.8) = 0.23 \text{ mg/l}$$

Therefore, the maximum 30-day average concentration and 24-hour maximum limitation are determined, respectively:

$$(0.12 \text{ mg/l}) (60 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.0072 \text{ kg/kg}$$

$$(0.23 \text{ mg/l}) (60 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.014 \text{ kg/kg}$$

b. Nickel

The long-term average concentration is determined for nickel by application of a 14 percent removal to 0.10 mg/l in Table 14-37 as follows:

$$(0.10 \text{ mg/l}) (1.0-0.14) = 0.086 \text{ mg/l}$$

The maximum 30-day concentration for nickel is:

$$(0.086 \text{ mg/l}) (2.0) = 0.17 \text{ mg/l},$$

and the 24-hour maximum concentration is:

$$(0.086 \text{ mg/l}) (3.8) = 0.33 \text{ mg/l}$$

Therefore, the maximum 30-day average concentration and 24-hour maximum limitation are determined, respectively:

$$(0.17 \text{ mg/l}) (60 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.010 \text{ kg/kg}$$

$$(0.33 \text{ mg/l}) (60 \text{ m}^3/\text{kg}) \left(\frac{\text{kg}/\text{m}^3}{(1000 \text{ mg/l})} \right) = 0.020 \text{ kg/kg}$$

c. Other Metals

The concentration basis for lead, zinc, cadmium, copper, antimony, and arsenic are determined in a similar manner to the primary pollutants. The following equation is used in conjunction with the concentration information in Table 14-37 and the percent removal presented in this section:

$$\begin{array}{lcl} \text{BPT long-term} & \times & \text{Percent remaining} = \text{NSPS long-term} \\ \text{average} & & 100 \quad \text{average} \\ \text{concentration} & & \text{concentration} \end{array}$$

The maximum 30-day average concentration and 24-hour maximum concentration are determined by using the appropriate variability factors in Table 14-37 and multiplying by the NSPS long-term average. For example, the long-term average for zinc is:

$$(0.20 \text{ mg/l}) (0.94) = 0.19 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.19 \text{ mg/l}) (3.1) = 0.59 \text{ mg/l}$$

The 24-hour maximum concentration is:

$$(0.19 \text{ mg/l}) (6.4) = 1.2 \text{ mg/l}$$

Similarly, the concentration bases are determined for the remaining toxic pollutants and are presented in Table 14-53.

Basis for Pretreatment Standards

Pretreatment is necessary because it provides better removal of pollutants than is achievable by a well operated POTW with secondary treatment installed, and thereby prevents pass-through that would occur in a POTW in the absence of pretreatment.

Existing Sources

Since there are no indirect dischargers in this subcategory, the Agency is excluding this subcategory from categorical PSES under the provisions of paragraph 8(b) of the Settlement Agreement.

New Sources

The Agency is promulgating PSNS that are equal to NSPS because these standards provide better removal of iron, chromium and nickel than is achieved by a well-operated POTW with secondary treatment installed and therefore iron, chromium and nickel would pass through a POTW in the absence of pretreatment. Pollutants regulated under PSNS are iron, chromium, and nickel. See Table 14-53.

SECTION 15

ALUMINUM FLUORIDE INDUSTRY

Industry Profile

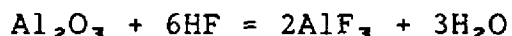
General Description

Aluminum fluoride is used as a raw material in the production of cryolite (sodium fluoroaluminate), which in turn is used in the production of aluminum. Aluminum fluoride is used also as a metallurgical flux (for welding rod coatings), as a ceramic flux (for glazes and enamels), and as a brazing flux (for aluminum fabrication).

The industry profile data for this subcategory are given in Table 15-1, while the status of regulations prior to promulgation of this new regulation is given in Table 15-2.

General Process Description and Raw Materials

In the dry process for the manufacture of aluminum fluoride, partially dehydrated alumina hydrate is reacted with hydrofluoric acid gas. The reaction is given as:



The product, aluminum fluoride, is formed as a solid, and is cooled with noncontact cooling water before being milled and shipped. The gases from the reactor are scrubbed with water to remove unreacted hydrofluoric acid before being vented to the atmosphere. A simplified flow diagram of the process is shown in Figure 15-1.

Water Use and Waste Source Characteristics

Water Use

Water is used in noncontact cooling of the product, for seals on vacuum pumps and for scrubbing the reacted gases before being vented to the atmosphere. Water is also used for leak and spill cleanup and equipment washdown. Table 15-3 summarizes water usage in the aluminum fluoride industry.

Waste Sources

A. Noncontact Cooling Water

Noncontact cooling water is used to cool the product coming out of the reactor. In some cases it is recirculated and the blowdown treated separately from other process contact wastewater or it is discharged without treatment. The water can be monitored for fluoride and if process contamination occurs, it

TABLE 15-1. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY ALUMINUM FLUORIDE

Total subcategory capacity rate	NA
Total subcategory production rate	134,700 kkg/year
Number of plants in this subcategory	5*
308 Data on file for	6
With total capacity of	204,800 kkg/year
With total production of	120,000 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	1,000 kkg/year
Maximum	45,600 kkg/year
Average production	24,300 kkg/year
Median production	35,500 kkg/year
Average capacity utilization	59 percent
Plant age range:	
Minimum	5 years
Maximum	21 years
Waste water flow range:	
Minimum	539 cubic meters/day
Maximum	2,200 cubic meters/day
Volume per unit product:	
Minimum	5 cubic meters/kkg
Maximum	12 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry." June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

NA = Not Available

* Seven plants were operating at the beginning of this study, but two closed down production after 1978.

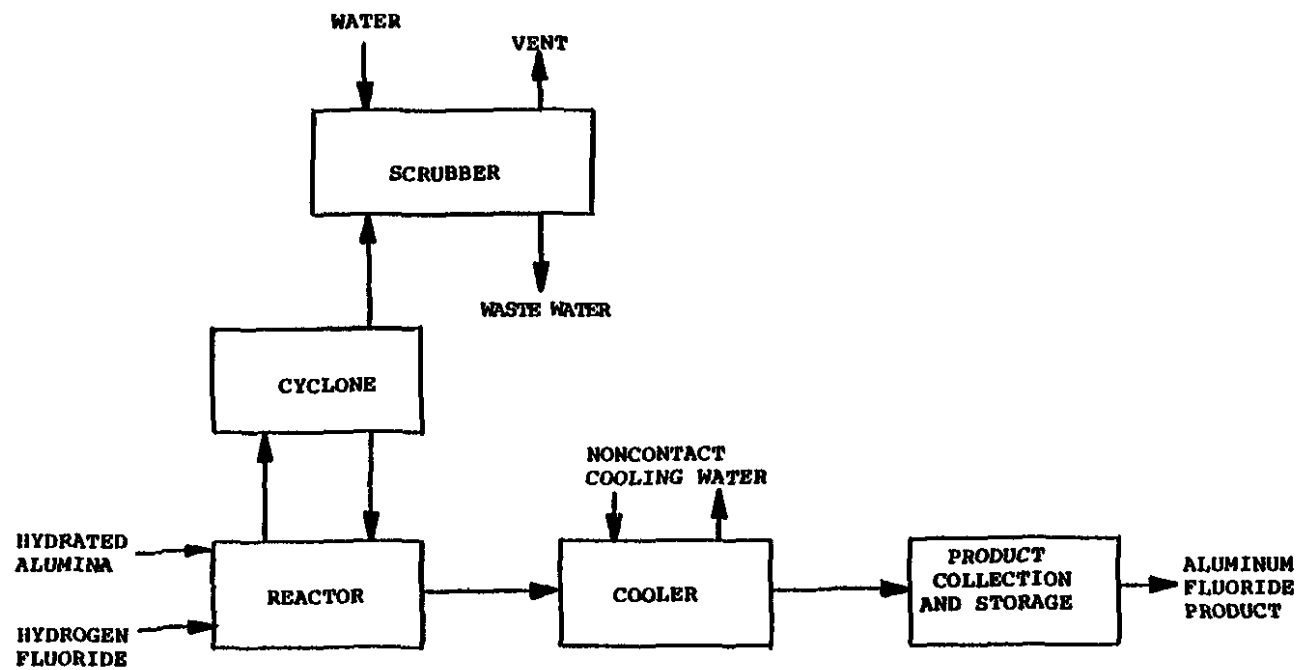


Figure 15-1. General process flow diagram for production of aluminum fluoride.

TABLE 15-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY Aluminum Fluoride

SUBPART W (40 CFR 415.230, 5/22/75)

		STANDARDS					
Product Process	Parameters	BPT/CRA *		BATEA *		NSPS *	
		Max. ¹	Avg. ²	Max.	Avg.	Max.	Avg.
		kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)
AlF ₃	Fluoride	0.68 (40) ³	0.34 (20)				
	TSS	0.86 (51)	0.43 (25)				
	Aluminum	0.34 (20)	0.17 (10)				

* Sections 415.230, 415.231, and 415.232 were revoked by the Agency (41 FR 51601, November 23, 1976).

¹Max. = Maximum of any one day.

²Avg. = Maximum average of daily values for thirty consecutive days.

³flow basis 17,000 l/kg.

TABLE 15-3. WATER USAGE IN THE ALUMINUM FLUORIDE SUBCATEGORY

Source	Water use per unit of production			
	(m ³ /kg of AlF ₃)			
	Plant # 837	Plant # 705 (2)	Plant # 188	Plant # 251 (2)
Non-contact cooling	14.5	NA (1)	6.95	NA
Indirect process contact (pumps, seals, leaks, spills)	12.2	1.15	NA	NA
Maintenance, e.g. cleaning and work area washdown	1.13	2.39	NA	1.02
Scrubber	3.45	8.92	3.46	18.7

(1) NA = Not Available

(2) Currently not manufacturing aluminum fluoride.

can be diverted to the wastewater treatment facility for fluoride removal.

B. Floor and Equipment Washings

The quantity and quality of wastewater generated from these operations varies and depend largely on the housekeeping practices at the individual plants.

C. Scrubber Wastewater

This is the major source of wastewater requiring treatment before discharge or recycle to the scrubber. It is contaminated with hydrofluoric acid, aluminum fluoride and aluminum oxide, and, in some cases, sulfuric acid and silicon tetrafluoride have been detected. These originate as impurities in the hydrofluoric acid used in the process. Table 15-4 presents the wastewater flows at different facilities in the subcategory. Noncontact cooling water is excluded from consideration since it normally does not contain pollutants.

D. Solid Wastes

In the aluminum fluoride production, hydrofluoric acid gas and solids, such as aluminum trihydrate and aluminum fluoride, escape with the vent gases. During scrubbing, the solids are suspended in the scrubber water, while hydrofluoric acid gas is dissolved. In the treatment facility, the wastewater is neutralized with lime and calcium fluoride precipitates out and settles with other suspended solids. In the majority of cases, the solids are retained in a lagoon for periods up to ten years. Table 15-5 gives a summary of the amounts of solids generated at two aluminum fluoride plants.

Different wastes from the aluminum fluoride process are intermixed before treatment. As mentioned earlier, scrubber water constitutes the major source of wastewater in the aluminum fluoride subcategory. If the production of aluminum fluoride is integrated with hydrofluoric acid, then the wastewaters from both plants are combined and treated.

Description of Plants Visited and Sampled

Screening

Plant #705 was visited in the screening phase of the program. Both hydrofluoric acid and aluminum fluoride are produced at this facility by the general processes described earlier. The wastewater from the hydrofluoric acid and aluminum fluoride plants is mixed and sent to the treatment facility. At the treatment facility the combined wastewater is neutralized with lime and sent to a series of settling ponds. The effluent from the last pond is given a final pH adjustment before a portion is discharged and the rest recycled to the process.

TABLE 15-4. WASTE WATER FLOW AT PLANTS #837, #705 AND #251
FOR ALUMINUM FLUORIDE SUBCATEGORY

Source	Flow rate per unit of production ⁽¹⁾ (m ³ /kgg of AlF ₃)		
	Plant #837	Plant #705 ⁽⁴⁾	Plant #251 ⁽⁴⁾
Scrubber water	3.45	8.92 ⁽²⁾	18.7 ⁽³⁾
Maintenance equipment cleaning and work area washdown	1.13	2.39 ⁽²⁾	1.02 ⁽³⁾
Total raw waste flow	4.58	11.3	19.7
Average of above three flows		11.9	

- (1) All flow information is from 308 Questionnaires and plant visits. Unit flow is calculated by dividing waste water flow in m³/day by production in kkg/day.
- (2) From Table 15-6 (see footnotes which describe basis of information).
- (3) From Table 15-7 (see footnotes which describe basis of information).
- (4) Currently not manufacturing aluminum fluoride.

TABLE 15-5. SOLIDS GENERATED AT PLANT #705 AND #251 PRODUCING
ALUMINUM FLUORIDE

Plant	Total Solids Generated(kg/kgg of AlF ₃)
#705 ⁽¹⁾	54 ⁽¹⁾
#251 ⁽¹⁾	69 ⁽¹⁾

- (1) Currently not manufacturing aluminum fluoride.

Figure 15-2 shows a simplified block diagram of the process including the wastewater treatment facility and sampling locations. Table 15-6 presents a summary of flow data of the sampled streams, and the data for important classical pollutant parameters.

Verification

Plant #705 was visited again and the same streams sampled in the screening phase also were sampled and analyzed in the verification phase. The variations in individual stream flows were small during the two phases of sampling. Table 15-6 summarizes the flow data and important conventional and nonconventional pollutant emissions. A second plant (Plant #251) was visited and sampled in the verification phase. Figure 15-3 is a simplified flow diagram of the aluminum fluoride manufacturing plant and the wastewater treatment facility showing the sampling locations. Table 15-7 presents the flow and pollution concentration data for the plant. The aluminum fluoride and hydrofluoric acid waste streams are combined and sent to a gypsum pond for suspended solids removal. The overflow from the pond is mixed with alkaline and acid streams from other plants for neutralization and pH adjustment before final discharge.

Summary of the Toxic Pollutant Data

Following is a list of toxic pollutants which identifies their maximum concentration levels as found in the raw process waste streams sampled during screening and verification.

Maximum Raw Waste Concentrations Observed ($\mu\text{g/l}$)

Pollutant	Screening Plant #705	Verification Plant #705 and #251
Arsenic	200	480
Selenium	68	97
Chromium	70	1100
Copper	120	250
Lead	25	91
Mercury	1.6	11
Nickel	150	290
Zinc	450	450
Cadmium	0.70	33
Antimony	0	3.0
Beryllium	0.80	0.80

Section 5 of this report describes the methodology of the screening and verification sampling program. In the aluminum fluoride industry, seven days of sampling were conducted at Plants #705 and #251. Seven sampling points were identified and studied for the subcategory. The evaluation of toxic pollutant content of these process-related waste streams was based on 637 analytical data points. The screening for toxic organic pollutants at Plant #705 generated an additional 645

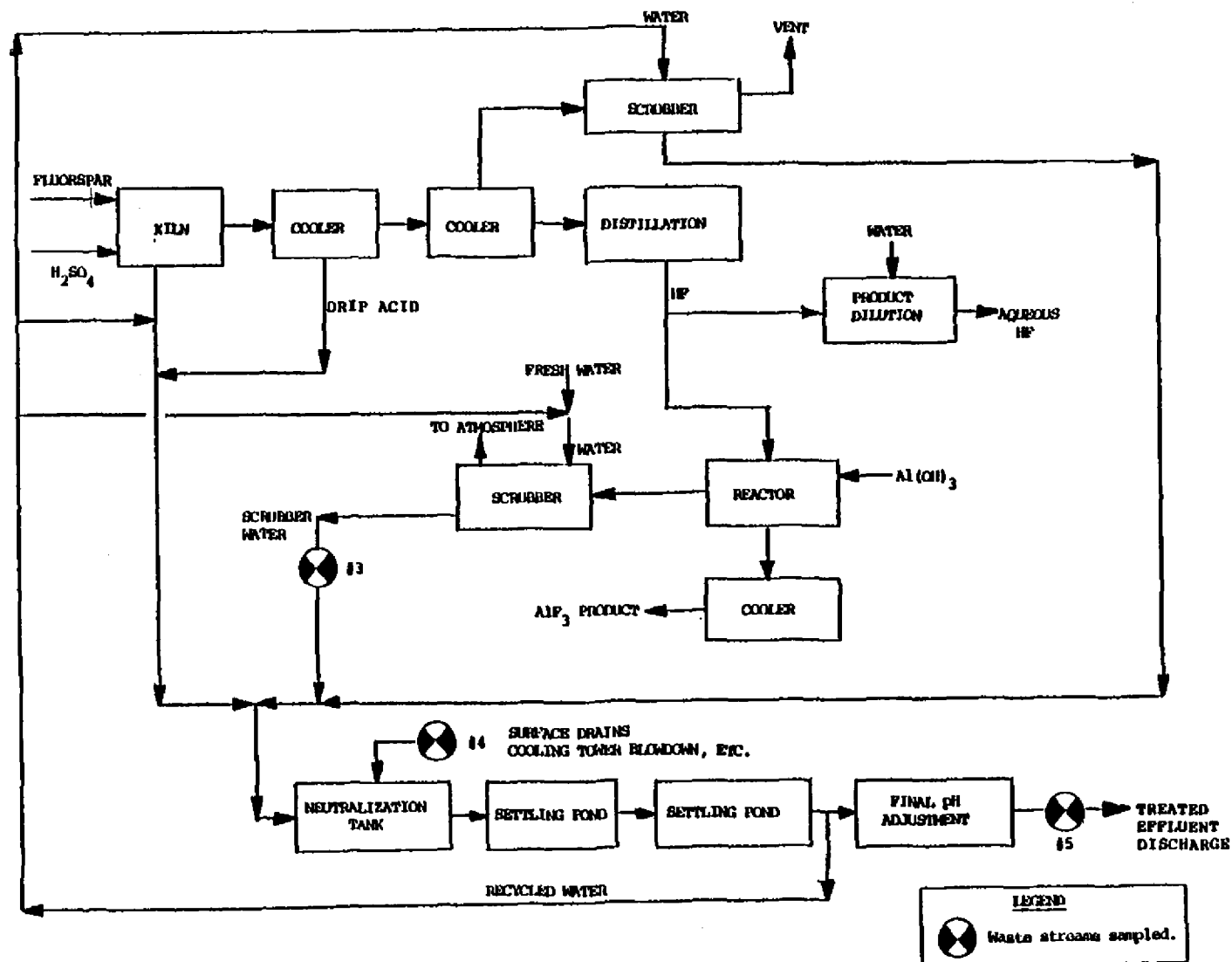


Figure 15-2. General process flow diagram at Plant #705 showing the sampling points (aluminum fluoride manufacture).

TABLE 15-6. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #705 PRODUCING ALUMINUM FLUORIDE

Sampling Phase	Sampled Stream No.	Sampled Stream Description	Unit Flow (m ³ /kkg)	Total Suspended Solids		Fluoride		Aluminum	
				(mg/l)	(3) (kg/kkg) (4)	(3) (mg/l)	(4) (kg/kkg)	(3) (mg/l)	(4) (kg/kkg)
Screening	3	AlF ₃ scrubber	8.92	13,000	120	530	4.7	780	7.0
	4 (1)	Surface drains, cooling tower, blowdown, etc.	2.39	200	0.48	350	0.82	40	0.10
	3&4	Total raw waste load	11.3	11,000 (5)	120	490	5.5	620	7.1
	5	Treated waste (2)	24	80	2.0	70	1.6	10	0.17
Verification Sampling	3	AlF ₃ scrubber	8.92	1,400	13	1400	12	460	4.1
	4 (1)	Surface drains, cooling tower, blowdown, etc.	2.39	200	0.48	170	0.40	27	0.060
	3&4	Total load	11.3	1,200 (5)	13	1100	13	370	4.1
	5	Treated waste (2)	24	2.0	0.048	20	0.55	1.0	0.012

- (1) Consists of waste water from HF and AlF₃ process. Flow indicated is estimated portion of total flow contributed by AlF₃ maintenance and washdown waste water from 308 Questionnaire. Total flow is 17.8 m³/kkg of product for both process wastes combined.
- (2) Consists of waste water from HF and AlF₃ process. Plant currently not manufacturing AlF₃.
- (3) Average of three daily composite samples during verification and single value obtained during screening.
- (4) kg/kkg of AlF₃.
- (5) Weighted average based on unit flows.

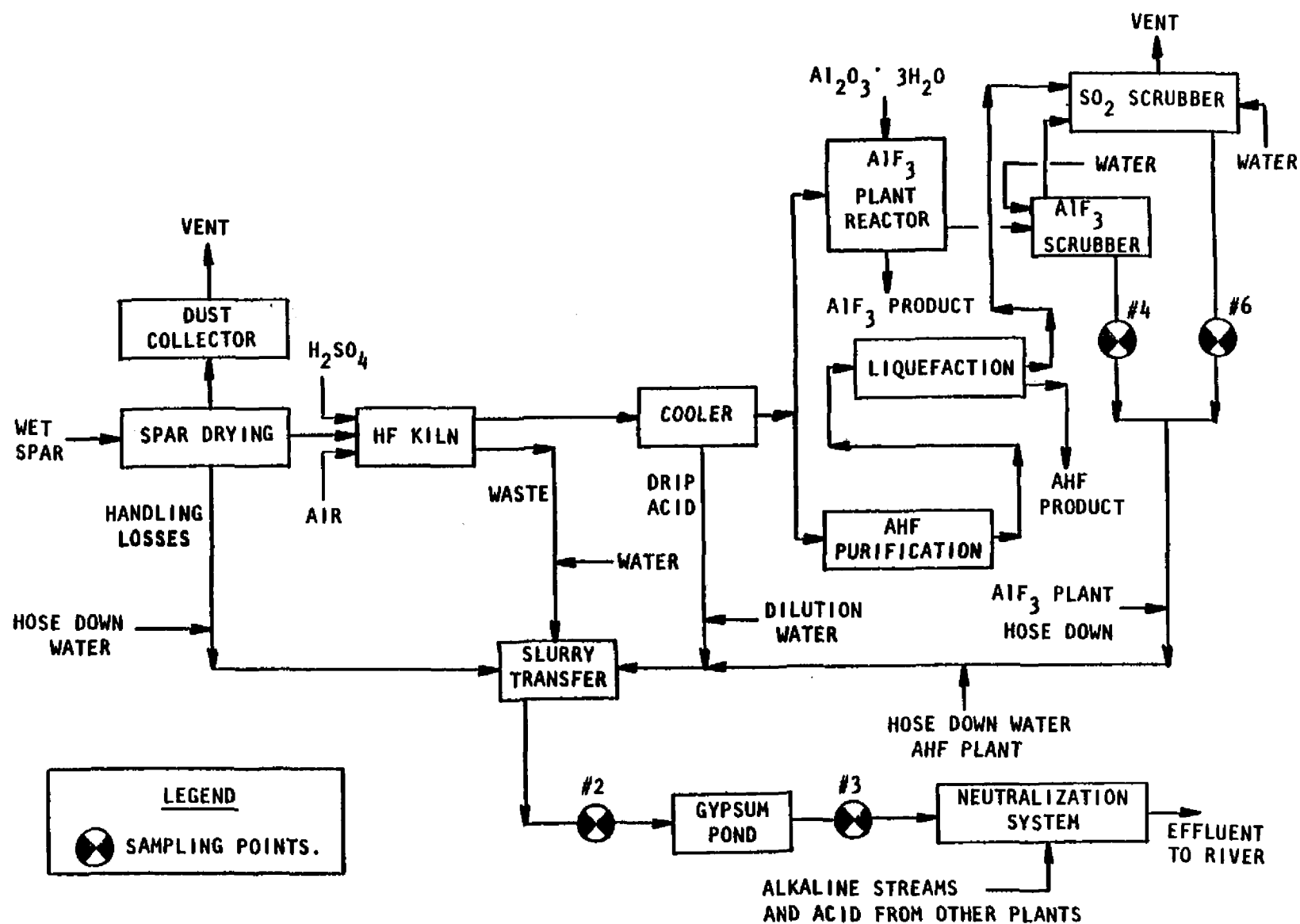


Figure 15-3. General process flow diagram at Plant #251 showing the sampling points. (aluminum fluoride manufacture).

TABLE 15-7. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED STREAMS
FOR PLANT #251 PRODUCING ALUMINUM FLUORIDE

Stream No.	Sampled Stream Description	Unit Flow (m ³ /kkg of AlF ₃)	Total Suspended Solids		Fluoride		Aluminum	
			(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)
Verification Sampling								
4	AlF ₃ scrubber water	12.6	1200	16	470	5.90	50	0.60
6	SO ₂ scrubber water (1)	6.10	0.0	0.0	20	0.14	0.20	0.0010
4&6	Total raw waste load	18.7	1200	16	320	6.0	50	0.60
2	Gypsum pond influent (2)	25.1	19,000	470	660	17	26	0.65
3	Gypsum pond effluent (2)	25.1	9.0	0.23	320	8.0	22	0.55

(1) One half flow of SO₂ scrubber water is assumed to contribute to the AlF₃ process since the total flow is common to the AlF₃ and HF process.

(2) Consists of hydrofluoric acid and aluminum fluoride waste water. Plant currently not manufacturing AlF₃.

analytical data points. The daily raw waste loads were calculated from the waste stream flow rates measured or estimated at the time of sampling and the measured pollutant concentration.

That is,

$$\text{Daily loading (as kg of pollutant per day)} = \frac{(C) (Q)}{1000}$$

where: C is the concentration of the pollutant expressed as mg/l (Note: $\text{kg/m}^3 = 1000 \text{ mg/l}$), and Q is the Aluminum Fluoride process - waste stream flow rate expressed as m^3/day . (m^3 , a cubic meter, is equal to 264.2 U.S. gallons)

Similarly, the unit loadings were calculated from the reported aluminum fluoride production rate, the waste stream flow rate, and the measured pollutant concentration.

$$\begin{array}{l} \text{Unit loading (as kg of pollutant} \\ \text{per kkg of aluminum fluoride)} \end{array} \approx \frac{(C) (Q)}{1000P}$$

where C and Q are the same as described above, and P is the aluminum fluoride production rate expressed as kkg/day. (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs.)

The P and Q factors are for the Aluminum Fluoride Process and thereby the Agency has segregated that portion of the effluent attributable only to the Aluminum Fluoride Process.

Tables 15-8 and 15-9 are tabulations of the raw waste and treated toxic pollutant concentrations and loads determined during the three plant visits. The loads and concentrations are based on the average of three composite samples during verification and one composite sampling during screening. These unit loads were used to determine the minimum, average, and maximum unit loading values presented in Table 15-10.

Based on the total annual production of 134,700 kkg/year in this subcategory and the average waste load generated per unit product in Table 15-10, the estimated total toxic pollutant raw waste loads generated each year for this subcategory are as follows:

TABLE 15-8. TOXIC POLLUTANT AVERAGE RAW WASTE LOADS AND CONCENTRATIONS

SUBCATEGORY		ALUMINUM FLUORIDE						
Pollutant	Screening		Verification				Average Concentration (mg/l)	Avg. Load ↓
	Plant #705		Plant #705		Plant #251			
	(mg/l) (1)	(kg/kkg) (2)	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)		
Arsenic	0.18	0.0020	0.18	0.0020	0.020	0.00030	0.13	
Selenium	0.050	0.0010	— (3)	— (3)	0.050	0.0010	0.050	
Chromium	0.030	0.00030	0.44	0.0050	— (3)	— (3)	0.24	
Copper	0.10	0.0010	0.070	0.0010	0.010	0.00010	0.060	
Lead	0.0050	0.00010	0.020	0.00020	0.010	0.00010	0.012	
Mercury	0.00040	0.0000040	0.00040	0.0000050	0.0030	0.000050	0.0013	
Nickel	0.11	0.0010	0.22	0.0030	0.010	0.00020	0.11	
Zinc	0.16	0.0020	0.080	0.0010	0.020	0.00030	0.090	
Cadmium	0.00020	0.0000020	0.010	0.00020	— (3)	— (3)	0.0050	
Antimony	— (3)	— (3)	0.00040	0.0000050	— (3)	— (3)	0.00040	
Beryllium	0.00020	0.0000020	— (3)	— (3)	— (3)	— (3)	0.00020	

(1) Concentrations based on average raw waste loads shown and total process production and waste flows.

(2) kg/kg of product.

(3) — below analytical detection limit.

TABLE 15-9. TOXIC POLLUTANT EFFLUENT CONCENTRATIONS DURING SAMPLING

SUBCATEGORY		ALUMINUM FLUORIDE		
Pollutant	Plant and Sampling Phase			Average (mg/l)
	#705 Screening (mg/l)	#705 Verification (mg/l)	#251 Verification (mg/l)	
Arsenic	ND ⁽¹⁾	ND	0.0050	< 0.0050
Selenium	ND	ND	0.070	< 0.070
Chromium	0.0070	0.040	0.22	0.090
Copper	0.10	0.0010	0.070	0.060
Lead	0.0020	0.020	0.030	0.020
Mercury	ND	ND	ND	ND
Nickel	0.050	ND	0.050	0.050
Zinc	0.0020	0.0010	ND	0.0020
Cadmium	0.0020	0.0010	ND	< 0.0020
Antimony	ND	ND	ND	ND
Beryllium	0.0020	ND	ND	< 0.0020

(1) ND -- Not Detected

TABLE 15-10. SUMMARY OF RAW WASTE LOADINGS FOUND IN SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY		ALUMINUM FLUORIDE				
Pollutant	Loading Range, kg/day		Unit Loading, kg/kg			No. of Plants Averaged
	Minimum	Maximum	Minimum	Average ⁽¹⁾	Maximum	
<u>Toxic</u>						
Arsenic	0.050	0.080	0.00030	0.0013	0.0020	3
Selenium	0.030	0.16	0.0010	0.0010	0.0010	2
Chromium	0.020	0.22	0.00030	0.0030	0.0050	2
Copper	0.020	0.050	0.00010	0.00070	0.0010	3
Lead	0.0030	0.020	0.00010	0.00015	0.00020	3
Mercury	0.026	0.0080	0.0000040	0.000020	0.000050	3
Nickel	0.026	0.12	0.00020	0.0013	0.0030	3
Zinc	0.040	0.080	0.00030	0.0010	0.0020	3
Cadmium	0.00010	0.0070	0.0000020	0.000080	0.00020	2
Antimony	NA ⁽²⁾	0.00020	NA	0.0000050	NA	1
Beryllium	NA	0.00010	NA	0.0000020	NA	1
<u>Conventional and Nonconventional</u>						
TSS	600	5400	13	50	119.0	3
Fluorine	250	980	5.5	8.1	13.0	3
Aluminum	100	320	0.60	3.9	7.0	3

(1) Average of unit loadings from Table 15-8.

(2) Not Applicable



<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Arsenic	180
Selenium	140
Chromium	400
Copper	94
Lead	20
Mercury	3.0
Nickel	180
Zinc	140
Cadmium	11
Antimony	0.70
Beryllium	0.30

Pollution Abatement Options

Toxic Pollutants of Concern

The toxic pollutants found in actual plant wastewaters are lead, mercury, cadmium, antimony, beryllium, copper, arsenic, chromium, nickel, zinc, and selenium. In the case of selenium, it is apparent that the source was the raw water supply and is therefore not regarded as a process-related pollutant, but control of selenium in the treated effluent may be required in some cases. The toxic pollutants of most concern are chromium and nickel.

Copper and chromium may be present as trace impurities in the hydrofluoric acid used to react with bauxite to form aluminum fluoride. Arsenic, zinc, and nickel may originate as impurities in the bauxite ore. Waste treatment processes should be designed to control TSS, fluoride, and the significant toxic metals. Lead, mercury, cadmium, antimony, and beryllium are eliminated as toxic pollutants of concern because levels observed are too low to be considered treatable.

Process Modification and Technology Transfer Options

- A. Total recycle of wastewater to the scrubbers is feasible if final neutralization is with soda ash. The calcium in the waste is precipitated in the treatment system as calcium carbonate and therefore scaling problems in pipes and scrubbers are reduced.
- B. Passage of the vent gases from the reactor through a cyclone prior to scrubbing with water will remove the aluminum oxide and aluminum fluoride particulates. The collected material in the cyclone can be recycled to the reactor. The installation of a cyclone will result in material recovery and will also reduce the suspended solids load going to the wastewater treatment facility.

Best Management Practices

- A. Rainfall runoff in plant areas, treatment facilities and other places susceptible to fluoride contamination can be collected and sent to the wastewater treatment facility.
- B. If solid wastes containing fluoride are stored on land, studies should be conducted to ascertain the risk of contaminating ground water. Where necessary, provisions can be made for collection and treatment of leachate, permeate, and runoff.
- C. Settling ponds in the wastewater treatment facility should be deep enough (or provided with baffles) to eliminate or reduce turbulence caused by wind and rainfall. This will reduce the incidence of weather-related plant upsets, and suspended solids limitations will be met more consistently.

Prevailing Control and Treatment Practices

Plant #705 practices lime neutralization and settling of the wastewaters. Since aluminum fluoride production is integrated with hydrofluoric acid production, the wastewaters from the two processes are combined before treatment. The plant does not treat noncontact cooling water.

At Plant #837 the tail gases are scrubbed with soda ash solution, and the resulting solution is sent to an adjacent facility for use. The water from the wet scrubbers on the hydrated alumina dryers is also sent to an adjacent facility for use. The wastewaters from area washdown are combined with other product wastewater, treated with hydrated lime and sent to a settling lagoon before discharge.

Plant #188 produces aluminum fluoride in small quantities and in batches. The wastewater from the batch operation is first sent to a collection pond. It then goes to a second pond where lime and alum are added and it finally enters a third pond where the pH is adjusted by recarbonation.

Plant #251 mixes the aluminum fluoride waste with hydrofluoric acid plant waste. The combined wastewater is sent to gypsum ponds for suspended solids removal. The supernatant is treated with an effluent from another plant for pH control and neutralization. Because of the presence of complex fluorides (from the HF process) in the waste waters, the plant is planning to use a new proprietary process in the near future to further reduce fluoride levels in the final effluent.

Advanced Treatment Technologies

Metal ions can be precipitated as hydroxides at alkaline pH levels, and in clarified solutions they may be exchanged for hydrogen or sodium ions by ion exchange. Metal ions at low levels may also be controlled by xanthate precipitation, although the process is not widely used. Sulfide precipitation will reduce copper, nickel, and

zinc to low levels but will not control chromium or arsenic. Although the mechanism is not clear, arsenic levels appear to be reduced in the lime neutralization process followed at most plants, perhaps by entrapment or adsorption of the oxide during the precipitation of calcium fluoride. A combination of lime and ferric sulfate coagulation is probably the most effective and practical method for reducing arsenic concentrations.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT, BAT and NSPS)

Neutralization with lime is widely used in the industry to remove the primary nonconventional pollutant as calcium fluoride. Because lime neutralization to pH 10 results in significant incidental removal of toxic pollutants, alkaline precipitation was chosen as the Level 1 technology. The flow diagram is shown in Figure 15-4.

B. Level 2

A higher removal of suspended metal hydroxides, TSS, and CaF_2 can be achieved by adding dual-media filtration to the Level 1 system. The flow diagram is shown in Figure 15-5.

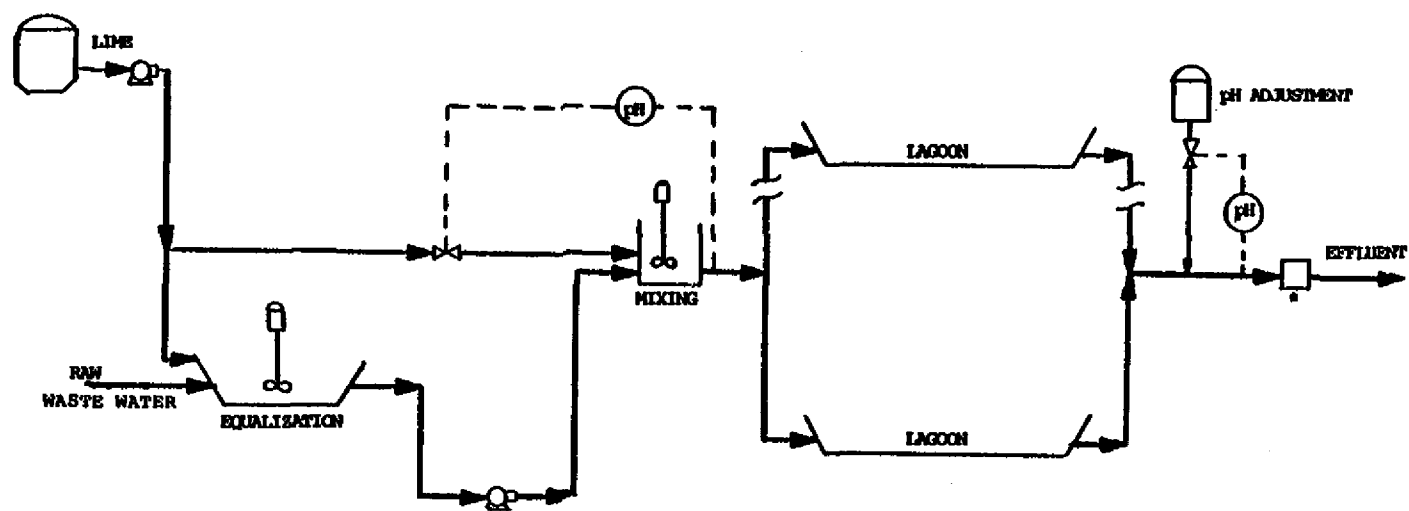
C. Level 3

Sulfide precipitation is added to the Level 2 treatment to attain a higher level of heavy metal removal. Chromium and selenium levels are not appreciably reduced although other toxic pollutants levels are reduced. The flow diagram is shown in Figure 15-6.

D. Level 4

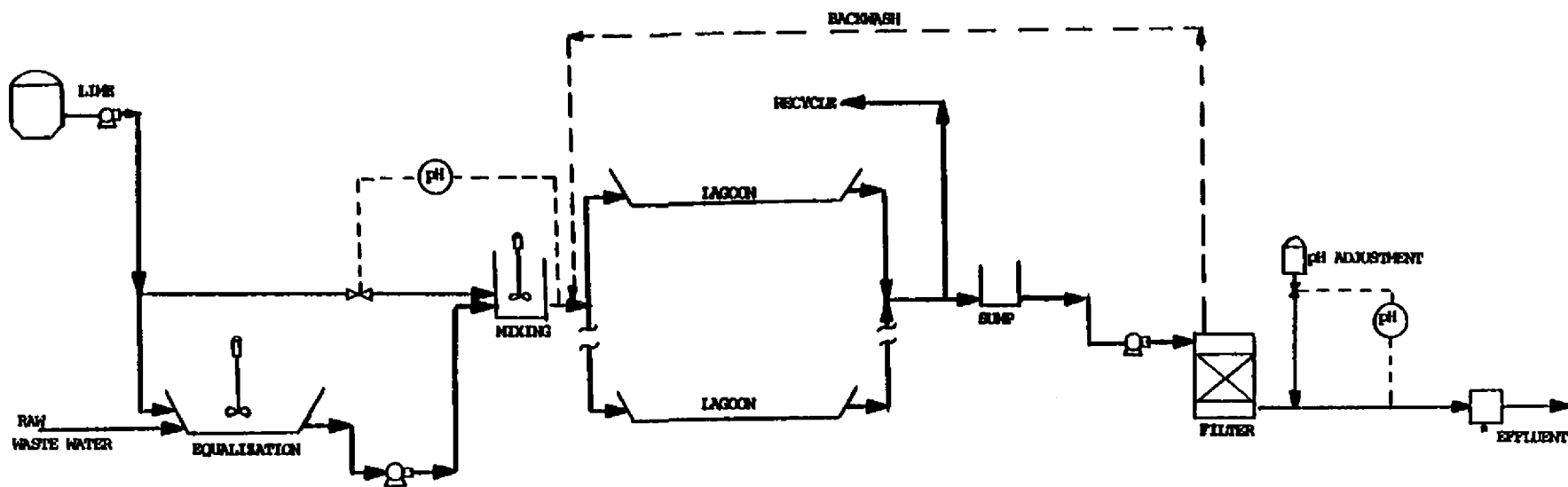
The technology is similar to Level 2, except that soda ash is substituted for part of the lime treatment, permitting partial recycling of effluent. Eighty percent recycle has been demonstrated and is used in the development of plant performance estimates. The flow diagram is shown in Figure 15-7.

A detailed cost comparison and performance evaluation of alternative levels of treatment were utilized in the development of the proposed regulations and were presented in the proposed Development Document (60).



*Includes flow monitoring, pH monitoring and sampler.

Figure 15-4. Level 1 waste water treatment for the aluminum fluoride subcategory.



*Includes flow monitoring, pH monitoring and sampler.

Figure 15-5. Level 2 waste water treatment for the aluminum fluoride subcategory.

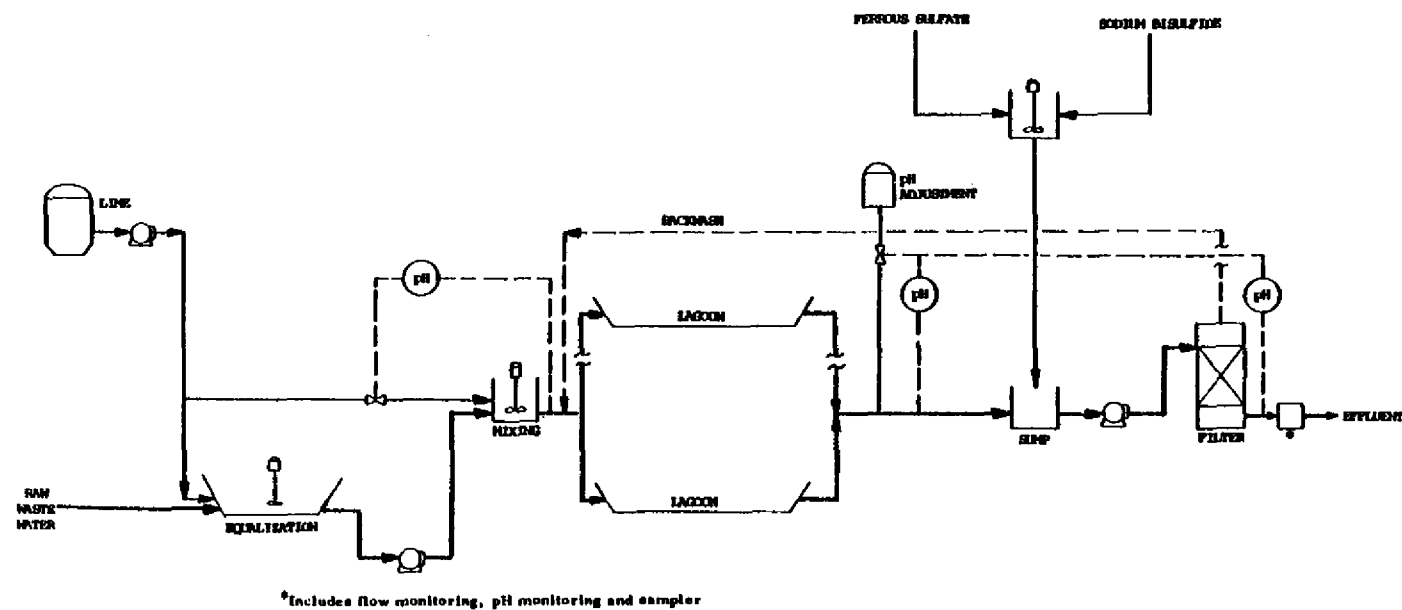


Figure 15-6. Level 3 waste water treatment for the aluminum fluoride subcategory.

Equipment for Different Treatment Levels

A. Equipment Functions

Level 1 consists of flow equalization with first stage lime application followed by second stage lime application and lagoon settling. The final pH is adjusted with hydrochloric acid to the 6-9 range before discharge through an effluent monitoring system.

In Level 2, dual-media filtration is added to provide better control of suspended solids, including heavy metal hydroxides, which are returned to the lagoons as filter backwash.

In Level 3, ferrous sulfide is prepared on site from ferrous sulfate and sodium bisulfide and is added ahead of the dual-media filter shown in Level 2, to reduce heavy metals (except chromium) to lower levels by sulfide precipitation.

Level 4 is a modification of Level 2 which allows partial recycling of final effluent by substituting soda ash for part of the lime treatment, and settling the resulting calcium carbonate in a clarifier before filtration. This step reduces the calcium saturation and permits recycling of effluent without serious scaling problems. Although a small blowdown of effluent is maintained for control of salinity the total mass discharge of toxic pollutants is less than that achieved in Level 2 due to the lower effluent flow rate.

B. Chemicals and Handling

In Level 1 (BPT) and in Level 2, two-stage neutralization is accomplished with lime alone, using conventional handling equipment to deliver milk of lime to two points of application. In Level 3, a mixture of ferrous sulfate and sodium bisulfide is prepared in a well-ventilated space and applied with a conventional solution feeder to the inlet of the Level 2 dual-media filter. With adequate ventilation and proper pH control in this chemical preparation, there are no unusual problems in chemical handling. In Level 4, soda ash is used to furnish part of the alkalinity, employing conventional dry chemical feeding equipment for this nonhazardous chemical.

C. Separation and Removal of Solids

At all levels of treatment the precipitated solids are removed mechanically from the lagoons at regular intervals and are piled in self-draining areas near the lagoons, on land provided for a ten-year operating period. Fluoride and toxic pollutants are in the insoluble or adsorbed form and do not constitute a hazard to the local environment when left at the plant site under controlled conditions, i.e., with leachate and permeate control.

D. Monitoring Requirements

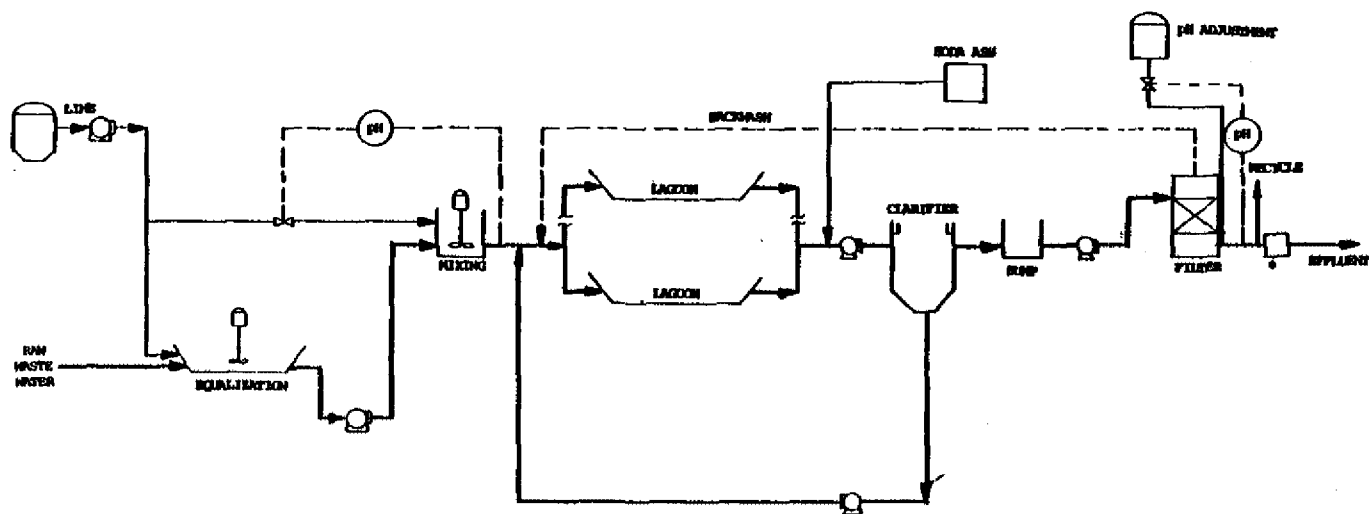


Figure 15-7. Level 4 waste water treatment for the aluminum fluoride subcategory.

Control of fluoride and toxic pollutants in the treatment process can be reasonably assured by pH and fluoride ion field testing equipment. At advanced levels very low values of toxic metals are detected best by atomic absorption methods, normally performed in commercial laboratories on carefully collected and composited samples.

Treatment Cost Estimates

General Discussion

A model plant concept was developed for the subcategory for treatment cost estimation purposes. The BPT treatment system specifications are outlined below.

A. Wastewater Flow

The range of wastewater data on file shows flow variations from 4.58 m³/kkg of AlF₃ to 19.7 m³/kkg of AlF₃ (see Table 15-4). Based on these values, a unit flow of 11.9 m³/kkg of AlF₃ was taken as the average for the wastewater treatment model plant for cost estimating purposes.

B. Production

Five plants manufacture aluminum fluoride at a total production rate of 120,000 kkg/yr. Individual plant production rates range from a minimum of 38 kkg/yr to a maximum of 45,600 kkg/yr with an average of 24,300 and a median of 35,500 kkg/yr. For wastewater treatment cost estimates, three production levels were selected as model plants. These three models reflect the production levels of the plants for which data is on file (excluding a small batch operation plant) and are 15,900 kkg/yr, 35,600 kg/yr and 45,800 kkg/yr.

C. Pollutant Loadings

Observed pollutant loadings varied from 14 to 27 kg/kkg of AlF₃ for suspended solids and from 5.4 to 39.5 kg/kkg of AlF₃ for fluoride. The data sources are as follows:

Source of Data	TSS (kg/kkg-AlF ₃)	F (kg/kkg-AlF ₃)
EPA-440/1-75-037	16-20	15-20
Screening and Verification Phase		
-Plant Data	14-27	5.4-40

For model plants, pollutant loadings of 20 kg of total suspended solids and 18 kg of fluoride per kkg of AlF₃ were used to establish treatment requirements.

D. Treatment Chemicals

Lime (CaO powder form) is added to precipitate fluoride and to raise the pH to a six to nine range. For each of the model plants, lime is added at 25 percent above the stoichiometric requirements for fluoride precipitation. For advanced treatment, ferrous sulfide is added to give a concentration of 10 ppm. This acts as a polishing step to remove additional trace metals from the effluent. For a more advanced level of treatment, soda ash is added in addition to lime (CaO). The soda ash dosage was assumed to be 770 kg/kkg.

E. Generation of Solids

From the pollutant loadings and treatment chemicals above, the waste treatment residue consists of 20 kg/kkg of suspended solids plus 46.2 kg/kkg from added chemicals. Thus, the total solids generated are 66.2 kg/kkg of product. After mechanical removal to self-draining piles, the combined fluoride (as CaF_2) is reasonably stable at the reaction pH reached during lime treatment.

F. Cost Estimates

The estimated treatment costs (BPT) for three different production models are given in Tables 15-11, 15-12, and 15-13. For these models, both the hydraulic and pollution loadings per unit of production are held constant over the entire range of production. A summary of the annual treatment costs is presented in Table 15-14. At this level of treatment, chemicals, labor, and amortization have significant impact on the annual costs.

Basis For Regulations

Evaluation of BPT Treatment Practices

EPA is setting BPT limitations based on Level 1 treatment. All plants in this subcategory have installed BPT technology. Pollutants limited by the BPT regulations are TSS, fluoride, chromium, nickel, and pH. The major pollutants previously regulated are TSS, fluoride, and aluminum. Aluminum is no longer considered a pollutant of concern due to its relatively nontoxic nature. The treatment selected as the basis for BPT regulations will actually benefit from the presence of aluminum which will precipitate under mildly alkaline conditions and act as a coagulant to aid the removal of toxic metals and suspended solids.

BPT Effluent Limitations

A. Technology Basis

The Agency is setting BPT limitations for which the technology basis is, or is equivalent to, equalization, lime neutralization/alkaline precipitation, solids removal by settling or thickening, final pH adjustment, and discharge of the

TABLE 15-11. MODEL PLANT TREATMENT COSTS

Subcategory Aluminum Fluoride Production 15,900 metric tons per year	
	(\$)
A. INVESTMENT COST	BPT
Site development	30,300
Equipment	198,000
Monitoring equipment	20,000
Subtotal	248,300
Contractor's O & P ^a	37,245
Subtotal	285,545
Engineering	57,109
Subtotal	342,654
Contingencies	34,265
Subtotal	376,919
Land	24,000
TOTAL INVESTMENT COST	400,919
B. OPERATION AND MAINTENANCE COST	
Labor and supervision	56,000
Energy	3,500
Chemicals	35,000
Maintenance	37,692
Taxes and insurance	12,028
Residual waste disposal	5,500
Monitoring, analysis and reporting	15,000
TOTAL OPERATION AND MAINTENANCE COST	164,720
C. AMORTIZATION OF INVESTMENT COST	61,325
TOTAL ANNUAL COST	226,044

^a Overhead and Profit

TABLE 15-12. MODEL PLANT TREATMENT COSTS

Subcategory	Aluminum Fluoride
Production	35,600 metric tons per year
	(\$)
A. INVESTMENT COST	BPT
Site development	45,900
Equipment	245,000
Monitoring equipment	20,000
Subtotal	310,900
Contractor's O & P ^a	46,635
Subtotal	357,535
Engineering	71,507
Subtotal	429,042
Contingencies	42,904
Subtotal	471,946
Land.....	42,000
TOTAL INVESTMENT COST	513,946
B. OPERATION AND MAINTENANCE COST	
Labor and supervision	56,000
Energy	5,500
Chemicals	80,000
Maintenance	47,195
Taxes and insurance	15,418
Residual waste disposal	12,500
Monitoring, analysis and reporting	15,000
TOTAL OPERATION AND MAINTENANCE COST	231,613
C. AMORTIZATION OF INVESTMENT COST	76,786
TOTAL ANNUAL COST	308,399

^a Overhead and Profit

TABLE 15-13. MODEL PLANT TREATMENT COSTS

Subcategory	Aluminum Fluoride	
Production	45,800 metric tons per year	
		(\$)
A. INVESTMENT COST		BPT
Site development	53,300	
Equipment	283,000	
Monitoring equipment	20,000	
Subtotal	356,300	
Contractor's O & P ^a	53,445	
Subtotal	409,745	
Engineering	81,949	
Subtotal	491,694	
Contingencies	49,169	
Subtotal	540,863	
Land	60,000	
TOTAL INVESTMENT COST	600,863	
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	
Energy	7,500	
Chemicals	100,000	
Maintenance	54,086	
Taxes and insurance	18,026	
Residual waste disposal	16,000	
Monitoring, analysis and reporting	15,000	
TOTAL OPERATION AND MAINTENANCE COST	266,612	
C. AMORTIZATION OF INVESTMENT COST	87,998	
TOTAL ANNUAL COST	354,611	

^a Overhead and Profit

TABLE 15-14. MODEL PLANT UNIT TREATMENT COSTS

Subcategory Aluminum Fluoride		
Annual Treatment Costs (\$/kkg)		
COST ITEM	PRODUCTION (kkg/yr)	LEVEL OF TREATMENT
		BPT
Annual Operation and Maintenance	15,900	10.36
	35,600	6.51
	45,800	5.82
Annual Amortization	15,900	3.86
	35,600	2.16
	45,800	1.92
Total Annual Cost	15,900	14.22
	35,600	8.66
	45,800	7.74

clarified effluent. This technology represents current practice in the Aluminum Fluoride industry and was therefore selected as the basis for the BPT effluent limitations.

B. Flow Basis

The basis of flow for BPT limitations is estimated from data provided in the 308-Questionnaires for three of the four complete plant responses received, including Plant #837, #251, and #705. Plant #188 was omitted in view of the batch process utilized for the manufacture of aluminum fluoride. The other three plants are continuous manufacturing processes.

The two major raw process wastewater sources contributing to the total plant flow estimates include scrubber and work area washdown. These wastewater sources are summarized in Table 15-4 for the three plants considered. The model plant flow for the AlF_3 industry is estimated as the average total raw wastewater flow for the three plants, and is used to estimate pollutant discharge loadings for the purpose of regulation. Exact measures of treated effluent from the aluminum fluoride industry are not available, since aluminum fluoride plants normally integrate process waste streams with those generated by the hydrofluoric acid process prior to treatment and discharge. The unit flow rates varied widely for the three plants in the range between 4.58 to 19.7 m^3/kg of product which is largely dependant on the scrubber design and water utilization. The AlF_3 process in Plant #251 shares an SO_2 scrubber with the anhydrous hydrofluoric acid process. Wastewater generation from this combined use scrubber was estimated on the basis of hydrofluoric acid utilization in the two processes.

The cleaning and work area washdown flow is similar for the three plants considered, ranging between 1.02 and 2.39 m^3/kg of product.

The average total flow for the three plants is 11.9 m^3/kg of product. This flow is used for the model plant in the aluminum fluoride subcategory.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific numerical effluent limitations are set was based on an evaluation of raw waste data from the screening and verification sampling program. Pollutant data from the plant sampled during screening was used to determine the need for verification sampling. Verification sampling of Plants #705 and #251 provided additional pollutant raw waste concentration data needed to assess the magnitude of the pollution potential.

For conventional pollutants, the Agency has selected pH and total suspended solids for specific treatment and control. Fluoride

was selected as the only nonconventional pollutant parameter because it is a major constituent in the process raw waste and is a pollutant of concern to the Agency. A limitation on aluminum is not set because this constituent of the process wastes will be effectively controlled by treatment required for removal of toxic metals.

Results of the screening and verification sampling are tabulated in Section 15 for the raw process waste stream. The pollutant concentration listed under verification is the highest value observed during sampling at the two plants visited. Toxic pollutants are listed based on their presence, during sampling, at detectable concentration levels. Pollutants from this list were considered candidates for regulation if their concentrations appeared at least once at approximately the lowest level estimated as treatable using any available technology appropriate for their removal. The only two metals which passed this test were chromium and nickel. The metals arsenic, copper, selenium, and zinc were never observed in the raw waste at concentrations equal to or above the lowest level estimated as treatable as presented in Table 8-11 and therefore are not regulated.

Specific numerical effluent loading limitations are set for chromium and nickel for which the average concentration levels (Table 15-8) are considered treatable for at least one plant visited during sampling.

No limitation is being set for aluminum because of its relatively low toxicity and its beneficial effects in removing toxic metals by coprecipitation. In addition, control of the major toxic metal ions should provide adequate control of the aluminum concentration, since the treatment pH for BPT is in the region considered optimal for alkaline precipitation of most metal hydroxides.

D. Basis of Pollutant Limitations

1. Conventional and Nonconventional Parameters

a. pH

The treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS and Fluoride

Pollutant limitations for TSS and fluoride were based on the evaluation of data for the Hydrofluoric Acid subcategory. This evaluation is described in Section 12 under "Basis of Pollutant Limitations." There is no data available from plants where the BPT treatment

performance can be evaluated for the treatment of raw aluminum fluoride process wastewater alone. The aluminum fluoride plants for which data is available integrate raw process wastewater with wastewaters generated from the hydrofluoric acid process.

In view of the similar wastewater characteristics, the effluent concentration from a common treatment system would be the same for TSS and fluoride whether it originates from the AlF_3 industry or the HF industry. Therefore, based on limitations established for the HF industry (Table 12-21), a maximum 30-day average concentration of 97 mg/l TSS and 53 mg/l fluoride are set for the AlF_3 industry. These are relatively high values that are unique to this industry. The variability factor ratio of 2.1 was selected based on the evaluation in the HF subcategory (Table 12-23). The unit effluent load limitation is determined as follows:

$$L \text{ (as kg/kkg)} = \frac{(Q) (C)}{1000}$$

where C is the maximum 30-day average concentration in mg/l, Q is the unit flow in m^3/kkg , and 1000 is the conversion factor for kg to grams. (Note: $kg/m^3 = 1000 \text{ mg/l}$.)

The 24-hour maximum is determined by the following relationship:

$$\begin{array}{ll} \text{Maximum 30-day average} \times \text{VFR} = \text{24-hour maximum} \\ \text{(concentration or unit loading)} & \text{(concentration or unit loading)} \end{array}$$

In this case, the daily maximum TSS concentration is $2.1 \times 97 \text{ mg/l} = 200 \text{ mg/l}$.

The 30-day average effluent is:

$$(97 \text{ mg/l}) (11.9 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 1.2 \text{ kg/kkg}$$

The 24-hour maximum effluent is:

$$(200 \text{ mg/l}) (11.9 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 2.4 \text{ kg/kkg}$$

In the same manner the concentration basis for fluorides is:

$$2.1 \times 53 \text{ mg/l} = 110 \text{ mg/l}.$$

The 30-day average effluent is:

$$(53 \text{ mg/l}) (11.9 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.63 \text{ kg/kg}$$

The 24-hour maximum effluent is:

$$(110 \text{ mg/l}) (11.9 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 1.3 \text{ kg/kg}$$

2. Toxic Pollutants

The effluent limitations set for the selected toxic pollutant control parameters are derived from three sources of information including 1) literature based treatability estimates (Section 8), 2) screening and verification sampling data, and 3) a limited amount of long-term monitoring data from Plant #251.

The sampling results represent raw process waste pollutants observed during three days of composite sampling at each of the plants verified. An assessment of treatment system performance was not possible in view of the lack of representative effluent data available in the subcategory. Effluent data obtained during verification sampling is for treated wastewater from the HF and AlF_3 processes combined, since no plant is available which treats AlF_3 wastes alone. Therefore, the screening and verification data may be used to determine candidate toxic pollutants for regulation without specifying achievable concentration limits which represent the AlF_3 plant performance alone. However, review of the combined HF and AlF_3 waste effluent data in Table 15-9 reveals that all toxic pollutants of concern are treatable within the levels of treatability defined in Section 8 for lime settling (BPT). Removal of toxic pollutants from one wastewater or the other would not differ in light of the similar nature of HF and AlF_3 wastes. Therefore, the literature estimates of treatability discussed in Section 8 have been used as the basis for determining specific numerical limitations for toxic pollutants.

a. Chromium

The literature treatability value of 0.32 mg/l from Table 8-13 for lime settling is considered to represent a long-term average concentration value for chromium in view of plant performance data in the HF and combined HF/ AlF_3 industries.

Since long-term monitoring data on chromium is not available, the variability factor ratio (VFR) of 3.3 was derived from the data in the nickel sulfate

industry. This is justified by the fact that nickel is one of the dominant metal pollutants selected for control in the AlF_3 subcategory and the wastewater characteristics from the AlF_3 and NiSO_4 industries can be assumed to be similar. Therefore,

$$\text{VFR} = \frac{\text{VF of daily measurements}}{\text{VF of 30-day averages}} = \frac{3.9}{1.2}$$

$$\text{VFR} = 3.3$$

The effluent limitations for chromium are determined as follows:

The maximum 30-day average is:

$$(0.32 \text{ mg/l}) (1.2) = 0.38 \text{ mg/l}$$

The 24-hour maximum concentration is:

$$(0.32 \text{ mg/l}) (3.9) = 1.3 \text{ mg/l}$$

The maximum 30-day average effluent limit is:

$$(0.38 \text{ mg/l}) (11.9 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0045 \text{ kg/kg}$$

The 24-hour maximum effluent limit is:

$$(1.3 \text{ mg/l}) (11.9 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.015 \text{ kg/kg}$$

The effluent limitations on chromium are presented in Table 15-15 for BPT treatment.

b. Nickel

For the purpose of regulation, a value of 0.17 mg/l was derived from the HF industry as the subcategory performance for nickel. The limitations are determined as follows:

The maximum 30-day average is:

$$(0.17 \text{ mg/l}) (1.2) = 0.20 \text{ mg/l}$$

The 24-hour maximum concentration is:

$$(0.20 \text{ mg/l}) (3.3) = 0.66 \text{ mg/l}$$

where 3.3 is the VFR as discussed for chromium.

The maximum 30-day average effluent limit is:

$$(0.20 \text{ mg/l}) (11.9 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0024 \text{ kg/kkg}$$

The 24-hour maximum effluent limit is:

$$(0.66 \text{ mg/l}) (11.9 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0079 \text{ kg/kkg}$$

c. Other Metals

The concentration bases for arsenic, copper, selenium, and zinc are also presented in Table 15-15. These pollutants are listed to serve as guidance in cases where these pollutants are found to be of water quality concern. The concentration limitations are also based on literature treatability levels presented in Table 8-11. However in every case these treatability levels were above raw waste concentrations observed for each of these metals.

Basis for the BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Effluent Limitations

A. The Application of Advanced Level Treatment

The Agency has analyzed the cost effectiveness of the base level systems (BPT) and the various advanced level options for conventional, nonconventional and toxic pollutant removal based on utilizing the cost estimates presented in this report. The economic impacts on the aluminum fluoride industry have been evaluated in detail and taken into consideration in the selection of the technology basis for the BAT regulations.

For BAT, EPA is setting limitations based on Level 1 treatment. Pollutants limited in the BAT regulations are fluoride, chromium, and nickel.

The Agency considered the use of treatment Level 2 (addition of dual-media filter) but did not adopt it because the installation of the filter is not very effective in the removal of TSS, fluorides and toxic metals. EPA also considered limitations based on Level 3 and 4 sulfide precipitation and use of soda ash to increase recycle, respectively. These options were rejected because they remove only small incremental amounts of toxic pollutants in this subcategory.

B. Technology Basis

For BAT, the Agency is setting the effluent limitation on fluoride and the toxic metals based on the BPT treatment system. Similar to the Hydrofluoric Acid Subcategory, the addition of dual-media filtration after alkaline precipitation and settling is not considered cost effective based on the conclusions made in Section 7 "Hydrofluoric Acid Subcategory" of EPA's "Treatability Studies for the Inorganic Chemicals Manufacturing Point Source Subcategory" (61) as referred to in Section 12 of this Development Document.

C. Flow Basis

The same flow established for BPT above is used in the development of the BAT effluent limitations. The flow used is 11.9 m³/kgg of product (Table 15-4).

D. Selection of Pollutants to be Regulated

The Agency has selected fluoride and the same two toxic pollutants identified in the BPT regulations for the BAT regulations. The rationale for their selection is discussed above.

E. Basis of Pollutant Limitations

The BAT limitations were set equal to BPT and are given in Table 15-15.

Basis for New Source Performance Standards

A. Technology Basis

For NSPS, the Agency set the same treatment technology as for BAT.

B. Flow Basis

The same flow established for BPT and BAT is used in the development of the NSPS effluent limitations.

TABLE 15-15. EFFLUENT LIMITATIONS

Aluminum Fluoride
Best Practicable Control Technology Currently Available*
Waste Water Flow: 11.9 m³/kkg

Pollutant	Subcategory Performance (mg/l)	VFR	Concentration Basis (1) (mg/l)		Effluent Limit (kg/kkg)	
			Max.		Max.	
			30-day avg.	24-hr. max.	30-day avg.	24 hr. max.

Conventional and
Nonconventional Pollutants:

Total Suspended Solids, TSS	57 ⁽²⁾	3.5/1.7	97	200	1.2	2.4
Fluoride	33 ⁽²⁾	3.4/1.6	53	110	0.63	1.3

Toxic Pollutants:

Arsenic	0.50 ⁽³⁾	3.9/1.2 ⁽⁵⁾	0.60	2.0	— ⁽⁶⁾	— ⁽⁶⁾
Chromium	0.32 ⁽³⁾	3.9/1.2 ⁽⁵⁾	0.38	1.3	0.0045	0.015
Copper	0.32 ⁽³⁾	3.9/1.2 ⁽⁵⁾	0.38	1.3	— ⁽⁶⁾	— ⁽⁶⁾
Nickel	0.17 ⁽³⁾	3.9/1.2 ⁽⁵⁾	0.20	0.66	0.0024	0.0079
Selenium	0.20 ⁽³⁾	3.9/1.2 ⁽⁵⁾	0.24	0.78	— ⁽⁶⁾	— ⁽⁶⁾
Zinc	0.55 ⁽³⁾	3.9/1.2 ⁽⁵⁾	0.66	2.2	— ⁽⁶⁾	— ⁽⁶⁾

(1) VFR: Ratio of the 24-hour variability factor to the 30-day variability factor

(2) Long term average construction based on the HF subcategory regulation (Section 12.7.2).

(3) The lower limit of treatability estimate (Table 8-11) and the industrial waste water treatment system performance (Table 8-12) are used as the basis for the long term average limitation and subcategory performance, since no plant is available where BPT treatment can be evaluated for the AlF₃ waste water alone.

(4) VFR based on HF subcategory evaluation.

(5) VFR based on limited long term data.

(6) No effluent limitation proposed.

* The BPT effluent limitations are also applicable to BAT except for the TSS limitations. The BPT limitations are also applicable for NSPS.

C. Selection of Pollutants to be Regulated

The Agency has selected TSS, fluoride and the same two toxic pollutants identified for the BAT regulations. The rationale for their selection is discussed above. The NSPS limitations are presented in Table 15-15.

Basis for Pretreatment Standards

The Agency is not promulgating PSES and PSNS because a well-operated POTW provides equal or better removal of chromium and nickel (the only toxic pollutants regulated under BAT for this subcategory) than is achieved by BAT for this subcategory, and therefore there is no pass-through of these toxic pollutants in the Aluminum Fluoride Subcategory. At present, there are no indirect dischargers in the Aluminum Fluoride subcategory.

SECTION 16

CHROME PIGMENTS INDUSTRY

Industry Profile

General Description

Chrome pigments are a family of inorganic compounds primarily used as colorants in a number of industries. These pigments are used in paints, ceramics, floorcovering products, ink, paper, and cements. However, certain chromium compounds (i.e., oxides) may be used as raw materials in the manufacture of certain metals and alloys. Chrome pigments vary substantially in their chemical makeup. The various types include chrome yellow, chrome green, chrome orange, molybdenum orange, anhydrous and hydrous chromium oxide and zinc yellow. The industry data profile is given in Table 16-1 and the status of the regulations prior to promulgation of this new regulation is given in Table 16-2.

Subcategorization

Several factors were originally considered in the subcategorization process, such as raw materials, products, manufacturing process, size and age of equipment, and water pollution control technology. It was concluded that if effluent limitations were to be tied to units of production, only subdivision by dominant product was viable as a method of primary subcategorization. Further subdivision was not warranted in the chrome pigment industry. A more detailed discussion of the subcategorization process may be found in Section 4.

General Process Description and Raw Materials

The general manufacturing process for each of the above compounds is given below.

A. Chromium Oxide

C

This pigment consists of two compounds: anhydrous and hydrated chrome oxide (Guigets Green). The amount of the anhydrous chromic oxide produced is approximately ten times the amount of hydrated chromic oxide produced. It is offered in a narrow range of shades from light yellowish to dark bluish green.

The anhydrous oxide is almost pure chromium oxide and the commercial grade consists of a minimum of 98.5 percent Cr_2O_3 . It is prepared by calcination of sodium dichromate with sulfur or carbon according to the reactions given below:



TABLE 16-1. SUBCATEGORY PROFILE DATA SUMMARY⁽¹⁾

SUBCATEGORY	CHROME PIGMENTS
Total subcategory capacity rate	73,500 kkg/year
Total subcategory production rate	73,500 kkg/year
Number of plants in this subcategory	12
308 Data on file for	5
With total capacity of	
With total production of	39,800 kkg/year
Representing capacity	
Representing production	62 percent
Plant production range: ⁽²⁾	
Minimum	100 kkg/year
Maximum	18,000 kkg/year
Average production	6,300 kkg/year
Median production	6,400 kkg/year
Average capacity utilization	78 percent
Plant age range:	
Minimum	38 years
Maximum	60 years
Wastewater flow range:	
Minimum	800 cubic meters/day
Maximum	11,363 cubic meters/day
Volume per unit product:	
Minimum	32 cubic meters/kkg
Maximum	170 cubic meters/kkg

(1) Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

(2) Based on production at 11 plants, all other figures are based on 308 Questionnaires.

TABLE 16-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY Chrome Pigments
 SUBPART AH (40 CFR 415.340, 5/22/75)

		STANDARDS					
Product Process	Para- meters	BPCTCA *		BATEA		NSPS	
		Max. ¹ kg/kg (mg/l)	Avg. ² kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)
Chrome Pigment	TSS	5.1 (76.1) *	1.7 (25.4)	Reserved		Reserved	
	Cr (T)	0.10 (1.5)	0.034 (0.5)				
	Cr ⁺⁶	0.010 (0.2)	0.0034 (0.1)				
	Pb	0.42 (6.3)	0.14 (2.1)				
	Zn	0.72 (10.8)	0.27 (4.0)				
	CN	0.010 (1.5)	0.0034 (0.5)				
	CN(A)	0.10 (0.2)	0.034 (0.1)				
	Fe	0.72 (10.8)	0.27 (4.0)				

* Sections 415.340, 415.341, and 415.342 were revoked by the Agency
 (41 FR 51601, November 23, 1976).

¹Max. = Maximum of any one day.

²Avg. = Average of daily values for thirty consecutive days.

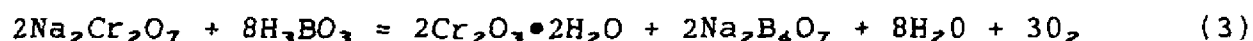
* flow basis 67,000 l/kg.



The use of sulfur as the reducing agent eliminates CO_2 and CO emissions but increases the sulfates in the raw waste as well as producing SO_2 and SO_3 in the off-gases. In the manufacturing process using sulfur, the raw materials consisting of sodium dichromate and sulfur are mixed with water and the resultant solution is fed to a kiln. The material is heated and the reacted materials from the kiln are slurried with water, filtered, washed, dried, ground, screened, and packaged. The effluent gases from the kiln containing sulfur dioxide and sulfur trioxide are wet scrubbed before venting to the atmosphere.

A general process flow diagram of the preparation of anhydrous chrome oxide is given in Figure 16-1.

Hydrated chromium oxide, $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ or $\text{Cr}_2\text{O}(\text{OH})_4$, also known as chromium hydrate and Guigets Green, is a brilliant bluish green. It is made by reacting sodium dichromate with boric acid as follows:



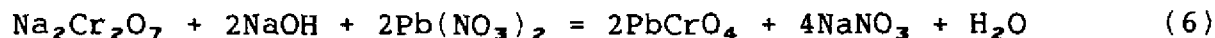
The raw materials are blended in a mixer and then heated in an oven at about 550 degrees C. The reacted material is slurried with water and filtered. The filtered solids are washed with water, dried, ground, screened, and packaged. The filtrate and the wash water are treated with sulfuric acid to recover boric acid according to the reaction given below:



A waste stream containing some boric acid and sodium sulfate is discharge from the boric acid unit. Figure 16-2 is a generalized flow diagram of the process.

B. Chrome Yellow and Chrome Orange

Chrome yellow is one of the more important synthetic pigments. The chrome yellows cover the range of hues from light greenish yellow to reddish medium yellow and consist mainly of lead chromate. They are made by reacting sodium dichromate, caustic soda, and lead nitrate. The reactions are given as:



Lead chromate is formed as a precipitate during the reaction. It is filtered and treated with chemicals for development of desired specific pigment properties, dried, milled, and packaged. The filtrate from the filtration operation is sent to the wastewater

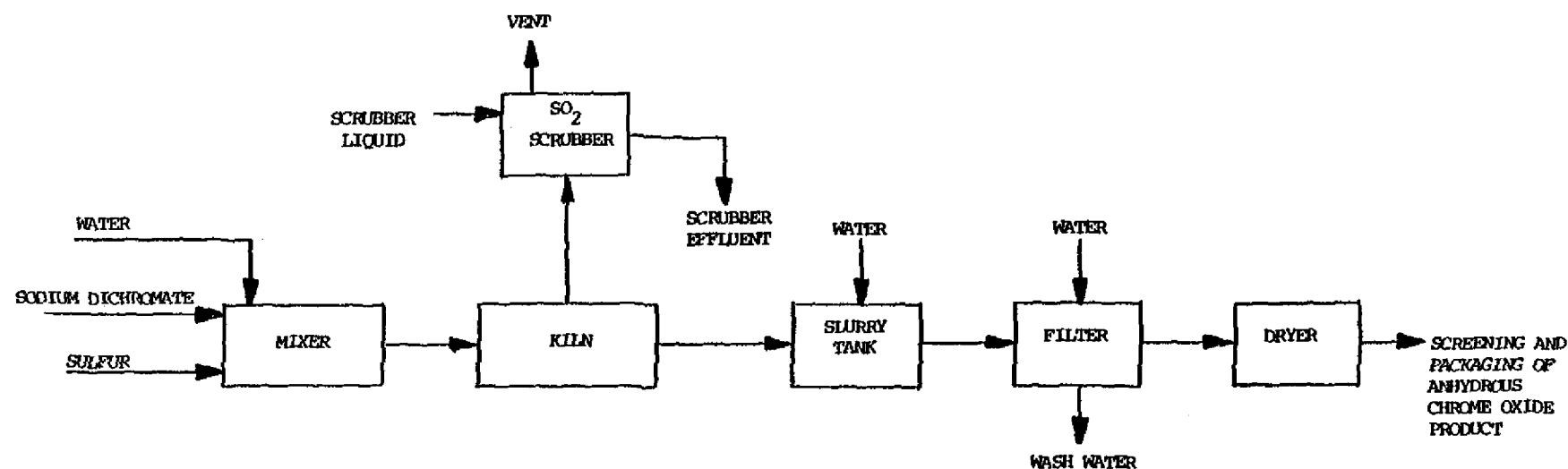


Figure 16-1. General process diagram for production of anhydrous chrome oxide.

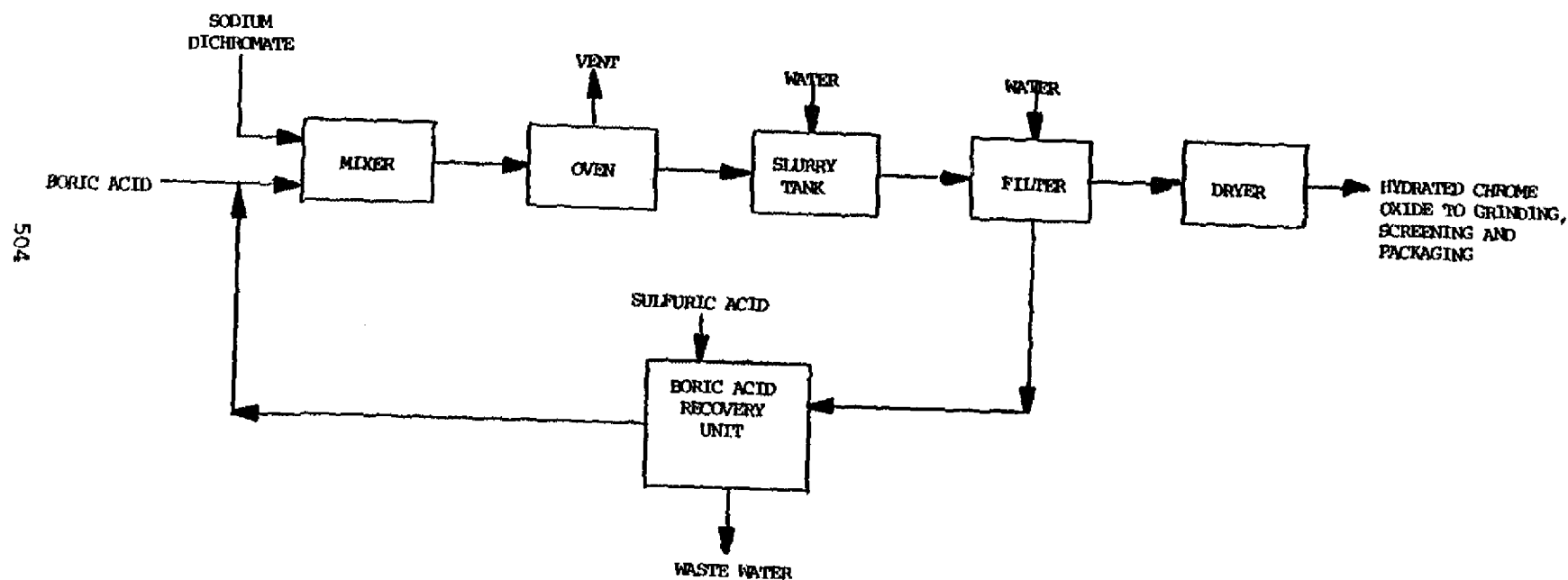


Figure 16-2. General process diagram for production of hydrated chromic oxide.

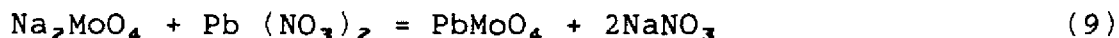
treatment facility. A flow diagram of the chrome yellow manufacturing process is shown in Figure 16-3.

C. Molybdenum Orange

Molybdenum orange is made by the coprecipitation of lead chromate (PbCrO_4) and lead molybdate (PbMoO_4). The resulting pigments are more brilliant than chrome oranges.

The process consists of dissolving molybdic oxide in aqueous sodium hydroxide and adding sodium chromate. The solution is mixed and reacted with a solution of lead nitrate. The precipitate from the reaction is filtered, washed, dried, milled and packaged. The filtrate is sent to the treatment facility.

The reactions are given as follows:



A simplified flow diagram for the manufacture of molybdenum orange is given in Figure 16-4.

D. Chrome Green

Chrome greens are a coprecipitate of chrome yellow and iron blues. They include a wide variety of hues from very light to very dark green. Iron blues are manufactured by reaction of aqueous solutions of iron sulfate and ammonium sulfate with sodium ferrocyanide. The precipitate formed is separated and oxidized with sodium chlorate or sodium chromate to form iron blues, $\text{Fe}(\text{NH}_4) \bullet \text{Fe}(\text{CN})_6$. Chrome green is produced by mechanically mixing chrome yellow and iron blue pigments in water. The coprecipitate formation of chrome green is given by:

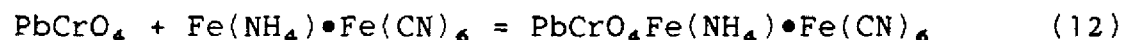


Figure 16-5 gives a process flow diagram for the manufacture of chrome green.

E. Zinc Yellow

Zinc yellow, also called zinc chromate, is a greenish yellow pigment. It is a complex compound of zinc, potassium, and chromium which has the approximate composition $4\text{ZnO} \bullet \text{K}_2\text{O} \bullet 4\text{Cr}_2\text{O}_7 \bullet 3\text{H}_2\text{O}$. It is made by the reaction of zinc oxide,

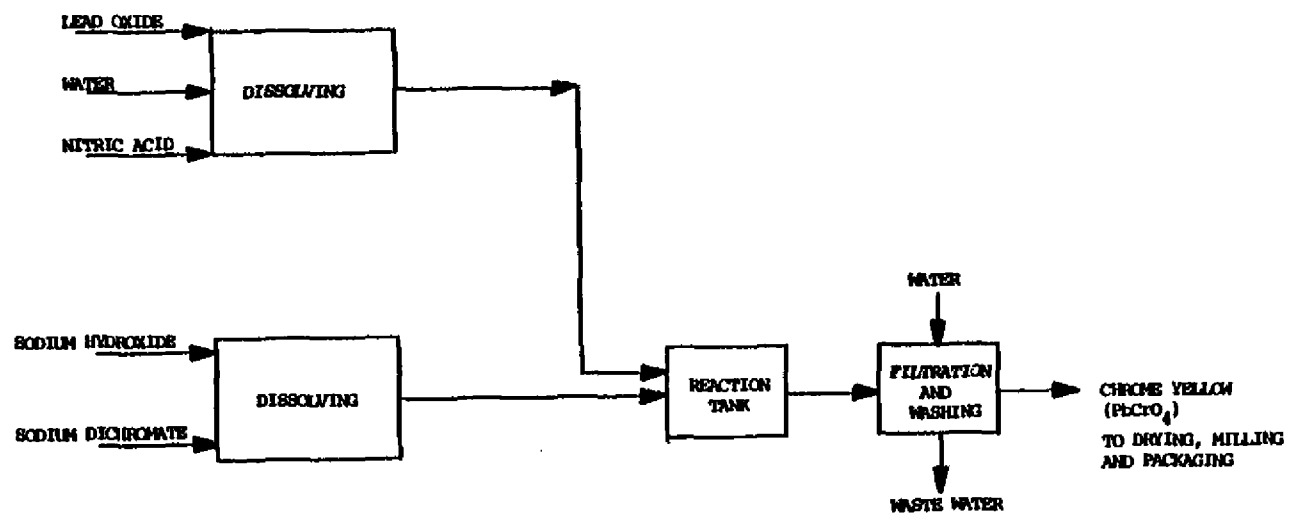


Figure 16-3. General process diagram for production of chrome yellow.

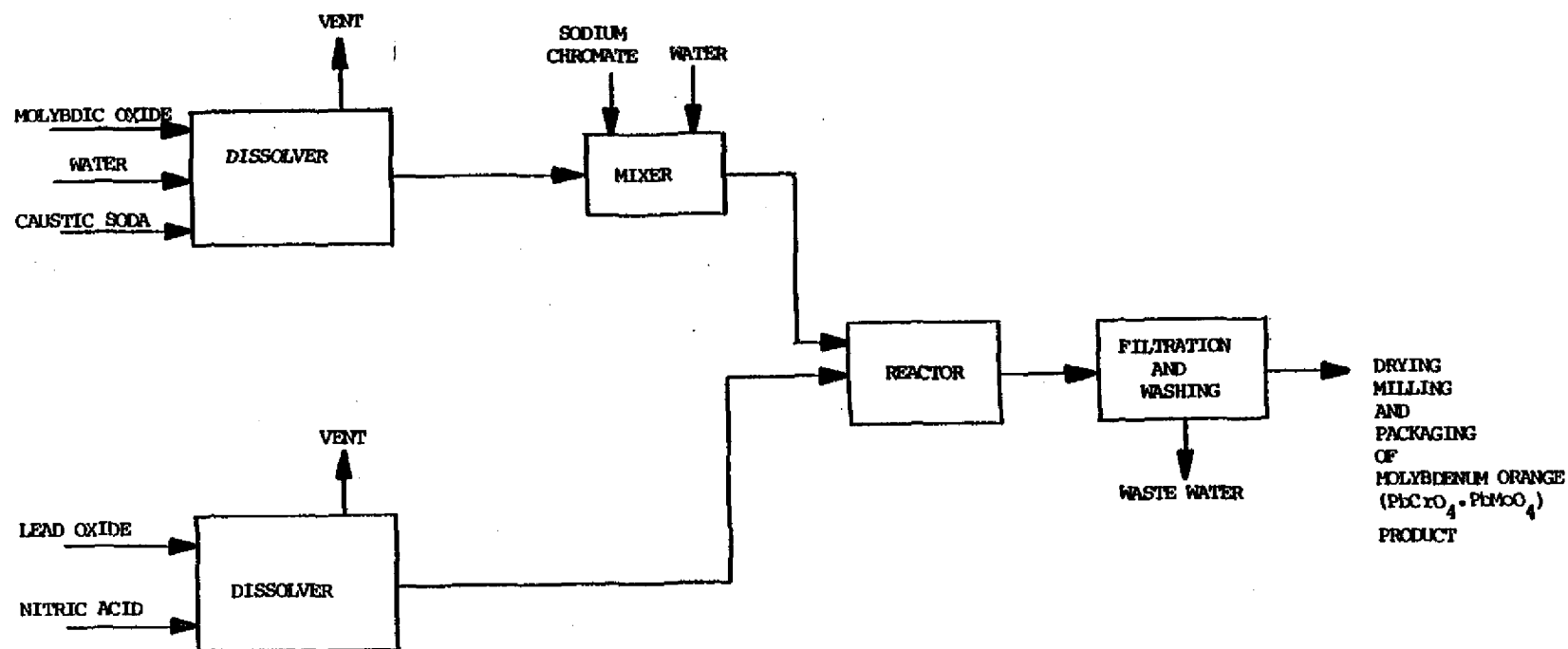
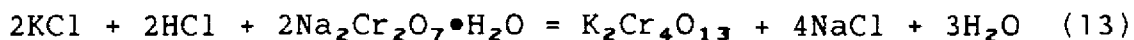


Figure 16-4. General process diagram for production of molybdenum orange.

hydrochloric acid, sodium dichromate, and potassium chloride. Zinc yellow is formed as a precipitate and is filtered, washed, dried, milled, and packaged for sale. The reactions are given as:



A general flow diagram of the manufacturing process is given in Figure 16-6.

Water Use And Waste Source Characteristics

Water Use

In the chrome pigments industry, water is used primarily for noncontract cooling, washing the precipitated product, and as boiler feed for steam generation. In some cases, water is introduced into the reactor along with the raw materials.

In addition, substantial quantities of water may be used in cleaning equipment. This occurs during product changes at plants manufacturing a number of pigments. This partially accounts for the increased unit water use at larger plants, since these plants have the most complex product mix.

In anhydrous and hydrated chrome oxide manufacture, water is used for slurring of the reaction product and in scrubbing the reactor vent gases. Table 16-3 is a summary of water usage at different pigment plants in the chrome pigments subcategory.

Waste Sources

Some plants produce different pigment products sequentially in the same equipment. At a few plants, the different pigment products are manufactured concurrently and the wastewaters combined and treated at a single facility. A generalized flow diagram applicable to all chrome pigment plants is given in Figure 16-7. The wastewater sources are similar for all pigment products except that at chrome oxide plants, an additional scrubber waste is generated. Table 16-4 gives the wastewater flow data summary for several plants. The quantity of wastewater and the pollutants are dependent of the raw materials used. The figures in Table 16-4 represent actual plant discharges.

The data sources for the plants used in the determination of unit flow values presented in Table 16-4 are outlined below:

Plant ~~14000~~ Data based on 308-Questionnaire submission. Only chrome pigment production and flows were included.

Plant ~~14000~~ Data based on 308-Questionnaire submission. Chrome pigment and iron blue production and flows were included.

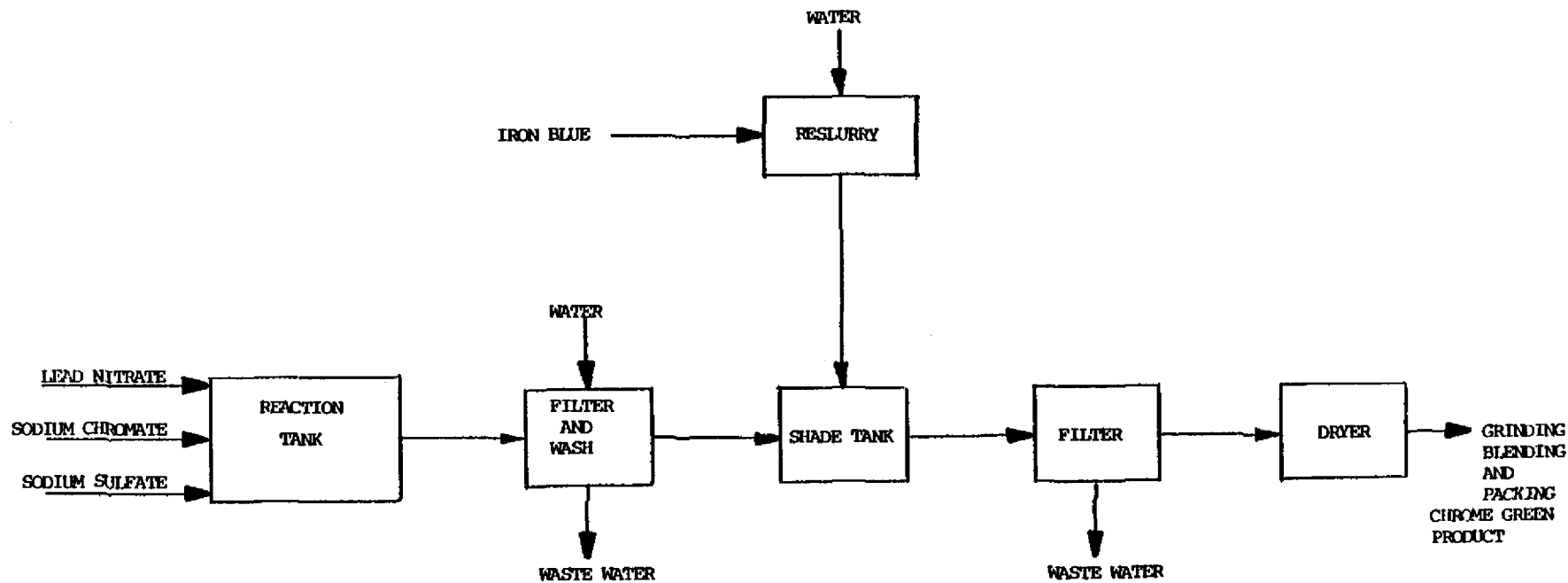


Figure 16-5. General process diagram for production of chrome green.

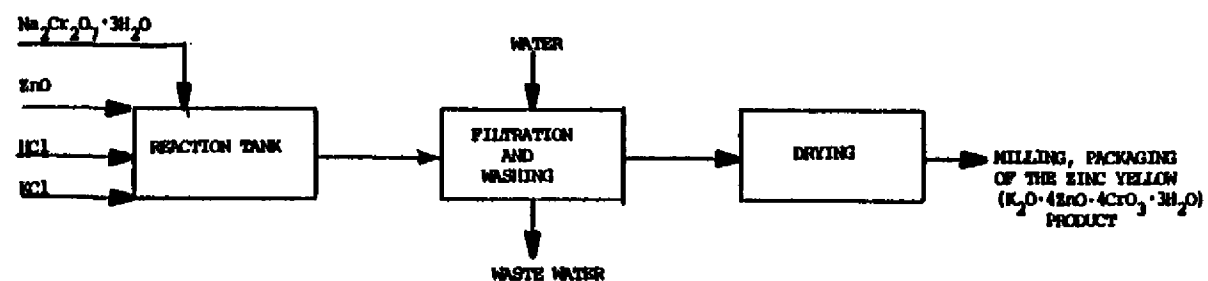


Figure 16-6. General process diagram for production of zinc yellow.

TABLE 16-3. WATER USAGE IN THE CHROME PIGMENTS SUBCATEGORY⁽¹⁾

USE	UNIT FLOW (m ³ /kkg)		
	Plant Designation		
	#464	#436	#214
Noncontact cooling	9.50	6.45	NA
Direct process contact	18.6	147	32.6
Indirect process contact	7.18	NA ⁽²⁾	NA
Maintenance	12.0	1.78	0.152
Scrubbers	3.30	9.56 ⁽³⁾	NA
Boiler Feed	2.52	11.1	0.152
Total	53.1	176	32.9

(1) Includes all chrome pigment product mixes. Values indicated only for those plants that reported complete information.

(2) NA - Not applicable.

(3) Iron blue pigment process.

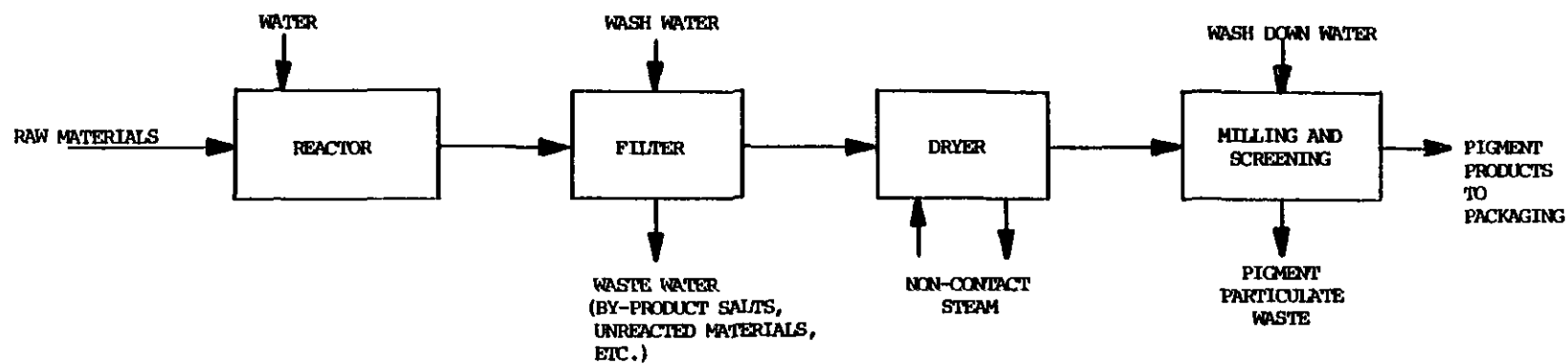


Figure 16-7. General process diagram for production of chrome pigment complexes.

Plant #436. Data based on 308-Questionnaire submission. Chrome pigment production and flows were included.

Plant #002. Data based on three days of sampling. Chrome pigment and organic pigment (20 percent) productions and flows were included.

Plant #894. Data based on three days of sampling. Chrome pigment, iron blue, and organic pigment (15 percent) productions and flow were included.

As previously discussed, various plants make several chrome pigments sequentially or concurrently. Thus the unit hydraulic load going to the treatment facility will be an average of all the waste loads from the different processes. The raw waste from a complex plant may contain nearly all of the following substances: sodium acetate, sodium chloride, sodium nitrate, sodium sulfate, potassium chloride; lead, iron, and zinc salts; soluble chromium and pigment particulates.

Description Of Plants

Screening

Plant #894 was visited during the screening phase of the program. The samples for this plant were analyzed for all toxic and conventional pollutants.

This plant produces over 100 products including organic pigments such as copper phthalocyanine, and all the wastes are combined and treated together. Treatment consists of hexavalent chromium reduction, equalization and neutralization, followed by clarification and filtration. Sulfur dioxide is added to reduce the hexavalent chromium to the trivalent state at a low pH prior to hydroxide precipitation. The backwash from the sand filters is cycled to the equalization tank, while the sludge from the clarifiers is passed through filter presses and then hauled to a landfill. The landfill has a bottom consisting of two clay layers sandwiching a gravel layer to allow for collection of leachate drainage. Any water from the sludge is trapped in the gravel layer, and is pumped out and returned to the plant for retreatment.

Verification

Two plants were visited during the verification phase of the program. The first plant, #002, has a rather large product mix. However, one of the larger continuous units can have a major impact on the raw waste characteristics. This unit either produces lead chromate or zinc chromate. During the sampling period, zinc chromate was being produced. All process wastewaters are treated continuously. First, the wastes are treated in an SO_2 reactor to convert hexavalent chromium to the trivalent state. The pH is then adjusted to 8.5 and then the waste is passed through precoated filters, followed by discharge to the sewer. Figure 16-8 shows the treatment flow diagram and sampling points. Table 16-5 shows the waste flows and pollutant

TABLE 16-4. SUMMARY OF WASTE WATER FLOW

SUBCATEGORY: CHROME PIGMENTS	
Plant Designation	Waste Water Flow ⁽¹⁾ (m ³ /kkg)
#464	41.1
#214	32.8
#436	149
#002	78.4 ⁽²⁾
#894	170 ⁽²⁾
Weighted Average Flow	105 ⁽³⁾

(1) Includes waste water from all pigment product mixes.

(2) Includes organic pigments.

(3) Weighted on the basis of production since unit waste flow is directly related to plant production:

$$\text{Weighted average} = \frac{\sum [(\text{unit flow}) (\text{production})]}{\sum (\text{production})}$$

$$\text{i.e.} = \frac{Q_1(P_1) + Q_2(P_2) + Q_3(P_3) + \dots + Q_n(P_n)}{P_1 + P_2 + P_3 + \dots + P_n}$$

Where Q = Unit flow and P = production (which is considered confidential information).

loadings. At sample point #2, half the sample was filtered through a glass fiber filter on a Buechner funnel to simulate the filtration process which was being bypassed at the time of sampling. Analyses were carried out on the filtered and unfiltered samples in order to make possible a comparison of the total and dissolved concentrations.

A review of the sampling data indicates that the waste treatment facility was not functioning properly during the period of sampling at Plant #002. The inadequacies observed in the treated effluent quality have been related to deficiencies in the treatment system design including 1) inadequate equalization and SO₂ contact facilities, and 2) inadequate clarification which in turn caused blinding of the filter and the subsequent need for filter bypass.

Plant #894 was also visited during the verification phase. The treatment system has been previously discussed. The major problem at this plant is the high unit water use rate. However, this was the only plant found with an adequately designed and operated treatment system in this subcategory.

During the verification phase, only certain pollutant parameters were analyzed. These were pH, cyanide, suspended solids, and toxic metals. No organics were analyzed during verification.

Figure 16-9 shows the treatment system flow diagram with the sampling points indicated. Table 16-6 gives waste flows and pollutant loadings.

Toxic Pollutant Concentrations

The toxic pollutants found above treatable concentrations in the raw wastes during sampling are given in the table below.

Maximum Concentration ($\mu\text{g/l}$)

Pollutant	Screening	Verification
		2 Plants
Cadmium	79	1,250
Cyanide	360	8,200
Chromium	55,000	349,000
Copper	7,500	4,700
Lead	36,000	69,000
Zinc	4,100	273,000
Antimony	7,700	1,475
Selenium	> 10	28
Silver	7	20
Nickel	160	740
Phenol*	73	
Bis (2 ethylhexyl)		
Phthalate*	>0.1	

* from organic pigment process

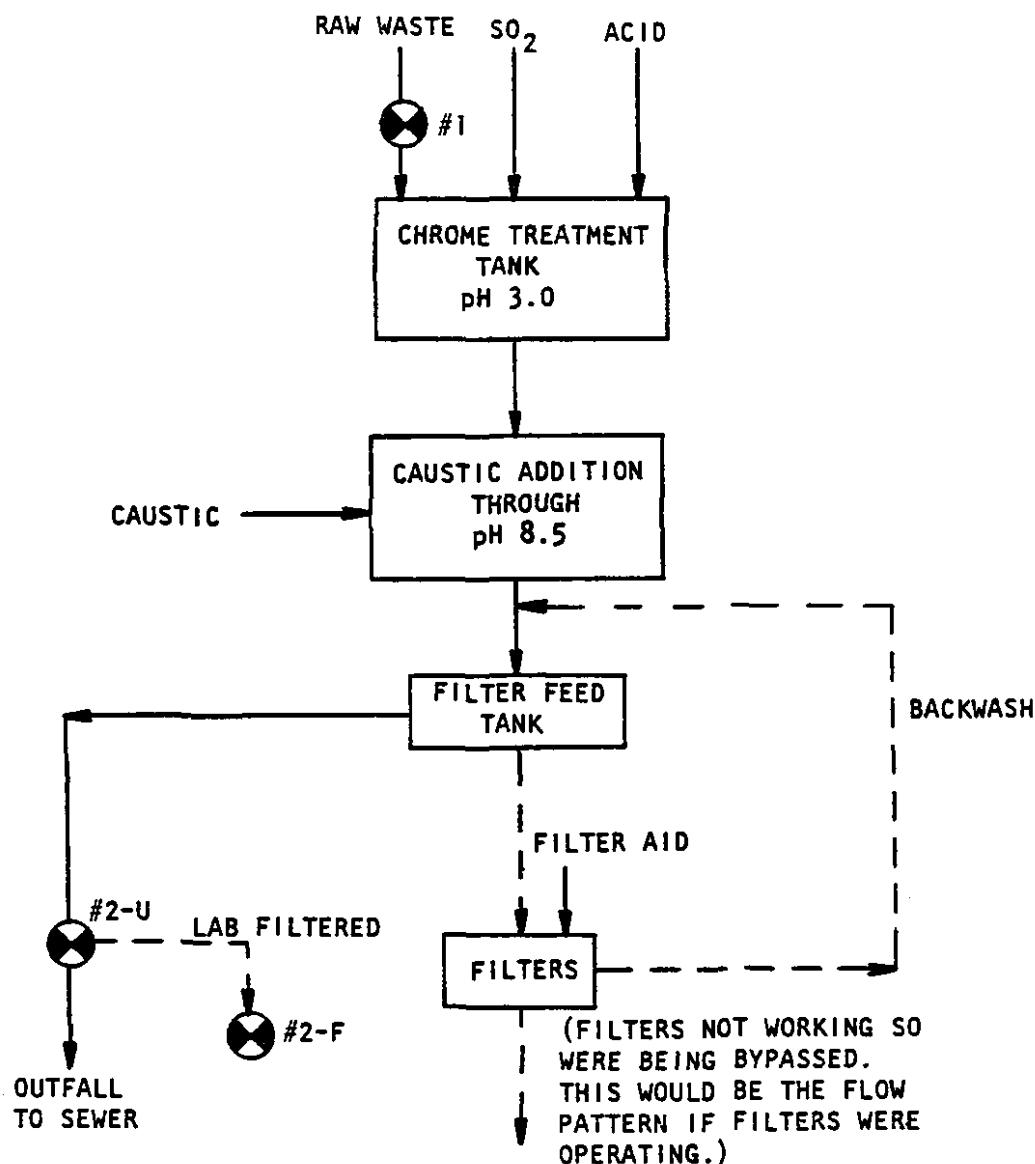


Figure 16-8. General waste water treatment process flow diagram at plant #002 showing the sampling points. (Chrome pigment manufacture.)

TABLE 16-5. FLOW, POLLUTANT CONCENTRATION AND LOAD
DATA OF THE SAMPLED WASTE STREAMS FOR PLANT # 002

SUBCATEGORY: CHROME PIGMENTS					
Conventional and Nonconventional Pollutants					
mg/l (kg/kg of chrome pigments)					
Stream #	Stream Description	Flow (m ³ /kkg)	TSS	Fe	Cr (VI)
1	Raw Waste	78.4	700 (55)	1.6 (0.13)	300 (24)
2-U	Unfiltered Treated Waste	78.4	970 (76)	2.3 (0.18)	120 (9.4)
2-F	Filtered Treated Waste	78.4	NA ⁽¹⁾	0.06 (0.0047)	NA ⁽¹⁾

(1) NA - Not available

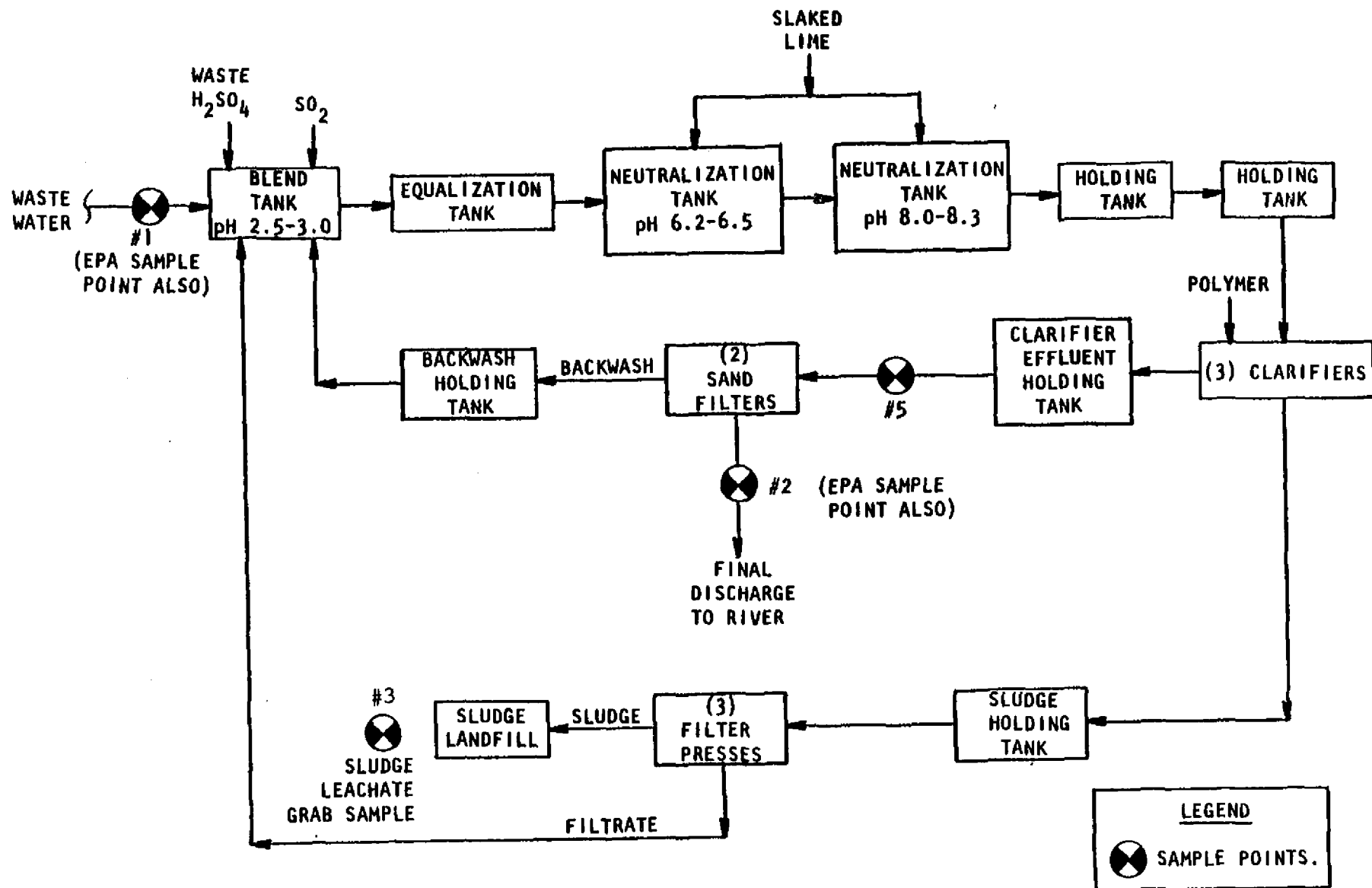


Figure 16-9. General waste water treatment process flow diagram at plant #894 showing the sampling points. (Chrome pigment manufacture.)

TABLE 16-6. FLOW, POLLUTANT, CONCENTRATION AND LOAD DATA FOR THE SAMPLED WASTE STREAMS AT PLANT # 894

SUBCATEGORY: CHROME PIGMENTS					
Conventional and Nonconventional Pollutants ⁽³⁾ mg/l (kg/kg of chrome pigments)					
Stream #	Stream Description	Flow (m ³ /kkg)	TSS	Fe	Cr (VI)
1	Raw Waste	170	770 (130)	48 (8.2)	ND ⁽²⁾
2	Final Discharge	170	3.9 (0.66)	0.30 (0.051)	0.023 (0.0039)
3	Leachate	NA ⁽¹⁾	ND ⁽²⁾	0.04 (NA)	ND ⁽²⁾
5	Sand Filter Influent	170	11 (1.9)	1.0 (0.17)	ND ⁽²⁾

(1) Not Applicable

(2) Not Detected

(3) Verification sampling which involves three 24-hour composite samples.

Screening data was obtained at Plant #894. Verification was completed at Plants #894 and #002. The only organic pollutant not listed above found in the raw waste above the protocol detectable limit (10 µg/l) was naphthalene at 14 µg/l. It should be noted, however, that some nitrobenzene (56 µg/l) and phthalates at levels up to 220 µg/l were found in the treated effluent and one raw water intake. Since they were not present in the raw wastes, it is presumed they are present as a result of sample contamination; i.e., plasticizer in Tygon Tubing. No organic pollutant sampling was made during verification.

Section 5 of this report describes the methodology of the screening and verification sampling program. In the chrome pigments industry, 9 days of sampling were conducted at Plants #894 and #002. This involved five different sampling points for raw and treated waste streams. The evaluation of toxic metals content of these process related waste streams was based on 195 analytical data points. The screening at Plant #894 for organic pollutants generated another 228 data points. The daily raw waste loads were calculated from the waste stream flow rates measured or estimated at the time of sampling and the measured concentration.

That is,

$$\text{Daily loading as } \frac{\text{kg of pollutant}}{\text{day}} = \frac{(C)(Q)}{1000}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: kg/m³ = 1000 mg/l), and

Q is the waste stream flow rate expressed in units of m³/day. (m³, a cubic meter, is equal to 264.2 U.S. gallons.)

Similarly, the unit loadings were calculated from the reported chrome pigments production rate, the waste stream flow rate, and the measured pollutant concentration.

$$\text{Unit loading (as kg of pollutant per kkg of chrome pigments)} = \frac{(C)(Q)}{(1000)(P)}$$

where C and Q are the same as described above, and P is the pigment production rate expressed in units of kkg/day. (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs.)

The minimum, average, and maximum values are based on data from those plants where the particular pollutant was found at concentrations greater than the analytical detection limits and significant in that it could conceivably be treated by an available treatment technology regardless of economic considerations.

In Table 16-7, the toxic pollutant raw waste data are presented as the average daily concentrations and the unit loading found at the

individual plants. The overall averages are also shown and were subsequently used in the calculations of the average daily loadings and the average unit loadings shown in Table 16-8 along with the corresponding minimum and maximum values. The toxic pollutant concentrations in the treated effluent are presented in Table 16-9 for the two plants visited during verification sampling.

Based on the total annual production from Table 16-1 of this subcategory and the average waste load generated per unit product from Table 16-8, the estimated total toxic pollutant raw waste loads generated each year for this subcategory are as follows:

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Antimony	42,000
Cadmium	8,000
Chromium	1,160,000
Copper (1)	54,000
Lead	252,000
Nickel (1)	1,400
Zinc	104,000
Mercury	260
Cyanide (1)	34,000
Phenol (1)	900
Phenolics (1)	1,500,000

(1) Probable Source is organic pigment process or other processes.

The waste load for zinc and lead in the above have been adjusted to reflect the fact that not all plants produce a chrome pigment containing lead, and most do not produce zinc yellow. For example, a plant that does not produce zinc yellow will have a very low level of zinc in the raw waste load. See the data for plant #894 in Table 16-7.

TABLE 16-7. TOXIC POLLUTANT RAW WASTE DATA

SUBCATEGORY: CHROME PIGMENTS				
Average Daily Pollutant Concentrations and Loadings at Plants Sampled (1)				
	<u>mg/l.</u>			
	(kg/kg of Chrome Pigments)			
Pollutant	Plant Designation			Overall Average
	#894(S) (2)	#894(V) (3)	#002(V)	
Antimony	7.7 (1.5)	0.76 (0.13)	1.4 (0.11)	3.3 (0.58)
Cadmium	0.79 (0.15)	0.88 (0.15)	0.20 (0.016)	0.62 (0.11)
Chromium	55 (10)	82 (14)	310 (24)	150 (16)
Copper	7.5 (1.4)	4.1 (0.70)	1.4 (0.11)	4.3 (0.74)
Lead	36 (6.8)	4.8 (0.82)	54 (4.2)	32 (3.9)
Nickel	0.16 (0.030)	0.017 (0.0028)	0.32 (0.025)	0.17 (0.019)
Zinc	4.1 (0.78)	4.2 (0.71)	163 (13)	57 (4.8)
Mercury	* *	0.042 (0.0072)	0.00043 (0.000034)	0.014 (0.0036)
Cyanide, CN	3.6 (0.68)	4.9 (0.84)	0.71 (0.056)	3.1 (0.53)
Cyanide, CN(A)	* *	0.88 (0.15)	* *	0.88 (0.15)

(1) The methodology of the sampling program is described in Section 5.1.2, and Section 16.3.3 presents the scope of sampling in the chrome pigments industry.

(2) S - Screening data from one 72-hour composite sample of individual or combined raw waste streams.

(3) V - verification data from three 24-hour composite samples, averaged, from each raw waste sampling point.

* Concentration below detection or no data available.

TABLE 16-8. SUMMARY OF RAW WASTE LOADINGS FOUND IN SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY CHROME PIGMENTS						
Pollutant	Loading Range, (kg/day)		Minimum	Unit Loading, (kg/kg) Average		No. of Plants Averaged ⁽²⁾
	Minimum	Maximum		Maximum		
<u>Toxic</u>						
Antimony	6.0	98	0.11	0.58	1.5	3
Cadmium	0.87	10	0.016	0.11	0.15	3
Chromium ⁽¹⁾	700	1300	10	16	24	3
Copper	6.1	96	0.11	0.74	1.4	3
Lead	55	459	0.82	3.9	6.8	3
Nickel	0.19	2.0	0.0028	0.019	0.030	3
Zinc	48	714	0.71	4.8	13 13	3
Mercury	0.0019	0.48	0.000034	0.0036	0.0072	2
Cyanide, CN	3.1	56	0.056	0.53	0.84	3
Cyanide, CN(A)	9.8			0.15		1
Phenol	0.93			0.014		1
Phenolics	8.8			0.13		1
<u>Conventional and Nonconventional</u>						
Total Suspended Solids, TSS	3100	8800	55	93	130	2
Fe	7.1	550	0.13	4.2	8.2	2
Hexavalent ⁽¹⁾ Chromium Cr+6	1300			24		1

(1) Hexavalent chromium is only one valent form of chromium.

(2) Only those plants where the pollutant was observed at significant levels were included.

TABLE 16-9. TOXIC POLLUTANT TREATED WASTE DATA ⁽¹⁾

SUBCATEGORY: CHROME PIGMENTS			
Pollutant (mg/l)	Plant Designation		Overall ⁽²⁾ Average Concentration
	#894	#002	
Antimony	0.30	0.43	0.37
Cadmium	0.0084	0.12	0.064
Chromium	0.33	130	65
Copper	0.035	0.077	0.056
Lead	0.11	1.5	0.81
Nickel	0.021	0.083	0.052
Zinc	0.058	117	59
Mercury	ND ⁽³⁾	ND	ND
Cyanide, CN	0.065	*	0.065
Cyanide, CN(A)	0.0067	*	0.0067

(1) Verification sampling concentration data, average of three 24-hour composite samples.

(2) Average of two plants shown during verification sampling.

(3) Not detected.

* No data

Pollution Abatement Options

Toxic Pollutants of Concern

The toxic pollutants found in significant amounts are mostly the heavy metals found in the products as well as the chromium ore and other raw materials. These metals are cadmium, chromium, copper, lead, zinc, antimony and nickel. In addition, some cyanide was found in raw wastes and treated effluents. This cyanide is a result of the manufacture of iron blues and, at one plant site, HCN. However, these guidelines do not apply to iron blues; they will be included in Phase II of the Inorganic Chemicals regulation development. There is significant removal of the cyanides in the chrome pigments treatment, however, probably due to the precipitation of ferrocyanides. The HCN manufacturing process is also regulated by another guideline (see Section 17). Some organic toxic pollutants were found during the screening phase. This was believed to be an anomaly caused by the sampling procedure, since they were also found in the raw intake water, treated effluent, and in the raw waste. In addition, any organics present are probably caused by organic pigments manufacture which is not regulated by this guideline, but will be regulated under the Organic Chemicals Category.

All the wastewaters generated in the Chrome Pigments Subcategory contain dissolved chromium and pigment particulates.

Additional pollutants that may be anticipated are given below for each major pigment group.

A. Chrome Yellow and Chrome Orange

The raw wastewater contains sodium acetate, sodium chloride, sodium nitrate, sodium sulfate, and lead salts.

B. Chrome Oxide

The aqueous process effluent contains sodium sulfate. If boric acid is used in the preparation of hydrated chromic oxide then the wastewater will contain sodium borate and boric acid.

C. Chrome Yellow and Chrome Orange

Additional pollutants present in the raw wastewater from chrome yellow and chrome orange manufacture include sodium acetate, sodium chloride, sodium nitrate, sodium sulfate, and lead salts.

D. Molybdenum Orange

Process waste effluents from the manufacture of molybdenum orange contain sodium chloride, sodium nitrate, sodium sulfate, chromium hydroxide, lead salts, and silica.

E. Chrome Green

The raw wastewater contains sodium nitrate. If iron blue is manufactured on-site as part of the process for chrome green manufacture, the wastewater also contains sodium chloride, ammonium sulfate, ferrous sulfate, sulfuric acid and iron blue pigment particulates.

F. Zinc Yellow

The raw wastes contain hydrochloric acid, sodium chloride, potassium chloride, and soluble zinc salts.

Process Modifications and Technology Transfer Options

The major process problem in the industry is the high rate of water use in some cases. This can be alleviated in a number of ways.

- A. Close attention to product quality in conjunction with reduction of product rinses.
- B. Reduction in equipment cleaning rinses by the following methodologies:
 - 1. Recycle of rinse waters.
 - 2. Minimizing of product changes by the use of better planning and increased number of units.

Equipment cleaning is known to contribute approximately 20 percent of the waste load volume at one plant (#002).

- C. Use of parallel treatment for individual product lines. This will allow the reuse of rinse waters and the recovery of products presently lost in waste sludges.
- D. The use of ion exchange and/or reverse osmosis on isolated wastewaters. This will allow total recovery of product as well as total reuse of wastewater. This system is in use on one line at Plant #409.

The above options were reviewed, but except for option 1 were not considered for inclusion in the treatment models due to the engineering required and their capital intensive nature.

Best Management Practices

- A. All storm water and surface area runoff from the plant site should be collected and sent to a treatment facility if the water is contaminated from process wastes. This contamination can be minimized by storage of chemicals indoors, proper air pollution control, and elimination of all spills.

- B. If the solids from the treatment plant are disposed of on-site, provision should be made to control leachates and permeates. It is possible to monitor the metal concentrations and when concentrations approach predetermined limits, the leachate can be pumped back to the treatment system for further treatment.

Prevailing Control and Treatment Practices

A description of the individual treatment facilities for those plants visited is given above. In addition, the following information was obtained for the remaining plants.

Plant #214 manufactures pigments and other chemicals. The plant does not have a wastewater treatment facility. After pH adjustment, waste is discharged to a POTW. Part of the process waste is recycled.

Plant #593 manufactures organic and inorganic chemicals. The existing combined wastewater treatment plant consists of lagoon, aeration, clarifiers, and filters. The sludge disposal is on-site landfill.

Plant #464 manufactures both organic and inorganic pigments. After pH adjustment, wastewater is discharged to a POTW.

Plant #101 manufactures inorganic ceramic pigments, color and porcelain. The existing combined wastewater treatment facility consists of a series of settling basins. Sludge disposal is to an off-site landfill. After pH adjustment, the final discharge is to a POTW.

Plant #502 manufactures both organic and inorganic pigments, of which chrome pigments are a small part. Treatment consists of pH adjustment prior to discharge.

Plant #436 manufactures several chemicals in addition to chrome pigments. The treatment system consists of neutralization with caustic and clarification in settling lagoons prior to discharge. Sludge is contract-hauled approximately once every three years.

Plant #409 manufactures specialty chemicals and inorganic pigments. The existing wastewater treatment facility consists of SO_2 reduction, clarification, filters and pH adjustment. Sludge disposal is to an off-site location.

Plant #997 manufactures chromic oxide and sulfuric acid. Production data is not available. The existing wastewater treatment facility consists of pH adjustment, SO_2 reduction and lagoons.

Plant #962 manufactures inorganic pigments (chrome yellow). The existing waste treatment plant consists of flocculation, clarification, and filters. After pH adjustment, the effluent is discharged to a POTW. Sludge is recycled to process.

Plant #200 manufactures small quantities of chrome pigments. Treatment is unknown.

In summary, a review of the existing treatment system descriptions indicates that the prevailing treatment practices appear insufficient except for the system at Plant #894. The major problems besides total lack of treatment is lack of sufficient residence time, lack of critical treatment units, and failure to collect all waste streams. As previously stated, only Plant #894 has a properly designed and operated treatment system. This system is basically the same as the Level 1 treatment system shown in Figure 16-10.

Advanced Treatment Technologies

The treatment technologies in use in the industry consist of segregation, equalization, SO₂ reduction, alkaline neutralization, clarification, and filtration. In addition, the following technologies were reviewed for model plant development: sulfide precipitation, ion exchange, reverse osmosis, and the xanthate process.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A careful review of the end-of-pipe treatment methods available to industry was made. As a result, the following methodology was set forth as the only treatment level for this subcategory. Originally, sulfide precipitation was considered as a level 2 addition to the level 1 technology. However, an Agency treatability study (61) indicated no significant improvement in pollutant reduction was achieved by this addition. The result of eliminating level 2 technologies from consideration is to set NSPS standards equal to those for BPT/BAT. Considerations made in establishing the level 1 model included:

- Effective reduction of pollutants.

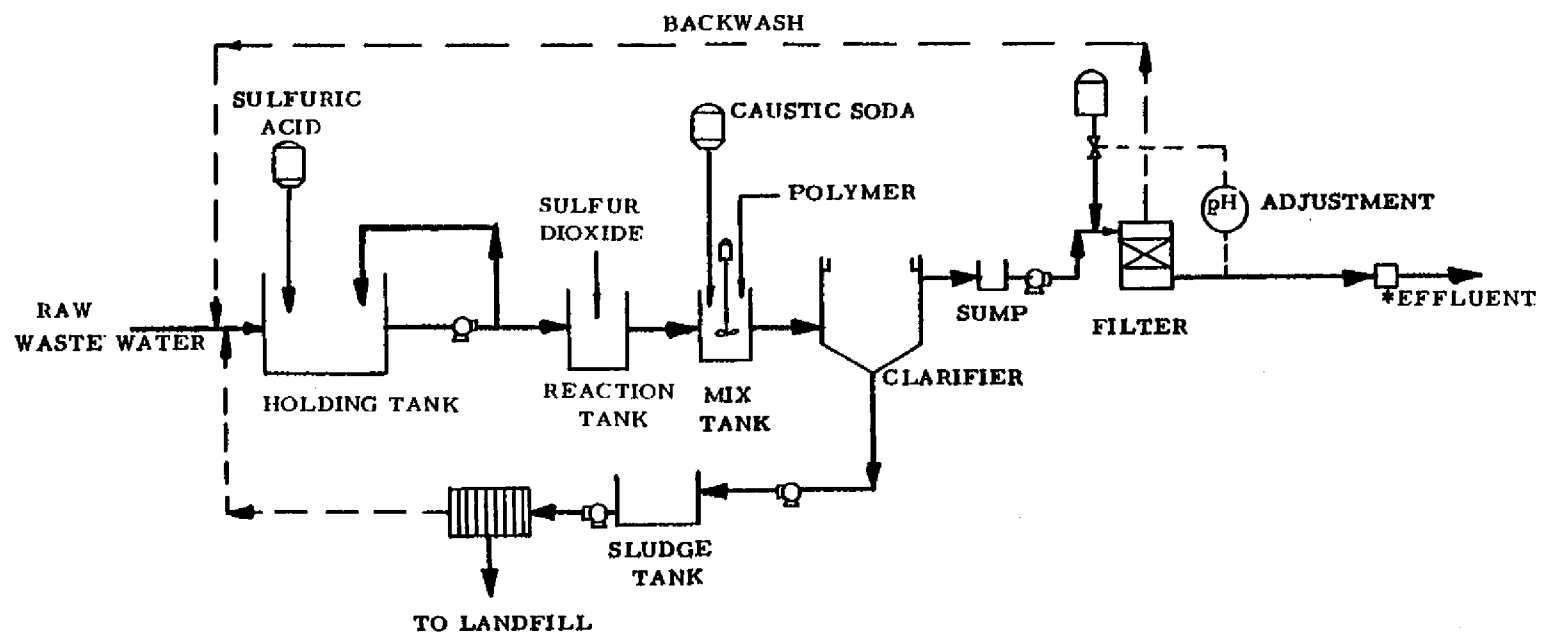
- Established treatment practices in the industry.

- The cost of technology.

- The adaptability of the model to different situations.

A. Level 1 (BPT/BAT/NSPS/PSES/PSNS)

Consists of equalization, SO₂ reduction, alkaline precipitation, clarification, and filtration. A flow diagram of the level 1 system is shown in Figure 16-10.



*Includes flow monitoring, pH monitoring and sampler.

Figure 16-10. Level 1 waste water treatment for chrome pigments.

B. Level 2

Sulfide treatment addition to BPT system has been dropped from consideration as a level 2 treatment. For a discussion of the proposed system and the cost evaluation see the Proposed Development Document (60). Figure 16-11 is a diagram of the proposed system.

Equipment for Treatment

A. Equipment Functions

In the model treatment system, the incoming wastes are acidified in a holding tank and then treated with sulfur dioxide solution in a reactor to convert hexavalent chromium to trivalent chromium. Caustic soda, lime, or other neutralizing agent is then added to neutralize the acid and precipitate heavy metal hydroxides and a polymeric coagulant is added to help settle the heavy metal hydroxides in a clarifier. The settled effluent is then filtered in a dual-media filter and discharged after pH adjustment to the range 6 to 9.

B. Chemicals and Handling

Sulfuric acid and caustic soda solutions are common industrial chemicals which are readily handled with conventional liquid feeding equipment. Sulfur dioxide is received as a compressed gas which is dissolved in water by modified gas chlorinator and fed to the reactor to maintain consistent reducing conditions. Polymer is fed by a standard package of holding tank, mixer, and feeder. With normal precautions there are no unusual hazards in handling chemicals for treatment of chrome pigment wastes.

C. Separation and Disposal of Solids

Solids from the clarifier, including recirculated filter backwash solids are dewatered in a filter press and hauled to a chemical landfill. Sludge filtrate is returned to the influent holding tank.

D. Monitoring Requirements

Internal process monitoring consists of maintaining proper pH levels in the holding tank and final effluent, using conventional field equipment. A reducing environment is maintained in the reactor, using an oxidation-reduction potential instrument and/or analysis for excess SO_2 . Periodic effluent analyses for chromium and heavy metals should be made on composite samples by atomic absorption methods, for official reporting purposes. Sulfide monitoring is generally unnecessary because dissolved sulfides should not exist in the presence of excess ferrous iron and oxygen.

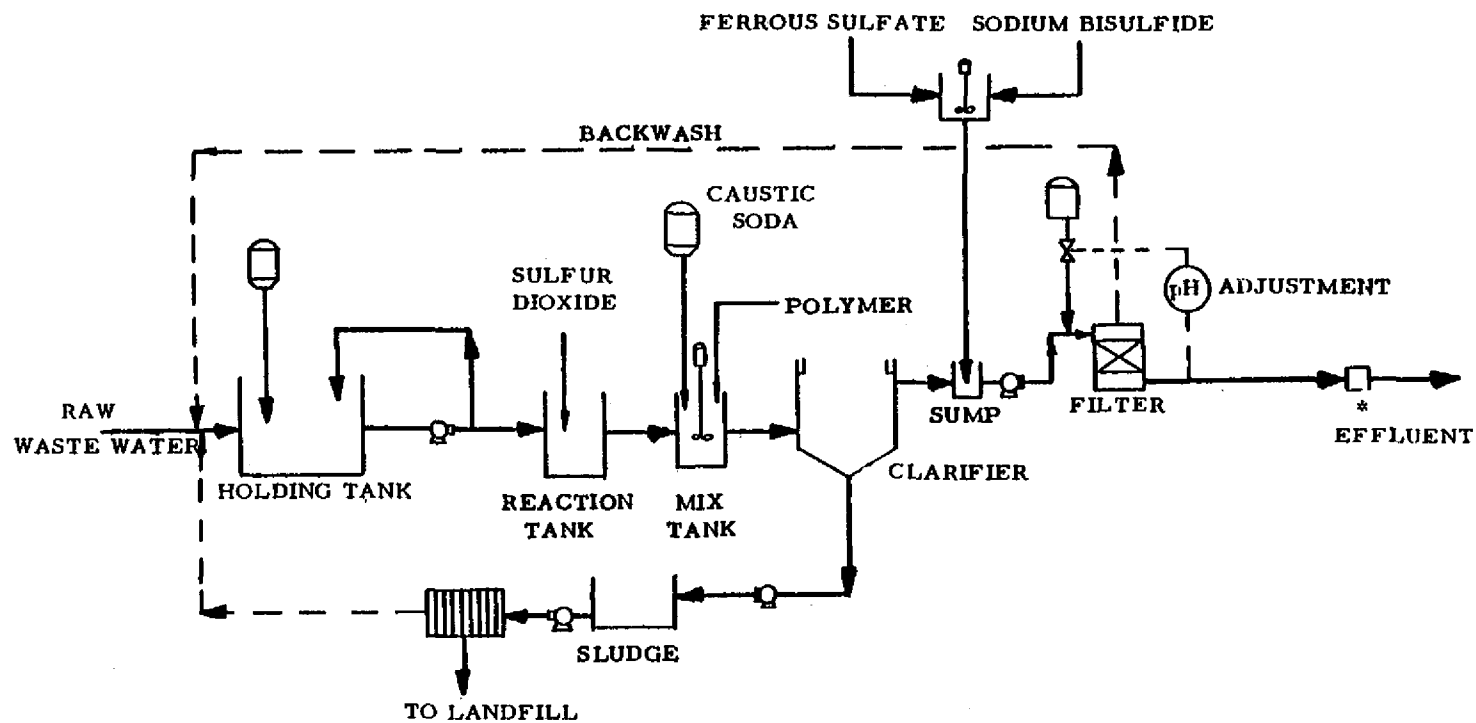


Figure 16-11. Level 2 waste water treatment for chrome pigments.

Treatment Cost Estimates

General Discussion

To prepare cost estimates, a model plant concept was developed and plant criteria developed for BPT (Level 1).

A. Wastewater Flow

The data for five plants with usable flow data is summarized in Table 16-4. This information was used on a production weighted basis to determine the average flow in the industry. This average was computed to be 105 m³/kkg (25,200 gal/ton). This value was used for sizing the model plants.

B. Chromium Pigment Production

Production in the chrome pigment subcategory ranges from a low of 500 kkg/year to a high of approximately 18,000 kkg/year. The mean production is approximately 7200 kkg/year. For the purposes of estimating treatment costs, four production levels were selected as model plants. These are 1500 kkg/year, 4000 kkg/year, 6000 kkg/year, and 18,000 kkg/year. These cover the entire range of production rates. Most plants produce many chrome pigment products on a continuous basis so the operational mode selected was continuous and assumed to run 350 days per year. Chrome pigments are usually produced in integrated facilities with the necessary flexibility to shift from one product or combination of products to another. The model plant was selected to reflect this type of complexity.

C. Wastewater Pollution Load

For the model plants, the loads are based on verification plant data. This data indicated an average loading of 16 kg/kkg chromates as chromium (Table 16-8). Total toxic metals loadings ranged from 12 kg/kkg to 47 kg/kkg. Total suspended solid loadings ranges from 55 kg/kkg to 130 kg/kkg (Table 16-8). The overall solid waste generation is expected to be 85 kg/kkg to 150 kg/kkg (dry solids). For the purpose of determining solid waste generation, a value of 105 kg/kkg (dry solids) was selected.

The estimated costs of the BPT system for the four models are given in Tables 16-10, 16-11, 16-12, and 16-13. For these models, both hydraulic and pollution loads per unit of production were held constant over the entire range of production.

In order to determine the accuracy of the treatment model, an attempt was made to compare the model costs against actual industry costs. Cost data were received on two plants, one with treatment installed and one in the design stage. No attempt was made to compare costs item by item since these specific costs may differ for the following reasons:

Variations in land costs.

Variations in hydraulic loading.

Varying costs of solid waste disposal.

Modifications to the existing wastewater treatment facility and other related costs

The following overall results were obtained:

	Annual Costs (\$/kkg)
Model Plant	89.75
Plant #002	85.38
Plant #894	91.03

The above data indicate a fair correlation between the model plant and site specific cost estimates.

Table 16-14 presents a summary of the unit cost distribution between amorization, operation, and maintenance cost components at various production levels.

For the model plant, the primary sources of wastewater are from product washings, slurring of reaction products, scrubbing of reactor vent gases, and washing of equipment due to product changes.

Model Plant Costs

The major costs for the Level 1 (BPT) model plant are equipment, labor, and chemical costs. Engineering design and equipment maintenance are also fairly large. The majority of the annual cost is tied up in operation and maintenance. This cost can approach 50 percent of the total capital cost.

Basis for Regulations

Evaluation of BPT Treatment Practices

A number of factors are anticipated to contribute to a wide variation in the effluent quality at chrome pigment plant treatment facilities. Consideration of these variations is included in establishing limitations in that the performance of the plant on which limitations are based is a large complex plant that encounters all of these factors. These include the following:

TABLE 16-10. MODEL PLANT TREATMENT COSTS

Subcategory	Chrome Pigments Production	1,500 metric tons per year	
			($\text{\$}$)
A. INVESTMENT COST			BPT BAT ^a
Site development		600	0
Equipment		317,000	0
Monitoring equipment		20,000	0
Subtotal		337,600	0
Contractor's O & P ^b		50,640	0
Subtotal		388,240	0
Engineering		77,648	0
Subtotal		465,888	0
Contingencies		46,589	0
Subtotal		512,477	0
Land		6,000	0
TOTAL INVESTMENT COST		518,477	0
B. OPERATION AND MAINTENANCE COST			
Labor and supervision		112,000	0
Energy		7,500	0
Chemicals		53,000	0
Maintenance		51,248	0
Taxes and insurance		15,554	0
Residual waste disposal		5,000	0
Monitoring, analysis and reporting		15,000	0
TOTAL OPERATION AND MAINTENANCE COST		259,302	0
C. AMORTIZATION OF INVESTMENT COST		83,380	0
TOTAL ANNUAL COST		342,682	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 16-11. MODEL PLANT TREATMENT COSTS

Subcategory	Chrome Pigments Production	4,000 metric tons per year	
			($\text{\$}$)
A. INVESTMENT COST		BPT	BAT ^a
Site development		1,200	0
Equipment		564,000	0
Monitoring equipment		20,000	0
Subtotal		585,200	0
Contractor's O & P ^b		87,780	0
Subtotal		672,980	0
Engineering		134,596	0
Subtotal		807,576	0
Contingencies		80,758	0
Subtotal		888,334	0
Land		12,000	0
TOTAL INVESTMENT COST		900,334	0
B. OPERATION AND MAINTENANCE COST			
Labor and supervision		112,000	0
Energy		15,000	0
Chemicals		141,500	0
Maintenance		88,833	0
Taxes and insurance		27,010	0
Residual waste disposal		15,000	0
Monitoring, analysis and reporting		15,000	0
TOTAL OPERATION AND MAINTENANCE COST		414,343	0
C. AMORTIZATION OF INVESTMENT COST		144,532	0
TOTAL ANNUAL COST		558,875	0

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 16-12. MODEL PLANT TREATMENT COSTS

Subcategory	Chrome Pigments	
Production	6,000 metric tons per year	
		(\$)
A. INVESTMENT COST	BPT	BAT^a
Site development	1,200	0
Equipment	738,000	0
Monitoring equipment	20,000	0
Subtotal	759,200	0
Contractor's O & P ^b	113,880	0
Subtotal	873,080	0
Engineering	174,616	0
Subtotal	1,047,696	0
Contingencies	104,770	0
Subtotal	1,152,466	0
Land	12,000	0
TOTAL INVESTMENT COST	1,164,466	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	112,000	0
Energy	20,000	0
Chemicals	211,500	0
Maintenance	115,247	0
Taxes and insurance	34,934	0
Residual waste disposal	20,000	0
Monitoring, analysis and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	528,681	0
C. AMORTIZATION OF INVESTMENT COST	187,506	0
TOTAL ANNUAL COST	716,187	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 16-13. MODEL PLANT TREATMENT COSTS

Subcategory	Chrome Pigments	
Production	18,000 metric tons per year	
		($\text{\$}$)
A. INVESTMENT COST	BPT	BAT ^a
Site development	1,800	0
Equipment	1,700,000	0
Monitoring equipment	20,000	0
Subtotal	1,721,800	0
Contractor's O & P ^b	258,270	0
Subtotal	1,980,070	0
Engineering	396,014	0
Subtotal	2,376,084	0
Contingencies	237,608	0
Subtotal	2,613,692	0
Land	18,000	0
TOTAL INVESTMENT COST	2,631,692	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	112,000	0
Energy	28,000	0
Chemicals	635,000	0
Maintenance	261,369	0
Taxes and insurance	78,951	0
Residual waste disposal	60,000	0
Monitoring, analysis and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	1,190,320	0
C. AMORTIZATION OF INVESTMENT COST	425,248	0
TOTAL ANNUAL COST	1,615,568	0

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

A. Product Changes

Changes in products require that equipment be thoroughly cleaned prior to reuse. Therefore, frequent product changes will result in higher waste flows.

B. Product Application

The final disposition of the product will affect the quality required. The higher the quality, the more water required for rinsing.

C. Air Pollution Control

Equipment will be required in many cases for control of the environment as well as off-site air compliance. Scrubbers will add some waste flow to the treatment system. This flow, however, is generally small.

D. Other Related Products

Many plants manufacture other types of pigments including iron blues and organic pigments. These products generate significant quantities of wastewater which tend to dilute chrome pigment wastes. However, these wastewaters were included in the computation of the unit waste flow. Therefore, the use of parallel treatment for existing facilities producing other pigments is not required at this time as long as chromium pigment production is the majority of the overall production. The following guidelines should be used in applying these regulations:

1. When determining the effluent loadings, the total production of a facility will be used as long as the chrome pigment production is in the majority.
2. When the chromium production is the minority of the overall production, the total production should be used for computing the effluent limits under the following conditions: the remaining production (other than chrome pigments) generates a wastewater containing significant amounts of toxic metals which will be removed by a chrome pigment treatment system.
3. For those facilities (existing sources) where chromium production is in the minority and the wastes from other sources do not contain metals above accepted levels of treatability, segregation and parallel treatment of chromium pigment wastes are recommended. However, the permitting authority or POTW must consider the following balancing factors:
 - a. The economic impact on the facility balanced against

TABLE 16-14 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Chrome Pigments

Annual Treatment Costs (\$/kg)

LEVEL OF TREATMENT

COST ITEM

PRODUCTION
(kg/yr)

BPT

Annual Operation
and Maintenance1,500
4,000
6,000
18,000172.87
103.59
88.11
66.13Annual
Amortization1,500
4,000
6,000
18,00055.59
36.13
31.25
23.62Total Annual
Cost1,500
4,000
6,000
18,000228.45
139.72
119.36
89.75

b. The environmental benefits of parallel treatment.

In addition to the above factors, the design and operation of the treatment facilities affect effluent quality. Important factors are equalization, SO₂ contact time and pH depression, SO₂ dose, proper neutralization, and adequate solids removal.

Table 16-15 is a summary of verification sampling and long-term effluent monitoring data at Plant #894 for the major pollutants of concern. Plant #002 sampling results are excluded from the subcategory performance evaluation, since the treatment system was not functioning properly as previously discussed.

The long-term monitoring data in Table 16-15 is for the maximum 30-day average long-term monitoring results. Sufficient data was not available to estimate long-term daily maximum values.

Plant #894 is the only known plant with Level 1 treatment system installed and operating. Table A-11a sets forth means, variability factors, and the maximum 30-day average performance. Maximum daily performance was not computed since the discrete sampling data was not available at the time of the evaluation. The performance evaluation in Table 16-5 is utilized for the development of regulations for TSS and applicable toxic metals.

As previously stated, only one plant of the existing twelve is known to have a Level 1 treatment system installed. This plant represents approximately 20-30 percent of total production. One other plant, with a different treatment system, meets the promulgated BPT/BAT limitations. Most other plants have some type of treatment installed, but none of these appear to be adequate. This technology is expected to remove 3,450,000 pounds per year of toxic metals.

Basis for BPT Effluent Limitations

A. Technology Basis

For BPT, the Agency is promulgating limitations based on equalization, reduction of hexavalent chromium followed by alkaline precipitation, and dual-media filtration. Reduction of flow by the methods given in this section was considered but not used since their application is site specific. However, they are quite viable options in most cases and could result in substantial treatment cost savings.

B. Flow Basis

The basis of flow for the BPT limitations is estimated from data provided in the 308-Questionnaires and plant visits during sampling. Table 16-4 presents the plant flow data used for the purpose of regulation. A weighted average flow was determined based on plant production. Plants producing a greater quantity

TABLE 16-15. SUMMARY OF LONG TERM AND VERIFICATION EFFLUENT SAMPLING RESULTS AT PLANT #894

SUBCATEGORY: CHROME PIGMENTS				
Pollutant	Verification (mg/l)	Sampling ⁽³⁾ (kg/kkg)	Achievable Performance ⁽⁴⁾	
			Max 30-day Avg (mg/l)	Avg (kg/kkg)
Total Suspended Solids, TSS	3.9	0.66	23	3.8
Iron	0.30	0.051	NA ⁽²⁾	NA
Antimony	0.30	0.051	NA	NA
Arsenic	ND ⁽¹⁾	ND	0.16	0.027
Cadmium	0.0084	0.0014	0.12	0.020
Chromium	0.33	0.056	0.73	0.12
Copper	0.035	0.0060	0.25	0.42
Lead	0.11	0.019	0.87	0.15
Mercury	ND	ND	0.0016	0.00027
Nickel	0.021	0.0036	NA	NA
Zinc	0.058	0.0099	0.074	0.013
Cyanide (CN-A)	0.065	0.011	0.068	0.012
Cyanide (Total)	0.0067	0.0011	0.31	0.053
Chromium (VI)	0.023	0.0039	0.30	0.051

(1) ND, Not Detected.

(2) NA, Not Available.

(3) From Tables 16-6 and 16-9.

(4) From Table A-11a, "Historical Effluent Monitoring Data Summary."

of chrome pigment product have a waste flow which has a greater influence on the average flow calculation. This approach for the determination of the average flow is substantiated by the unit waste flow which is related to the plant production rate.

Since plants in the chrome pigments subcategory do not segregate wastewaters from the various pigment processes for treatment, the basis of flow for the purpose of regulation includes all process related wastewater combined. The flow basis is 105 m³/kkg from Table 16-4. This flow does not include any recycle or reuse of wastewaters other than some incidental recycle being done at five plants included in the data base.

C. Selection Basis for Pollutants to be Regulated

The selection of pollutants for which specific numerical effluent limitations are set was based on an evaluation of raw waste data from the screening and verification sampling program. Pollutant data from the plants sampled during screening was used to determine the need for verification sampling. Verification sampling at Plants #002 and #894 provided additional pollutant raw waste concentration data needed to assess the magnitude of the pollution potential.

Results of the screening and verification sampling are tabulated in this section for the raw process waste streams. The pollutant concentration listed under verification is the highest value observed during sampling at the two plants visited.

Toxic pollutants are listed based on their presence at significant concentration levels during sampling. Pollutants from this list were considered for regulation if their concentrations appeared to equal or exceed in at least one instance the lowest level estimated as treatable using any available technology appropriate for their removal, ignoring economic considerations.

The relative significance of the toxic pollutants was estimated based on the total annual raw waste load for each pollutant which appears in a Table in this section. The total annual load is based on the average concentration observed during screening and verification which is tabulated in Table 16-8, in addition to the estimated annual production of 73,500 kkg of product for the industry.

Specific numerical effluent loading limitations had been proposed for those pollutants which appeared at average concentration levels (Table 16-7) considered to be treatable for at least one plant visited during sampling.

On the basis of concentration and total annual raw waste loads determined during sampling, chromium, zinc, lead, copper, antimony, cadmium, nickel and mercury have been identified in

chrome pigment wastes at treatable levels (mercury is treatable by sulfide precipitation which was rejected as the basis for BAT). These metals were all considered for regulation, however, final regulations include limitations on chrome (total), zinc, and lead only. Organic pollutants and cyanide are not included, since they are considered products of iron blue, organic pigments, or HCN production as discussed above. In addition, these parameters will be covered by future regulations in other subcategories.

The Agency's decision to restrict metals regulation to chrome, lead, and zinc was made in light of the performance characteristics of the treatment technology for this subcategory, and the nature of the waste involved. The performance of this technology is such that control of certain "key" metals will result in sufficient control of the remaining metals. This is discussed in detail in Section 8.

The treatment technology designed for removal of the more prominent metals in this subcategory, namely chrome, zinc and lead, will ensure control of all the toxic metals originally considered for regulation. Performance data from this subcategory substantiates this (Tables 16-15 and 16-16).

The Agency is also aware that specific plants may have unusually high loadings for one or more of the unregulated metals. In these instances, limitations should be set on a case by case basis. Table 16-16 includes guidance for copper, antimony, nickel, cadmium, and mercury concentrations for those cases where additional control is deemed necessary.

Hexavalent chromium was excluded from consideration in the final regulations. The complexity and subsequent accuracy of the analysis may cause misleading conclusions if hexavalent chromium is used as an effluent monitoring parameter. Sulfur dioxide reduction under acidic conditions will convert hexavalent chromium to its trivalent form which can be conveniently verified by analysis of total chromium in the treated effluent. Chromium cannot be removed by alkaline precipitation unless it is in the trivalent form. Therefore, if the SO_2 reduction step fails to reduce the hexavalent chromium it will become apparent in the effluent total chromium concentration.

Basis of Pollutant Limitations

A. Conventional and Nonconventional Parameters

1. pH

The treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

2. Total Suspended Solids (TSS)

Review of the long-term monitoring and verification sampling data in Table 16-15 indicates a maximum 30-day average TSS discharge of 3.8 kg/kg for the purpose of the limitation determination. The 30-day average concentration basis is then determined as follows:

$$\frac{(3.8 \text{ kg/kg}) (1000 \text{ mg/l})}{(105 \text{ m}^3/\text{kg}) (\text{kg/m}^3)} = 36 \text{ mg/l}$$

The 24-hour maximum loading limitation is determined by the following relationship:

$$\begin{array}{l} \text{Maximum 30-day} \\ \text{average loading} \\ \text{or concentration} \end{array} \times \text{VFR} = \begin{array}{l} \text{24-hour maximum} \\ \text{loading or} \\ \text{concentration} \end{array}$$

The variability factor ratio (VFR) is estimated from the Titanium Dioxide Sulfate Process subcategory based on 30-day average and daily variability factors for zinc. The long-term monitoring data on zinc showed daily average concentrations ranging from 0.010 to 1.14 mg/l during a period of more than two years (Tables A-9a-1 and A-9c-1 in Appendix A). This range of values for zinc nearly spans the observed range of toxic metal concentrations found in the effluent from Chrome Pigments Plant #894 (Table 16-15). The VFR of 2.1 for zinc in the TiO_2 Sulfate Process reflects the overall metal removal performance of alkaline precipitation followed by settling and discharge without filtration. The choice of VFR is also supported by a statistical evaluation of data developed in the Agency Treatability Study (61). For the chrome pigments subcategory, the study data indicated a VFR of 2.3 for chrome concentrations in treated, but unfiltered wastes from a level 1 system. Therefore, a VFR of 2.4 is applied to the Chrome Pigments industry as a conservative estimate of the performance of a similar treatment technology which does include a final filtration step. Therefore, the 24-hour maximum limitation becomes,

$$(3.8 \text{ kg/kg}) (2.4) = 9.1 \text{ kg/kg}$$

3. Other Pollutants

The concentration basis for iron is also presented in Table 16-15. This concentration is intended to serve as guidance in cases where iron is found to be of serious concern.

B. Toxic Pollutants

The effluent limitations proposed for the selected toxic pollutant control parameters are derived from three sources of information including 1) screening and verification sampling

TABLE 16-16. EFFLUENT LIMITATIONS
 Chrome Pigments
 Best Practicable Control Technology Currently Available*
 Waste Water Flow: 105 m³/kkg

Pollutant	Subcategory Performance (mg/l) ⁽¹⁾	VFR ⁽²⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kkg)	
			Max. 30-day Avg.	24-hr Max.	Max. 30-day Avg.	24-hr Max.
<u>Conventional and Nonconventional Pollutants</u>						
Total Suspended Solids, TSS	18.1	4.8/2.0 ⁽³⁾	36	87	3.8	9.1
Iron	0.30 ⁽⁴⁾	4.4/1.8 ⁽⁶⁾	0.54	1.3	—	—
<u>Toxic Pollutants</u>						
Chromium	0.71	4.1/1.7	1.2	2.9	0.13	0.31
Zinc	0.71 ⁽⁵⁾	4.1/1.7	1.2	2.9	0.13	0.31
Lead	0.66	5.0/2.1	1.4	3.4	0.15	0.36
Antimony	0.40 ⁽⁷⁾	4.4/1.8 ⁽⁶⁾	0.72	1.7	—	—
Cadmium	0.13	3.8/1.6	0.20	0.49	—	—
Copper	0.21	4.6/1.9	0.41	0.99	—	—
Nickel	0.30 ⁽⁸⁾	4.4/1.8 ⁽⁶⁾	0.54	1.3	—	—

- (1) Subcategory long-term average concentrations adjusted for model plant flow, unless otherwise indicated.
- (2) VFR: Ratio of the 24-hour variability factor to the 30-day average variability factor.
- (3) VFR of 2.4 from long-term evaluation in Titanium Dioxide Subcategory, verified by analysis of chrome pigments subcategory results from an Agency Treatability Study (61). 30-day variability factors from Table A-11A in Appendix A unless otherwise specified.
- (4) Verification sampling results based on three 24-hour composite effluent samples, adjusted for model plant flow.
- (5) Long-term averages for zinc, which include zinc chromate production are not available; therefore, limitations are set equal to those for chrome.
- (6) Variability factors based on average of those for other parameters since no long-term data available.
- (7) Lower limit of treatability estimate (Table 8-11).
- (8) Estimated achievable long-term average (Table 8-13).
- (*) Conventional and nonconventional pollutant limitations apply also to NSPS. Toxic pollutant limitations apply also to BAT, PSES, and PSNS.

data, 2) literature based treatability estimates (Section 8), and 3) a limited amount of long-term monitoring data at Plant #894.

The sampling results represent plant performance observed during three days of sampling. The sampling data was used primarily to select the pollutants of concern, and in the case of antimony and nickel the sampling results were used to estimate the 30-day average concentration in view of the lack of long-term monitoring data for these two pollutants.

The sampling data for Plant #894 appears to demonstrate that in some cases the effluent quality for metal pollutants are considerably better for BPT treatment than indicated by literature treatability in Section 8. This high degree of incidental removal supports the contention that applying effluent limitations just to the dominant metal pollutants, assures effective control of the other metals.

The VFR used to determine the proposed 24-hour maximum limitations is based on long-term data for zinc in the Titanium Dioxide subcategory, which is supported by analysis of treatability results for this subcategory (61).

1. Chromium

The raw waste concentration for chromium was observed as high as 370 mg/l and averaged 150 mg/l during sampling (Table 16-7). The long-term monitoring results indicate a maximum 30-day average discharge of 0.13 kg/kkg which is the limitation basis. The concentration basis then becomes:

$$\frac{(0.13 \text{ kg/kkg}) (1000 \text{ mg/l})}{(105 \text{ m}^3/\text{kkg}) (\text{kg/m}^3)} = 1.2 \text{ mg/l}$$

The 24-hour maximum is determined as follows:

$$(0.13 \text{ kg/kkg}) (2.4) = 0.31 \text{ kg/kkg}$$

where the VFR is set equal to 2.4 based on data from the TiO_2 subcategory and the Treatability Study (61).

2. Zinc

Zinc limitations were set equal to chromium. Tables 16-7 and 16-9 indicate that the removals of zinc and chromium are similar at Plant #002 where zinc is found at very high raw waste concentrations.

3. Lead

The raw waste concentration for lead was observed as high as 69 mg/l and averaged 32 mg/l during sampling. The long-term monitoring results indicate a maximum 30-day average

discharge of 0.15 kg/kkg which is used as the 30-day average limitation. The concentration basis then becomes:

$$\frac{(0.15 \text{ kg/kkg})(100 \text{ mg/l})}{(105 \text{ m}^3/\text{kkg}) (\text{kg/m}^3)} = 1.4 \text{ mg/l}$$

The 24-hour maximum limitation then becomes:

$$(0.15 \text{ kg/kkg}) (2.4) = 0.36 \text{ kg/kkg.}$$

4. Copper

The raw waste concentration for copper was observed as high as 6.2 mg/l and averaged 4.3 mg/l during sampling. The long-term monitoring results indicate a maximum 30-day average discharge of 0.042 kg/kkg. Therefore, the concentration basis becomes:

$$\frac{(0.043 \text{ kg/kkg}) (1000 \text{ mg/l})}{(105 \text{ m}^3/\text{kkg}) (\text{kg/m}^3)} = 0.41 \text{ mg/l}$$

5. Antimony

The raw waste concentration for antimony was observed as high as 7.7 mg/l and averaged 3.3 mg/l during sampling. Since no long-term data is available, the lower limit of treatability (Table 8-11) for antimony is used to determine the concentration basis. This then becomes:

$$(0.4 \text{ mg/l}) (1.8) = 0.72 \text{ mg/l}$$

where 1.8 is an estimated 30-day average variability factor for antimony, obtained by averaging known factors for pollutants in the subcategory (Table 16-16).

6. Cadmium

The raw waste concentration for cadmium was observed as high as 1.3 mg/l and averaged 0.62 mg/l during sampling. The long-term monitoring results indicate a maximum 30-day average discharge of 0.021 kg/kkg. The concentration basis then becomes:

$$\frac{(0.021 \text{ kg/kkg}) (1000 \text{ mg/l})}{(105 \text{ m}^3/\text{kkg}) (\text{kg/m}^3)} = 0.20 \text{ mg/l}$$

7. Nickel

The raw waste concentration for nickel was observed as high as 0.74 mg/l and averaged 0.17 mg/l during sampling. The verification sampling results indicate an achievable concentration of 0.021 mg/l which compares to an industry

long-term average of 0.30 mg/l (Table 8-13). Therefore, the concentration basis becomes:

$$(0.30 \text{ mg/l}) (1.8) = 0.54 \text{ mg/l}$$

where, again, 1.8 is an estimated 30-day average variability factor for nickel in this subcategory.

The limitations are summarized in Table 16-16 for BPT.

Basis for BCT Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Effluent Limitations

A. The Application of Advanced Level Treatment

Utilizing the cost estimates presented in this report, the Agency has analyzed the cost effectiveness of the base level systems (BPT) and various advanced level options for conventional, nonconventional, and toxic pollutant removal. The economic impacts on the Chrome Pigments Industry have been evaluated in detail and taken into consideration in the selection of the technology basis for the BAT regulations.

The Agency is promulgating BAT limitations based on treatment consisting of Level 1 technology which is equivalent to BPT. The implementation of BPT/BAT will remove 2,400,000 pounds of toxic metals annually. The two plants currently meeting the promulgated BPT/BAT limitations are removing an additional 900,000 pounds per year of toxic metals.

B. Technology Basis

For BAT, the Agency is utilizing the identical technology basis discussed for BPT in this section. BAT includes no additional treatment because the Agency has concluded, based on the Treatability Study (61) results, that sulfide treatment after alkaline precipitation does not significantly increase treatment performance, and, therefore, does not justify costs associated with such additional treatment technology.

C. Flow Basis

The unit flow of 105 m³/kkg is also used for BAT.

D. Selection of Pollutants to be Regulated

The basis of pollutant selection is discussed for BPT above. For BAT, the toxic metals shown in Table 16-16 are selected for regulation. These include chromium, zinc and lead.

E. Basis of Pollutant Limitations

The basis of the limitations are discussed in detail under BPT above.

Basis for New Source Performance Standards

A. Application of Advanced Level Treatment

Chrome pigment industry wastes primarily contain toxic metal pollutants which are particularly amenable to removal by alkaline precipitation and sulfide precipitation. Almost all plants combine wastewater from the chrome pigment process with wastewater from unrelated processes. The Agency proposes that for new sources, the wastewater from the chrome pigments process be segregated from wastewater from other processes unless the other wastewater contains toxic metal pollutants. Segregation and separate treatment of the wastewaters can conceivably reduce treatment costs, and simplify the treatment of metals without complications from unrelated wastewater constituents not amenable to metals treatment.

B. Technology Basis

For New Source Performance Standards (NSPS), the agency is setting limitations based on the identical technology basis discussed for BPT above. The Agency also recommends that all unrelated wastewater sources which are not amenable to metals treatment be segregated before treatment as previously discussed.

C. Flow Basis

The basis for the unit flow used for the purpose of setting limitations is 105 m³/kkg and does not differ from BPT.

D. Selection of Pollutants to be Regulated

The same conventional, nonconventional, and toxic pollutants selected for BPT are also considered here for the NSPS limitations. These include TSS, pH, iron, and the same eight toxic metal pollutants.

E. Basis of Pollutant Limitations

The basis of the limitations are discussed in detail under BPT above.

Basis for Pretreatment Standards

The Agency is promulgating PSES and PSNS that are equal to BPT limitations because BPT provides better removal of chromium, lead, and zinc than is achieved by a POTW and, therefore, these toxic pollutants would pass through a POTW in the absence of pretreatment. In particular, 1.4 million pounds per year of hexavalent chromium from existing sources would pass through in the absence of pretreatment. The promulgated pretreatment regulations will remove over 1.3 million pounds of hexavalent chromium per year. Pollutants regulated under PSES and PSNS are chromium, lead, and zinc.

Existing Sources

There are currently eight indirect discharge chrome pigment plants in the subcategory. For Pretreatment Standards for Existing Sources (PSES), the Agency is setting limitations based on BPT described above. The pollutants to be limited are chromium, zinc, and lead as presented in Table 16-16.

We are excluding small plants discharging less than 210,000 m³ process wastewater per year to POTW from compliance with these PSES. They will be subject only to the general pretreatment standards in 40 CFR Part 403. The exclusion is intended to apply to plants producing less than 2000 kkg per year, but we have established a flow basis for the convenience of POTW's, since water use is much easier to monitor than production. The annual flow basis for the exclusion was calculated by multiplying the unit flow, 105 m³/kkg, by 2000 kkg per year: (105 m³/kkg) (2000 kkg/year) = 210,000 m³/year. Plants discharging less than 210,00 m³ process wastewater per year produce less than 2000 kkg per year chrome pigments. There would be very significant economic impacts on this segment of the industry if they were required to comply with these PSES. See the Preamble to the Regulation and the Economic Impact Analysis of Pollution Control Technologies for Segments of the Inorganic Chemicals Manufacturing Industry, EPA 440/2-81-023.

New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is setting limitations based on NSPS. The pollutants are indicated in Table 16-16.

SECTION 17

HYDROGEN CYANIDE INDUSTRY

Industry Profile

General Description

Over 50 percent of the Hydrogen Cyanide manufactured is produced by the Andrussow process, while about 40 percent is a by-product from acrylonitrile manufacture. A major portion of the production is used in the manufacture of methyl methacrylate, plexiglas molding and extrusion powders, and surface coating resins. It is also used as a fumigant for orchards and tree crops. The industrial data profile for this industry is given in Table 17-1, while the status of regulations prior to promulgation of this new regulation is given in Table 17-2.

Subcategorization

The method of primary subcategorization chosen for the inorganic chemicals point source category was subdivision by dominant product. Other factors taken into consideration for subcategorization included: raw materials used, manufacturing process employed, geographical location, size and age of equipment and facility involved, non-water-quality aspects of waste characteristics, water pollution control technology, treatment costs, energy requirements and solid waste disposal. A detailed discussion of these factors is given in Section 4.

Hydrogen cyanide (HCN) is made from two different processes, the Andrussow process and as a by-product of acrylonitrile manufacture. In the Andrussow process, air, ammonia and natural gas are reacted to produce the dominant product, hydrogen cyanide. Water-borne wastes from the process consist principally of ammonia and sulfates in addition to cyanide and nitriles. The primary product in the other process is acrylonitrile ($\text{CH}_2=\text{CHCN}$) and the hydrogen cyanide is a by-product.

The Hydrogen Cyanide Subcategory in this regulation is confined to the Andrussow process. Since hydrogen cyanide is a by-product of the acrylonitrile manufacturing process, this process will be covered in the organic chemicals manufacturing category with the primary product.

General Process Description and Raw Materials

The raw materials are reacted at elevated temperature (900-1000 degrees C) over a platinum catalyst. The reaction is given as:

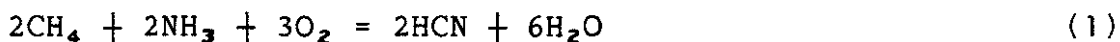


TABLE 17-1.

SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY		HYDROGEN CYANIDE*
Total subcategory capacity rate		289,000 kkg/year
Total subcategory production rate		166,000 kkg/year
No. of plants in this subcategory		7
Plant age range:		
	Minimum	5 years
	Maximum	30 years
308 Data** on file for		2
With total capacity of		179,000 kkg/year
With total production of		116,000 kkg/year
Representing capacity		62 percent
Representing production		70 percent
Average production		57,800 kkg/year
Average capacity utilization		65 percent
Waste water flow per unit product		
	Minimum	10 m ³ /kkg of HCN
	Maximum	57 m ³ /kkg of HCN

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry", June 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry March, 1980.

* Includes data from plants using Andrussow Process and from plants recovering HCN as a byproduct from the manufacture of acrylonitrile.

**Includes data from plants using Andrussow Process.

TABLE 17-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY		HYDROGEN CYANIDE					
SUBPART		AP (40 CFR 415.420, 5/22/75)					
STANDARDS							
Product	Param- eters	BPCTCA*		BATEA		NSPS	
		Max. ¹ kg/kg (mg/l)	Avg. ² kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)
Process							
Andrussow Process	TSS	2.4 (48.0)**	1.2 (24.0)				
	CN	0.005 (1.0)	0.025 (0.5)				
	CN(A)	0.005 (0.1)	0.005 (0.05)				
	BOD ₅	3.6 (72.0)	1.8 (36.0)				
	NH ₃ -N	0.36 (7.2)	0.18 (3.6)				

* Sections 415.420, 415.421, and 415.422 were revoked by the Agency (41 FR 10681, February 23, 1977).

¹Max. = Maximum of any one day.

²Avg. = Average of daily values for thirty consecutive days shall not exceed.

** flow basis 50,000 l/kg.

The source of methane is natural gas containing 50 to 100 percent methane by volume. In addition to hydrogen cyanide, the reacted gases contain ammonia, nitrogen, carbon monoxide, carbon dioxide, hydrogen, and small amounts of oxygen, as well as traces of organic nitriles formed from non-methane hydrocarbon components of natural gas. The reactor gases are cooled and then scrubbed in one of two processes which are used to remove the unreacted ammonia. In one patented process the gases are scrubbed with phosphate liquor, the resulting solution is decomposed and the phosphate solution is recirculated. The recovered ammonia is recycled to the reactor. In the second process sulfuric acid is used to absorb ammonia from the reactor gases. At one plant the resulting ammonium sulfate solution is used for the manufacture of another product.

The hydrogen cyanide is removed from the ammonia scrubber effluent gases by absorption in cold water, and the waste gases are vented to the atmosphere. The absorbed solution containing hydrogen cyanide, water, and other contaminants is distilled to produce HCN gas of over 99 percent purity.

The water produced during the initial reaction (Equation 1) of the formation of hydrogen cyanide is purged with the distillation bottom stream and is either recycled to the absorber or discharged to the treatment facility. In order to be recycled, the distillation bottom water has to be cooled by refrigeration prior to reuse in the HCN absorber unit. At plant locations where cold water is readily available in large quantities, it can be used on a once-through basis with a significant savings in energy costs. Figure 17-1 presents a general block diagram for the manufacture of hydrogen cyanide by the Andrussow process.

Water Use and Waste Source Characteristics

Water Use

Water is used in noncontact cooling in the absorber, pump seal quenches, flare stack flushes, for washdown and cleanup of tank cars, for absorption of the product from reactor gases, and for washing equipment and cleaning up leaks and spills. Table 17-3 gives the detailed water consumption at one plant and also the total consumption at two plants. There is a pronounced difference in water usage at these two plants due to the use of refrigeration at Plant #782 which makes possible the recycling of absorber water from the distillation unit back to the absorber. This practice is energy intensive but is required in locations where an abundant supply of cool water is not available. Plant #765 has such a supply and uses absorber water on a once-through basis. In this case, a much larger flow must be treated prior to discharge.

Waste Sources

The following are sources of wastewater produced from the manufacture of hydrogen cyanide by the Andrussow process:

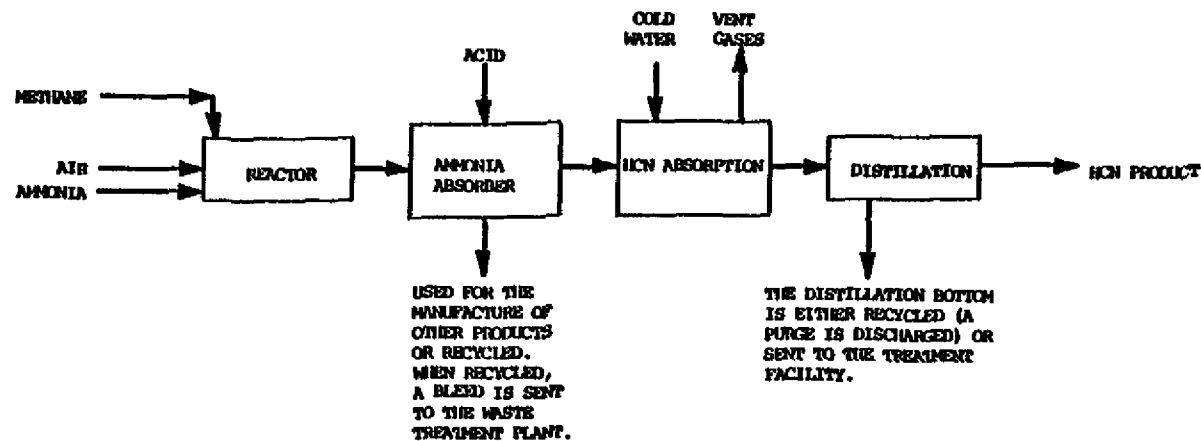


Figure 17-1. General process flow diagram for production of hydrogen cyanide by the Andrussow process.

TABLE 17-3. WATER USAGE IN HYDROGEN CYANIDE - ANDRUSSOW PROCESS
SUBCATEGORY

Plant	Water Usage, (m ³ /kkg of HCN)	
	Total Consumption	Noncontact Cooling
#782 ⁽¹⁾	29.5	18.9
#765	58.3	8.00

(1) Detail water usage (m³/kkg) at Plant #782 is:

Noncontact cooling	=	18.9
Direct process contact	=	7.45
Indirect process contact (pumps, seals, leaks, spills, etc.)	=	0.71
Maintenance, e.g. cleaning and work area washdown	=	0.31
Noncontact ancillary uses (boilers, utilities, etc.)	=	0.67
Exported steam	=	1.44

A. Distillation Bottoms

The wastewater contains ammonia, hydrogen cyanide, and small amounts of organic nitriles. The water consists of the water produced by the reaction plus scrubber water used for the absorption of HCN. The absorption water bottoms are either recycled to the HCN absorber or discharged to the treatment facility. Even if the distillation bottom stream is recycled to the absorber, a portion of it is discharged to stop the buildup of impurities.

B. Scrubber Streams

If the ammonia scrubber liquid is recycled, a portion of it has to be purged to control the accumulation of impurities. The bleed contains the acid used from scrubbing and minor amounts of organic nitriles. The scrubber solution can also be used for the manufacture of other products in which case nothing is discharged to the treatment plant.

C. Other Wastewater

This includes leaks and spills, equipment and tank car washings, noncontact cooling water blowdown and rainfall runoff. The tank cars are washed out with dilute acid or alkali to remove any contaminants present, which, if allowed to remain in the tank car, can polymerize the hydrogen cyanide causing safety hazards due to possible explosion during shipment. The noncontact cooling water may be contaminated with the product as a result of leaks. The recirculated cooling water is monitored for cyanide and the cooling tower blowdown is discharged to the wastewater treatment facility. During shutdown, the equipment is drained to avoid freeze-up and the resulting wastewater is discharged to the treatment facility.

The quantity of wastewater produced and treated at two plants producing hydrogen cyanide by the Andrussow process is given in Table 17-4. The large variation in flow exists because the water used to absorb the hydrogen cyanide from the reactor gases in Plant #765 is not recycled. As discussed earlier, that plant is situated where sufficient cold water is available for once-through use. Since the cold water is readily available at a low cost, the water used for absorption is discharged. A similar plant practicing recycling, in the absence of available cold water, can achieve a total waste effluent of 7.1 m³/kgg of HCN.

Description of Plants Visited and Sampled

Screening

Plant #765 was visited and the wastewater sampled during the screening phase of the program. The combined wastes consist of distillation bottoms, ammonia recovery purge liquor, tank car washings, leaks,

TABLE 17-4. WASTE FLOW DATA FOR HCN PRODUCTION BY THE ANDRUSSOW PROCESS

Plant	Total waste going to the treatment facility (m ³ /kkg)
#765	57
#782	9.9*

*The breakdown and flow of the different waste streams comprising the total is given below:

<u>Source</u>	<u>Unit Flow (m³/kkg)</u>
Recovery and purification	6.3
Pump seal quenches	0.58
Flare stack flushes	0.09
Sample hoods	0.02
NH ₃ stripper caustic	0.24
Steam condensate from NH ₃ stripper	0.90
Freeze protection	0.06
Washdowns and cleanup	0.25
Boiler blowdown and condensate	1.48

spills and equipment clean out, purge from the noncontact cooling water system, and stormwater runoff. These combined wastes are commingled with the other cyanide product wastewaters and sent to the alkaline chlorination treatment facility. The first unit of the treatment facility is a trench where the pH of the wastewater is raised to the range of 8.5 to 11 with dilute caustic soda. The caustic is added under controlled mixing conditions with continuous automatic pH recording and caustic feed adjustment. The pH-adjusted wastewater is sent to two 8-hour retention ponds. Chlorination is accomplished by adding sodium hypochlorite at the pond entrance. The chlorinated wastewater from the 8-hour ponds are alternately discharged to another small pond having one hour of detention and equipped with baffles and agitators. Caustic and chlorine are added as required in the one-hour pond to achieve the low levels of cyanide desired. The effluent from the pond is discharged to a POTW. The pond contains a flow controller/analyzer, which will block the discharge from the pond when a high cyanide level is detected in the treated effluent. Figure 17-2 is a flow diagram of the treatment process indicating the sampling location used during the screening program.

Composite sampling conducted consisted of one 48-hour composite sample for nonvolatile organics, metals, and mercury and one 24-hour composite sample of BOD₅, TSS, TDS, NH₃, Fe, Cr, Zn, Cu, and settleable solids. Grab samples for volatile organics, cyanide, phenols, temperature and pH were collected on two consecutive days at each sampling location. Table 17-5 gives the flow data and concentration and unit loads of ammonia-nitrogen, total cyanide and thallium, for the sampled streams. We believe that thallium is not contributed by the hydrogen cyanide manufacturing process.

Verification

Plant #765 was sampled again in the verification phase. One additional stream of hydrogen cyanide wastewater was sampled in the verification phase at a point upstream of mixing with other cyanide produce wastewater. This stream is identified in Figure 17-2. The variation in the flow of the streams in the two sampling phases was small. Table 17-6 gives the flow and pollutant data of the sampled streams.

The second hydrogen cyanide plant sampled in the verification phase was Plant #782. The wastewater from the hydrogen cyanide plant mainly consists of blowdown from the distillation column which is combined with a portion of the other product wastewater and sent to an ammonia stripper. Effluent from the ammonia stripper is mixed with the rest of the process wastewater from other products and sent to a single stage biological system. The primary treatment facility consists of grit removal, oil skimmers, and pH adjustment. The effluent from primary treatment goes through an oil separator and into an aerated lagoon. Effluent from the lagoon is flocculated and sent to a clarifier. The overflow from the clarifier is sent to a final settling basin before final discharge. The surface drainage

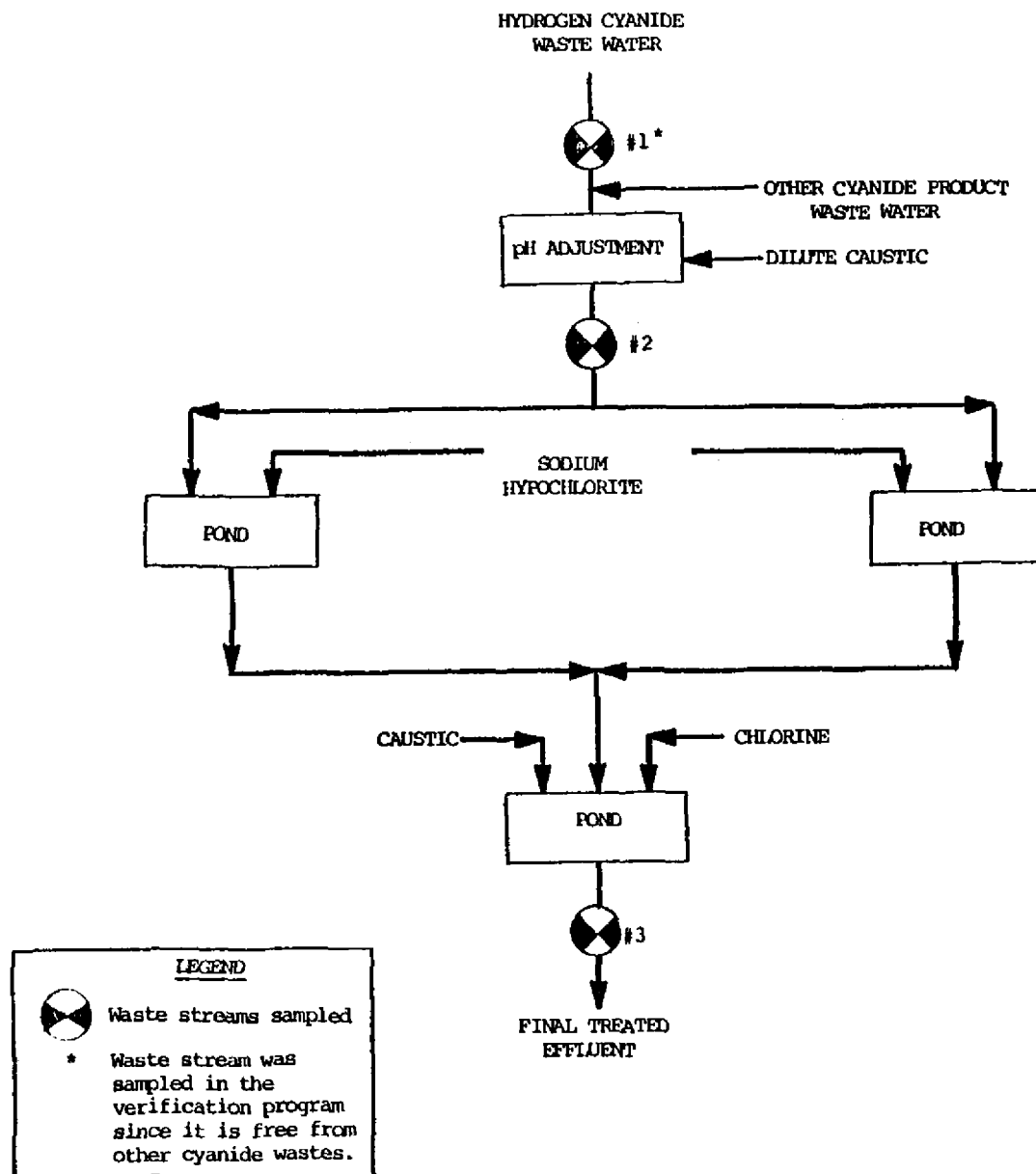


Figure 17-2. General waste water treatment process flow diagram at plant #765 showing the sampling points. (Hydrogen cyanide manufacture.)

TABLE 17-5. FLOW AND POLLUTANT DATA OF THE RAW AND TREATED WASTE
STREAMS OF PLANT #765 PRODUCING HYDROGEN CYANIDE BY
ANDRUSSOW PROCESS

Stream Description	Unit Flow (m ³ /kkg)	NH ₃ -N		Total Cyanide		Thallium	
		($\frac{\text{mg}}{\text{l}}$)	($\frac{\text{kg}}{\text{kkg}}^{(1)}$)	($\frac{\text{mg}}{\text{l}}$)	($\frac{\text{kg}}{\text{kkg}}^{(1)}$)	($\frac{\text{mg}}{\text{l}}$)	($\frac{\text{kg}}{\text{kkg}}^{(1)}$)
#2 Influent to Treatment	57 ⁽²⁾	7.8	4.4 ⁽³⁾	107	6.1 ⁽³⁾	.028	0.0016 ⁽³⁾
#3 Treatment (Alkaline Chlorination) Effluent	57 ⁽²⁾	3.5	2.0 ⁽³⁾	0.36	0.020 ⁽³⁾	.010	0.00057 ⁽³⁾

$$(1) \text{ Unit Load} = \text{Unit Flow} \left(57 \frac{\text{m}^3}{\text{kkg}} \right) \times \text{pollutant concentration in mg/l} \times \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) \\ \text{in kg/kkg}$$

(2) The stream is a commingled waste water. The flow given is the amount contributed by the HCN process.

(3) The pollutant load was calculated by apportioning the mass emitted between the two waste streams on the basis of measured flows. This is clearly a very approximate process and the results must be used with caution.

consisting of runoff, wash down, etc., from the hydrogen cyanide and other process areas is collected separately. The water is sent first to a surface pond where it undergoes a two-stage pH adjustment and then is piped to a trickling filter. It then merges with the treated process wastewaters in the clarifier. A general flow diagram of the treatment process including streams sampled is shown in Figure 17-3.

Table 17-7 gives flow and concentration data of the sampled streams. In Table 17-8, the unit waste flow and unit pollutant loads are given for the raw and treated effluent. Because of intermixing of various product wastewater streams, the unit pollutant loads (especially for treated effluent) were calculated based on hydraulic loadings and the method used is only an approximation. The principal process wastewater from the hydrogen cyanide plant is the waste from the recovery and purification operation and represents a unit flow of 6.3 m³/kkg of HCN. The total wastewater flow going to the treatment facility from the hydrogen cyanide plant is approximately 9.9 m³/kkg of HCN, consisting of both process contact and noncontact effluents.

In calculating the pollutant loads, (Table 17-8) the loss or gain of water to the treatment system such as evaporation, loss through filtered solids, precipitation, and the water introduced by treatment chemicals has not been included because it was considered insignificant in comparison to other factors.

Toxic Pollutant Concentrations

Total cyanide and thallium were the toxic pollutants detected in the raw waste from Plant #765 which was sampled in the screening phase. We believe that thallium in the wastewater is not contributed from the hydrogen cyanide process.

The HCN wastewater at Plant #765 is mixed with other product wastewater and the combined flow was sampled upstream of the treatment system. It is probable that thallium is contributed from these other product wastewaters.

The raw waste stream was not analyzed for free cyanide. The same plant was sampled again with another plant in the verification phase. In addition to total cyanide, free cyanide was found in significant concentrations in the raw process waste sources from the two HCN plants. Free cyanide in the wastewater consists of hydrogen cyanide, sodium or potassium cyanide and cyanogen chloride which may be present as a result of chlorination (especially in the treated effluent). Total cyanide includes the free cyanide and cyanides found in metal complexes (such as sodium ferrocyanide or sodium ferricyanide). No toxic organic pollutants were found in significant concentrations in the HCN plant raw waste sampled. The concentrations of the toxic pollutants found in the raw wastewater in the screening and verification were:

TABLE 17-6. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #765 PRODUCING HYDROGEN CYANIDE

Stream Description	Unit Flow (m ³ /kgg of HCN)	TSS Load (kg/kgg of HCN)	NH ₃ -N Load (kg/kgg of HCN)	CN(A) (kg/kgg of HCN)	CN(T) (kg/kgg of HCN)
#1 Raw HCN waste	57	1.1	27	0.82	1.6
#2 Influent to the pond (1)	57 (1)	NA	11(2)	0.39(2)	1.6
#3 Treated effluent from the final pond	57(2), (3)	1.9(2)	7.1(2)	NA	0.00015

- (1) The stream is comingled wastewater. The flow given is the amount contributed by the HCN process.
- (2) The pollutant load was calculated by apportioning the mass emitted between the waste streams on the basis of measured flows. This is clearly a very approximate process and the results must be used with caution.
- (3) The addition or loss of water from rainfall, addition of chemicals and evaporation has not been estimated.

NA = Not Available

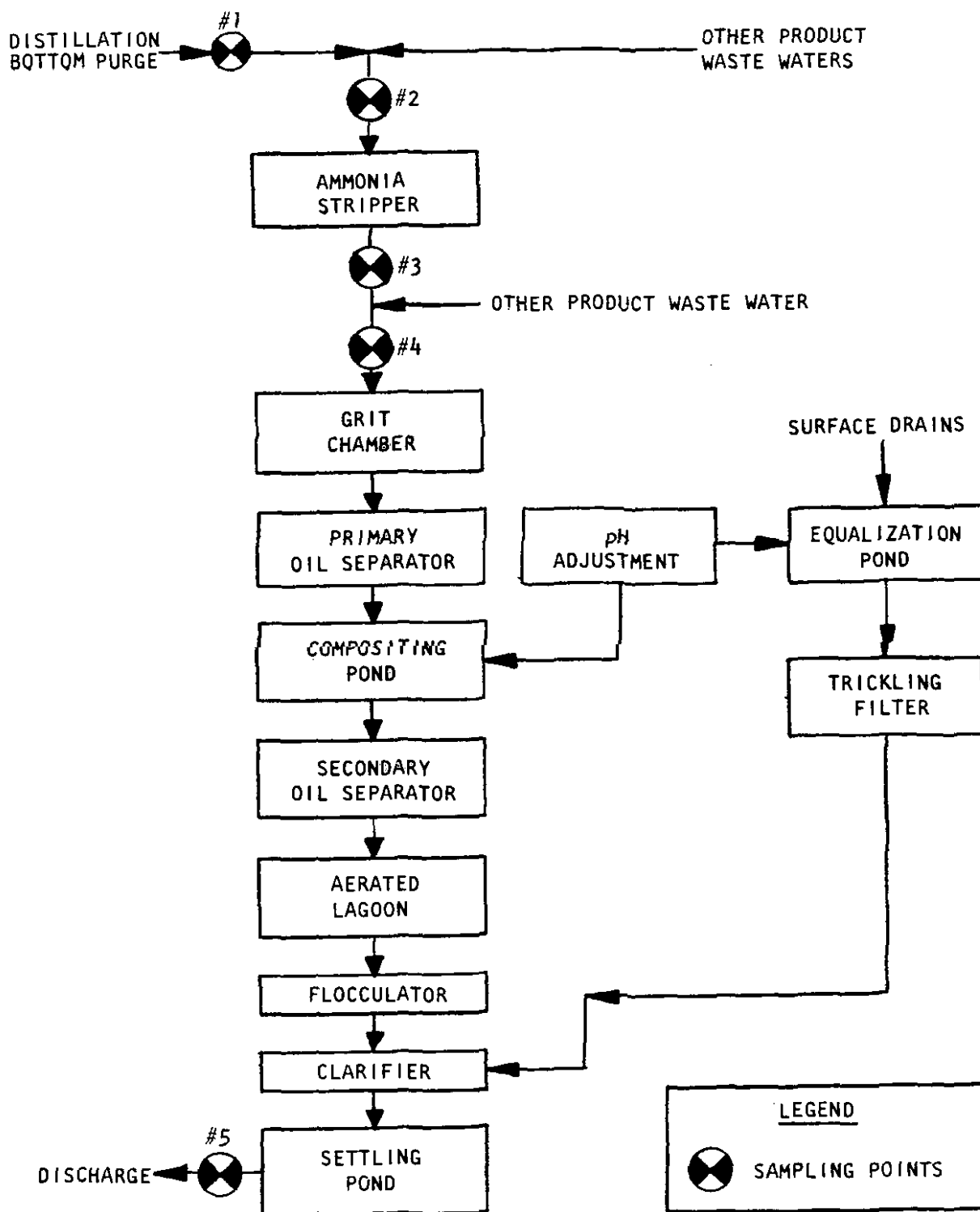


Figure 17-3. General waste water treatment process flow diagram at plant #782 showing sampling points. (Hydrogen cyanide manufacture.)

Table 17-7. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #782 PRODUCING HYDROGEN CYANIDE

Stream No.	Waste Stream Description	Flow m ³ /day	CN(T)	CN(A) (mg/l)	NH ₃ -N	TSS
1	Distillation ⁽¹⁾ bottom purge	(6.3) ⁽²⁾	71	62	886	24
2	Ammonia stripper ⁽³⁾ influent	5400	167	145	410	76
3	Ammonia stripper ⁽³⁾ effluent	5400	51	41	41	162
4	Influent to ⁽³⁾ primary treatment facility	6400	31	7.0	1380	110
5	Final treated ⁽³⁾ effluent	NA	2.2	1.7	5.6	74

(1) - The total waste is composed of the blowdown from three distillation columns. Three 24-hour composite samples were collected for each unit. The pollutant concentration value (given in mg/l) is an average of the three composited samples for the three waste stream sources.

(2) - The value given is the total unit flow in m³/kg of HCN for the three purge streams.

(3) - The stream is combined wastewater. It includes the waste effluents from hydrogen cyanide and other products.

TABLE 17-8. UNIT FLOW AND UNIT POLLUTANT LOADING FOR RAW AND TREATED WASTE EFFLUENTS AT PLANT #782

Unit Pollutant Loading (kg/kg) (1)					
Stream	Unit Flow (m ³ /kkg)	Total Cyanide CN _(T)	Free Cyanide CN _(A)	Ammonia-N NH ₃ -N	Total Suspended Solids TSS
Process raw wastewater (distillation bottom purge)	6.3	0.45	0.39	5.6	0.15
Process wastewater treated effluent	6.3 ⁽²⁾	0.014	0.011	0.035	0.47
Total HCN wastewater treated effluent ⁽²⁾	9.9 ⁽³⁾	0.022	0.017	0.055	0.74

(1) Unit pollutant load = unit flow x pollutant concentration x $\frac{\text{kg/3}}{1000 \text{ mg/l}}$
 (m³/kkg) (in mg/l from Table 17-7)

(2) The pollutant load was calculated by apportioning the mass emitted from the total treated effluent (which includes other product wastewater) on the basis of measured flow contributed by the HCN process. This is clearly an approximate process and the results must be used with caution.

(3) The wastewater flow consists of direct process contact and noncontact effluent from the HCN plant going to the treatment system.

Maximum Raw Waste Concentration Observed
($\mu\text{g/l}$)

<u>Pollutant</u>	<u>Screening Plant #765</u>	<u>Verification Plants #765, #782</u>
Thallium	25	Not Determined
Cyanide (Total)	166,000	186,000
Cyanide (Free)	Not Determined	172,000

The general sampling methodology used in the screening and verification program is described in Section 5. A total of nine days of sampling was conducted at Plants #765 (sampled twice) and #782. Thirteen wastewater sampling points were involved which included the raw wastewater, combined wastewater, and combined treated effluent streams. The evaluation of the toxic metal and toxic organic pollutant content of these process streams was based on total analytical data points from both the screening and verification phases.

The daily toxic pollutant waste load in the raw waste was calculated from the effluent waste flow rate and the measured pollutant concentration of the toxic pollutant.

This is given by:

$$\text{Daily loading (as kg of pollutant per day)} = \frac{(C)(Q)}{(1000)}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: $\text{kg/m}^3 = 1000 \text{ mg/l}$), and

Q is the waste stream flow rate expressed in units of m^3/day (m^3 , a cubic meter, is equal to 264.2 U.S. gallons).

Similarly, the unit loadings were calculated from the reported hydrogen cyanide production rate, the waste stream flow rate, and the measured pollutant concentration.

$$\text{Unit loading (as kg of pollutant per kkg of hydrogen cyanide)} = \frac{(C)(Q)}{1000P}$$

where C and Q are the same as described above, and P is the hydrogen cyanide production rate expressed in units of kgg/day (kgg is 1000 kg, a metric ton, which is equal to 2205 lbs).

In the case of two or more process waste streams going to the treatment system the daily raw waste load of the toxic pollutant was calculated by determining the combined pollutant load of the individual streams.

Table 17-9 gives the toxic, conventional and nonconventional pollutant loadings of the raw waste for Plants #765 and #782 which were sampled in the screening and verification phases. The overall average pollutant loads for the sampled plants are given in the last column of the table.

The approximate toxic pollutant generated per year by the entire subcategory is estimated by multiplying the overall average unit pollutant loading (Table 17-9) with the hydrogen cyanide subcategory production from Table 17-1 (165,500 kkg/yr).

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Cyanide (Free)	100,000
Cyanide (Total)	450,000

Toxic Pollutants of Concern

The toxic pollutants of concern in the HCN raw waste are free (or oxidizable) cyanide and total cyanide. Free (or oxidizable) cyanide is cyanide amenable to chlorination, and is designated in the regulation as Cyanide A. No organic toxic pollutants of significance were found in the raw waste of the sampled plants.

Process Modifications and Technology Transfer Options

Process modifications have not been identified for the subcategory.

Best Management Practices

No best management practices have been identified for the subcategory.

Prevailing Control and Treatment Practices

Out of a total of seven plants currently producing hydrogen cyanide by the Andrussow Process, 308 data are available for only two. The production at these two plants constitutes more than 70 percent of the total subcategory production. Since the two plants produce a significant amount of the total subcategory production, their wastewater treatment technologies are taken as the subcategory treatment practices. The two plants were visited to review the treatment systems and to collect waste effluent samples.

Plant #765 has a high volume effluent because the water used to absorb the reactor gases is not recycled since low cost cold water is readily available at the site. The wastewater consisting of scrubber purge, absorption water, and plant runoff is mixed with other cyanide product wastewaters and sent to an alkaline chlorination system. The pH of the wastewater is raised to about 10 with dilute caustic in an inlet trench and then it is discharged to one of two 8-hour ponds as sodium hypochlorite is added to oxidize the cyanide to cyanate. The chlorinated wastewater is transferred to a small pond equipped with

TABLE 17-9. SUMMARY OF POLLUTANT RAW WASTE LOADING FOUND IN SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY		HYDROGEN CYANIDE		
Average Daily Pollutant Loading and Concentrations at Plants Sampled				
kg/kg of HCN (mg/l)				
Pollutant	#765(s)	# 765(v)	# 782(v)	Overall Average
<u>TOXIC</u>				
Free Cyanide	NA	0.82 (14)	0.39 (62)	0.61
Total Cyanide	6.1 (110)	1.6 (29)	0.45 (71)	2.7
<u>Conventional and Nonconventional</u>				
TSS	NA	2.0 (35)	0.15 (24)	1.1
NH ₃ -N	4.4 (78)	27 (480)	5.6 (890)	12

(S) = Sampled in screening phase

(V) = Sampled in verification phase

agitators and baffles before final discharge to a POTW. Caustic or chlorine is added to the final pond to achieve the desired low levels of cyanide. The treatment system is shown in Figure 17-2.

Plant #782 uses a single-stage biological treatment system for the treatment of effluent from the hydrogen cyanide plant. The process wastewater from the HCN plant consists mainly of distillation column blowdown and is combined with other cyanide product wastewater and sent to an ammonia stripper. The effluent from the stripper combines with other product wastewaters and is treated by means of a grit chamber, an oil separator, a compositing pond, a second oil separator, an aerated lagoon, a flocculator and a final clarifier. The overflow from the clarifier is sent to a final settling basin before discharge. The runoff from the HCN plant and other product manufacturing areas is combined and sent to a pond for a two-stage pH adjustment. The effluent from the pond is treated by a trickling filter and clarifier, and the clarifier effluent is mixed with the treated process wastewater. A general block diagram of the treatment system is shown in Figure 17-3.

Advanced Treatment Technologies

The three pollutants of concern in hydrogen cyanide plant effluents are cyanide, ammonia, and chlorine. The treatment technologies for cyanide removal include alkaline chlorination, biological treatment, ozonation, wet air oxidation, electrolytic decomposition, acidification, activated carbon, permanganate oxidation, lime reaction with sulfur, radiation, evaporative recovery, catalytic oxidation and ion exchange. Except for alkaline chlorination and biological treatment, the remaining treatment technologies are not effective or advantageous for one or more of the following reasons:

- A. The technology has low cyanide removal efficiency.
- B. The technology cannot treat wastewater with high cyanide concentrations.
- C. The technology has air pollution problems.
- D. The technology has high operating costs.

The free cyanide in the raw waste is readily oxidizable and exerts a chlorine demand. Sufficient chlorine is added to react with ammonia and to oxidize cyanide. The presence of large amounts of ammonia will increase the cost of chlorination. If costs are too extensive, residual ammonia in the raw waste effluent can be reduced by steam or air stripping before alkaline chlorination to reduce the amount of chlorine required.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT)

Two-stage alkaline chlorination followed by pH adjustment was chosen for the removal of cyanide from the raw waste effluents. The technology is being practiced in the industry. The flow diagram of the treatment system is shown in Figure 17-4.

B. Level 2 (BAT)

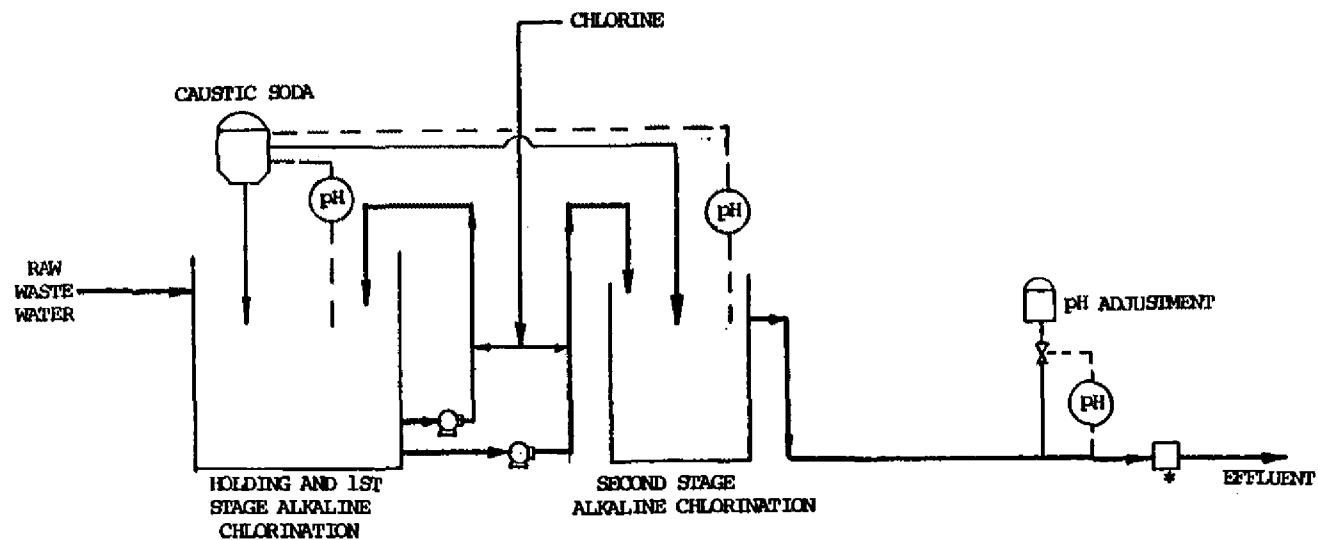
The treatment is the same as BPT (Level 1) except that residual chlorine is reduced to a lower level by treatment with sulfur dioxide. Chlorine in adequate amounts is added to oxidize cyanide. Where practiced, steam or air stripping of ammonia has not been considered as a part of the treatment system since the value of the recovered ammonia is the justification for doing it. It has been assumed to be process related. The general flow diagram of the treatment process is given in Figure 17-5.

Addition of chlorine to remove ammonia ("break-point chlorination") is not intended for either Level 1 or Level 2. Break-point chlorination for ammonia removal generally is very expensive. In this industry, ammonia control, where necessary, should be accomplished by steam or air stripping and recovery and reuse of the ammonia. The achievable concentrations of ammonia in the final effluent from a hydrogen cyanide plant with cyanide removal after ammonia recovery are presented below for guidance.

Equipment for Different Treatment Levels

A. Equipment Functions

In level 1, the raw wastewater enters a holding tank equipped with an external pump and recirculation system. Caustic soda and chlorine are added and the tank contents are mixed by the recirculation pump. Following this first stage alkaline chlorination, the wastewater is chlorinated further in a second tank which is equipped with automatic pH control. The final effluent is neutralized to pH 6-10.5 before discharge. In Level 2, cyanide control is accomplished using the same equipment as in Level 1. To remove excess chlorine before discharge, sulfur dioxide is fed into the chlorinated wastewater by a modified gas chlorinator, with oxidation-reduction potential control. Solutions of sulfur dioxide in water are acidic, so the addition of sulfur dioxide to react with the residual chlorine will tend to neutralize the alkalinity of the wastewater, thus reducing the amount of sulfuric acid that must be added for final pH adjustment. As in Level 1, the effluent is then adjusted to pH 6-10.5 before discharge.



* Includes flow monitoring, pH monitoring and sampler.

Figure 17-4. Level 1 waste water treatment for hydrogen cyanide subcategory.

B. Chemicals and Handling

Caustic soda solution, chlorine, sulfur dioxide, and sulfuric acid are used in the waste treatment process. Caustic soda and sulfuric acid are common industrial chemicals which pose no specific hazards when handled by conventional corrosion-resistant feeding equipment. Chlorine and sulfur dioxide are received in one-ton containers as liquified gases, and are fed as water solutions by vacuum-controlled equipment designed for the specific chemical. No unusual chemical feeding or handling problems are anticipated, provided precautions are taken to prevent gas leaks and to guard against corrosive attack.

C. Separation and Removal of Solids

Since few solids are produced in the treatment process, there is no significant sludge disposal problem.

D. Monitoring Requirements

Internal process monitoring is done largely with automatic sensing and control equipment for regulating pH and chlorine/sulfur dioxide residuals. Field tests for cyanide and/or chlorine in the effluent should be made regularly by the operator, and 24-hour composite effluent samples should be collected and analyzed for cyanide as required in local or NPDES permits.

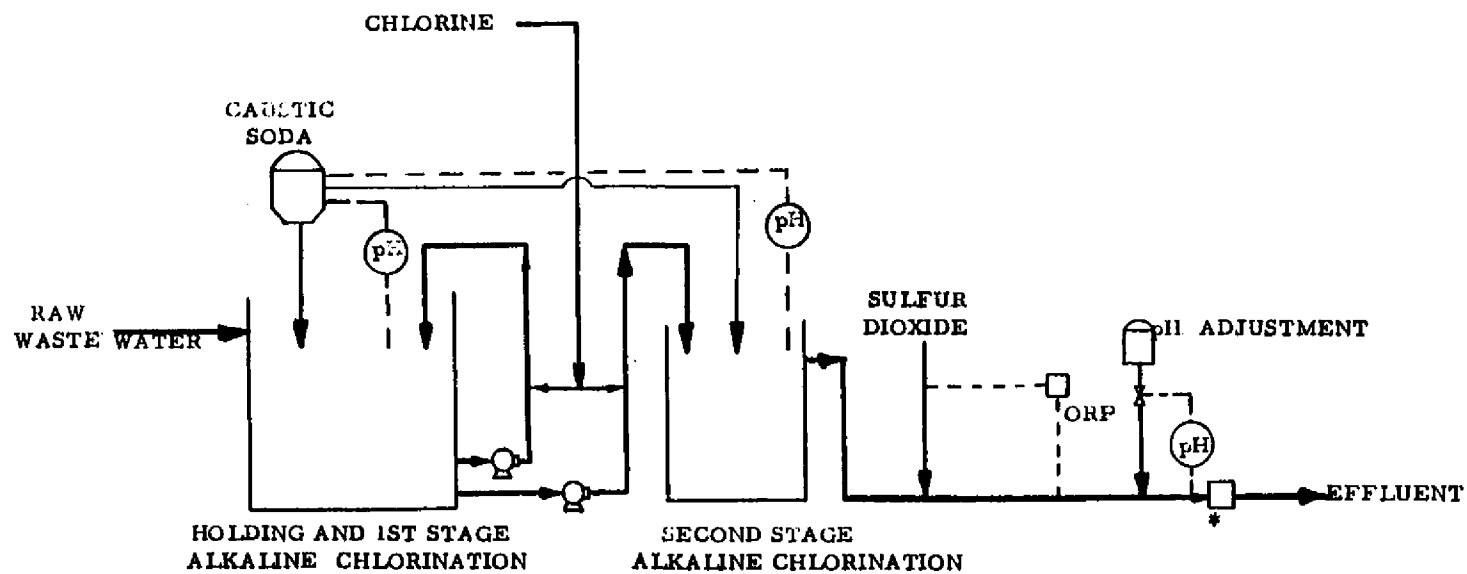
Treatment Cost Estimates

General Discussion

A model plant concept was developed as a basis for estimating treatment costs. For conceptual design a representative unit waste flow (cubic meters per kkg of HCN) was selected, together with three different HCN production rates. The latter were chosen to cover most of the subcategory production range. The selected daily HCN production for the model plant was multiplied by the selected unit flow to obtain the volume of wastewater passing to the treatment system. The selected unit raw waste pollutant load was also multiplied by the model plant production rate to determine the pollutant load on the treatment system. Capital and equipment costs were then calculated based on developed conceptual design parameters for each model plant production rate.

A. Wastewater Flow

The unit process wastewater flows for the two plants visited in this study are 6.3 m³/kkg of HCN (Plant #782) and 57 m³/kkg of HCN (Plant #765). The difference results from the different absorption water discharge practices at the two plants. The model plant has been developed using the larger unit flow rate of 57 cubic meter/kkg of HCN, since this is a more conservative



* Includes flow monitoring, pH monitoring and sampler.

ORP = Oxidation Reduction Potential Control

Figure 17-5. Level 2 waste water treatment for hydrogen cyanide subcategory.

approach. The Agency considered developing effluent limits for two different levels of flow but rejected it because of the cost, complexity, and difficulty in implementing the approach.

B. Production

For wastewater treatment cost estimates, three production levels were selected for the model plant. These are 31,800, 50,900 and 63,600 kkg/yr.

C. Wastewater Pollutant Load

The three pollutants of concern in the subcategory are cyanide (oxidizable and total), ammonia, and chlorine. Chlorine is not present in the raw waste but is added during alkaline chlorination treatment. The average value of 0.61 kg of free cyanide/kg of product HCN and 12 kg of NH_3 /kg of product HCN (Table 17-9) developed from the screening and verification results were used for the model plant raw waste loads.

D. Chemicals Used

At the BPT level of treatment, alkaline chlorination requires 33 kg of chlorine (most to react with ammonia) and 5.0 kg of caustic per kkg of product HCN. For BAT treatment, 9.0 kg of SO_2 per kkg of product HCN is used for dechlorination in addition to the chemicals used for BPT treatment.

E. Solids Generated

Few, if any, solids are produced in treating HCN production wastes.

The estimated costs for the three model plants at different production levels are given in Tables 17-10, 17-11, and 17-12. As mentioned earlier, both the hydraulic and pollutant loads per unit of production are held constant over the entire range of production.

The costs shown in Tables 17-10, 17-11, and 17-12 at each level of treatment correspond to BPT (Level 1) with incremental costs to meet the more stringent BAT requirements.

Basis for Regulations

Evaluation of BPT Treatment Practices

A total of seven plants produce hydrogen cyanide by the Andrussow Process. At one facility the raw wastes from the hydrogen cyanide plant are combined with the waste from an organic cyanide process and sent to a biological treatment system to reduce organic and cyanide pollutants. Four of the other six HCN producers (using the Andrussow Process) use alkaline chlorination for treatment of raw waste

effluents. There is no available information concerning the treatment practices at the other two plants.

Basis for BPT Limitations

A. Technology Basis

The predominant treatment practice for raw waste effluent in the HCN subcategory is alkaline chlorination. The Agency is therefore promulgating BPT effluent limitations based on alkaliine chlorination to destroy cyanide amenable to treatment by chlorination (free cyanide or Cyanide A).

B. Flow Basis

The effluent limitations are based on the high flow (57 m³/kgg of HCN) model, that is, with no recycle of absorber water. A low flow basis (7 m³/kgg of HCN based on the flow of Plant #782) was rejected as being too energy intensive due to the need for refrigerative cooling of the recycled absorber water. The water going to the model plant treatment system is assumed to consist of process and contact cooling waste effluents, leaks and spills, and storm water run-off. The boiler blowdown and noncontact cooling water (once through or blowdown discharge in case of closed loop) are not included in the flow basis.

C. Selection of Pollutants to be Regulated

The selection of pollutants on which specific limitations are promulgated is based on the evaluation of raw waste composition as determined during the screening and verification programs.

Plant #765 was sampled during the screening phase and the presence of toxic pollutants in significant concentrations established the need for verification sampling. Two plants were sampled in the verification phase. Free cyanide, total cyanide, and ammonia were found in the raw waste at concentrations high enough to be treatable (Table 17-9) using available treatment technology options. These were therefore selected for regulation. Chlorine concentrations in the effluent are not affected by BPT treatment technology and therefore no BPT limit is promulgated for this parameter. Thallium is best controlled by management practices developed by the permitting authority on a case-by-case basis.

D. Basis of Pollutant Limitations

1. Conventional and nonconventional parameters

a. pH

The treated effluent is to be controlled within the pH range of 6.0 to 10.5. This limitation is based on the

TABLE 17-10. MODEL PLANT TREATMENT COSTS

Subcategory	Hydrogen Cyanide Production 31,800 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	6,000	0
Equipment	850,000	125,000
Monitoring equipment	20,000	0
Subtotal	876,000	125,000
Contractor's O & P ^b	131,400	18,750
Subtotal	1,007,400	143,750
Engineering	201,480	28,750
Subtotal	1,208,880	172,500
Contingencies	120,888	17,250
Subtotal	1,329,768	189,750
Land	6,000	0
TOTAL INVESTMENT COST	1,335,768	189,750
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	84,000	14,000
Energy	9,000	3,100
Chemicals	296,000	97,000
Maintenance	132,977	18,975
Taxes and insurance	40,073	5,693
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	577,050	146,268
C. AMORTIZATION OF INVESTMENT COST	216,353	30,872
TOTAL ANNUAL COST	793,403	177,140

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 17-11. MODEL PLANT TREATMENT COSTS

Subcategory	Hydrogen Cyanide	
Production	50,900 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	6,000	0
Equipment	1,340,000	135,000
Monitoring equipment	20,000	0
Subtotal	1,366,000	135,000
Contractor's O & P ^b	204,900	20,250
Subtotal	1,570,900	155,250
Engineering	314,180	31,050
Subtotal	1,885,080	186,300
Contingencies	188,508	18,630
Subtotal	2,073,588	204,930
Land	6,000	0
TOTAL INVESTMENT COST	2,079,588	204,930
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	84,000	14,000
Energy	9,800	3,100
Chemicals	476,000	154,000
Maintenance	207,359	20,493
Taxes and insurance	62,388	6,148
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	854,546	205,241
C. AMORTIZATION OF INVESTMENT COST	337,373	33,342
TOTAL ANNUAL COST	1,191,919	238,583

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 17-12. MODEL PLANT TREATMENT COSTS

Subcategory	Hydrogen Cyanide Production 63,600 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	9,000	0
Equipment	1,600,000	190,000
Monitoring equipment	20,000	0
Subtotal	1,629,000	190,000
Contractor's O & P ^b	244,350	28,500
Subtotal	1,873,350	218,500
Engineering	374,670	43,700
Subtotal	2,248,020	262,200
Contingencies	224,802	26,220
Subtotal	2,472,822	288,420
Land	9,000	0
TOTAL INVESTMENT COST	2,481,822	288,420
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	84,000	14,000
Energy	11,500	4,600
Chemicals	592,000	191,000
Maintenance	247,282	28,842
Taxes and insurance	74,455	8,653
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	1,024,237	254,595
C. AMORTIZATION OF INVESTMENT COST	402,328	46,926
TOTAL ANNUAL COST	1,426,565	301,521

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 17-13 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Hydrogen Cyanide

		Annual Treatment Costs (\$/kgg)	
		LEVEL OF TREATMENT	
COST ITEM	PRODUCTION (kgg/yr)	BPT	BAT*
Annual Operation and Maintenance	31,800	18.15	4.60
	50,900	16.79	4.03
	63,600	16.10	4.00
Annual Amortization	31,800	6.80	0.97
	50,900	6.63	0.66
	63,600	6.33	0.74
Total Annual Cost	31,800	24.95	5.57
	50,900	23.42	4.69
	63,600	22.43	4.74

*Represents the incremental cost above BPT

data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS

The concentration of suspended solids found during sampling of the raw wastewater was low. No additional solids are produced in the treatment technology and no provision presently exists in the existing or model treatment systems for the removal of solids. The maximum concentration of 35 mg/l of TSS was found in the raw waste during screening and verification sampling (Table 17-9). However, 35 mg/l was accepted as the long term average concentration on the basis of historical data shown in Table A-13a. The variability factors estimated for ammonia (Table 17-14) are used to calculate the concentration bases and effluent limit.

The TSS maximum 30-day average concentration is:

$$(35 \text{ mg/l}) (1.6) = 56 \text{ mg/l}$$

and the TSS maximum 30-day average effluent limit is given by:

$$(56 \text{ mg/l}) (57 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 3.2 \text{ kg/kg}$$

The TSS 24-hour maximum concentration is given by:

$$(35 \text{ mg/l}) (4.2) = 150 \text{ mg/l}$$

and the TSS 24-hour maximum effluent limit is given by:

$$(150 \text{ mg/l}) (57 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 8.6 \text{ kg/kg}$$

c. Ammonia

The Agency is not promulgating effluent limitations for ammonia in the discharge for the reasons described above. However, we are providing guidance for use by permit writers and POTW's in cases where the discharge of ammonia is of concern. This guidance is based on performance data from plant #765. Plant #765 has recently submitted one and one-half years of monitoring data on the treated effluent for ammonia. Plant #765 uses a proprietary process for removal of ammonia, however, the same performance can be achieved by steam stripping. The variability factors for the daily data and 30-day averages were calculated from the long-term data as shown in Table 17-14. The long-term average

TABLE 17-14. STATISTICAL ANALYSIS OF HISTORICAL EFFLUENT
MONITORING DATA ON FREE CYANIDE AND AMMONIA
FROM PLANT #765

Pollutant	Time Period	Monitoring Frequency	N	\bar{X}	S ⁽¹⁾	CV ⁽²⁾	VF
			No.	Mean (mg/l)	Std Dev (mg/l)	Coeff. of Variation	Variability Factor
Free Cyanide	9-79	Daily	512	0.20	0.36	1.8	8.0 ⁽³⁾
	to 7-80	30-day average	11	0.21	0.087	0.40	1.7 ⁽⁴⁾
Ammonia	1-79	Daily	540	45	42	0.93	4.2 ⁽³⁾
	to 7-80	30-day average	11	52	19	0.36	1.6 ⁽⁴⁾

For free cyanide and ammonia, the long-term monitoring data were screened of outliers. In the first place, values recorded as zero were interpreted to mean "inability to measure pollutant" and were rejected prior to the statistical analysis. For the remaining data, the reported measurements of oxidizable CN were screened by the use of the t-statistic

$$t = \max ((X \max - \bar{X}) / s, (\bar{X} - X \min) / s)$$

for extreme values as outliers. Screening was performed on a month-by-month basis, and any datum with a calculated t value exceeding the 99% confidence limits from the t distribution was concluded to be an outlier. Given rejection of a value, recomputation of statistical measures for that month was performed.

- (1) Arithmetic standard deviation, S

$$\text{where } S^2 = \sum (X - \bar{X})^2 / (N-1)$$

For 30-day averages, this is the standard error of the mean

- (2) $CV = S / \bar{X}$

- (3) For daily measurements, VF is calculated by

$$\ln(VF) = S' (2.33 - 0.5S')$$

Where $(S')^2 = \ln(1 + (CV)^2)$. S' is the moments estimator of the scale parameter of the lognormal distribution and 2.33 is the Z value corresponding to 99th percentile

- (4) For 30-day average data, $VF = (1 + 1.64 (CV))$

Where 1.64 is the Z value for the 95th percentile.

concentration of 52 mg/l was used as the basis for guidance. The estimated variability factors and model plant flow rate were used in calculating the concentration bases as follows:

The maximum 30-day average concentration basis for ammonia is given by:

$$(52\text{mg/l}) (1.6) = 83 \text{ mg/l}$$

The 24-hour maximum concentration is given by:

$$(52 \text{ mg/l}) (4.2) = 220 \text{ mg/l}$$

2. Toxic Pollutants

The toxic pollutants promulgated for regulation are free cyanide and total cyanide.

a. Free Cyanide

Plant #765 practices alkaline chlorination and has recently submitted almost one year of monitoring data on the treated effluent for free cyanide. The samples were properly stabilized before analysis. The variability factors for the daily data and 30-day averages were calculated from the long-term data as shown in Table 17-14. The long-term average concentration of 0.21 mg/l (Table 17-14) was used as the basis for the limitations. The estimated variability factors and model plant flow rate were used in calculating the concentration bases and effluent limitations.

The maximum 30-day average concentration basis for free cyanide is given by:

$$(0.21 \text{ mg/l}) (1.7) = 0.36 \text{ mg/l}$$

The 24-hour maximum concentration is given by:

$$(0.21 \text{ mg/l}) (8.0) = 1.7 \text{ mg/l}$$

The maximum 30-day average effluent limitation is calculated by:

$$(0.36 \text{ mg/l}) (57 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.021 \text{ kg/kkg}$$

The 24-hour maximum effluent limitation is given by:

$$(1.7 \text{ mg/l}) (57 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.10 \text{ kg/kkg}$$

b. Total Cyanide

The variability factors for total cyanide for daily data and 30-day averages were estimated from a 28-day study conducted by Plant #765 and are given in Table 17-15. In the case of the 30-day average variability factor, it was necessary to apply a different approach which requires estimation of the 30-day average arithmetic standard deviation. This approach, also used in the Treatability Study (61), is necessary when 30-day average data is not available. The approach for determining the estimated 30-day average standard deviation is as follows:

Estimated 30-day Average Standard Deviation =

$$\frac{\text{24-hour Measurement Standard Deviation}}{30}$$

The limitations for total cyanide are derived from the average unit effluent load (0.19 kg/kkg given in Table 17-15), variability factors estimated from the 28-day test, and model plant flow of 57 m³/kkg.

The maximum 30-day average effluent for total cyanide limitation is calculated by:

$$(0.19 \text{ kg/kkg}) (1.2) = 0.23 \text{ kg/kkg}$$

The total cyanide 24-hour maximum effluent limitation is given by:

$$(0.19 \text{ kg/kkg}) (3.4) = 0.65 \text{ kg/kkg}$$

The total cyanide maximum 30-day average concentration basis is:

$$(0.23 \text{ kg/kkg}) \frac{1}{(57 \text{ m}^3/\text{kkg})} \frac{(1000 \text{ mg/l})}{(\text{kg}/\text{m}^3)} = 4.0 \text{ mg/l}$$

The total cyanide 24-hour maximum concentration basis is:

$$(0.65 \text{ kg/kkg}) \frac{1}{(57 \text{ m}^3/\text{kkg})} \frac{(1000 \text{ mg/l})}{(\text{kg}/\text{m}^3)} = 11 \text{ mg/l}$$

The final effluent limitations for Hydrogen Cyanide produced by the Andrussov Process are summarized in

TABLE 17-15. STATISTICAL ANALYSIS OF THE 28-DAY EFFLUENT
SAMPLING RESULTS ON TOTAL CYANIDE
FROM PLANT #765

Total Cyanide	
<u>Daily Data</u>	
No. of points	25
Average Unit Load	0.192
kg/kg of HCN	
Std. Deviation(S)	0.128
Std. Deviation (S')	0.61
Variability Factor	3.44
<u>30-Day Average Data</u>	
The Standard error	
of the mean (A)	0.023
Coefficient of	
variation for the mean(CV)	0.119
Variability factor	1.19
<u>Variability Factor Ratio</u>	
V.F.R.	2.9

Table 17-16 for toxic, conventional, and nonconventional pollutants.

Basis for BCT Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. The dechlorination technology added to BPT for BAT does not remove additional conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Limitations

The Agency considered different advanced level technologies and their cost effectiveness relative to the base level system (BPT) for the removal of toxic, conventional, and nonconventional pollutants. For BAT, the Agency is utilizing Level 2 technology which includes dechlorination before final discharge.

The Agency also considered break point chlorination for essentially complete destruction of cyanide and ammonia removal. However, the operational costs were too high. The reduction of effluent load to the treatment system by recycling the absorber water was also considered and was found to be too energy intensive and too costly. Therefore the only cost effective treatment technology beyond BPT was found to be dechlorination.

A. Technology Basis

For BAT, the Agency is promulgating limitations based on BPT with the addition of dechlorination (Figure 17-5, Level 2). Control of chlorine in the discharge is uniformly inadequate in this industry. Its control in BAT is believed to be appropriate because of its well-documented toxicity to aquatic life. The basis for the chlorine limit is transfer of technology from the chlor-alkali industry (Appendix A). This transfer is appropriate because the chlorine in both streams is amenable to the same treatment for removal and removal is not inhibited by the presence of other chemicals in either of the waste streams.

B. Flow Basis

The BPT effluent discharge rate of 57 m³/kgg of HCN has been used as the basis for the BAT model plant.

TABLE 17-16. EFFLUENT LIMITATIONS
HYDROGEN CYANIDE (ANDRUSSOW PROCESS)
Best Practicable Control Technology Currently Available
Wastewater Flow: 57 m³/kkg of HCN

Pollutant	Subcategory Performance (mg/l)	Daily Variability Factor	Concentration Basis (mg/l)		Effluent Limit (kg/kkg)	
		30-day Variability Factor	Max. 30-day Avg.	24-hr. Max.	Max. 30-day Avg.	24-hr. Max.
<u>Conventional/ Nonconventional Pollutants</u>						
Total Suspended Solids	35 ⁽¹⁾	4.2/1.6	56	150	3.2	8.6
Ammonia-N	52 ⁽²⁾	4.2/1.6	83	220	--(5)	--(5)
<u>Toxic pollutants:</u>						
Free Cyanide ⁽⁴⁾	0.21 ⁽²⁾	8.0/1.7	0.36	1.7	0.021	0.10
Total Cyanide ⁽⁴⁾	3.3 ⁽³⁾	3.4/1.2	4.0	11	0.23	0.65

(1) Average effluent concentration from monitoring data (Table A-13a).

(2) Average based on recently received long-term monitoring data submitted by Plant #765 (Table 17-14).

(3) Average based on a 28-day sampling data submitted by Plant #765 (Table 17-15).

(4) Also applicable for PSNS limitations.

(5) No effluent limitation has been established.

C. Selection of Pollutants to be Regulated

For the BAT regulation, the Agency has selected chlorine in addition to the pollutants identified in BPT.

D. Basis of Pollutant Limitations

1. Nonconventional Pollutants

The nonconventional pollutant promulgated for regulation is total residual chlorine. For total residual chlorine the BAT regulation is based on long-term monitoring data from the chlor-alkali industry given in Appendix A. The long-term average concentration is 0.64 mg/l. The daily and 30-day variability factors are 2.3 and 1.4, respectively.

The 24-hour maximum concentration is:

$$(0.64 \text{ mg/l}) (2.3) = 1.5 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.64 \text{ mg/l}) (1.4) = 0.90 \text{ mg/l}$$

The determination of load limitations for total residual chlorine (kg/kkg) was calculated based on the unit flow rate of 57 m³/kkg, thus the 24-hour maximum limit is given by:

$$(1.5 \text{ mg/l}) (57 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.086 \text{ kg/kkg}$$

The maximum 30-day average was calculated similarly,

$$(0.9 \text{ mg/l}) (57 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.051 \text{ kg/kkg}$$

2. Toxic Pollutants

The Agency has selected the same limitations for free cyanide and total cyanide as those promulgated for BPT because Level 2 technology does not affect either of these pollutant parameters.

The nonconventional and toxic pollutant limitations for BAT are summarized in Table 17-17.

Basis for New Source Performance Standards

Level 2 treatment technology (also promulgated for BAT) was selected as the basis for NSPS limitations. The pollutants to be controlled for NSPS are pH, total suspended solids, total residual chlorine, free cyanide, and total cyanide. The NSPS limitations are given in Table 17-18. For pH, the NSPS limitation is 6.0 to 10.5

TABLE 17-17. EFFLUENT LIMITATIONS
HYDROGEN CYANIDE (ANDRUSSOW PROCESS)
Best Available Technology
Waste Water Flow: 57 m³/kkg of HCN

Pollutant	Subcategory Performance (mg/l)	Daily Variability Factor	Concentration Basis (mg/l)		Effluent Limit (kg/kkg)	
		30-day Variability Factor	Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
<u>Nonconventional pollutants:</u>						
Ammonia-N ⁽¹⁾	52	4.2/1.6	83	220	-- (4)	-- (4)
Total Residual Chlorine ⁽²⁾	0.64	2.3/1.4	0.90	1.5	0.051	0.086
<u>Toxic pollutants:</u>						
Free Cyanide ⁽¹⁾	0.21	8.0/1.7	0.36	1.7	0.021	0.10
Total Cyanide ⁽²⁾	3.3 ⁽³⁾	3.4/1.2	4.0	11	0.23	0.65

(1) Average based on recently received long-term monitoring data submitted by Plant #765 (Table 17-14).

(2) Average based on long-term monitoring data from the chlor-alkali industry given in Appendix A.

(3) Average based on a 28-day sampling data submitted by Plant #765 (Table 17-15).

(4) No effluent limitation has been established.

Basis for Pretreatment Standards

Pretreatment is required because NSPS provides better removal of free and total cyanide than is achieved by a well-operated POTW with secondary treatment installed and therefore these pollutants may pass through a POTW in the absence of pretreatment.

A. Existing Sources

The Agency is excluding this subcategory from Pretreatment Standards for Existing Sources (PSES) under the provisions of paragraph 8(b)(ii) of the Settlement Agreement because the concentrations of toxic pollutants in the effluent to POTW from the one existing indirect discharger are below treatable levels.

B. New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is promulgating limitations based on NSPS excluding dechlorination of the final plant effluent. Dechlorination is not required because influent to a POTW is often chlorinated. The pollutants to be regulated are free cyanide and total cyanide as summarized in Table 17-16.

TABLE 17-18. EFFLUENT LIMITATIONS
 HYDROGEN CYANIDE (ANDRUSSOW PROCESS)
 New Source Performance Standards
 Waste Water Flow: 57 m³/kkg of HCN

Pollutant	Subcategory Performance (mg/l)	Daily Variability Factor	Concentration Basis (mg/l)		Effluent Limit (kg/kkg)	
		30-day Variability Factor	Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
<u>Conventional and nonconventional pollutants:</u>						
Total Suspended Solids, TSS	35	4.2/1.6	56	150	3.2	8.6
Total Residual Chlorine	0.64	2.3/1.4	0.90	1.5	0.051	0.086
Ammonia-N	52	4.2/1.6	83	220	-- (*)	-- (*)
<u>Toxic pollutants:</u>						
Free Cyanide	0.21	8.0/1.7	0.36	1.7	0.021	0.10
Total Cyanide	3.3	3.4/1.2	4.0	11	0.23	0.65

* No effluent limitation has been established.

SECTION 18

SODIUM DICHROMATE INDUSTRY

Industry Profile

General Description

Most of the sodium dichromate produced is used in the chromic acid and chrome pigment industries. It is used for leather tanning and metal treatment as well as a corrosion inhibitor.

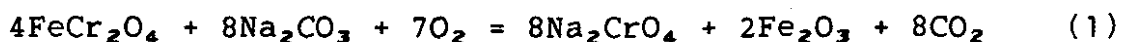
The industry profile data for this subcategory are given in Table 18-1, and the status of regulations prior to promulgation of this new regulation is given in Table 18-2.

Subcategorization

Subcategorization in the sodium dichromate industry is established on the basis of the manufactured product. This follows from the requirement that the effluent limitations are to be tied to units of production. Furthermore, for the two plants discharging process wastewater in the dichromate subcategory, the characteristics of the wastewater are similar and therefore the same treatment technology can be applied. Subcategorization is discussed in more detail in Section 4 of this report.

General Process Description and Raw Materials

The starting materials for the preparation of sodium dichromate are chromite ore, limestone and soda ash. When the above materials are reacted, sodium chromate is formed which is reacted with sulfuric acid to produce sodium dichromate. The reactions are given as:



Chromite ore is a chromium iron oxide containing ferrous chromite (FeCr_2O_4 or FeOCr_2O_3). Small amounts of alumina, silica and magnesia are present. For the preparation of sodium chromate and finally, sodium dichromate, high grade chromite ores are used containing approximately 50 percent Cr_2O_3 . These ores are imported from South Africa.

At the plant site, the ore is ground to a fine powder, mixed with soda ash and calcined in rotary kilns at 1100 to 1150 degrees C. The reacted product is leached with hot water in a leachate tank. The thickener underflow is filtered and the filtrate recycled to the leachate tank or thickener. The solid filter cake is dried in rotary kilns. The alumina present in the thickener overflow is hydrolyzed

TABLE 18-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	SODIUM DICHROMATE
Total subcategory capacity rate	140,000 kkg/year
Total subcategory production rate	136,500 kkg/year
Number of plants in this subcategory	3
308 Data on file for	3
With total capacity of	NA
With total production of	112,000 kkg/year
Representing capacity	NA
Representing production	82 percent
Plant production range:	
Minimum	20,700 kkg/year
Maximum	66,800 kkg/year
Average production	37,300 kkg/year
Median production	24,800 kkg/year
Average capacity utilization	77 percent
Plant age range:	
Minimum	7 years
Maximum	28 years
Waste water flow range:	
Minimum	455 cubic meters/day
Maximum	720 cubic meters/day
Volume per unit product:	
Minimum	4 cubic meters/kkg
Maximum	8 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

NA = Not Available

TABLE 18-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY		SODIUM DICHROMATE					
SUBPART		Q (40 CFR 415.170, 3/12/74)					
STANDARDS							
		BPCTCA		BATEA*		NSPS	
		Max. (1)	Avg. (2)	Max.	Avg.	Max.	Avg.
Product		kg/kkg	kg/kkg	kg/kkg	kg/kkg	kg/kkg	kg/kkg
Process	Parameters	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Na ₂ Cr ₂ O ₇	TSS	0.44 (52)	0.22 (26)	No discharge of pwwp ³		0.30	0.15
	Cr ⁺⁶	0.0090 ⁽⁴⁾ (0.11)	0.00050 (0.060)	No discharge of pwwp ³		0.0090 ⁽⁴⁾	0.00050
	Cr(T)	0.0088 (1.0)	0.0044 (0.50)	No discharge of pwwp ³		0.0088	0.0044

* Section 415.173 was remanded and reserved (41 CFR 51606, November 23, 1976).

¹ Max. = Maximum of any one day.

² Avg. = Maximum average of daily values for thirty consecutive days.

³ pwwp = Process wastewater pollutants.

⁴ The published value in 40 CFR 415.172 and 415.175 is incorrect and should be 0.0009 kg/kkg.

and removed from the chromate solution as precipitated aluminum hydrate in slurry form. The solution is centrifuged and the centrate is evaporated, to give a concentrated solution of sodium chromite, which is reacted with sulfuric acid to give sodium dichromate and sodium sulfate. Sodium sulfate crystallizes as anhydrous sodium sulfate from the boiling solution, and the crystals are removed by filtration. The filtrate is concentrated in multiple effect evaporators. The residual sodium sulfates separate out as solids from each of the evaporators while the hot concentrated solution of sodium dichromate from the last effect of the evaporator is fed to a water-cooled crystallizer. Sodium dichromate crystallizes out and is centrifuged. The centrate, or mother liquor, is returned to the evaporator. The sodium dichromate crystals separated in the centrifuge are dried in a rotary drum dryer and then packaged for sale or stored for use. Figure 18-1 presents a generalized flow diagram for the production of sodium dichromate.

Water Use and Waste Source Characteristics

Water Use

Water is used for noncontact cooling, in leaching, for scrubbing vent gases and for process steam for heating. Water use information provided in 308-Questionnaires is given in Table 18-3. It is possible that the figures given in the 308-Questionnaires may be the amount going to each unit operation and not the amount added as makeup water. The quantities seem unusually high for an industry practicing extensive recycling of water, as this one does.

Waste Sources

A. Spent Ore

The unreacted ore is removed from the process as a sludge. The solids contain chromium and other impurities originally present in the ore. The waste is disposed as a solid waste in a suitable landfill or is slurried with water and sent to the treatment facility.

B. Noncontact Cooling Water and Cooling Tower Blowdown

The noncontact cooling water is either used on a once-through basis and discharged or is recycled and the blowdown discharged to the treatment facility. In addition to dissolved sulfate and chloride, the blowdown may contain chromates.

C. Boiler Blowdown

The steam used for heating is recovered as condensate, while the boiler blowdown is discharged to the treatment facility. It may become contaminated with chromium escaping from the process area and hence should be sent to the wastewater treatment facility for treatment.

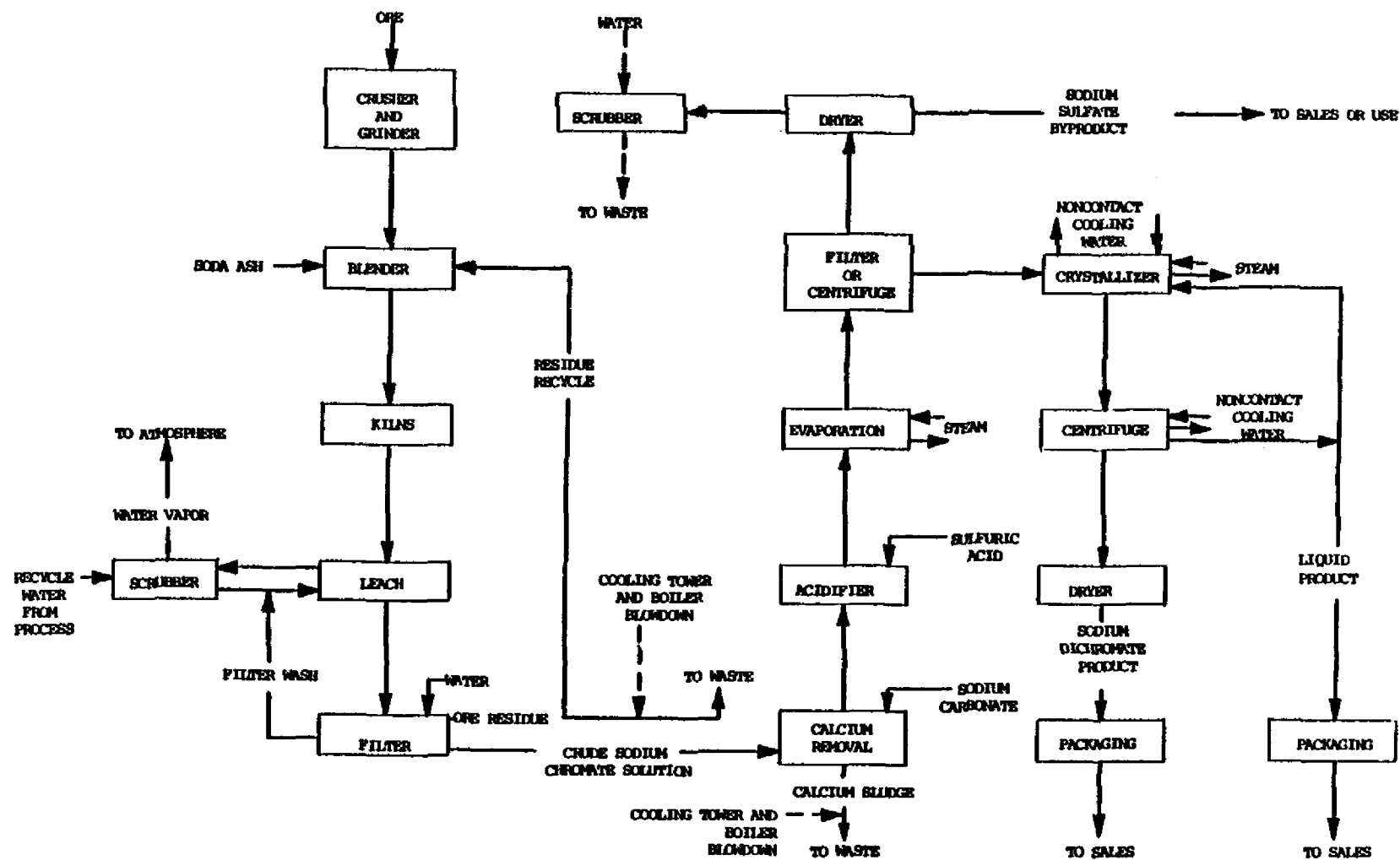


Figure 18-1. General process diagram for production of sodium dichromate.

TABLE 18-3. WATER USAGE IN SODIUM DICHROMATE SUBCATEGORY

Source	Water usage at plants, (m^3/kg of $\text{Na}_2\text{Cr}_2\text{O}_7$)		
	Plant #398	Plant #376 ⁽³⁾	Plant #493
Noncontact cooling	277	11.39	5.7
Noncontact ancillary uses	0.5	NA	3.12
Direct process contact ⁽¹⁾	5.7 ⁽²⁾	7.83 ⁽⁴⁾	2.85
Indirect process contact (pumps, seals, leaks and spills)	0.9 ⁽²⁾	4.16	0.2
Maintenance, e.g. cleaning and work area washdown	0.5 ⁽²⁾		0.2
Air pollution control	2.5 ⁽²⁾	NA	1.0
Total contact waste water influent to treatment	9.6 ⁽²⁾	11.59	4.25

NA = Not Available

(1) Up to 50 percent solids

(2) Total recovery and recycle is practiced at this plant.

(3) Plant is no longer in operation.

(4) Due to a high evaporation rate, there is no discharge from the primary pond during 9 to 10 months of the year. There was no primary pond effluent at the time of sampling and only $4.16 \text{ m}^3/\text{kg}$ of the indirect contact sources were being treated and discharged.

The majority of aqueous streams resulting from the manufacture of sodium dichromate are recycled. Streams recycled include condensates from product evaporation and drying; product recovery filtrates; air pollution control scrubber effluents from product drying, leaching and roasting kilns; filter wash waters; and equipment and process area washdowns. At two plants the wastewater, consisting of boiler and noncontact cooling tower blowdown, is used to slurry the spent ore residue to the wastewater treatment facility. At one plant, the only wastewater resulting from process operations is the noncontact cooling water, which is used on a once-through basis.

Description of Plants Visited and Sampled

Screening

Three sodium dichromate plants were visited and the wastewater streams sampled. Plant #493 was sampled in the screening phase and Plants #376 and #398 were sampled in the verification phase.

At Plant #493, the wastewater going to the treatment facility includes the boiler and cooling tower blowdown and a small volume of effluent from a scrubber on a by-product sodium sulfate operation. The total waste includes the spent ore residue, which is also sent to the treatment facility. At the treatment facility, the alkaline wastewaters are reacted with imported acidic industrial waste (pickle liquor containing ferrous iron) at an elevated temperature in a reactor. The chromium is reduced and precipitated during the reaction. The reacted waste is sent to clarifiers via holding tanks. In the clarifiers, large quantities of water are used to wash the precipitated solids in a countercurrent fashion. The final clarifier overflow, which is the treated effluent, is filtered and discharged and the clarifier underflow is disposed of in a quarry. Figure 18-2 is a block diagram of the treatment process and indicates which streams were sampled. Table 18-4 gives the flow data and pollutant emissions of the streams sampled.

Verification

At Plant #376, sodium sulfide is used for simultaneous chromate reduction and precipitation. The wastewaters at this plant are segregated into two streams. One stream consists of the cooling tower and boiler blowdown and is used for slurring the spent ore residue to the treatment facility. The second waste stream consists of stormwater runoff from both the solids disposal areas and the production areas. The first wastewater stream is mixed with sodium sulfide during transportation and sent to a diked containment and settling pond system. The sulfide reduces the hexavalent chromium to trivalent chromium, which in turn is precipitated as chromium hydroxide. The solids are settled in the pond, and the overflow from the ponds is mixed with the second waste stream and reacted with sufficient alkaline sodium sulfide to reduce the chromate and precipitate chromium hydroxide. The reacted solution is sent to a

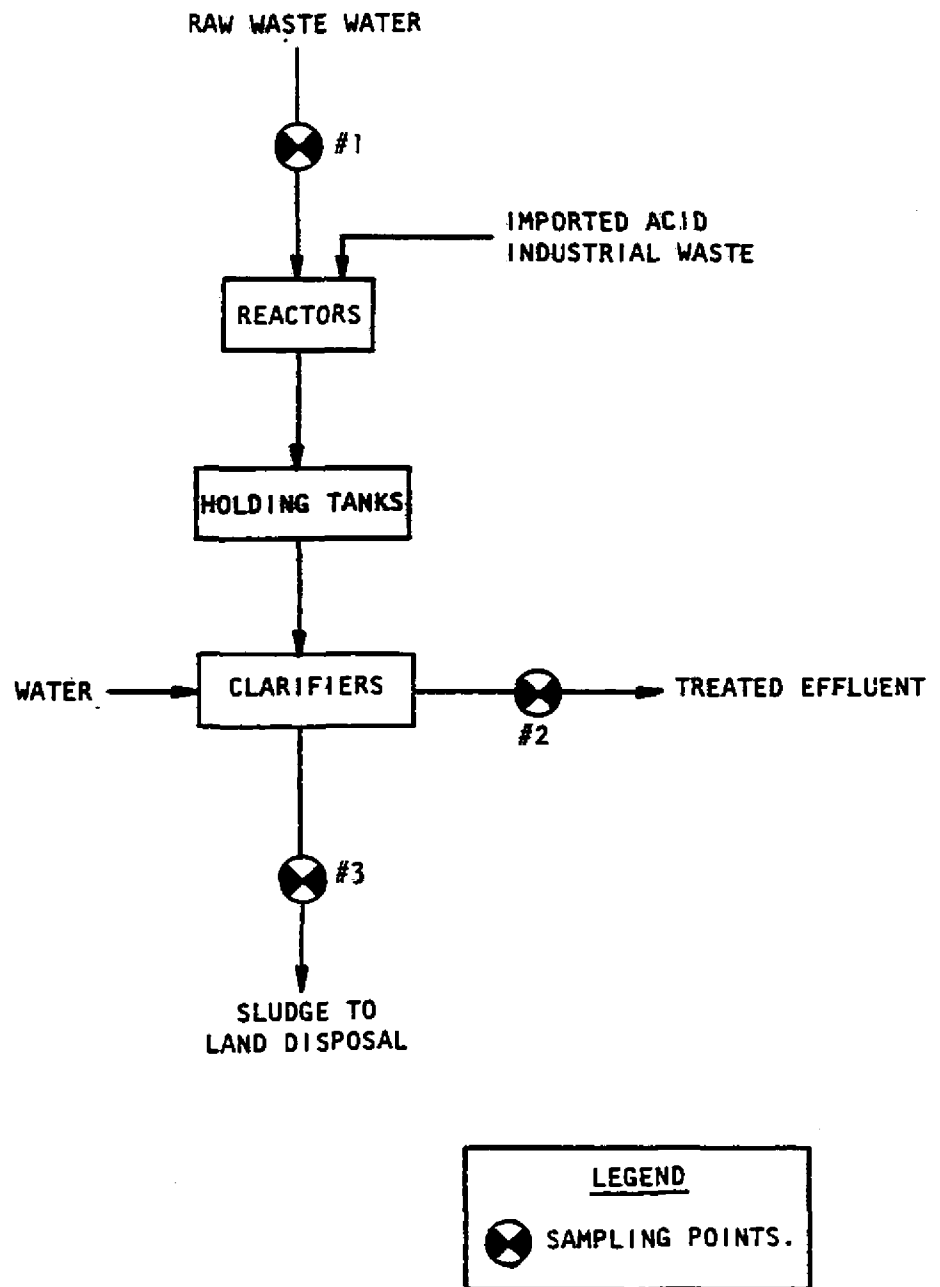


Figure 18-2. General waste water treatment process flow diagram at Plant #493 showing the sampling points. (Sodium dichromate manufacture).

TABLE 18-4. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #493 PRODUCING SODIUM DICHROMATE

Stream No.	Waste Stream Discription	Unit Flow (m ³ /kkg of Na ₂ Cr ₂ O ₇)	TSS Load (kg/kkg of Na ₂ Cr ₂ O ₇)	Cr ⁺⁶ Load (kg/kkg of Na ₂ Cr ₂ O ₇)	Chromium Load (kg/kkg of Na ₂ Cr ₂ O ₇)
1	Raw Waste Water	4.25	183	3.5	3.30
2	Treated Effluent	28.91*	0.018	0.0001	0.072

* This value includes the flow from the sodium dichromate plant, imported acid used for neutralization, and the water used for washing the solids.

settling pond where the suspended solids are settled and the overflow discharged. A simplified flow diagram of the wastewater treatment process is given in Figure 18-3. Table 18-5 gives the flow data and pollutant emissions for the streams sampled.

Plant #376 has implemented some changes in the process technology and treatment system since the time of sampling. The dichromate production was converted from a "high-lime" process to a "no-lime" process, using only chromite ore and soda ash as the raw materials. This requires additional treatment facilities to be installed for removal of impurities from the product solution, which is treated with acid and lime to remove aluminum and vanadium, respectively. At the time of sampling, the data obtained from this plant was considered a valid part of the data base for assessing the pollution potential of the industry and evaluating viable treatment options. The chromate reduction technology being used was evidently subject to periodic problems associated with the hazard of the H₂S gas production. This has been confirmed in treatability studies conducted by the Agency. With proper operation of the treatment system this problem can be avoided.

At Plant #398, the only effluent produced is the noncontact cooling water. The noncontact cooling water is used on a once-through basis and is discharged without treatment through two outfalls. The solid waste residuals from the leaching process are trucked to a state-licensed hazardous waste landfill area. The amount of solid waste residue disposed of is approximately 290 kg/kg of product. Table 18-6 gives the unit flow data and pollutant emissions for the process effluent.

Toxic Pollutant Concentrations and Loadings

Toxic pollutants detected in the raw wastes during sampling were as follows:

Maximum Concentrations Observed (µg/l)

<u>Pollutants</u>	<u>Screening</u>	<u>Verification (2 Plants)</u>
Chromium (Total)	250,000	310,000
Chromium (Hexavalent)	---	150,000
Nickel	13,000	1,300
Zinc	580	1,200
Copper	35	240
Lead	9	24
Silver	<0.50	230*
Arsenic	<10	<5
Selenium	<5	140**

* Found at one plant only

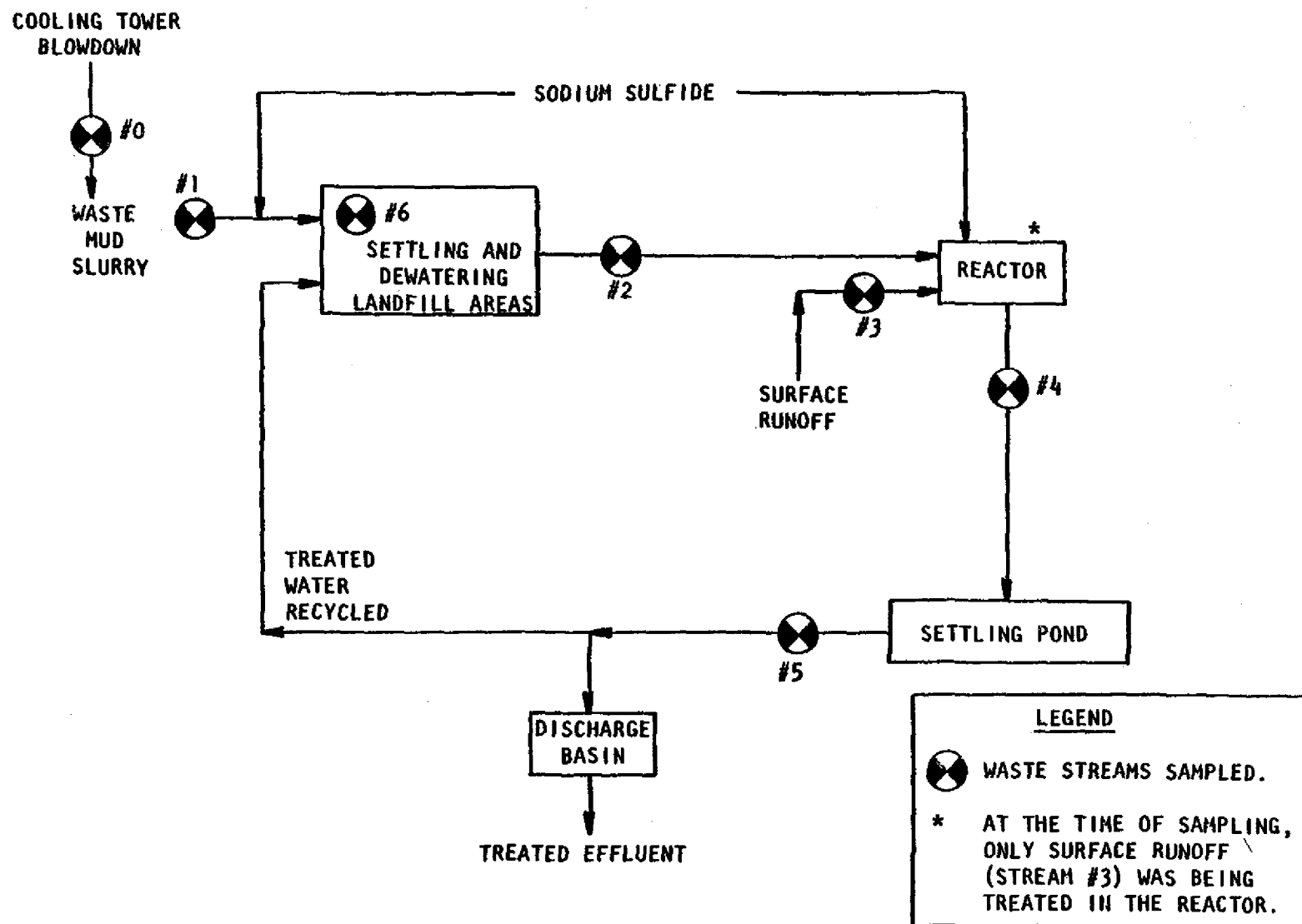


Figure 18-3. General waste water treatment process flow diagram at Plant #376 showing the sampling points. (Sodium dichromate manufacture)

TABLE 18-5. FLOW AND POLLUTANT LOADING DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #376 PRODUCING SODIUM DICHROMATE

Stream No.	Waste Stream	Average Observed Loadings			
		Unit Flow (m ³ /kkg of Na ₂ Cr ₂ O ₇)	TSS Load (kg/kkg of Na ₂ Cr ₂ O ₇)	Cr ⁺⁶ Load (kg/kkg of Na ₂ Cr ₂ O ₇)	Chromium Load (kg/kkg of Na ₂ Cr ₂ O ₇)
1	Mud Slurry Waste	7.85	3988	0.407	1.041
2	Primary Pond* Effluent	NA	0.591	NA	0.808
3	Surface Runoff	4.16	0.621	0.057	0.55
4	Reactor Effluent		7.942	NA	0.77
5	Pond Effluent		0.046	< 0.00004	0.0034

* Due to a high evaporation rate, there is normally no discharge from the primary pond for 9 or 10 months of the year.

NA = Not available

TABLE 18-6. FLOW AND POLLUTANT LOADING DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #398 PRODUCING SODIUM DICHROMATE

Stream No.	Waste Stream Description	Unit Flow	Average Observed Loadings		
			TSS Load	Cr ⁺⁶ Load	Chromium Load
		(m ³ /kkg of Na ₂ Cr ₂ O ₇)	(kg/kkg of Na ₂ Cr ₂ O ₇)	(kg/kkg of Na ₂ Cr ₂ O ₇)	(kg/kkg of Na ₂ Cr ₂ O ₇)
1	Noncontact cooling water	71	0.426	NNI*	NNI*
2	Noncontact cooling water	206	0.55	NNI*	NNI*

* NNI= No net increase of the pollutant load, compared to the intake source.

**** Noncontact cooling water at one plant only**

Individual plant average raw waste loads per unit product found in sampling can be found in Table 18-7. A summary of daily and unit product raw waste loads for all plants sampled can be found in Table 18-8.

Based on the total annual production of this subcategory and the average waste load generated per unit product, the estimated total pollutant raw waste loads generated each year for this subcategory are as follows:

Total Subcategory Raw Waste Load Generation

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Chromium (Total)	290,000
Cr (Hexavalent)	210,000
Nickel	3,700
Zinc	330
Copper	55
Silver	20
Lead	< 8.2
Selenium	4.0
Arsenic	< 5.0

Pollution Abatement Options

Toxic Pollutants of Concern

The most significant toxic pollutants found are the primary pollutant, chromium, and the common heavy metals often present as impurities in the chromium ore, notably zinc and nickel. In controlling these metals by the processes chosen for the treatment models, incidental removal of other trace toxic metals also occurs.

The existing BPT regulations control pH, TSS, and chromium (Table 18-2). In the new promulgated regulations, effluent limitations on nickel are added to the BPT-based regulations. Based on the discussion in Section 8, there is no BAT effluent limitation set for zinc, which is also removed in the hydroxide precipitation by controlling chromium. Although copper, silver, selenium, lead, and arsenic were detected in trace quantities (Section 18 and Tables 18-7 and 18-8), these five toxic pollutants did not occur at treatable concentrations and, therefore, no regulations on them are being set.

Process Modifications and Technology Transfer Options

Appropriate process modifications can be made where opportunities exist for recycle of chrome-bearing wastewaters for recovery and reuse in the process or for use in other product manufacturing operations. Plant #398 currently practices extensive recovery of chromium values

TABLE 18-7.

TOXIC POLLUTANT RAW WASTE DATA

SUBCATEGORY

SODIUM DICHROMATE

POLLUTANT

AVERAGE RAW WASTE INFLUENT

	PLANT #493		PLANT #376 (✓)	
	(mg/l)	(kg/kg)	(mg/l)	(kg/kg)
Chromium, Cr	250.0	0.94	420.0	3.30
Copper, Cu	0.035	0.00013	0.085	0.00067
Lead, Pb	0.0090	0.000030	0.011	0.000090
Nickel, Ni	1.25	0.0047	0.64	0.0050
Zinc, Zn	0.580	0.0022	0.318	0.0025
Silver, Ag	< 0.005	< 0.00002	0.036	0.00028
Selenium, Se	< 0.005	< 0.00002	< 0.005	< 0.00004
Arsenic, As	< 0.010	< 0.00004	< 0.005	< 0.00004

TABLE 18-8.

SUMMARY OF RAW WASTE LOADINGS FOUND IN
SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY		SODIUM DICHROMATE		
Pollutant	Unit Loading, (kg/kg)			No. of Plants
	Minimum	Average	Maximum	
<u>Toxic</u>				
Chromium, total	0.94	2.12	3.30	2
Chromium, Hexavalent	0.47	1.6	2.6	3
Copper	0.00013	0.0004	0.00067	2
Nickel	0.0047	0.027	0.050	2
Silver	0.000020	0.00015	0.00028	2
Zinc	0.0022	0.0024	0.0025	2
Selenium	*	< 0.00003	*	2
Arsenic	*	< 0.00004	*	2
<u>Conventional</u>				
TSS	140	2100	4000	2

* Concentrations were at or below the detection limits

for use in other processes and has no discharge of direct process contact wastewaters.

Best Management Practices

Extensive recycle and reuse of process contact wastewater limits effluent generation at sodium dichromate plants. At two facilities, cooling water blowdown streams are used to slurry spent ore residues and the resultant waste stream is treated for the removal of chromium prior to discharge. At the remaining plant, ore residues are removed as a solid waste and only once through noncontact cooling water is discharged.

Prevailing Control and Treatment Practices

At the time of verification sampling, Plant #376 was using alkaline sodium sulfide (or bisulfide) for the reduction of hexavalent chromium, followed by precipitation of metal sulfides and hydroxides. Problems experienced by the plant included intermittent, low level H_2S gas generation and incomplete reduction of the chromates. These problems were mitigated by the physical layout of the treatment system and lagoons and the long retention time afforded by the evaporation ponds during most of the year.

At Plant #493, the treatment technology employed is the reduction of chromate wastes with an acidic ferrous iron solution (waste pickle liquor), followed by lime addition for metal hydroxide precipitation, settling, and filtration. Overall, this technology is roughly equivalent to the sulfide reduction/alkaline precipitation technique used by Plant #376 and has the advantage of not risking operator exposure to hydrogen sulfide gas.

Advanced Treatment Technologies

In addition to the chromate reduction and metal removal techniques practiced in the sodium dichromate industry, consideration was given to other advanced treatment technologies considered to be equal to or better than the proposed BAT. These technologies include:

- The use of sulfur dioxide for chromite reduction.

- Ferrite coprecipitation i.e., the addition of ferrous iron (e.g., waste pickle liquor) and aeration at about pH 5-6 for both chromate reduction and metals precipitation.

- Ion exchange systems.

- Xanthate precipitation.

These options are not considered viable at this time because there is not sufficient information on performance and cost effectiveness.

Selection of Appropriate Technology and Equipment

Technology for Different Treatment Levels

Alkaline precipitation or reaction with hydroxide will separate nickel and zinc from solution. Hexavalent chromium must be reduced to its trivalent form before it can be precipitated as the hydroxide. Although ion exchange or xanthates can remove metals from clarified solutions they are inappropriate for treating raw waste slurries from this industry.

A. Level 1 (BPT, BAT, NSPS)

The system utilizes pickle liquor containing ferrous iron and hydrochloric acid added to the raw wastes to reduce hexavalent chromium to its trivalent form in a first-stage lagoon. The lagoon effluent is then subjected to alkaline precipitation of trivalent chromium, followed by solids separation in a clarifier and by pH adjustment of the overflow before discharge. Other reducing agents may be utilized instead of ferrous iron for the reduction of hexavalent chromium such as sodium sulfide or sulfur dioxide. Using either of these reagents, chromate reduction under acid conditions would be followed by pH adjustment with lime or caustic to obtain alkaline precipitation of the metal hydroxides. A number of operational difficulties were associated with the treatment with sodium sulfide. Based on the Treatability Studies on the dichromate subcategory (61), it was found that at pH levels above 8, the addition of sodium sulfide required excessive reaction times to reduce chromate to the trivalent form. At pH levels below 8, the evolution of H_2S gas poses a potential safety hazard for the plant operator. The flow diagram for the ferrous iron-based option for Level 1 is shown in Figure 18-4.

B. Level 2

Dual-media filtration is added to achieve a higher level of suspended solids removal, including metallic hydroxides which may have passed through the clarifier. The effluent is adjusted to a pH range of 6 to 9 as in Level 1. At proposal, Level 2 was selected as a possible BAT and NSPS treatment because it was being practiced by one plant in the industry and it could provide a method of removing additional quantities of toxic metals from the wastewater. However, the incremental cost of dual-media filtration applied to Level 1 is measurably more costly for the Sodium Dichromate Subcategory than other subcategories and does not significantly improve effluent quality. The Treatability Studies on the dichromate subcategory (61) showed that dual-media filtration is only marginally effective in reducing toxic metals and TSS beyond BPT. Therefore, this level has not been selected as the basis for BAT or NSPS. The flow diagram for the ferrous iron-based option for Level 2 is shown in Figure 18-5.

C. Equipment Functions

The raw waste flows into an equalizing lagoon, where the influent flows are measured by a magnetic flow meter which controls application of pickle liquor solution into the influent pipeline. Hexavalent chromium is converted to the less toxic trivalent form and together with inert solids passes to the first-stage lagoon. A second application of ferrous iron is made in the lagoon outflow, and lime is added to precipitate trivalent chromium and residual trace metals prior to clarification. In Level 1 the clarifier effluent is adjusted to pH 6 to 9 and released. In the Level 2 system a dual-media filter is added to remove additional suspended material from the overflow. Clarifier underflow and filter backwash are returned to the equalizing lagoon influent, to be settled in the lagoon.

D. Chemicals and Handling

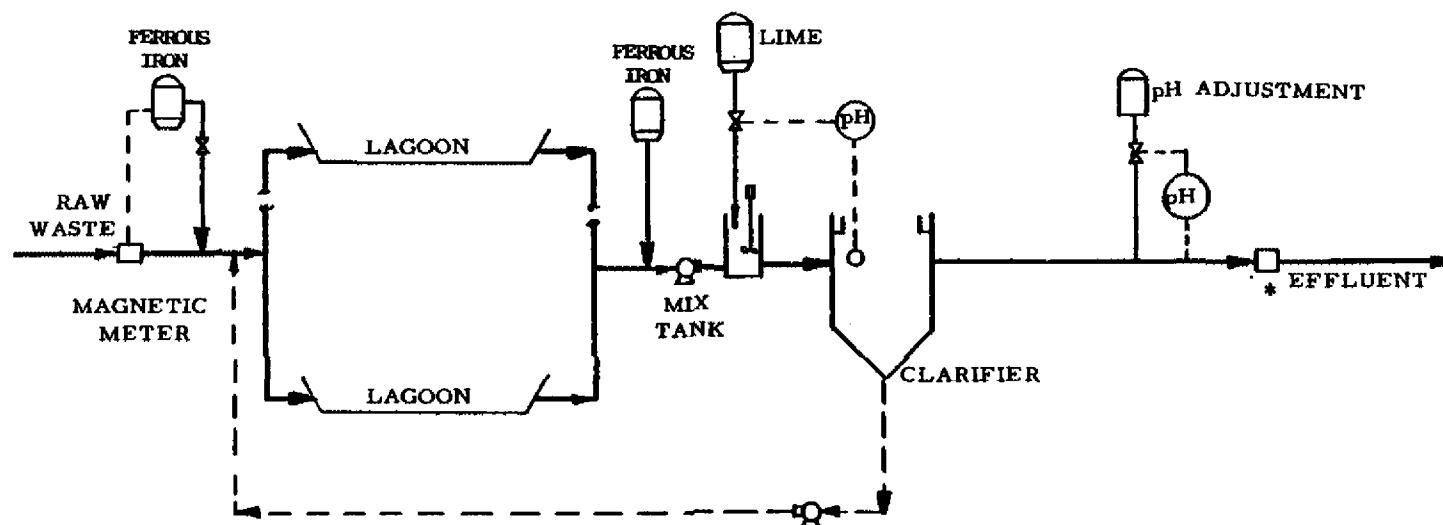
Ferrous chloride, hydrochloric acid and lime are used in the treatment process. The ferrous chloride and hydrochloric acid solution can be applied at the influent pipeline in proportion to flow. Lime slurry is fed through conventional equipment ahead of the clarifier. Hydrochloric acid is used (instead of sulfuric acid) to minimize the formation of gypsum scale which could result from heavy use of lime followed by sulfuric acid.

E. Separation and Disposal of Solids

As a basis for estimating model plant costs, influent suspended solids, metallic hydroxide precipitates, and filter backwash are returned to, or left in, the influent lagoon(s). As each lagoon becomes filled with solids it is decanted from each filled lagoon and the solid material must be periodically removed to a chemical landfill.

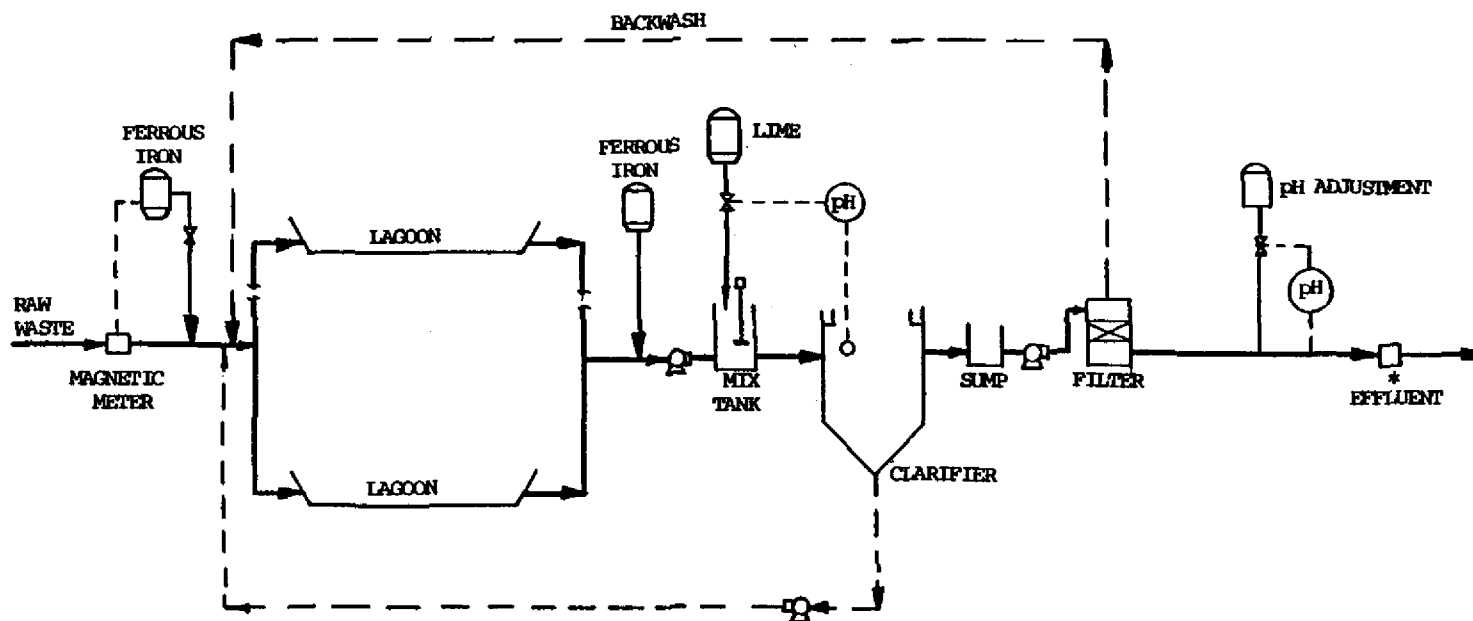
F. Monitoring Requirements

Internal process monitoring should include both routine testing to maintain reducing conditions and a pH above 7 in the influent lagoons, and simple field determination of pH to assure that the optimum level is reached for precipitation of chromic hydroxide. Routine testing of the effluent should also be performed at the site to show that hexavalent chromium is being consistently reduced to trivalent chromium and that total chromium in the final effluent does not exceed the allowable limit. Periodic composite effluent samples should be analyzed for total chromium by the atomic absorption method for official reporting purposes.



* Includes flow monitoring, pH monitoring and sampler.

Figure 18-4. Level 1 waste water treatment for sodium dichromate subcategory.



* Includes flow monitoring, pH monitoring and sampler.

Figure 18-5. Level 2 waste water treatment for sodium dichromate subcategory.

Treatment Cost Estimates

General Discussion

Model plant specifications were selected for the purpose of cost estimation. The rationale for the selection of model plant characteristics is as follows:

A. Production

At the time of sampling, five industrial plants produced sodium dichromate at a total production rate of approximately 140,000 kkg/year. Two of these plants have discontinued production. Production and wastewater flow data, from which model plant characteristics are derived, are on file for three plants which produce a total of 112,000 kkg/year, or approximately 80 percent of the United States production. For wastewater treatment cost estimates, three production levels were selected. These are 20,000 kkg/year, 50,000 kkg/year and 70,000 kkg/year.

B. Wastewater Flow

Unit waste flows for three plants either treating or recycling their wastewaters are approximately 9.6, 11.59, and 4.25 m³/kkg of product. For the model plant, 8.5 m³/kkg of sodium dichromate was used as the wastewater flow.

C. Pollutant Loading

For the model plant, it is assumed that the spent ore residues are slurried and transported to the treatment facility, since this is the prevalent practice at two plants. The spent ore (waste-generated residue) at Plant #969 is 290 kg/kkg Na₂Cr₂O₇. The hexavalent chromium loading in the wastewater varies from 0.5 to 14 kg/kkg of Na₂Cr₂O₇. Pollutant loadings used for the model plants are suspended solids (spent ore residue) at 290 kg/kkg Na₂Cr₂O₇ produced, and hexavalent chromium at 5.0 kg/kkg.

D. Chemicals Required

To reduce hexavalent chromium to trivalent chromium a ferrous chloride dosage of 4.3 g/l is needed, but to allow for reaction with other metals, a model dosage of 5.0 g/l was used. This is equivalent to 42.5 kg/kkg of product in a unit flow of 8.5 m³/kkg. To raise the pH to 9.5, 1.7 g/l of lime is needed, equivalent to 15 kg/kkg of product. For final neutralization, HCl is used in the amount of 10 percent of the lime dosage.

E. Solids Generated

Total dry solids produced from treatment are 260 kg/kkg of sodium dichromate.

F. Model Plant Control Costs

The cost estimates of three models having different production levels are presented in Tables 18-9, 18-10, and 18-11.

Table 18-12 gives a summary of the unit cost distribution between amortization, and the operation and maintenance cost components at various production rates and levels of treatment.

At the first level of treatment, investment costs are high because sludge lagoons costs are provided for a ten-year period. Therefore, amortization is the major portion of the total annual costs. In place of annual cost for the residual waste (sludge) disposal, a large investment in land is shown. At the second level of treatment, labor and amortization have significant impact on the additional annual costs.

Basis for Regulations

BPT Effluent Limitations

A. Technology Basis

BPT regulations for the Sodium Dichromate subcategory are presently in effect, 40 CFR 415.172 (Table 18-2). The technology basis for the existing BPT is ferrous reduction of hexavalent chromium, followed by alkaline precipitation of metals and clarification. As an alternative to the use of ferrous iron, the reduction of hexavalent chromium may be accomplished by reaction with sodium sulfide or sulfur dioxide under acidic conditions. All three plants in this subcategory have installed BPT technology and are meeting the limits.

The control of suspended solids is necessary to the achievement of good effluent quality after precipitation of heavy metals. In the Sodium Dichromate subcategory, it can be assumed that chromium is a significant constituent in the suspended solids discharged. For this reason, only one advanced treatment alternative, addition of a filtration unit for solids control, has been considered.

B. Response to Remand Issues

The zero discharge requirements originally promulgated as BAT for sodium dichromate production were remanded on the basis of inadequate technical and economic justification for the evaporative technology required to eliminate discharge. A control and treatment alternative, which allows wastewater discharge, has been identified and the performance levels achievable have been demonstrated.

TABLE 18-9. MODEL PLANT TREATMENT COSTS

Subcategory Production	Sodium dichromate 20,000 metric tons per year	
	(\$)	
A. INVESTMENT COST	Level 1	Level 2 ^a
Site development	608,700	0
Equipment	185,000	38,000
Monitoring equipment	20,000	0
Subtotal	813,700	38,000
Contractor's O & P ^b	122,055	5,700
Subtotal	935,755	43,700
Engineering	187,151	8,740
Subtotal	1,122,906	52,440
Contingencies	112,291	5,244
Subtotal	1,235,197	57,684
Land	156,000	0
TOTAL INVESTMENT COST	1,391,197	57,684
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	14,000
Energy	2,500	600
Chemicals	17,000	0
Maintenance	123,520	5,768
Taxes and insurance	41,736	1,731
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	255,756	29,599
C. AMORTIZATION OF INVESTMENT COST	200,966	9,385
TOTAL ANNUAL COST	456,722	38,984

^a Represents the incremental cost above that for BPT treatment^b Overhead and Profit

TABLE 18-10. MODEL PLANT TREATMENT COSTS

Subcategory	Sodium dichromate	
Production	50,000 metric tons per year	
	(\$)	
A. INVESTMENT COST	Level 1	Level 2 ^a
Site development	1,300,000	0
Equipment	315,000	89,000
Monitoring equipment	20,000	0
Subtotal	1,635,000	89,000
Contractor's O & P ^b	245,250	13,350
Subtotal	1,880,250	102,350
Engineering	376,050	20,470
Subtotal	2,256,300	122,820
Contingencies	225,630	12,282
Subtotal	2,481,930	135,102
Land	252,000	0
TOTAL INVESTMENT COST	2,733,930	135,102
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	14,000
Energy	2,800	1,000
Chemicals	42,000	0
Maintenance	248,193	13,510
Taxes and insurance	82,018	4,053
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	446,011	40,063
C. AMORTIZATION OF INVESTMENT COST	403,810	21,981
TOTAL ANNUAL COST	849,821	62,044

^a Represents the incremental cost above that for BPT treatment^b Overhead and Profit

TABLE 18-11. MODEL PLANT TREATMENT COSTS

Subcategory		Sodium dichromate	
Production		70,000 metric tons per year	
		(\$)	
A. INVESTMENT COST		Level 1	Level 2 ^a
Site development		1,766,000	0
Equipment		405,000	105,000
Monitoring equipment		20,000	0
Subtotal		2,191,000	105,000
Contractor's O & P ^b		328,650	15,750
Subtotal		2,519,650	120,750
Engineering		503,930	24,150
Subtotal		3,023,580	144,900
Contingencies		302,358	14,490
Subtotal		3,325,938	159,390
Land		324,000	0
TOTAL INVESTMENT COST		3,649,938	159,390
B. OPERATION AND MAINTENANCE COST			
Labor and supervision		56,000	14,000
Energy		2,800	1,000
Chemicals		58,000	0
Maintenance		332,594	15,939
Taxes and insurance		109,498	4,782
Residual waste disposal		0	0
Monitoring, analysis and reporting		15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST		573,892	43,221
C. AMORTIZATION OF INVESTMENT COST		541,130	25,933
TOTAL ANNUAL COST		1,115,022	69,153

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 18-12 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Sodium Dichromate

		Annual Treatment Costs (\$/kg)	
		LEVEL OF TREATMENT	
COST ITEM	PRODUCTION (kg/yr)	Level 1	Level 2
Annual Operation and Maintenance	20,000	12.79	1.48
	50,000	8.92	0.80
	70,000	8.20	0.62
Annual Amortization	20,000	10.05	0.47
	50,000	8.08	0.44
	70,000	7.73	0.37
Total Annual Cost	20,000	22.84	1.95
	50,000	17.00	1.24
	70,000	15.93	0.99

*Represents the incremental cost above BPT

C. Flow Basis

The model plant waste flow rate is based on the raw waste influent data obtained from three plants as shown in Table 18-3. The flow rate selected, 8.5 m³/kkg, is the average of the flows for these three plants. All three plants are included in the flow averaging because the waste sources were typical for the industry at the time of sampling and represent the range of inflow rates expected to be handled by a BPT treatment system.

D. Selection of Pollutants to be Regulated

For BPT regulations the Agency is retaining the pollutants that are presently limited under 40 CFR 415.172, which are pH, total suspended solids (TSS), hexavalent chromium (CrVI), and total chromium (Cr) and is adding nickel. The significance of these pollutants is substantiated by the screening and verification data presented in Section 18.

The available treatment technology for the removal of chromium from wastewater necessitates the reduction of hexavalent chromium (chromate or dichromate) to the trivalent state which can then be precipitated as chromic hydroxide, Cr(OH)₃. Thus, from the regulatory point of view, an effluent limitation on the discharge of total chromium effectively limits hexavalent chromium as well. But, placing limitations on both forms of chromium in the Sodium Dichromate subcategory is consistent with the primary objective of controlling specifically the highly toxic hexavalent form by means of a two-step treatment process. In light of the potential analytical difficulties associated with the measurement of hexavalent chromium discussed in Section 5, monitoring both the hexavalent chromium and the total chromium content of the treated effluent provides an additional assurance that high chromate levels would not go undetected. As treatment system performance data are accumulated, support may develop for a decreased monitoring requirement or the elimination of effluent limitations on hexavalent chromium.

Nickel is included in the limitations since it provides a means of controlling the group of toxic metals represented by removal at slightly higher pH values than for chromium. A detailed discussion of the two toxic metal groups represented by nickel and chromium is in Section 8. Control of nickel and chromium will ensure that toxic metals that may occasionally occur at treatable levels will be adequately controlled.

E. Basis for Pollutant Limitations

1. Conventional Parameters -

a. pH

After final pH adjustment, the BPT treated effluent is to be held within the pH range of 6 to 9. The pH limitation is based on Appendix B of the proposed Development Document (60) and a study report, "An Assessment of pH Control of Process Waters in Selected Plants" by JRB Associates, Inc. (52).

b. TSS

The present study substantiates the basis for the existing BPT limitation on total suspended solids. The treated effluent sampling data from two plants presented in Table 18-13 suggest that the TSS concentrations found in sampling represent achievable performance of a well operated BPT system. This is in agreement with the 26 mg/l TSS which is the concentration basis for the existing maximum 30-day average effluent limitation (Table 18-2). For comparison, Table A-11a summarizes the long-term data available from another subcategory where a similar BPT is applied. Plant #376 discharged an average TSS of 11 mg/l without filtration. Monitoring data from Plant #493 shown at the bottom of Table 18-13 indicates that 25 mg/ is an achievable maximum 30-day average for TSS with filtration. Thus, individual plant performance can be seen as a function of a very large number of operating variables and waste characteristics. In general, the available performance data support the achievability of the existing regulations.

The variability factor ratio (VFR) of 2.0 is derived from the long-term data on chromium as presented in Tables A-9a-1, and following. This VFR value is used for TSS and chromium because a significant proportion of the TSS is composed of suspended metal hydroxides resulting from BPT treatment. For TSS, the maximum 30-day average limitation is related to the concentration basis and the model plant flow as follows:

$$\frac{(26 \text{ mg/l}) (8.5 \text{ m}^3/\text{kkg})}{(1000 \text{ mg/l})} \left(\frac{\text{kg}}{\text{m}^3} \right) = 0.22 \text{ kg/kkg}$$

and the daily maximum limitation is obtained by multiplying by the VFR;

$$(2.0) (0.22 \text{ kg/kkg}) = 0.44 \text{ kg/kkg}$$

2. Toxic Pollutants

a. Chromium

For BPT, the Agency is retaining the existing limitations on total and hexavalent chromium as given in 40 CFR 415.172 (Table 18-2). For hexavalent chromium, the observed performance level of 0.004 mg/l was below the accepted lower

TABLE 18-13. EFFLUENT SAMPLING DATA FROM
SODIUM DICHROMATE PLANTS

Pollutant	Screening & Verification Data			
	Plant #376		Plant #493	
	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)
Total Suspended Solids, TSS	11	0.046	2.0	0.0085
Hexavalent Chromium, Cr (VI)	< 0.01	< 0.00004	0.004	0.00002
Total Chromium, Cr (T)	0.81	0.0034	2.5	0.011
Copper, Cu	0.012	0.00005	0.016	0.00007
Nickel, Ni	0.20	0.00083	0.090	0.00038
Selenium, Se	< 0.005	< 0.00002	0.10	0.00043
Silver, Ag	0.015	0.00006	< 0.007	< 0.00003
Zinc, Zn	0.008	0.0003	0.11	0.00047
Flow (m ³ /kkg)	4.16		4.25	
Long Term Monitoring Data-Maximum 30-Day Averages				
	Plant #493 (1) (2)			
	(mg/l)			(kg/kkg)
TSS	25			0.11
Cr (VI)	0.023			0.00010
Cr (T)	0.072			0.00031

(1) Filtered effluent data reported in response to 308-Questionnaire (12-22-76)

(2) The number of samples is unknown.

limit of treatability (0.05 mg/l) from Table 8-11. The treatability level was the basis of the 30-day average concentration basis of 0.060 mg/l used for the existing BPT regulations (Tables 18-2 and 18-14).

The VFR of 4.0/2.0 used for total chromium is confirmed by long-term data (Tables A-9a-1, and following) on alkaline precipitation of chromium in another subcategory where a 1.8 value was determined for similar BPT technology.

The existing 24-hour maximum effluent limitation that was published for hexavalent chromium is in error as it appears in 40 CFR 415.172. The correct value is 0.0009 kg/kg reflecting an overall VFR value of approximately 1.8 for the residual hexavalent chromium remaining after the two-step treatment process.

For total chromium, the maximum 30-day average limitation is:

$$\frac{(0.50 \text{ mg/l}) (8.5 \text{ m /kg}) (\text{kg/m}^3)}{(1000 \text{ mg/l})} = 0.0044 \text{ kg/kg}$$

and, by applying the VFR value of 2.0, the daily maximum is:

$$(2.0) (0.0044 \text{ kg/kg}) = 0.0088 \text{ kg/kg}$$

For hexavalent chromium, the maximum 30-day average limitation is:

$$\frac{(0.60 \text{ mg/l}) (8.5 \text{ m /kg}) (\text{kg/m}^3)}{(1000 \text{ mg/l})} = 0.00050 \text{ kg/kg}$$

and the 24-hour maximum is obtained using the VFR value of 1.8, that is:

$$(1.8) (0.00050 \text{ kg/kg}) = 0.00090 \text{ kg/kg}$$

b. Nickel

The long-term average nickel concentration was selected from Table 8-12 which presents the industrial wastewater system performance. The variability factors are based on the primary pollutant chromium.

The maximum 30-day average concentration basis for nickel is,

$$(0.20 \text{ mg/l}) (2.0) = 0.40 \text{ mg/l}$$

The 24-hour maximum concentration basis for nickel is,

$$(0.20 \text{ mg/l}) (4.0) = 0.80 \text{ mg/l}$$

TABLE 18-14. EFFLUENT LIMITATIONS*
SODIUM DICHROMATE
Best Practicable Control Technology Currently Available
Wastewater Flow: 8.5 m³/kg

Pollutant	Subcategory Performance (mg/l)	VFR ⁽¹⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kkg)	
			Max.		Max.	
			30-day Avg.	24-hr. Max.	30-day Avg.	24-hr. Max.
<u>Conventional Pollutants:</u>						
Total Suspended Solids	25 ⁽³⁾	2.0	26	52	0.22	0.44 ⁽²⁾
<u>Toxic Pollutants:</u>						
Total Chromium ⁽⁸⁾	0.25 ⁽⁴⁾	4.0/2.0 ⁽⁵⁾	0.50	1.0	0.0044	0.0088 ⁽²⁾
Hexavalent Chromium ⁽⁸⁾	0.050 ⁽⁵⁾	1.8 ⁽⁶⁾	0.060	0.11	0.00050	0.00090 ⁽²⁾
Nickel ⁽⁸⁾	0.20 ⁽⁴⁾	4.0/2.0 ⁽⁵⁾	0.40	0.80	0.0034	0.0068
Zinc	0.50 ⁽⁴⁾	2.0	0.50	1.0	-- ⁽⁷⁾	-- ⁽⁷⁾

(1) VFR: Ratio of the 24-hour variability factor to the 30-day variability factor.

(2) Existing regulations, 40 CFR 415.72 (Table 18-2).

(3) Long-term monitoring 30-day averages from Plant #493 (Table 18-13).

(4) Industrial Wastewater System Performance (Table 8-12).

(5) The VFR used in original regulation is confirmed by long-term data on alkaline precipitation of chromium in another subcategory (Tables A-9a-1, etc.)

(6) VFR used in original regulation.

(7) No limitations.

(8) Applicable to BAT, and PSNS.

* - Also applicable to New Source Performance Standards (NSPS).

The maximum 30-day average limitation for nickel is,

$$\frac{(0.40 \text{ mg/l}) (8.5 \text{ mg/kg}) (\text{kg/m}^3)}{(1000 \text{ mg/l})} = 0.0034 \text{ kg/kg}$$

The 24-hour maximum limitation for nickel is,

$$\frac{(0.80 \text{ mg/l}) (8.5 \text{ m}^3/\text{kg}) (\text{kg/m}^3)}{(1000 \text{ mg/l})} = 0.0068 \text{ kg/kg}$$

c. Other Metals

The concentration basis for zinc is also given in Table 18-14. This and other similar metals will be effectively removed by the BPT alkaline precipitation step. Copper, silver, selenium, arsenic, and lead did not occur at concentrations high enough to be treatable and are therefore not regulated. An adequate removal of these metals is expected with a BPT treatment system specifically designed to provide optimum conditions for the precipitation of nickel and chromium.

BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

BAT Effluent Limitations

For BAT, the Agency is setting limitations equal to BPT, since the cost of dual-media filtration is too high to justify the relatively small additional toxic metal removal. The pollutants limited include hexavalent chromium, total chromium and nickel which are the same as presented in Table 18-14.

NSPS Effluent Limitations

For NSPS, the Agency is setting limitations equal to BPT, since the cost of dual-media filtration is too high to justify the relatively small additional toxic metal removal. The pollutants limited include TSS, total chromium, hexavalent chromium, and nickel which are the same as presented in Table 18-14.

Pretreatment Standards

The Agency is promulgating pretreatment regulations that are equal to NSPS in order to provide better removal of toxic metals than is achieved by a well-operated POTW with secondary treatment installed. These pollutants would pass through a POTW in the absence of pretreatment.

A. Existing Sources

The Agency is excluding this subcategory from pretreatment standard for existing sources (PSES) under the provisions of paragraph 8(b) of the Settlement Agreement because there are no existing indirect dischargers.

B. New Sources

There is an existing pretreatment standard for new sources (PSNS) in effect (40 CFR 415.176) which is based on BPT treatment. The Agency is retaining this BPT treatment for NSPS and is limiting total chromium, hexavalent chromium, and nickel as presented in Table 18-14.

SECTION 19

CARBON DIOXIDE INDUSTRY

Summary of Determinations

We have determined that no further effort need be given to developing BPT, BAT, NSPS, and Pretreatment regulations for the Carbon Dioxide Subcategory. The basis for this determination is that no toxic pollutants were found at significant levels in the process related wastewater during the screening of one plant. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Assessment of the Water Pollution Potential

Production Processes and Effluent

Carbon dioxide is produced in gaseous, liquid, or solid form. Most of the carbon dioxide is produced as a by-product of ammonia production. A major portion of the carbon dioxide is used captively for producing urea and secondary recovery of oil and natural gas. It is also used for refrigeration, in the food industry for the carbonation of beverages, in fire extinguishing equipment, and oil well stimulation.

The process wastewater is derived from gas scrubbing and condensation. The only toxic pollutant found at a significant concentration in the raw waste during screening at one plant was zinc (910 $\mu\text{g/l}$). When the data was reviewed with plant personnel, it was discovered that the zinc level was due to zinc corrosion inhibitors and was not process related. Control of zinc from this type of source is best achieved by management on a case-by-case basis by the permitting authority. The subcategory profile data is given in Table 19-1.

Maximum concentration of toxic pollutants found in screening at one plant were:

<u>Pollutant</u>	<u>$\mu\text{g/l}$</u>
Zinc	910
Copper	75
Chromium	31

Status of Regulations

Subpart AF has been reserved for this subcategory.

TABLE 19-1. - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY CARBON DIOXIDE

Total subcategory capacity rate	12,194,000 kkg/year
Total subcategory production rate	1,819,000 kkg/year
Number of plants in this subcategory	105
308 Data on file for	12
With total capacity of	713,947 kkg/year
With total production of	558,667 kkg/year
Representing capacity	59 percent
Representing production	31 percent
Plant production range:	
Minimum	1,600 kkg/year
Maximum	155,000 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	6 years
Maximum	50 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

NA = Not Available

SECTION 20

CARBON MONOXIDE AND BY-PRODUCT HYDROGEN INDUSTRY

Summary of Determinations

We have determined that no further effort need be given to developing BAT, NSPS, and Pretreatment regulations for the Carbon Monoxide and By-Product Hydrogen Subcategory. The basis for this determination is that no toxic pollutants were found at significant levels in the process related wastewater during the screening of one plant. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Assessment of the Water Pollution Potential

Production Processes and Effluents

Carbon monoxide is produced as a result of production of hydrogen by refining natural gas. It is also recovered from several gas sources including partial combustion of oil or natural gas, coke oven gas, blast furnace gas, water gas, and methane reformer gas.

The major use of carbon monoxide is for the manufacture of methanol. It is also used in the production of ammonia, acetic acid, zinc white pigments, and for reducing oxides for special steels and nickel refining.

The industry profile data is given in Table 20-1.

Toxic pollutants detected in the raw waste during screening at one plant were:

<u>Pollutant</u>	<u>Concentration (μg/l)</u>
Chromium	2590
Zinc	820
Silver	1.4
Mercury	1.2

The only pollutants of significance in terms of waste loads are chrome and zinc. However, those result from the additives used in cooling water to inhibit corrosion, and are not process related. Control of zinc and chromium from this type of source is best achieved by best management practices on a case-by-case basis by the permitting authority.

Status of Regulations

Subpart AG has been reserved for this subcategory.

TABLE 20-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY		CARBON MONOXIDE AND BY-PRODUCT HYDROGEN
<hr/>		
Total subcategory capacity rate		
Total subcategory production rate		277,200 kkg/year
Number of plants in this subcategory		5
308 Data on file for		5
With total capacity of		
With total production of		112,400 kkg/year
Representing capacity		
Representing production		40 percent
Plant production range:		
Minimum		47 kkg/year
Maximum		63,000 kkg/year
Average production		NA
Median production		NA
Average capacity utilization		NA
Plant age range:		
Minimum		8 years
Maximum		19 years
Waste water flow range:		
Minimum		NA
Maximum		NA
Volume per unit product:		
Minimum		NA
Maximum		NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

NA = Not Available

SECTION 21

COPPER SULFATE INDUSTRY

Industrial Profile

General Description

Most of the copper sulfate produced is sold in the merchant market, consequently captive use is very small. Copper sulfate is produced either as a liquid solution or dried crystals. It is used in agriculture as a pesticide, and as an additive to copper-deficient soils. It is also used in electroplating and petroleum refining, and as a preservative for wood. Of the 16 plants in this industry, four plants produce copper sulfate in significant quantities and account for 70 percent of the total U.S. production. Two of these facilities account for over 50 percent.

The industrial profile data for this subcategory are given in Table 21-1. The status of regulations prior to promulgation of this regulation is summarized in Table 21-2.

Subcategorization

Primary subcategorization originally chosen for the inorganic chemicals manufacturing category was based on the dominant chemical produced. Other factors that were considered for subcategorization were: raw materials, manufacturing processes, size and age of plants and equipment, geographical location, water pollution control technology and solid waste handling. A detailed discussion of these factors is given in Section 4 of this document.

In the original study in 1974, the Agency had further subcategorized the copper sulfate process by raw material, promulgating regulations for pure copper and one for copper slag and copper refinery waste. The conclusion made in this study was that there was no need to subcategorize the copper sulfate industry beyond the dominant product. This is because pure raw materials make complete recycle possible, and using them will allow a plant to comply with effluent limitations without operation of a treatment system, if the production process is properly operated and maintained. Both types of raw material will be adequately covered under one regulation.

General Process Description and Raw Materials

Copper sulfate is produced by reacting copper with sulfuric acid, air and water. The general reaction is:



TABLE 21-1. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	COPPER SULFATE
Total subcategory capacity rate	Indeterminate
Total subcategory production rate	27,300 kkg/year
Number of plants in this subcategory	16
308 Data on file for	10
With total capacity of	33,850 kkg/year
With total production of	21,420 kkg/year
Representing capacity	
Representing production	78 percent
Plant production range:	
Minimum	45 kkg/year
Maximum	9,100 kkg/year
Average production	2,100 kkg/year
Median production	790 kkg/year
Average capacity utilization	63 percent
Plant age range:	
Minimum	3 years
Maximum	52 years
Waste water flow range:	
Minimum	0 cubic meters/day
Maximum	45 cubic meters/day
Volume per unit product:	
Minimum	0 cubic meter/kkg
Maximum	23 cubic meter/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

TABLE 21-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY Copper Sulfate

SUBPART AJ (40 CFR 415.360, 5/22/75)

STANDARDS							
Product Process	Para- meters	BPCTCA		BATEA		NSPS	
		Max. (1) kg/kg (mg/l)	Avg. (2) kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)
Pure Raw Materials Process	Cu	0.0006	0.0002				
Recovery Process	TSS	0.069	0.023				
	Cu	0.003	0.001				
	Ni	0.006	0.002				
	Se	0.0015	0.0005				

(1)- Max. = Maximum of any one day.

(2)- Avg. = Maximum average of daily values for thirty consecutive days.

Various forms of copper feed material are used, from pure copper to copper slag. The purity of raw materials significantly effects the quality and quantity of raw waste generated. One plant does not start with copper metal but uses a waste stream from a copper refinery which consists of copper, sulfuric acid, and a small amount of nickel. The solution needs to be strengthened by the addition of more copper but the same general equation applies.

Copper metal and/or copper refinery waste stream, steam, water, sulfuric acid and air are treated in oxidizer tanks at 100°C to produce a solution of copper sulfate. This solution is partially concentrated by evaporation.

If pure copper is used as a raw material, the resulting copper sulfate solution is pure enough to be either sold, or fed to crystallizers producing copper sulfate crystals. If impure copper feed, or copper refinery waste is used, the concentrated copper sulfate solution is filtered to remove other metal impurities. This purified solution can be sold as is or fed to the crystallizer. Copper sulfate crystals are recovered by centrifugation, dried at approximately 110°C, screened and then packed dry for sale. The mother liquor is recycled to the evaporator or crystallizer with some being purged to prevent impurities buildup. The purges are usually sold for metal recovery.

Figure 21-1 shows a general process flow diagram for the manufacture of copper sulfate.

Water Use and Waste Source Characteristics

Water Use

Water is used in direct contact with copper sulfate production as the reaction medium. A portion of it is evaporated to the atmosphere during crystallization, while the remainder becomes part of the dry product as its water of crystallization (hydration). Noncontact cooling water, including steam condensate, constitutes the major water use. This is used to cool the reactor and crystallizers. Water is also used for pump seals and washdowns. Table 21-3 gives a summary of plant water usages found in this study for facilities where information was available from 308-Questionnaire responses and previous documents.

Waste Sources

A. Noncontact Cooling Water

Noncontact cooling water is used to cool the crystallizers and constitutes one of the main wastes. This waste stream should not be contaminated by process leaks, and therefore can be discharged without treatment.

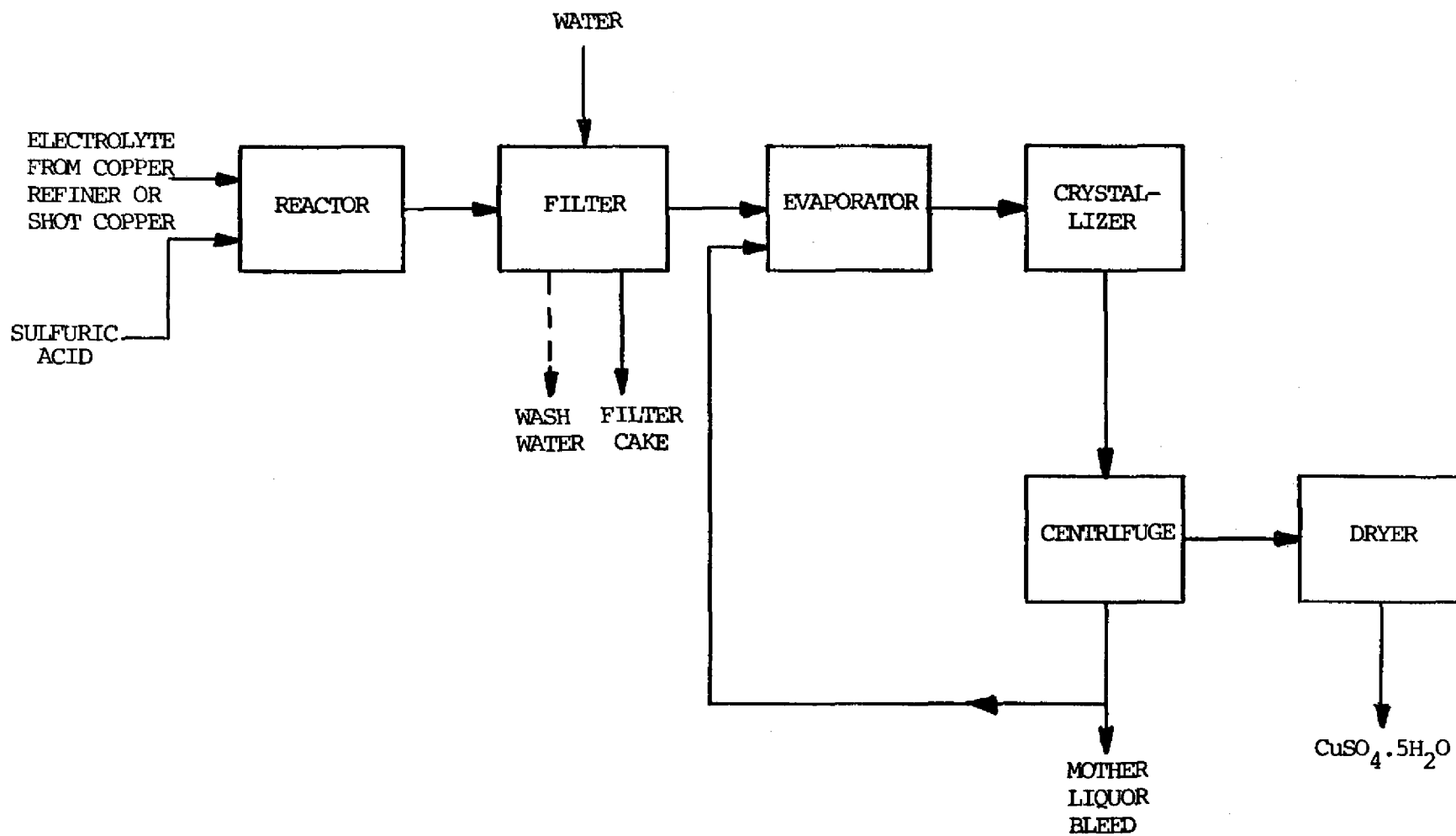


Figure 21-1. General process flow diagram of the manufacture of copper sulfate.

TABLE 21-3. WATER USAGE IN COPPER SULFATE SUBCATEGORY

Source	Water Usage at Plants (m ³ /kg)				
	#034	#284	#313 ⁽¹⁾	#069	#571
Process Contact	*	1.21 ⁽²⁾	24.8	3.30	0.075
Noncontact Cooling	19.6	0	37.3	105	0
Maintenance Cleaning and Washdown, Pumps Seals and Leaks	1.25 ⁽²⁾	0.35	0.28	3.77	0.017
Steam	38.6	0	0	0	0
Air Pollution Control	0	0.52	0	0	0

(1) Includes uses for other processes

(2) Maximum - includes groundwater infiltration

* Utilizes feed solution from another industry

B. Washdowns, Leaks, and Spills

Washdown, pump seal leaks, and spills are sources of contact wastewater. These flows, however, are relatively small and intermittent, and do not represent a major waste source. Wastewaters emanating from this source are either combined with the mother liquor, or treated and discharged.

C. Mother Liquor Purges

A small portion of the mother liquor is purged periodically from the process to prevent buildup of metal impurities. The amount of purge is variable and depends on the purity of feedstock. These purges are processed to separate metallic salts, particularly those of copper and nickel, from the impurities. These recovered metallic salts are used for other processes while the impurities are disposed of at an approved landfill.

D. Steam Condensate

A few plants use evaporators to concentrate the production solution. Steam condensate is an additional noncontact wastewater formed in the process. This can also be discharged without treatment.

E. Sludge

Solid waste is generated in product purification by the filtration step. This is necessary only for plants utilizing impure copper, or copper refinery waste, as raw material. These filter sludges contain metallic impurities or copper sulfides and need disposal at an approved landfill.

Plants that produce copper sulfate in liquid form have no direct contact waste streams from the process. Plants utilizing pure copper feedstock are able to recycle most contact wastewaters and generally have no discharge of contact wastes. Table 21-4 summarizes the quantities of wastewater that go to the treatment facility, their sources, and the handling practices for plants which do not discharge wastewaters. The data was taken from 308-Questionnaire responses, previous development documents, and industry visits.

Description of Plants Visited and Sampled

Screening

Plant #034 was visited and process wastewater and effluent samples were collected and analyzed for conventional and toxic pollutants. The process used at this plant is similar to that described earlier, for one which utilizes a waste stream from a copper refining facility as its feedstock. The feedstock is strengthened by the addition of copper shot. The filter cake and wash water are sent to a settler

TABLE 21-4. WASTE WATER FLOW FOR THE COPPER SULFATE SUBCATEGORY

Plant	Avg. Waste Water Flow to Treatment (m ³ /kkg of CuSO ₄)	Waste Water Handling Practice
#034	0.94	Segregated treatment of CuSO ₄ waste (lime treatment)
#284	0.52	Waste streams and treatment are combined with other mining, milling and man- ufacturing process wastes.
#313	23.4*	Waste streams and treatment are combined with other metal process wastes.
#069	4.01	Waste streams are combined with waste from other re- agent grade processes and discharged to sewer.
#571	0	No discharge of waste from the process (recycle)
#885	0	No discharge of waste from the process (recycle)
#458	0	No discharge of waste from the process (recycle)
#100	0	No discharge of waste from the process (recycle)
#969	0	No discharge of waste from the process (recycle)
#050	0	No discharge of waste from the process (recycle)

* Flow is for the combined waste from all process per kkg of CuSO₄.
Actual amount of flow contributed by CuSO₄ process is unavailable.

where the cake and wash water are finally separated. The decant of the settler is recycled back to the reactor, while the settled sludge is sent to another process for melting. Mother liquor purges from the centrifuge are also sent to other processes. Leaks, spills and washdown water flow down to a sump in the basement of the facility where it collects with contaminated groundwater, and is then pumped to holding tanks. About one quarter of this wastewater volume is comprised of contaminated groundwater from the immediate area. From the holding tanks, the waste goes to the treatment facility where it is treated with lime, filtered and discharged to a collection tank.

The uncontaminated steam condensate from the evaporator, and noncontact cooling water from the crystallizer, are combined with the effluent from the lime treatment in a collection tank. The combined stream passes through a cloth filter for final polishing and is discharged to a sewer. The filter residue from the filter press is hauled to an approved landfill site. Figure 21-2 shows the general process and treatment flow diagram with the location of the sampling points. Table 21-5 presents flow data, total suspended solids (TSS), and copper and nickel emissions for the various waste streams sampled during screening.

Verification

Plant #034 was sampled again during the verification phase. Prior to this, the system was changed so that only the effluent from lime treatment goes to the collection tank and through the cloth filter. This effluent then combines with the steam condensate and noncontact cooling water waste streams after the cloth filter and discharges to the sewer.

Figure 21-2 also shows this change, and the subsequent new sample points for verification phase sampling. Table 21-5 also gives flow and discharge data for various waste streams sampled during verification.

Plant #034 was the only plant sampled for the copper sulfate subcategory. During the program, an attempt was made to locate other candidates for sampling. A search was conducted using the 308-Questionnaires, published materials and the telephone. Out of the 17 other facilities, 11 have no discharge of process wastewaters (practice recycle); four plants were large multi-product complexes with combined waste treatment systems where segregation of copper sulfate process wastes was impossible; and two plants produced only reagent grade product, and are therefore low volume producers.

Toxic Pollutant Concentrations

The following toxic pollutants were found at detectable concentrations in the raw waste samples at copper sulfate Plant #034 during screening and verification sampling.

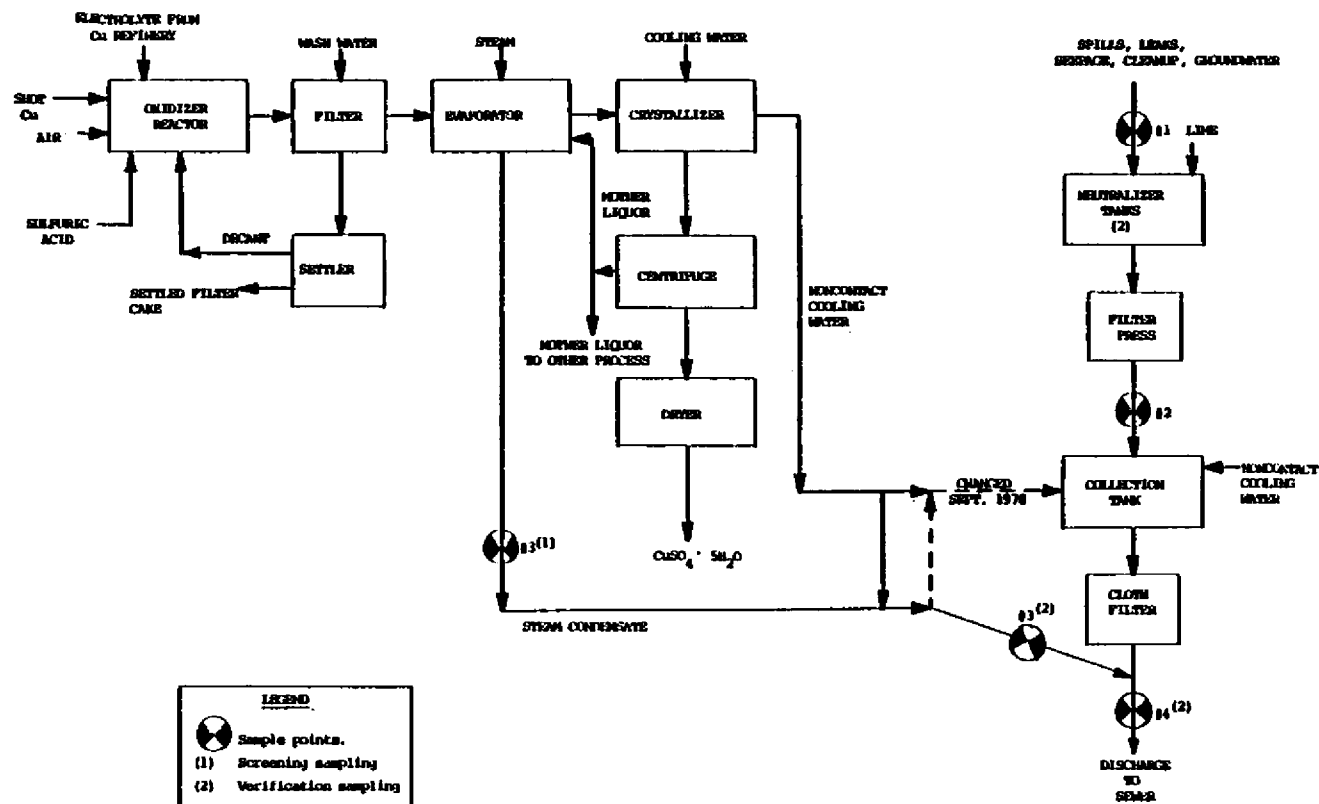


Figure 21-2. General process flow diagram at plant #034 showing the sampling points.
(Copper sulfate manufacture.)

TABLE 21-5. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #034 PRODUCING COPPER SULFATE

Stream No.	Sampled Stream Description	Unit Flow (m ³ /kg of CuSO ₄)	TSS	Cu (all in kg/kg of CuSO ₄)	Ni
<u>Screening (1)</u>					
1	CuSO ₄ waste *	1.25	0.087	4.2	0.25
2	Effluent from lime treatment	1.25	0.078	0.010	0.00053
3	Steam Condensate	0.209	0.00021	0.00016	0.000025
<u>Verification (2)</u>					
1	CuSO ₄ waste *	1.25	1.8	5.0	0.20
2	Effluent from lime treatment	1.25	0.030	0.0042	0.00038
3	Noncontact Cooling Water and Steam Condensate	14.2	0.11	0.024	0.0020

(1) From grab samples composited during the period of batch manufacturing and treatment process.

(2) Average of three daily grab samples composited during the period of batch manufacturing and treatment process.

* Infiltration of ground water into the collection sump was suspected at the time of sampling.

Maximum Raw Waste Concentration Observed
($\mu\text{g/l}$)

<u>Pollutant</u>	<u>Screening</u>	<u>Verification</u>
Antimony	330	1,300
Arsenic	3,500	127,000
Cadmium	870	2,500
Chromium	140	940
Copper	1,850,000	3,940,000
Lead	180	2,200
Nickel	112,000	136,000
Zinc	11,000	17,000
1,1,1-trichloroethane	240	NA

NA = Not analyzed

A large portion of the raw wastewater at this plant consists of groundwater which seeps and collects in the basement, along with leaks and washdown water from the process. The groundwater is contaminated from the surrounding area which is heavily industrialized. The trichloroethane is presumed to be external contamination because this chemical is not used in the process.

No other organic toxic pollutants were found at significant concentrations during screening sampling. Consequently, no organic toxic pollutants were analyzed for in the verification phase.

Section 5 of this report describes the methodology of the screening and verification sampling program. In the copper sulfate industry, a total of six days of sampling were conducted at Plant #034. Five different sampling points were involved covering the various raw wastes, and the intermediate and treated effluent streams. The evaluation of toxic metal content of these process related waste streams was based on 221 analytical data points. The screening for toxic organic pollutants at Plant #034 generated an additional 456 analytical data points. The unit loadings were calculated from the waste stream flow rates measured or estimated at the time of sampling, the measured pollutant concentration, and the reported copper sulfate production rate.

That is,

$$\text{Unit loading (as kg of pollutant per kkg of copper sulfate)} = \frac{(C) (Q)}{1000 (P)}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: $\text{kg/m}^3 = \text{mg/l}$),

Q is the waste stream flow rate expressed in units of m^3/day . (m^3 , a cubic meter, is equal to 264.2 U.S. gallons), and

P is the copper sulfate production rate expressed in units of kkg/day (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs).

The average values are based on data from Plant #034 where the particular pollutant was found at concentrations greater than the analytical detection limits and in significant concentrations since it could be treated by an available treatment technology.

In Table 21-6, the toxic pollutant raw waste data are presented as the average daily concentrations and the unit loading found during each sampling at Plant #034. The overall averages are also shown. It is this overall average which is used as the average raw waste load from the copper sulfate process in various calculations.

Based on the total annual production rate of this subcategory and the average waste load generated per unit product, the estimated total pollutant raw waste loads generated each year for this subcategory are as follows:

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Antimony	26
Arsenic	1,400
Cadmium	74
Chromium	15
Copper	124,000
Lead	30
Nickel	6,200
Zinc	700

Pollution Abatement Options

Toxic Pollutants of Concern

The principal pollutant of concern is copper. The other toxic pollutants found in plant wastewaters are closely related to the purity of the copper and acid sources. The heavy metals cadmium, nickel, zinc and, to a lesser extent, antimony, chromium and lead, which were found during field sampling, may originate as trace impurities in copper scrap and other impure copper sources. Plants utilizing pure copper shot would not experience a buildup of these impurities in the mother liquor, and consequently would not generate a waste stream containing these impurities. Arsenic was also found in fairly high concentrations in the raw wastewater. A possible source of arsenic, and other copper ore trace metals, is the use of sulfuric acid made from sulfur dioxide produced in the roasting of copper sulfide ore. 1,1,1-trichloroethane was found and several other trace organic toxic pollutants were found in the raw waste at Plant #034 which contains infiltrated groundwater. The general area around Plant #034 is heavily industrialized. The local groundwater is known to be contaminated with various organic compounds. Since there are no known organic compounds used in the feedstock, or copper sulfate process

TABLE 21-6. RAW WASTE DATA

Subcategory: Copper Sulfate

Average Daily Pollutant Concentrations and Loadings found during Sampling of Plant #034⁽¹⁾

Pollutant	(mg/l) (kg/kg of CuSO ₄ ·5H ₂ O)		
	Screening ⁽²⁾	Verification ⁽³⁾	Overall Average ⁽⁴⁾
<u>TOXIC</u>			
Antimony, Sb	0.31 0.00069	0.54 0.0012	0.44 0.00095
Arsenic, As	3.5 0.0078	44.0 0.097	24.0 0.052
Cadmium, Cd	0.87 0.0019	1.6 0.0035	1.2 0.0027
Copper, Cu	1900 4.2	2200 5.0	2000 4.5
Lead, Pb	0.18 0.00039	0.78 0.0018	0.48 0.0011
Nickel, Ni	110 0.25	91.0 0.20	102 0.23
Zinc, Zn	11.0 0.024	12.0 0.027	12.0 0.026
Chromium, Cr	0.14 0.000030	0.36 0.000080	0.25 0.00055
Selenium, Se	< 0.011 < 0.000024	< 0.0050 < 0.000011	< 0.008 < 0.000018
<u>CONVENTIONAL</u>			
TSS	39.0 0.087	790 1.80	410 0.92

(1) The methodology of the sampling program is described in Section 5.1.2, and Section 21.1.2 presents the scope of sampling in the Copper Sulfate industry.

(2) Screening data from one 72-hour grab composite sample of individual or combined raw waste streams.

(3) Verification data from three 24-hour grab composite samples, averaged.

(4) When averaging values indicated as "less than" (<), the absolute value was used and the resulting average was indicated as a "less than" value.

itself, the organic toxic pollutants found at Plant #034 are atypical and are related to the contaminated groundwater. Selenium was not detected in the raw waste at Plant #034. However, the average concentration of selenium was 0.1 mg/l in the treated effluent for all sampling trips. This phenomenon was also observed in previous studies at this plant. The increase in selenium occurs in the treatment operation and the source is presently unknown. It is apparent that copper, arsenic, cadmium, chromium, lead, antimony, nickel and zinc are typical pollutants encountered in copper sulfate wastewaters, and that selenium appears only in the effluent after lime treatment.

Process Modifications and Technology Transfer Options

Mechanical scrapers could be installed on filters in plants using impure raw materials. This would eliminate the need for backwashing and the wastewater from this source would be eliminated. Installation of these scrapers would constitute a small capital cost.

Best Management Practices

The best technology available for the treatment of copper sulfate waste, where pure copper is used as the raw material, is total recycle of process waste. This would require floor dikes, plumbing and sumps to segregate the wastes, and pumps and piping for recycle.

The best technology for waste treatment where copper sulfate is prepared from impure copper sources or copper refinery by-product is collection of waste mother liquor and process spills, washdowns, etc., followed by lime precipitation of metals, settling of suspended solids and filtration. This would require installing dikes, sewers, a treatment tank, a settling tank, filter presses, and associated piping and pumps (2).

Prevailing Control and Treatment Practices

Plant #034 collects leaks, spills and washdown water in a basement sump and pumps it to holding tanks having a combined volume of 6000 gallons. The batch is treated using lime neutralization and precipitation and is filtered by a filter press. The filtrate, after mixing with other streams, is polished further by passing through a cloth filter and is finally discharged to a sewer. The filter cake is hauled to a landfill.

Plant #284 sends mother liquor purges and filter sludges to other processes. Wastewaters from maintenance and dust control are combined with a multitude of other process wastes and treated by lime neutralization with aeration, followed by clarification before discharge.

Plant #069, which produces a reagent grade product, sends periodic purges and washdown water to a combined collection system with waste water from various other products. Treatment consists of neutralization and equalization of the wastes and discharge to a POTW.

Plant #313 also combines its wastewaters from copper sulfate production with wastes from various other metal processes and presently discharges the combined waste, after settling, to a pond. A treatment system is being designed which uses lime precipitation at pH 10 followed by gravity separation and centrifugation to thicken the sludge. The waste will then be neutralized to pH 6.5-7.5 and discharged.

Plants #100, #969, #050, #458, #885, and #571 have no discharge of wastewater from the copper sulfate process.

Advanced Treatment Technologies

Copper, nickel, cadmium and zinc can be separated from solution by alkaline precipitation at pH values from 7.2 (copper) to 9.7 (cadmium). Alternatively, sulfide precipitation can be used. These metals can also be removed from clarified solutions by ion exchange, but the metal ions remaining on the exchange resins or in the regenerant solutions may create additional disposal problems. Removal of trace metal concentrations by the xanthate process, although possible, has not been used widely. Some reduction of arsenic concentrations at high pH levels has been reported, although the removal mechanism is not clear. More effective arsenic removal would require the addition of ferric chloride during alkaline or sulfide precipitation of the process wastes.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT, BAT, NSPS)

Alkaline precipitation using caustic soda in a batch process was considered as the most effective technology for removal of heavy metals and arsenic. The Agency selected Level 1 technology as the basis for BPT because it represents the prevailing treatment practice in this industry. All direct dischargers have BPT installed. To accommodate a 40-hour, five-day production schedule, the wastes are received in daily batches, and are raised to pH 10, mixed, and settled. At the end of the workweek, the batch is filtered and the pH adjusted to a range of 6 to 9. Figure 21-3 shows the schematic flow diagram for Level 1 treatment.

B. Level 2

In the Level 2 treatment, the Level 1 system is supplemented by the addition of ferrous sulfide in the reaction vessel following alkaline precipitation, to increase the precipitation of trace metals. Metallic hydroxides are allowed to form and settle in the bottom of the reaction vessel. Then ferrous sulfide is mixed in the reactor with residual metals. Following completion of sulfide precipitation, filter aid is added while the mixture is

being filtered through a filter press. As in Level 1, the pH is adjusted and the filter effluent is discharged until the weekly batch is exhausted.

This technology was not recommended, however, because Level 1 afforded adequate control and the additional reduction was not sufficient to offset the additional cost. Figure 21-4 shows the schematic flow diagram for Level 2 treatment. Further information on estimated treatment system operation, costs and effectiveness, may be found in the proposed Development Document (60).

Equipment for Different Treatment Levels

A. Equipment Functions

At both levels the models are designed for batch operation. Each day's wastes are transferred from holding sumps to a reaction vessel for storage. At the end of a workweek the BPT treatment of the accumulated waste consists of raising the pH to 10 with caustic soda, mixing, and applying filter aid while filtering in a filter press. After pH adjustment to the 6 to 9 range, the filter effluent is discharged. In the Level 2 model the equipment remains the same but precipitation is accomplished in two steps.

B. Chemicals Used and Handling Precautions

Caustic soda solution is added manually to each batch until the proper pH level is reached. In Level 2, batches of ferrous sulfide are prepared by mixing ferrous sulfate and sodium bisulfide in a well-ventilated area. Inert filter aid is applied as a filter precoat and is added continuously during the filtering process. With normal precautions there are no special chemical handling problems in the treatment of copper sulfate wastes.

C. Separation and Removal of Solids

All solids in both levels are collected as filter cake in the filter press. At both levels the dewatered cake containing metallic hydroxides, metallic sulfides, and spent filter aid is hauled to an off-site chemical landfill.

D. Monitoring Requirements

Alkaline precipitation of the heavy metals is assured by bringing the reaction vessel contents to the proper pH, as determined by the operator, using field pH equipment. Periodic specific analyses of the final effluent for toxic pollutants can be made by atomic absorption methods through a commercial laboratory.

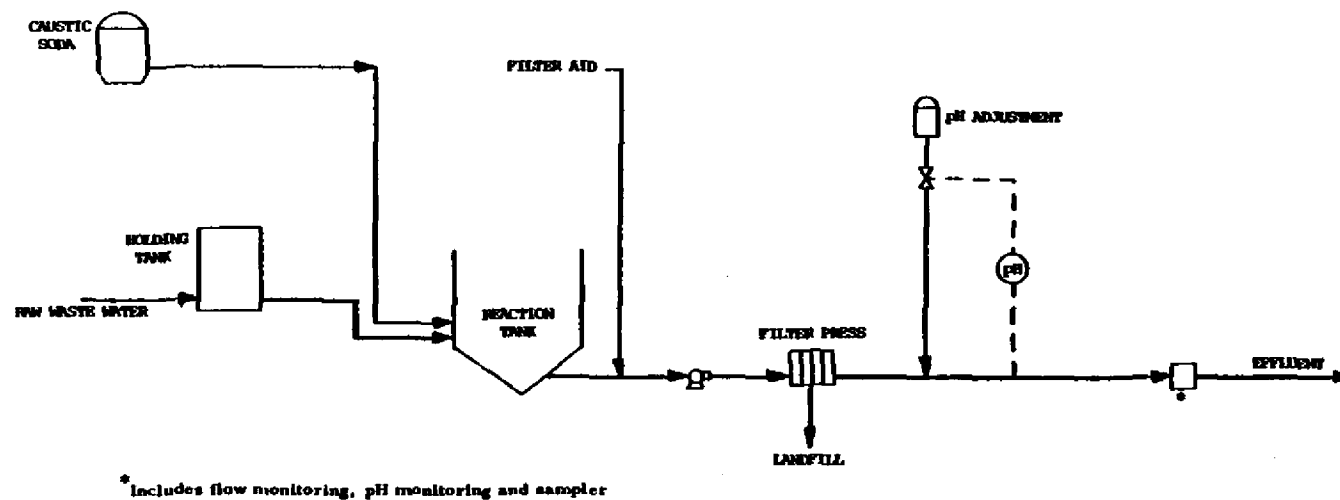


Figure 21-3. Level 1 waste water treatment for copper sulfate subcategory - batch process.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed for Level 1 technology. The BPT model treatment consists of:

Collection of wastewaters in a batch according to the production mode.

Hydroxide treatment to precipitate metals, followed by settling and filtration.

pH adjustment before discharge.

A. Production

Copper sulfate production ranges from 45 kkg/yr to 9100 kkg/yr in ten plants for which 308-Questionnaires were available. The average of the ten plants is 2100 kkg/yr and the median production is 790 kkg/yr. The operational mode for all these plants is assumed to be batch and to run 250 days per year.

For wastewater treatment cost estimates, one production level was chosen as the model plant. This is the average production of 2100 kkg/year. One production level is sufficient because the wastewaters will be collected in batches and treated as necessary when the batch tanks are full. The amount of wastewater to be treated at any one time is then independent of the production rate, although it will determine the frequency of treatment. All known plants with production rates below the model plant rate have no discharge of wastewaters from the copper sulfate process.

B. Wastewater Flow

The data on Table 21-4 for plants with a wastewater discharge shows a unit flow range from 0.52 m³/kkg of CuSO₄ to over 23 m³/kkg of CuSO₄. One plant flow is for reagent grade CuSO₄ and so cannot be considered a normal waste flow. Only Plant #034 has separate treatment for CuSO₄ wastewater, and the flow is the median of those normal processes sending wastewater for treatment. The wastewater unit flow used for the model plant is 0.94 m³/kkg of CuSO₄. All the other plants except #034 have either no discharge of wastewater, combine their wastes with other process wastes or produce reagent grade products.

C. Solid Waste Generation

Copper hydroxide from filtration is the only solid waste that required disposal. This waste must be disposed of in a chemical landfill since the solids may contain other contaminants or become oxidized and begin to migrate into the soil or

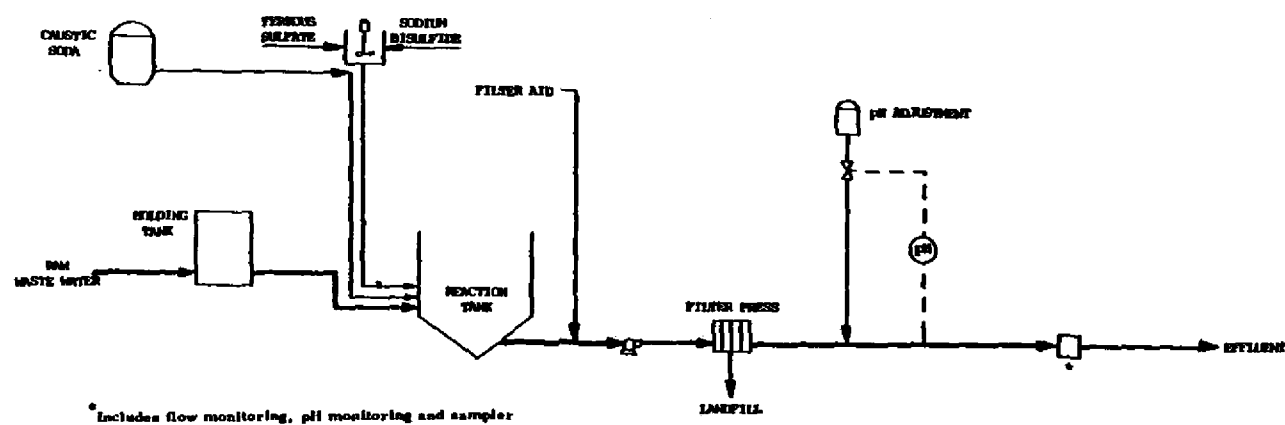


Figure 21-4. Level 2 waste water treatment for copper sulfate subcategory - batch process.

groundwater. Slimes from the mother liquor and copper sulfate solid wastes are all recycled or sent to another facility for metal recovery. There is no solid waste generation from processes using pure copper raw material.

Based on sludge production of 5 lbs/day for 250 days/yr in the model plant, the annual solids production is 558 kg, equivalent to unit solids generation of 0.27 kg/kg of product.

D. Treatment Chemicals

Caustic soda is required to precipitate metals and for pH adjustment. For the model plant, the assumed caustic soda dosage was 0.33 kg/kg of copper sulfate.

Model Plant Cost Estimates

The cost estimate of the model plant having one level of treatment (BPT) and one level of production is presented in Table 21-7. Table 21-8 gives a summary of the unit cost distribution between amortization and operation and maintenance cost components for Level 1 treatment.

Cost estimates developed for the first level of treatment (BPT, BAT, NSPS) indicate that amortization and labor constitute a major portion of the annual costs.

Basis for Regulations

Evaluation of BPT Treatment Practices

Copper sulfate can be manufactured using pure copper as the raw material or an impure copper raw material. Waste loads emanating from the two sources differ greatly in that total recycle of process wastes can be accomplished at plants using a pure copper source, while at plants using an impure raw material, waste streams need to be removed to some extent to avoid buildup of contaminants in the process.

Based on the process technology of total recycle at plants in this study using pure raw material, the industry practices indicate that the degree of waste control attainable is zero discharge of process wastes.

A. Pollutant Removal with BPT Treatment

BPT technology for copper sulfate plants utilizing impure raw materials is equivalent to Treatment Level 1. Table 21-9 presents a summary of long-term effluent monitoring data for Plant #034 on total suspended solids (TSS), copper, nickel, zinc, arsenic and selenium. Means, standard deviations, and variability factors are given where sufficient data are available. These performance characteristics are later utilized for the development of the regulations.

Table 21-10 presents the toxic and conventional pollutant data for effluent from the two samplings at Plant #034 in the same manner as Table 21-6 did for raw waste data. The ability of BPT treatment to remove toxic pollutants can be estimated by comparing the overall averages from Table 21-6 and 21-10. This comparison is presented in Table 21-11 which also expresses the removal efficiency as the calculated average percent removal observed at this plant.

Table 21-11 shows that the treatment efficiency for removal of copper, nickel, arsenic, cadmium and zinc is above 99.5 percent, while removal for antimony is just slightly over 80 percent. The toxic pollution concentrations were at or below the lower limit of concentration achieved by alkaline precipitation with the exception of copper and nickel. These toxic metal pollutants comprised the majority of the treatment loading which suggests that the optimum conditions for metal hydroxide formation were not being attained at the time of sampling. The thirteenfold increase in selenium concentrations in the treated effluent should be noted. This phenomenon was observed in previous studies at this and other plants. The observed concentrations appear to remain at the lowest achievable concentration for alkaline precipitation. The source is presently unknown, but it is suggested that the selenium may be introduced in the treatment chemicals.

Treatment system performance data was unavailable for other facilities generating a waste discharge because they combine their wastes with other process wastes for treatment.

Basis for BPT Effluent Limitations

The BPT regulations for the Copper Sulfate Subcategory were promulgated in 40 CFR 415.363 and are presently in effect (see Table 21-2). The technology basis for the existing BPT is alkaline precipitation plus filtration and final pH adjustment before discharge. Of the 16 plants in this subcategory, 10 are reported to have no discharge, five are direct dischargers, and one is an indirect discharger. All direct dischargers have BPT technology installed.

In the existing BPT regulations, the Agency has different limitations for pure and impure raw materials processes. The Agency has eliminated this distinction for BPT and is not establishing different limits for these processes in the BAT, BCT, NSPS, PSES and PSNS regulations. This is because both processes are adequately covered by one regulation, since the pure raw material process should, with proper operation and design, comply without end of pipe treatment.

A. Flow Basis

The model plant BPT treatment system is based on an inflow rate of 0.94 m³/kkg. This is derived from the average flow of Plant #034, and was the median of plants with a wastewater discharge

TABLE 21-7. MODEL PLANT TREATMENT COSTS

Subcategory Copper Sulfate Production 2,100 metric tons per year			
		(\$)	
A. INVESTMENT COST		BPT	BAT ^a
Site development		1,800	0
Equipment		61,500	0
Monitoring equipment		20,000	0
Subtotal		83,300	0
Contractor's O & P ^b		12,495	0
Subtotal		95,795	0
Engineering		19,159	0
Subtotal		114,954	0
Contingencies		11,495	0
Subtotal		126,449	0
Land		1,800	0
TOTAL INVESTMENT COST		128,249	0
B. OPERATION AND MAINTENANCE COST			
Labor and supervision		8,000	0
Energy		30	0
Chemicals		1,000	0
Maintenance		12,645	0
Taxes and insurance		3,847	0
Residual waste disposal		100	0
Monitoring, analysis and reporting		5,000	0
TOTAL OPERATION AND MAINTENANCE COST		30,622	0
C. AMORTIZATION OF INVESTMENT COST		20,573	0
TOTAL ANNUAL COST		51,196	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 21-8 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Copper Sulfate

Annual Treatment Costs (\$/kg)

LEVEL OF TREATMENT

COST ITEM	PRODUCTION (kg/yr)	BPT	BAT*	NSPS
-----------	-----------------------	-----	------	------

Annual Operation and Maintenance	2,100	14.58	NA	NA
-------------------------------------	-------	-------	----	----

Annual Amortization	2,100	9.80	NA	NA
------------------------	-------	------	----	----

Total Annual Cost	2,100	24.38	NA	NA
----------------------	-------	-------	----	----

*Represents the incremental cost above BPT. All plants presently meet BPT which is equal to BAT/NSPS in this subcategory.

TABLE 21-9. SUMMARY OF LONG TERM MONITORING DATA FROM PLANT #034⁽¹⁾

Pollutant	Number of Months	Long Term Averages		VF ⁽²⁾
		(mg/l)	(kg/kg)	
Total Suspended Solids (TSS)	16	25.0	0.093	2.4
Copper	16	4.4	0.016	1.6
Nickel	16	0.36	0.0013	2.2
Zinc	16	0.12	0.00044	2.4
Arsenic	16	0.0012	0.0000044	3.4
Selenium	15	0.0073	0.000027	6.2
Lead	16	0.033	0.00012	2.5

(1) Values are for monthly measurements of the treated effluent combined with noncontract cooling water and steam condensate discharges.

(2) For 30-day average measurements, a normal distribution is obtained and the variability factor is found by the expression, $VF = 1.0 + Z \left(\frac{S}{\bar{X}} \right)$ where \bar{X} is the arithmetic mean and S is the arithmetic standard deviation. When the value of Z is 1.64, the variability factor is for 95 percentile which is used to set the proposed maximum 30-day average effluent limitation. Refer to Section 8.2 for detailed discussion.

from industrial grade CuSO_4 manufacturing processes. Four other plants with wastewater discharges combine their waste with other processes for treatment. All other plants either produce reagent grade product, or have no discharge.

B. Selection Basis for Pollutants to be Regulated

The selection of pollutants for which numerical effluent limitations were established was based on an evaluation of raw waste data from the screening and verification sampling program. The two major factors considered were: 1) individual raw waste concentrations, and 2) the total subcategory raw waste loadings.

1. Raw Waste Pollutant Concentrations

A tabular summary of maximum raw waste concentrations found in sampling is presented above. Data from screening sampling was used to determine the need for verification sampling. The maximum concentrations found during both screening and verification are shown for comparison. As previously discussed, selenium was not found in the raw waste although it was present in the effluent. For each pollutant, the maximum concentration observed gave a preliminary indication of its potential significance in the subcategory. On this basis, the preliminary selection of candidates for regulation includes copper, nickel, zinc, arsenic, cadmium, antimony, 1-1-1-trichloroethane, and lead in decreasing order of their apparent pollution potential. These pollutants were observed at least once during screening at concentrations considered treatable in the industry using one of the available treatment technology options. The source of trichloroethane is presumed to be groundwater contamination. It is not process related, and was not considered for verification. In verification, the same metals found during screening appeared along with the addition of chromium. The other metals found exhibited maximum concentrations that were considerably lower than those treatable by available technologies.

2. Total Subcategory Raw Waste Pollutant Loadings

Pollutant raw waste loading data were used to evaluate the overall magnitude of the pollution potential for the subcategory. Data from the plant sampled are summarized in Table 21-6. This information, coupled with the estimated total copper sulfate production rate of 27,300 kkg/year, yielded the approximate total annual pollutant loading rates for the subcategory shown above. This method of ranking the pollution potential of the observed toxic metals confirms the dominance of the eight toxic metals and ranks them as copper, nickel, arsenic, zinc, cadmium, lead, antimony and chromium in terms of both total mass loading and treatable raw waste concentrations. The existing BPT regulations

TABLE 21-10. TREATED EFFLUENT DATA

Subcategory: Copper Sulfate

Average Daily Pollutant Concentrations and Loadings Found During Sampling of Plant #034⁽¹⁾

Toxic Pollutants	(mg/l) (kg/kg of CuSO ₄ · 5H ₂ O)		
	Screening ⁽²⁾	Verification ⁽³⁾	Overall Average ⁽⁴⁾
Antimony	0.036 0.00008	0.12 0.00027	0.08 0.00018
Arsenic	< 0.02 < 0.00004	0.057 0.00013	0.038 0.000085
Cadmium	0.001 0.000002	0.0042 0.0000089	0.0026 0.0000054
Chromium	0.005 0.00001	0.017 0.000038	0.011 0.000024
Copper	4.6 0.010	1.9 0.0042	3.3 0.0072
Lead	0.005 0.00001	< 0.031 < 0.000069	< 0.018 0.00004
Nickel	0.24 0.00053	0.17 0.00038	0.20 0.00046
Zinc	0.016 0.000036	0.02 0.000044	0.018 0.00004
Selenium	0.10 0.00022	0.11 0.00024	0.10 0.00023
<u>Conventional Pollutant</u>			
TSS	35.0 0.078	13.7 0.03	24.0 0.054

- (1) The effluent data presented here corresponds to the raw waste data shown in Table 21-6. The methodology of the sampling program is described in Section 5.1.2, and the scope of sampling in the industry is described in Section 21.3.3 Copper Sulfate.
- (2) Screening data from one 72-hour grab composite sample of treated effluent.
- (3) Verification data from three 24-hour grab composite samples, averaged.
- (4) When averaging values indicated as "less than" (<), the absolute value was used and the resulting average was indicated as a "less than" value.

TABLE 21-11. AVERAGE POLLUTANT LEVELS AND REMOVAL EFFICIENCY FOR PLANT #034

Subcategory: Copper Sulfate

Waste Water Flow = 1.25 m³/kkg

Pollutant	Raw Waste (mg/l)	Raw Waste (kg/kkg)	Treated Effluent * (mg/l)	Treated Effluent * (kg/kkg)	Percent Removal
TSS	410	0.92	24.0	0.054	94
Copper	2000	4.5	3.3	0.0072	99 +
Nickel	102	0.23	0.20	0.00046	99 +
Antimony	0.44	0.00095	0.08	0.00018	81.6
Arsenic	24.0	0.052	0.038	0.000085	99 +
Cadmium	1.2	0.0027	0.0026	0.0000054	99 +
Chromium	0.25	0.00055	0.011	0.000024	96
Lead	0.48	0.0011	< 0.018	0.00004	96
Selenium	< 0.008	0.000018	0.10	0.00023	Effluent > Influent
Zinc	12.0	0.026	0.018	0.00004	99 +

* Before combining with noncontact cooling and steam condensate streams.

included selenium limitations, although selenium was not found to be a significant pollutant in raw wastes at Plant #034. However, its continued presence in the effluent from alkaline treatment in significant concentrations indicates that selenium should continue to be included in the pollutants to be regulated.

3. Final Selection of Pollutants to be Regulated

Originally, limitations were proposed for all the previously mentioned significant toxic pollutants. The Agency has now decided to promulgate regulations on copper, nickel and selenium. Copper and nickel are the most predominant toxic metals in the wastewater of this subcategory. The nature of the treatment technology used by this industry is such that the control of the dominant metals will ensure control of all the toxic pollutants of concern. Further elaboration of this subject may be found in Section 8 of this document. It was also decided that selenium should continue to be regulated where it is shown to be present in the effluent and posing a potential problem. At plants where selenium is not found at significant concentrations in the effluent, the limitations would not apply. Because selenium was found only in the effluent, and not in the raw waste at treatable levels, it may not be directly related to the manufacturing process.

Section 8 indicates that toxic metals can be divided into two groups for pH optimization of alkaline precipitation, and that control of one or more of the metals in each of these groups, will ensure control of others in that group (see Table 8-14). By controlling both copper and nickel, the two different metal groups are covered. Therefore, because these two metals (copper and nickel) are the predominant toxic pollutants in the raw waste, control of these parameters will ensure control of all the metals previously considered for limitations. The data from all the samplings at Plant #034 supports this.

Optimization of treatment conditions for nickel and copper removal may cause a lack in performance of chromium control. However, because of the relatively low incoming chromium concentrations, the control of chromium should be adequate. Although arsenic is not in either of the two groups, and the incoming concentrations were the highest after copper and nickel, the results of the sampling data show excellent arsenic removal and very low effluent concentrations. Table 8-14 and Figure 7-1 indicate a pH around 10 would be optimum for the control of pollutants in this subcategory.

C. Basis of Pollutant Limitations

The BPT Effluent Limitations are presented in Table 21-12. Since the existing BPT limitations are being retained, the concentration bases for the maximum 30-day average and the daily maximum are back calculated from the pollutant mass limitations by applying the model plant flow rate of 0.94 m³/kkg. The variability factors used are consistent with those estimated from the statistical analysis of treatability data (61).

1. Conventional Pollutant Limitations

a. pH

The treated effluent is to be controlled within the range of pH 6.0 to 9.0. This limitation is based on data presented in Appendix B of the proposed Development Document (60) and the JRB study (52).

b. TSS

The existing BPT maximum 30-day average TSS limitation is 0.023 kg/kkg. The corresponding concentration basis is:

$$\frac{(0.023 \text{ kg/kkg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kkg}) (\text{kg/m}^3)} = 24 \text{ mg/l}$$

The existing BPT daily maximum TSS limitation is 0.069 kg/kkg and the concentration basis is:

$$\frac{(0.069 \text{ kg/kkg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kkg}) (\text{kg/m}^3)} = 73 \text{ mg/l}$$

The long-term average for TSS is calculated from the daily maximum concentration and the estimated variability factor for daily measurements as follows:

$$\frac{(73 \text{ mg/l})}{(3.6)} = 20 \text{ mg/l}$$

2. Toxic Pollutants

The effluent limitations for the selected toxic pollutants are based on the existing BPT regulations for the Copper Sulfate Subcategory. However, the separate limitation on copper for the pure raw material process is being dropped and the present limitations on TSS, copper, nickel, and selenium for the recovery process (Table 21-2) will apply to both processes.

a. Copper

The existing BPT maximum 30-day average effluent limitation on copper is 0.0010 kg/kg. Applying the model plant unit flow rate of 0.94 m³/kg, the concentration basis is calculated as follows:

$$\frac{(0.0010 \text{ kg/kg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kg}) (\text{kg/m}^3)} = 1.1 \text{ mg/l}$$

Similarly, the existing BPT daily maximum limitation is 0.0030 kg/kg, and the concentration basis becomes:

$$\frac{(0.0030 \text{ kg/kg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kg}) (\text{kg/m}^3)} = 3.2 \text{ mg/l}$$

The long-term average for copper is then determined from the estimated variability factor for daily measurements:

$$\frac{(3.2 \text{ mg/l})}{(3.6)} = 0.89 \text{ mg/l}$$

b. Nickel

The existing BPT maximum 30-day average effluent limitation on nickel is 0.0020 kg/kg. Using the model plant unit flow rate of 0.94 m³/kg, the concentration basis is calculated as:

$$\frac{(0.0020 \text{ kg/kg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kg}) (\text{kg/m}^3)} = 2.1 \text{ mg/l}$$

The existing BPT daily maximum limitation is 0.0060 kg/kg and the corresponding basis is:

$$\frac{(0.0060 \text{ kg/kg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kg}) (\text{kg/m}^3)} = 6.3 \text{ mg/l}$$

The expected long-term average concentration is determined from the estimated variability factor for daily measurement:

$$\frac{(6.4 \text{ mg/l})}{(3.6)} = 1.8 \text{ mg/l}$$

c. Selenium

The existing BPT maximum 30/day average limitation on selenium is 0.00050 kg/kg. The concentration basis is calculated as:

TABLE 21-12. EFFLUENT LIMITATIONS
Copper Sulfate
Best Practicable Control Technology Currently Available ⁽¹⁾
Waste Water Flow; 0.94 m³/kg of CuSO₄

Pollutant	Subcategory Performance (mg/l)	VFR (2)	Concentration Basis (mg/l)		Effluent Limit (kg/kg)	
			Max. 30-day Avg.	24-hr. Max.	Max. 30-day Avg.	24-hr. Max.
<u>Conventional Pollutant:</u>						
TSS	20	3.6/1.2	24	73	0.023	0.069
<u>Toxic Pollutants:</u>						
Copper	0.89	3.6/1.2	1.1	3.2	0.0010	0.0030
Nickel	1.8	3.6/1.2	2.1	6.4	0.0020	0.0060
Selenium	0.44	3.6/1.2	0.53	1.6	0.00050	0.0015

(1) Based on the existing BPT limitations, 40 CFR 415.360. Also applicable to NSPS.

(2) Ratio of the variability factor for daily measurements to the variability factor for 30-day average.

$$\frac{(0.00050 \text{ kg/kg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kg}) (\text{ kg/m}^3)} = 0.53 \text{ mg/l}$$

The existing BPT daily maximum limitation is 0.0015 kg/kg and the concentration basis is:

$$\frac{(0.0015 \text{ kg/kg}) (1000 \text{ mg/l})}{(0.94 \text{ m}^3/\text{kg}) (\text{ kg/m}^3)} = 1.6 \text{ mg/l}$$

The expected long-term average is then determined from the estimated variability factor for daily measurements:

$$\frac{(1.6 \text{ mg/l})}{(3.6)} = 0.44 \text{ mg/l}$$

Basis for BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Effluent Limitations

The Agency is promulgating BAT limitations that are equal to the existing BPT limitations for the selected toxic pollutants (copper, nickel, and selenium) as indicated in Table 21-13. Also shown in Table 21-13 are concentration guidance values for the other toxic pollutants (arsenic, cadmium, zinc, chromium, lead, and antimony) which do not have effluent limitations. The basis for these guidance values are developed below where treatability based performance estimates for Level 1 treatment are presented.

When the BAT regulations were recently proposed (60), the Agency had considered requiring more stringent limitations for the toxic pollutants because the results of treatability studies (61) indicated that Level 1 treatment system performance was better than the previous BPT data base suggested. However, the actual achievability of this improved performance is not sufficiently substantiated at present to warrant the promulgation of more stringent limitations and, therefore, the existing BPT limitations, with the Level 1 treatment technology basis, are being promulgated for BAT.

The Agency also considered control treatment Level 2 (sulfide precipitation), but rejected this treatment because it removes only a small additional amount of toxic metals which did not justify the additional cost.

Basis for New Source Performance Standards

The Agency is promulgating New Source Performance Standards (NSPS) based on treatment technology equivalent to BPT/BAT for the Copper Sulfate Subcategory. The conventional pollutant limitations for TSS are the same as shown for the existing BPT (BPCTCA) regulations in Tables 21-2 and 21-12. Also, pH is limited to the range 6 to 9 as based on data presented in Appendix B of the proposed Development Document (60) and the JRB study (52). The toxic pollutant parameters to be regulated are those identified in the development of the BPT/BAT regulations as shown in Table 21-12 and the specific numerical limitations proposed for NSPS are identical to those indicated for BPT/BAT.

Basis for Pretreatment Standards

There is an existing PSES regulation, 40 CFR 415.364, which is based on BPT. The Agency is amending that section in these final regulations to establish the same effluent concentrations as were used for the basis on BPT. In the original regulation, the concentrations for copper were 0.5 mg/l as the maximum 30-day average and 1.0 mg/l as the daily maximum. For nickel, the concentrations were 1.0 mg/l as the maximum 30-day average and 2.0 mg/l as the daily maximum. Under the amended PSES regulation, the concentrations for copper become 1.2 mg/l and 3.2 mg/l for the maximum 30-day average and daily maximum, respectively, and for nickel, 2.1 mg/l and 6.4 mg/l as shown in Table 21-13. Selenium is also regulated under the amended PSES regulation.

For new sources, the Agency is setting PSNS equal to NSPS as indicated in Table 21-13. Copper, nickel, and selenium are regulated.

Pretreatment standards are necessary because BAT provides better removal of toxic metals than is achieved by a well-operated POTW with secondary treatment installed and, therefore, these pollutants would pass through a POTW in the absence of pretreatment.

Basis for Level 1 Treatment Performance

A. Technology Basis

The screening and verification data were collected when the filter in the treatment system was not operating properly; hence the treated effluent data were not representative of the performance achievable with precipitation/filtration technology and, therefore, the basis for Level 1 performance was derived from other sources of performance data. The treatability study results (61) are summarized and incorporated with other data submitted by industry, as well as the sampling data, and

TABLE 21-13. EFFLUENT LIMITATIONS
Copper Sulfate
Best Available Technology (1)
Waste Water Flow: 0.94 m³/kg of CuSO₄

Pollutant	Subcategory Performance (mg/l)	VFR (2)	Concentration Basis (mg/l)		Effluent Limit (kg/kg)	
			Max. 30-day Avg.	24-hr. Max.	Max. 30-day Avg.	24-hr. Max.
Copper	0.89	3.6/1.2	1.2	3.2	0.0010	0.0030
Nickel	1.8	3.6/1.2	2.1	6.4	0.0020	0.0060
Selenium	0.44	3.6/1.2	0.53	1.6	0.00050	0.0015
Arsenic	0.20	4.0/1.2	0.24	0.80	— (3)	— (3)
Cadmium	0.10	4.0/1.2	0.12	0.40	— (3)	— (3)
Zinc	0.20	3.5/1.2	0.24	0.70	— (3)	— (3)
Chromium	0.16	3.5/1.2	0.20	0.56	— (3)	— (3)
Lead	0.050	3.5/1.2	0.060	0.18	— (3)	— (3)
Antimony	0.40	4.0/1.2	0.48	1.6	— (3)	— (3)

(1) Also applicable to PSES and PSNS.

(2) Ratio of the variability factor for daily measurements to the variability factor for 30-day averages.

(3) No effluent limitation has been established.

presented in Tables 8-12 and 8-13. Where there was insufficient data on a particular pollutant from these sources, the published literature treatability data from Table 8-11 was used to estimate performance.

The flow basis and the selection of pollutant parameters is the same as that presented for the BPT limitations in this section.

B. Basis of Pollutant Control Guidance

1. Toxic Pollutants

The effluent control guidance for the selected toxic pollutants are derived from estimated industry achievable long-term averages (Tables 8-12 and 8-13), and literature based treatability estimates (Table 8-11). This is necessary because plant performance data from long-term monitoring (Table 21-9) and the screening and verification sampling (Table 21-10) do not reflect optimum operation of a BPT system for removal of copper and nickel. In addition, these sources show effluent concentrations below the lower limit of treatability estimates for all the other toxic metals.

Estimated effluent mass loadings for copper, nickel and selenium are shown in Table 21-14 along with the corresponding concentration basis. The performance levels estimated on the basis of treatability data are better than are presently achieved by dischargers in the Copper Sulfate industry and the Agency does not have sufficient evidence that the improved performance can actually be achieved in practice. The estimated performance is for guidance purposes only. Also shown are the recommended concentration bases for the other toxic metals. These are included as a guidance reference, should the control of one or more of these metals be found necessary in specific cases.

The concentration bases for copper, cadmium, zinc and chromium are derived from estimated achievable long-term industrial averages (Tables 8-12 and 8-13). Concentration bases for nickel and arsenic are derived from the observed concentrations from sampling of several Level 1 treatment systems, supported by industry averages, while those for the remaining metals of concern were derived from the lower limit of the literature treatability estimates (Table 8-11). This approach is used to estimate achievable performance and provides for wider variations in the influent quality that may be associated with different purities of copper feed material or other process variables.

Variability factors used to calculate the maximum 30-day average and the daily maximum concentrations from long-term

averages were determined by statistical analysis of data presented in the Treatability Study (61) for the Copper Sulfate Subcategory.

a. Copper

The estimated achievable long-term average for copper indicated in Table 8-13 is 0.30 mg/l. This reflects industry performance using Level 1 technology. This is below the effluent level found during sampling of Plant #034, indicating that the system was not being run at its optimum performance. Therefore, using this concentration value and a 30-day variability factor of 1.2 from the copper sulfate treatability results for copper (61), the maximum 30-day concentration basis is:

$$(0.30 \text{ mg/l}) (1.2) = 0.36 \text{ mg/l}$$

The 24-hour maximum variability factor derived from the copper sulfate Treatability Study for copper (61) was found to be 3.5. Therefore, using this variability factor and the long-term average concentration of 0.30 mg/l, the daily maximum concentration is:

$$(0.30 \text{ mg/l}) (3.5) = 1.1 \text{ mg/l}$$

The effluent loadings for copper were determined using a model plant flow of 0.94 m³/kkg, with the maximum 30-day average concentration calculated as follows:

$$(0.36 \text{ mg/l}) (0.94 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.00034 \text{ kg/kkg}$$

The variability factor ratio is the ratio of the daily maximum variability factor and the 30-day average variability factor or:

$$\text{VFR} = \frac{\text{VF of daily measurements}}{\text{VF of 30-day averages}}$$

For copper the VFR is equal to:

$$\text{VFR} = \frac{3.5}{1.2} = 2.9$$

Therefore, the 24-hour maximum is calculated to be:

$$(2.9) (0.00034 \text{ kg/kkg}) = 0.0010 \text{ kg/kkg}$$

TABLE 21-14. GUIDANCE FOR EFFLUENT CONTROL
Copper Sulfate
Level 1 Technology
Waste Water Flow: 0.94 m³/kgg of CuSO₄

Pollutant	Long-Term Average (mg/l)	VFR (4)	Concentration Basis (mg/l)		Effluent Loading (kg/kgg)	
			Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
Copper	0.30 ⁽¹⁾	3.5/1.2	0.36	1.1	-- (5)	-- (5)
Nickel	0.20 ⁽²⁾	4.0/1.2	0.24	0.80	-- (5)	-- (5)
Selenium	0.10 ⁽³⁾	4.0/1.2	0.12	0.40	-- (5)	-- (5)
Arsenic	0.20 ⁽²⁾	4.0/1.2	0.24	0.80	-- (5)	-- (5)
Cadmium	0.10 ⁽²⁾	4.0/1.2	0.12	0.40	-- (5)	-- (5)
Zinc	0.20 ⁽¹⁾	3.5/1.2	0.24	0.70	-- (5)	-- (5)
Chromium	0.16 ⁽¹⁾	3.5/1.2	0.20	0.56	-- (5)	-- (5)
Lead	0.050 ⁽³⁾	3.5/1.2	0.060	0.18	-- (5)	-- (5)
Antimony	0.40 ⁽³⁾	4.0/1.2	0.48	1.6	-- (5)	-- (5)

(1) Industry Long-Term Average (Table 8-13).

(2) Industry and Treatability Data (Table 8-12).

(3) Lower limit of literature treatability data (Table 8-11).

(4) Variability Factor Ratio: the ratio of the daily variability factor to the monthly variability factor based on statistical analysis of treatability study data for copper sulfate (61).

(5) Indicates no control specification is needed.

b. Nickel

The observed concentration of nickel in the effluent samples from Level 1 treatment for both copper sulfate and nickel sulfate was 0.20 mg/l. This supported by other industry data using Level 1 technology (Table 8-12) and is used as the estimated achievable long-term average. The 30-day average variability factor for nickel is also 1.2, and the daily maximum variability was 4.0. Therefore, the calculation of the maximum 30-day average concentration basis is:

$$(0.20 \text{ mg/l}) (1.2) = 0.24 \text{ mg/l}$$

and the 24-hour maximum concentration is:

$$(0.20 \text{ mg/l}) (4.0) = 0.80 \text{ mg/l}$$

The VFR for nickel is calculated as:

$$\frac{4.0}{1.2} = 3.3$$

Therefore, the maximum 30-day average based on a flow of 0.94 m³/kkg is:

$$(0.24 \text{ mg/l}) (0.94 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.00023 \text{ kg/kkg}$$

and the 24-hour maximum is:

$$(3.3) (0.00023 \text{ kg/kkg}) = 0.00076 \text{ kg/kkg}$$

c. Selenium

Long-term monitoring and sampling data indicate effluent quality either at or below the lower limit of the estimated literature treatability data (Table 8-11). This lower limit of 0.1 mg/l was used as the long-term average concentration because there was insufficient industry data in Tables 8-12 and 8-13. Using the same variability factors and rationale applied to nickel, the maximum 30-day average concentration basis is:

$$(0.10 \text{ mg/l}) (1.2) = 0.12 \text{ mg/l}$$

and the 24-hour maximum concentration is:

$$(0.10 \text{ mg/l}) (4.0) = 0.40 \text{ mg/l}$$

The effluent loading for the maximum 30-day average is:

$$(0.12 \text{ mg/l}) (0.94 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.00011 \text{ kg/kg}$$

and for the 24-hour maximum:

$$(3.3) (0.00011 \text{ kg/kg}) = 0.00038 \text{ kg/kg}$$

d. Arsenic

From the data in Table 8-12, the observed concentration of arsenic in the effluent of Level 1 treatment for copper indicated a value of 0.20 mg/l. Using the variability factors from nickel, the maximum 30-day average concentration basis is:

$$(0.20 \text{ mg/l}) (1.2) = 0.24 \text{ mg/l}$$

and the 24-hour maximum is:

$$(0.20 \text{ mg/l}) (4.0) = 0.80 \text{ mg/l}$$

e. Cadmium

Industry data from metal finishing indicates an effluent value of 0.10 mg/l using Level 1 technology. This was used as the long-term average concentration basis rather than the lower limit of literature treatability estimates to account for more variation in influent and treatment operation. Again, using variability factors for nickel, the maximum 30-day average concentration basis is:

$$(0.10 \text{ mg/l}) (1.2) = 0.12 \text{ mg/l}$$

and the 24-hour maximum basis is:

$$(0.10 \text{ mg/l}) (4.0) = 0.40 \text{ mg/l}$$

f. Zinc

Industry averages from Tables 8-12 and 8-13 indicate a long-term average concentration of 0.20 mg/l. Again, using the variability factors for copper, the maximum 30-day average concentration basis is:

$$(0.20 \text{ mg/l}) (1.2) = 0.24 \text{ mg/l}$$

and the 24-hour maximum concentration basis is:

$$(0.20 \text{ mg/l}) (3.5) = 0.70 \text{ mg/l}$$

g. Chromium

Industry averages from Tables 8-12 and 8-13 indicate a long-term average concentration of 0.16 mg/l. Again, using the variability factors for copper, the maximum 30-day average concentration basis is:

$$(0.16 \text{ mg/l}) (1.2) = 0.20 \text{ mg/l}$$

and the 24-hour maximum concentration is:

$$(0.16 \text{ mg/l}) (3.5) = 0.56 \text{ mg/l}$$

h. Lead

From Table 8-11, the lower limit of treatability from literature data shows a value of 0.05 mg/l. This was used as the achievable long-term average concentration for the same reasons as selenium. Using the variability factors for copper, the maximum 30-day average concentration basis is:

$$(0.05 \text{ mg/l}) (1.2) = 0.060 \text{ mg/l}$$

and the 24-hour maximum concentration basis is:

$$(0.05 \text{ mg/l}) (3.5) = 0.18 \text{ mg/l}$$

i. Antimony

The long-term average concentration value of 0.40 mg/l was taken from the lower limit of literature treatability data (Table 8-11) for the same reasons as selenium. Using the variability factors for nickel, the maximum 30-day average concentration basis is:

$$(0.40 \text{ mg/l}) (1.2) = 0.48 \text{ mg/l}$$

and the 24-hour maximum concentration basis is:

$$(0.40 \text{ mg/l}) (4.0) = 1.6 \text{ mg/l}$$

SECTION 22

NICKEL SULFATE INDUSTRY

Industrial Profile

General Description

Most of the nickel sulfate produced is sold in the merchant market. The major use of nickel sulfate is in the metal plating industry, but it is also used in the dyeing and printing of fabrics, and for producing a patina on zinc and brass.

The industry profile data summary is given in Table 22-1, while the status of regulations is summarized in Table 22-2.

Subcategorization

Several factors were originally considered in the subcategorization process, such as raw materials, products, manufacturing process, size and age of equipment, and water pollution control technology. The conclusion was made that if effluent limitations were to be tied to units of production, only subdivision by dominant product was viable as a method of primary subcategorization. Option was left for further subdivision, if necessary; however, this was not warranted in the nickel sulfate industry.

General Process Description and Raw Materials

Nickel sulfate is produced by reacting various forms of nickel with sulfuric acid. The general reaction is:



Two different types of raw materials are used to produce nickel sulfate. Pure nickel or nickel oxide powder may be used as a pure material source, while spent nickel catalysts, nickel plating solutions or residues are impure sources.

The nickel sulfate produced when pure raw materials are used is filtered and sold or processed further. This is done by heating the solution to 300°C in a crystallizer to produce a solid nickel sulfate product. This must be classified, dried, and screened before it is ready for sale.

The use of impure raw materials produces a nickel sulfate solution which must be treated sequentially with oxidizers, lime, and sulfides to precipitate impurities which are then removed by filtration. The nickel sulfate solution can be sold or it may be crystallized, and the crystals classified, dried, and screened to produce solid nickel sulfate for sale. Figure 22-1 shows a general process flow diagram for the manufacture of nickel sulfate.

TABLE 22-1. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	NICKEL SULFATE
Total subcategory capacity rate (1)	Indeterminant
Total subcategory production rate (1)	6,350 kkg/year
Number of plants in this subcategory (2)	11
308 Data on file for	6
With total capacity of	17,700 kkg/year
With total production of	12,650 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	NA
Minimum	45 kkg/year
Maximum	5,900 kkg/year
Average production	2,100 kkg/year
Medium production	1,600 kkg/year
Average capacity utilization	71.5
Plant age range:	
Minimum	3
Maximum	48
Waste water flow range:	
Minimum	1.5 cubic meters/day
Maximum	17.0 cubic meters/day
Volume per unit product:	
Minimum	0.42 cubic meters/kkg
Maximum	0.72 cubic meters/kkg

(1) = "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

(2) = Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977

NA = Not Available

TABLE 22-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY Nickel Sulfate
 SUBPART AU (40 CFR 415.470, 5/22/75)

		STANDARDS					
Product Process	Para- meters	BPTCA		BATEA		NSPS	
		Max. ¹ kg/kg (mg/l)	Avg. ² kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)
Pure Raw Materials	Ni	No discharge of pwp ³		No discharge of pwp		No discharge of pwp	
	TSS	No discharge of pwp		No discharge of pwp		No discharge of pwp	
Impure Raw Materials	Ni	0.006	0.002				
	TSS	0.096	0.032				

¹Max. = Maximum of any one day.

²Avg. = Average of daily values for thirty consecutive days.

³pwp = Process wastewater pollutants.

Water Use and Waste Source Characteristics

Water Use

Noncontact cooling water is used for nickel sulfate production in the reactor and crystallizers, and constitutes the major water use. Water is used in direct process contact as a reaction component. A portion of this water goes into the dry product as its water of crystallization and the remainder is evaporated into the atmosphere. Small amounts of water are used for maintenance purposes, washdowns, cleanups, etc., and several plants use water in scrubbers for dust control. Table 22-3 gives a summary of water usage for plants where information was available from 308-Questionnaires and previous documents.

Waste Sources

A. Noncontact Cooling Water

Noncontact cooling is the main source of wastewater. This stream is usually not treated before discharge.

B. Direct Process Contact

Plants which use impure nickel raw materials generate a filter sludge which is treated as a solid waste. They also generate a small filter backwash waste stream with high impurity levels which must be treated before discharge. The filter sludges from processes using pure nickel can be recycled back to the process. Mother liquor, and wastewater streams from dust control are also recycled back to the process.

C. Maintenance

Washdowns, cleanups, spills, and pump leaks are periodic streams and account for the remaining wastes produced by nickel sulfate plants.

Table 22-3 also shows the unit flow of total wastewater generated from the nickel sulfate process at each plant where this information was available.

Description of Plants Visited and Sampled

Screening

Plant #369 was visited and process wastewater and effluent samples were collected and analyzed for conventional and toxic pollutants. The process used at Plant #369 is similar to that described earlier and utilizes nickel oxide powder feedstock. Mother liquor is recycled back to the reactor. Sources of wastewater consist of small quantities of mother liquor from the filter press, washdown water, leaks, and spills. Wastewater from the process area is collected in a

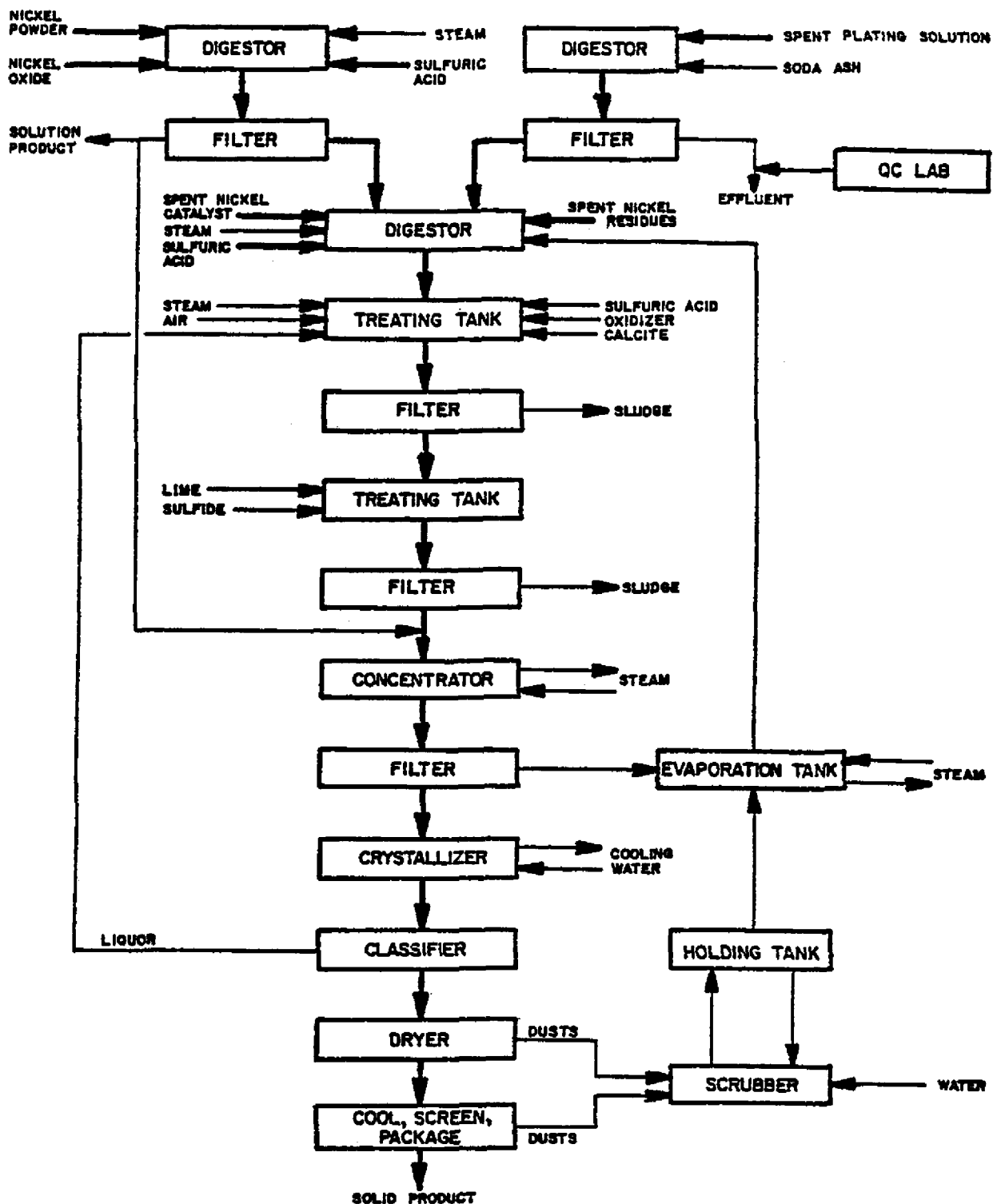


Figure 22-1. General process flow diagram for nickel sulfate manufacture.

TABLE 22-3. WATER USE IN THE NICKEL SULFATE SUBCATEGORY

Source	Water Uses at Plants (m ³ /kkg)					
	#313*	#069	#572	#369	#120	#603*
Direct Process Contact	24.8	0.0098	0.35	0.751	4.01	814
Noncontact Cooling Water	37.3	1.67	4.98	0.417	13.6	2035
Maintenance Cleaning and Washdowns, Pumps, Seals and Leaks	0.278	0.00196	0.896	0.094	Nil	Nil
Air Pollution Control Waste Water	0.278	0	0.498	0.094	1.28	0
Waste Water Flow to Treatment	23.4 ⁽¹⁾	.0196 ⁽¹⁾	20.3 ^{(1)*}	0.42 ⁽²⁾	0.72 ⁽²⁾	NA

* = Flow data includes uses for other products.

(1)= Data source: 308-Questionnaires

(2)= Data source: Plant visits

NA = Not Available

tank and treated as a batch by adjusting the pH to about 12.5 using sodium hydroxide. The precipitated metal hydroxides are allowed to settle, and the supernatant is decanted to another tank, checked for quality and discharged to a POTW. The sludge is hauled away to an approved landfill. Figure 22-2 shows a general treatment system flow diagram with the location of the sampling points. Table 22-4 gives data on flow, total suspended solids (TSS), and nickel and copper emissions for the waste streams sampled during screening.

Verification

Plants #572 and #120 were visited and sampled during the verification phase of the program. At Plant #572, pure nickel oxide is used as the raw feedstock. The wastewater streams discharge on a batch basis and are collected together in a floor drain. The wastes consist of washdowns, leaks, and air scrubber water which are collected in an equalization tank. In the equalization tank, alkaline wastes from another process are mixed in and the pH is raised to 10. Solids are allowed to settle and the clear supernatant is discharged to a POTW.

Plant #120 uses nickel oxide powder and impure nickel as raw materials. Wastewaters from the nickel sulfate process emanate from the filter wash, air scrubber, washdowns, and leaks, and are sent to the treatment system. The raw wastes are mixed with other plant nickel raw wastes prior to treatment. This consists of pH adjustment to precipitate nickel and other trace metals followed by sand filtration.

Figures 22-3 and 22-4 show the general treatment system flow diagram with the waste streams sampled for Plants #572 and #120, respectively. Table 22-4 also shows the waste stream flow and waste characteristics for both plants. The data for Plant #572 are presented on a concentration basis only, because a representative flow value for the sampling point was unavailable.

Summary of Toxic Pollutant Data

Seven toxic pollutants were found at detectable concentrations in the raw waste sample from nickel sulfate at Plant #369. Six of these toxic metals were verified in the raw waste at two other nickel sulfate plants. In addition, two more toxic pollutants were observed at detectable concentrations in the raw waste during verification sampling. No toxic organics were found at detectable concentrations in the raw waste at Plant #369. Consequently, organic toxic pollutants were not sought in the verification phase. The results were:

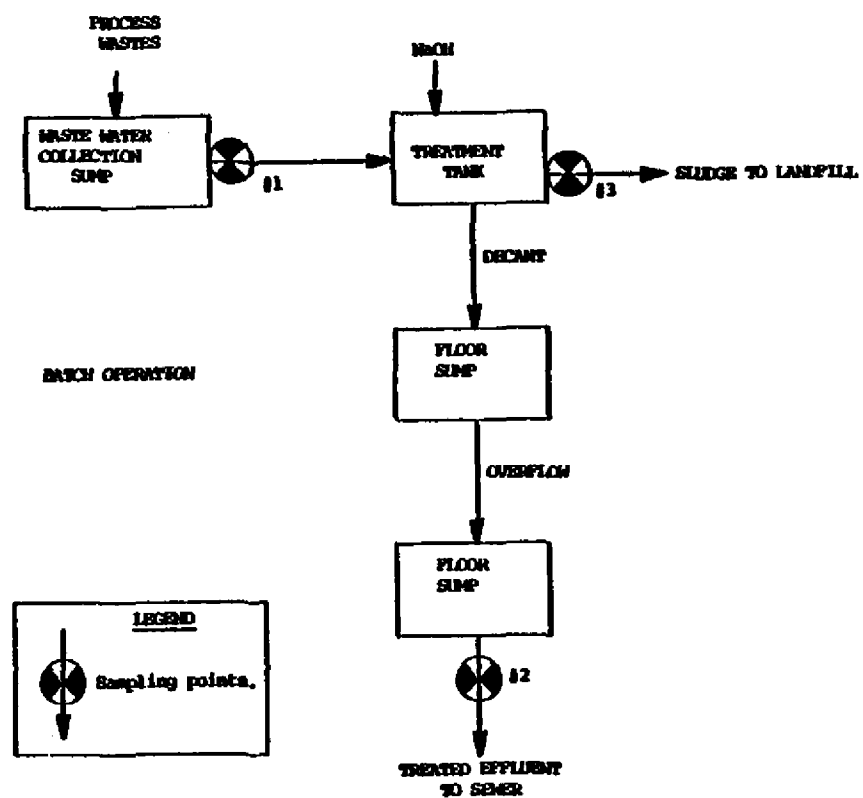
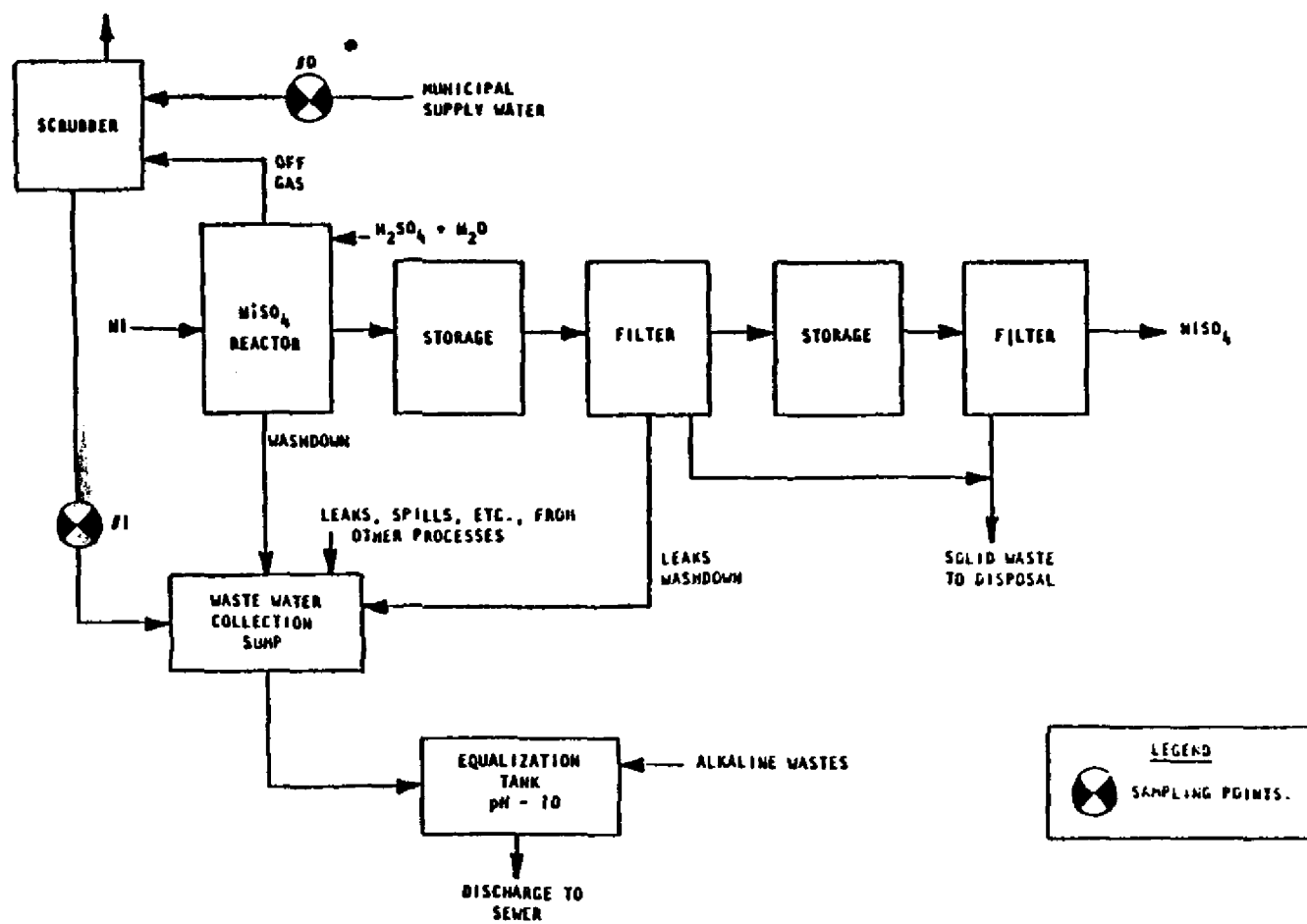


Figure 22-2. General waste water treatment process flow diagram showing sampling points at plant #369. (Nickel sulfate subcategory.)

TABLE 22-4. FLOW AND POLLUTANT CONCENTRATION DATA OF THE SAMPLED WASTE STREAMS FOR PLANTS PRODUCING NICKEL SULFATE

SUBCATEGORY		NICKEL SULFATE			
Stream No.	Sampled Stream Description	Flow (m ³ /kkg of NiSO ₄)	TSS (kg/kkg of NiSO ₄)	Ni (kg/kkg of NiSO ₄)	Cu (kg/kkg of NiSO ₄)
Screening Data ⁽¹⁾ Plant #369					
1	Raw untreated waste	0.42	0.093	0.073	0.030
2	Treated waste	0.42	0.045	0.00058	0.0076
Verification Data					
Plant #120 ⁽²⁾					
1	Raw NiSO ₄ waste	0.72	0.031	0.035	0.00016
2	All Nickel raw wastes*	0.72	0.05	0.0089	<0.0000036
3	Treated effluent*	0.72	0.0031	0.00014	0.000031
Plant #572 ⁽³⁾ (mg/l)					
1	Scrubber waste		3.2	1100	.04

- (1) = One grab sample of each waste water stream representing a composited batch sample of that day's nickel sulfate production.
- (2) = Average of three 24-hour composite samples of each waste water stream.
- (3) = Flow data was unavailable. Only waste water quality is presented here.
- * = The stream is a commingled waste water. The flow given is the amount contributed by the nickel sulfate plant.



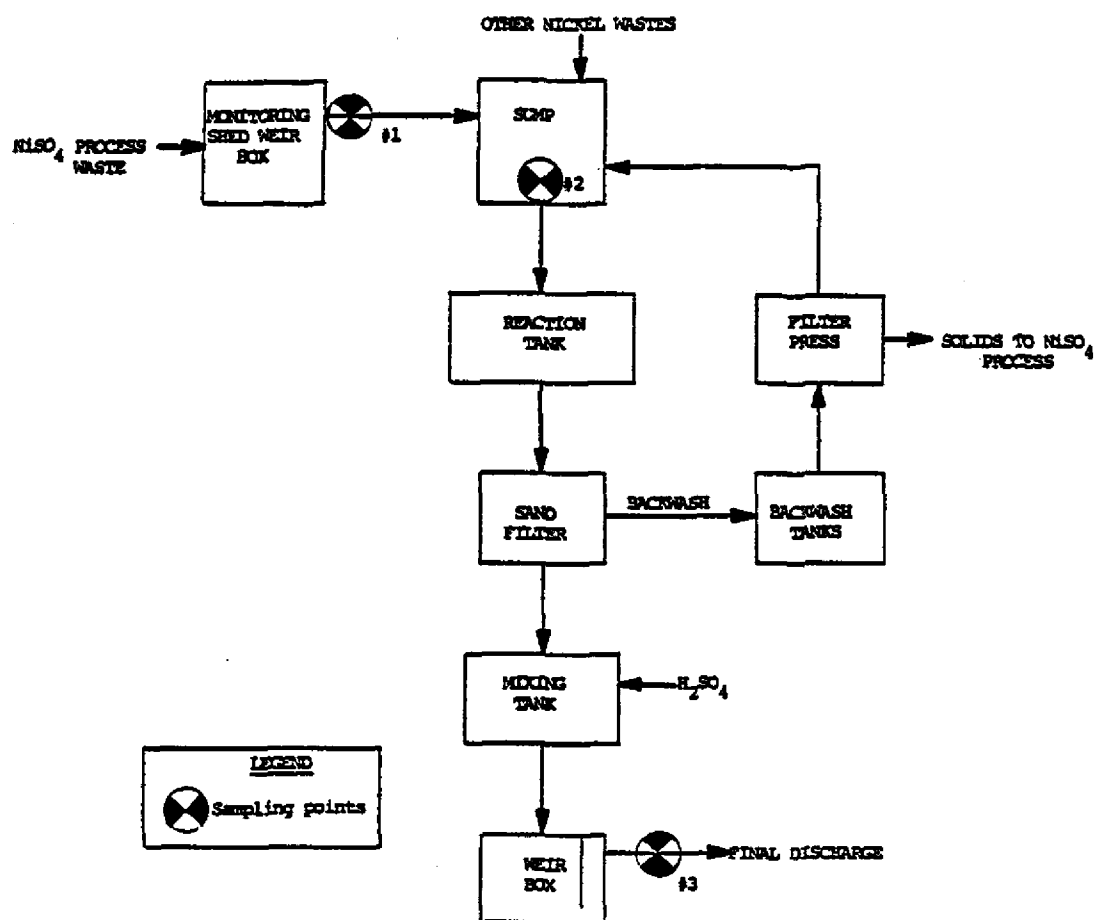


Figure 22-4. General waste water treatment process flow diagram at plant #120 showing the sampling points. (Nickel sulfate manufacture.)

Maximum Concentration Observed
($\mu\text{g/l}$)

Pollutant	Screening Plant #369	Verification (2 Plants) Plants #572 and #120
Nickel	175,500	1,115,000
Copper	73,300	355
Chromium	1,300	20
Antimony	476	18
Lead	55	120
Mercury	1.0	10
Cadmium	9.0	160
Selenium	10	141
Zinc	430	382

Section 5 of this report describes the methodology of the screening and verification sampling program. In the nickel sulfate industry, a total of seven days of sampling were conducted at Plants #369, #572 and #120. Nine different sampling points were involved covering the raw waste source, the various raw waste streams, and the treated effluents at these plants. The evaluation of toxic metal content of these process-related waste streams was based on 195 analytical data points. The screening for toxic organic pollutants at Plant #369 generated an additional 342 analytical data points. The unit loadings were calculated from the reported nickel sulfate production rate, the waste stream flow rate measured or estimated at the time of sampling, and the measured pollutant concentration.

That is,

$$\text{Unit loading (as kg of pollutant per kkg of nickel sulfate)} = \frac{(C)(Q)}{1000(P)}$$

where:

C is the concentration of the pollutant expressed in limits of mg/l (Note: kg/m^3 , = 1000 mg/l), and

Q is the waste stream flow rate expressed in units of m^3/day , (m^3 , a cubic meter, is equal to 264.2 U.S. gallons) and P is the nickel sulfate production rate expressed in units of kgg/day (kgg is 1000 kg , a metric ton, which is equal to 2205 pounds).

The average values are based on data from those plants where the particular pollutant was found at detectable concentrations.

In Table 22-5, the toxic pollutant raw waste data are presented as the average daily concentrations and the unit loading found at the

individual plants, with the exception of Plant #572 which presents only the concentrations. The overall averages are also shown and are calculated only for Plants #369 and #120, because they represent total composited wastewater from the entire NiSO_4 process, while Plant #572 data are for one of several sources.

Based on the total annual production rate of this subcategory (See Table 22-1) and the average waste load generated per unit product, the estimated total pollutant raw waste loads generated each year for this subcategory are as follows:

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Antimony	1.27
Arsenic	0.22
Cadmium	0.018
Chromium	1.72
Copper	95.2
Lead	0.19
Nickel	343
Selenium	< 0.17
Zinc	0.48

Mercury is not included in this list as it was found at a detectable concentration only in the one stream at Plant #572. This stream is shared with another nickel compound process using different source materials. Cross contamination is suspected. Since mercury was found below detectable concentrations in all other nickel sulfate waste water, using Plant #572 would yield an erroneously high average. This would subsequently show an unrepresentative yearly waste load in the previous table. Based on the reliable data, mercury is not a pollutant of concern in the nickel sulfate industry.

Pollution Abatement Options

Toxic Pollutants of Concern

The toxic pollutants present in a nickel sulfate process wastewater depend upon the purity of the sources and the nature of the raw materials being used, which vary with time.

If impure raw materials are used, most of the heavy metal impurities will be removed in the purification process, handled and disposed of as solid sludge. These impurities build up in the mother liquor and subsequently appear in purges, leaks, and washdowns. The toxic metals such as nickel and copper, and to a lesser extent antimony, arsenic, cadmium, chromium, lead, selenium, and zinc found in the wastewaters during sampling originate in the raw material source. Pure raw materials make complete recycle possible, allowing plants using these materials to comply with the effluent limitations without operation of a treatment system provided the manufacturing process used is properly designed, operated, and maintained.

TABLE 22-5. TOXIC POLLUTANT RAW WASTE DATA

SUBCATEGORY: Nickel Sulfate

Average Daily Pollutant Concentrations and Loadings at
Plants Sampled (1)

Pollutant	(mg/l) (Kkg of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$)			Overall (3)+ Average
	#369 (S)	#120 (V)	#572 (2) <i>0.05</i>	
Antimony	0.48 0.00020	* <i>0.00020</i>	0.018	0.48 0.00020
Arsenic	* <i>0.000035</i>	0.049 0.000035	* <i>0.000035</i>	0.049 0.000035
Cadmium	0.009 0.0000038	0.0027 0.0000019	0.16	0.0058 0.0000028
Chromium	1.3 0.00054	0.012 0.0000086	*	0.66 0.00027
Copper	73.3 0.030	0.22 0.00016	0.04	36.8 0.015
Lead	0.055 0.000022	0.052 0.000038	0.097	0.054 0.000030
Mercury	*	*	0.01	*
Nickel	176 0.073	49.2 0.035	1100	112 0.054
Selenium	< 0.010 < 0.0000041	0.069 0.00005	0.009	< 0.04 < 0.000027
Thallium	0.021 0.0000088	* <i>0.0000088</i>	*	0.021 0.0000088
Zinc	0.27 0.00011	0.055 0.00004	0.38	0.16 0.000075

(S) - Screening data from one grab composite sample of the batch process combined raw waste streams.

(V) - Verification data from three 24-hour composite samples, averaged, from each raw waste sampling point.

* - Concentration below significant level.

(1) - The methodology of the sampling program is described in Section 5.1.2, and Section 22.3.3 presents the scope of sampling in the Nickel Sulfate industry.

(2) - Data for Plant #572 is presented in concentration basis only.

(3) - Average of Plants #369 and #120 only.

+ - When averaging values indicated as "less than" (<), the absolute value was used and the resulting average was indicated as a "less than" value.

Wastewater quality for an air pollution control scrubber at Plant #572 is shown in Table 22-5. However, this source is not used to evaluate raw waste data, since it is only one of several sources and does not represent a total wastewater stream. This scrubber also serves in another nickel compound manufacturing process alternately with nickel sulfate so it cannot be considered totally representative of the process of interest.

No toxic organic pollutants were found in the process-related waste streams at significant concentrations.

Process Modifications and Technology Transfer Options

Mechanical scrapers should be installed on filters at plants which use impure raw materials. This would eliminate the backwash and reduce the amount of wastewater produced. Solids would need to be disposed of in a secure landfill. Installation of the scrapers would incur only a small capital cost.

Best Management Practices

The best technology for the treatment of wastewater from processes using pure raw materials is recycle of all process waters. To implement this treatment, recycle piping and pumping are needed.

The best technology available where nickel sulfate is manufactured from impure plating solutions is caustic soda addition to precipitate nickel and other metallic hydroxides, followed by sand filtration to remove the suspended solids. This requires installing treatment tanks, filters, pH control equipment, and related piping and pumps.

Prevailing Control and Treatment Practices

Plant #369 sends filter leaks and wash water to a collection tank. When the batch manufacturing process is complete, the collected waste is treated with caustic soda to pH 12.5. The metals are precipitated as hydroxides, settled, and the sludge disposed of at an approved landfill. The supernatant is sampled and analyzed before discharge to a POTW.

Plant #120 wastewaters are generated from leaks, washdowns, filter wash, and air scrubbers. These are combined with other nickel process wastes and treated with caustic soda to precipitate trace metals. The waste is then treated by filtration followed by pH adjustment prior to final discharge.

Plant #572 also combines wastes from the air scrubbers, leaks, and washdowns. These wastewaters are sent to an equalization tank where they are mixed with alkaline wastes to raise the pH to 10. After settling, the wastewaters are discharged to a POTW.

Plant #069, which produces a reagent grade product, sends periodic purges and washdown water to a combined collection system with

wastewater from numerous other products. Treatment consists of neutralization and equalization of the wastes prior to discharge to a POTW.

Plant #313 also combines its wastewaters from nickel sulfate production with wastes from various other metal processes and presently discharges the combined waste after a period of settling in a pond. A treatment system is being designed which uses lime precipitation at pH 10 followed by gravity separation. Centrifugation is to be used to thicken the sludge. The clarified wastewater will then be neutralized to pH 6.5 - 7.5 and discharged.

Plant #603 has no discharge of wastewaters from the nickel sulfate process.

Advanced Treatment Technologies

Alkaline precipitation will remove nickel and most other heavy metals from solution, allowing them to be settled and filtered in successive steps. Nickel and the common heavy metals (except chromium) can also be precipitated as metallic sulfides, for later separation by settling and filtration. Sulfide precipitation generally yields lower concentrations of the metals in the final effluent.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT, BAT, NSPS)

Level 1 consists of alkaline precipitation with caustic soda, followed by filtration. The system is operated as a batch process. This technology is generally the treatment practice in place within this industry. For evaluating Level 1 treatment, the Agency has developed two models--one for high production plants (7,000 kkg/year), and another for low (900 kkg/year) and medium production (4,000 kkg/year) plants--the difference being in the method of filtration. Flow diagrams for these models are shown in Figures 22-5 and 22-6.

B. Level 2

In proposed Level 2 treatment, the Level 1 system was to be supplemented by the additional step of sulfide precipitation with ferrous sulfide after alkaline precipitation. However, this technology was not employed, because Level 1 affords adequate control and the additional pollutant reduction was not sufficient to offset the additional cost. Proposed models for this technology are shown in Figures 22-7 and 22-8. Further information on estimated treatment system operation costs and effectiveness may be found in the proposed Development Document (60).

Equipment for Different Production Levels

A. Equipment Functions

In both Level 1 models, wastes are received in a one-day holding tank or wastewater collection sump which is drained each day to a reaction vessel. At the end of a normal work week, the contents of the reaction vessel are raised to about pH 10 with caustic soda and thoroughly mixed. In the high production model, the contents of the reaction tank are allowed to settle and the supernatant is filtered through a dual-media filter, while the precipitates are filtered through a high pressure filter. Filtrate from the dual-media filter is adjusted to a pH from 6-9 and is discharged as a final effluent. Filtrate from the high pressure filter is recycled to the holding tank.

In the low and medium production models, the entire contents of the reaction tank are sent through the high pressure filter after mixing. The filtrate is adjusted for pH and discharged, while sludge is sent to a landfill. Filter backwash is recycled to the holding tank.

B. Chemicals and Handling

Caustic soda in solution form is used for alkaline precipitation to form insoluble metallic hydroxides. The choice of caustic soda avoids precipitating calcium sulfate, as would occur with lime application. Caustic soda solution is handled in conventional equipment, or is drawn in batches from shipping containers when small volumes are needed.

C. Separation and Removal of Solids

In the low and midrange production models at both levels, essentially all solids are collected in a filter press, which is cleaned periodically. The dewatered sludge is hauled to a chemical landfill. In the larger model plant, backwash from cleaning the dual-media filter returns to the influent holding tank, from which the suspended solids pass via the reaction tank to the sludge filter press.

D. Monitoring Requirements

Satisfactory separation of heavy metals can be assured by maintaining the proper reaction pH, which can be determined manually on each batch, using simple field equipment. For reporting purposes, occasional monitoring of nickel and copper in the effluent should be done by atomic absorption methods.

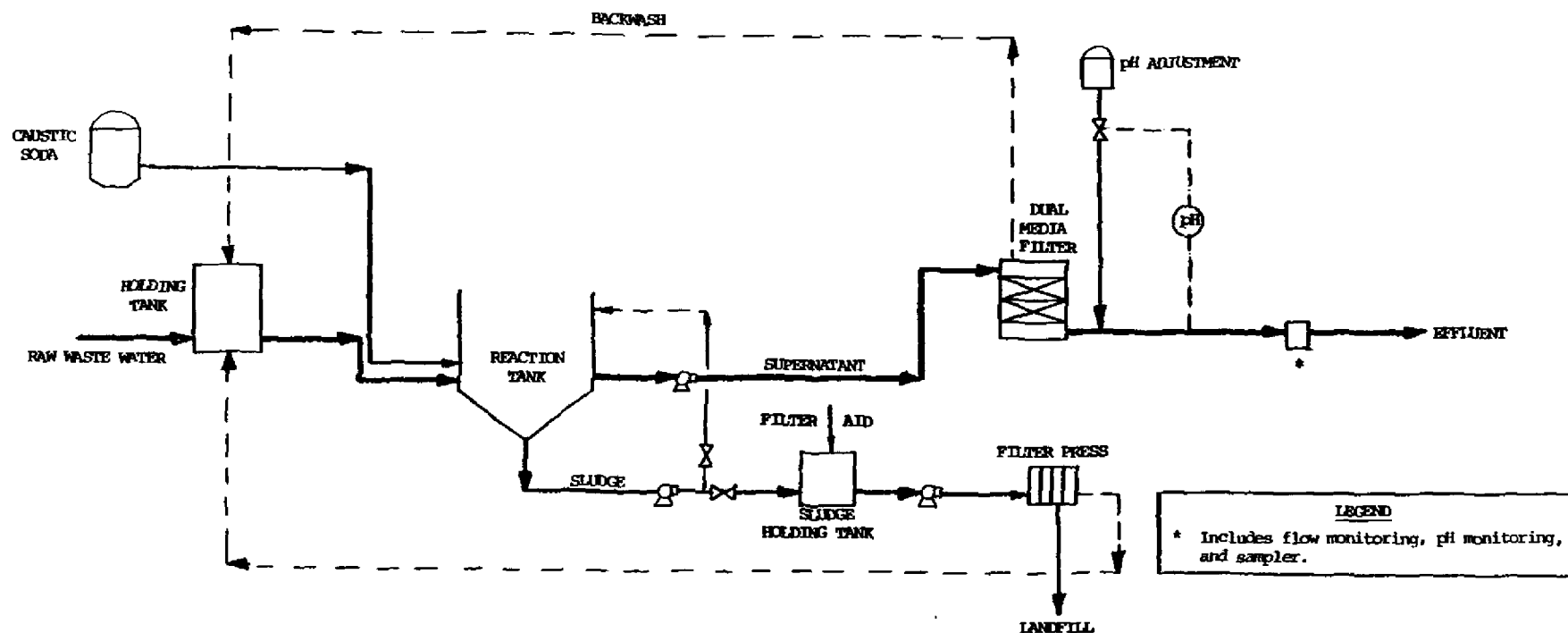


Figure 22-5. Level 1 waste water treatment for the nickel sulfate subcategory — high production model — batch process.

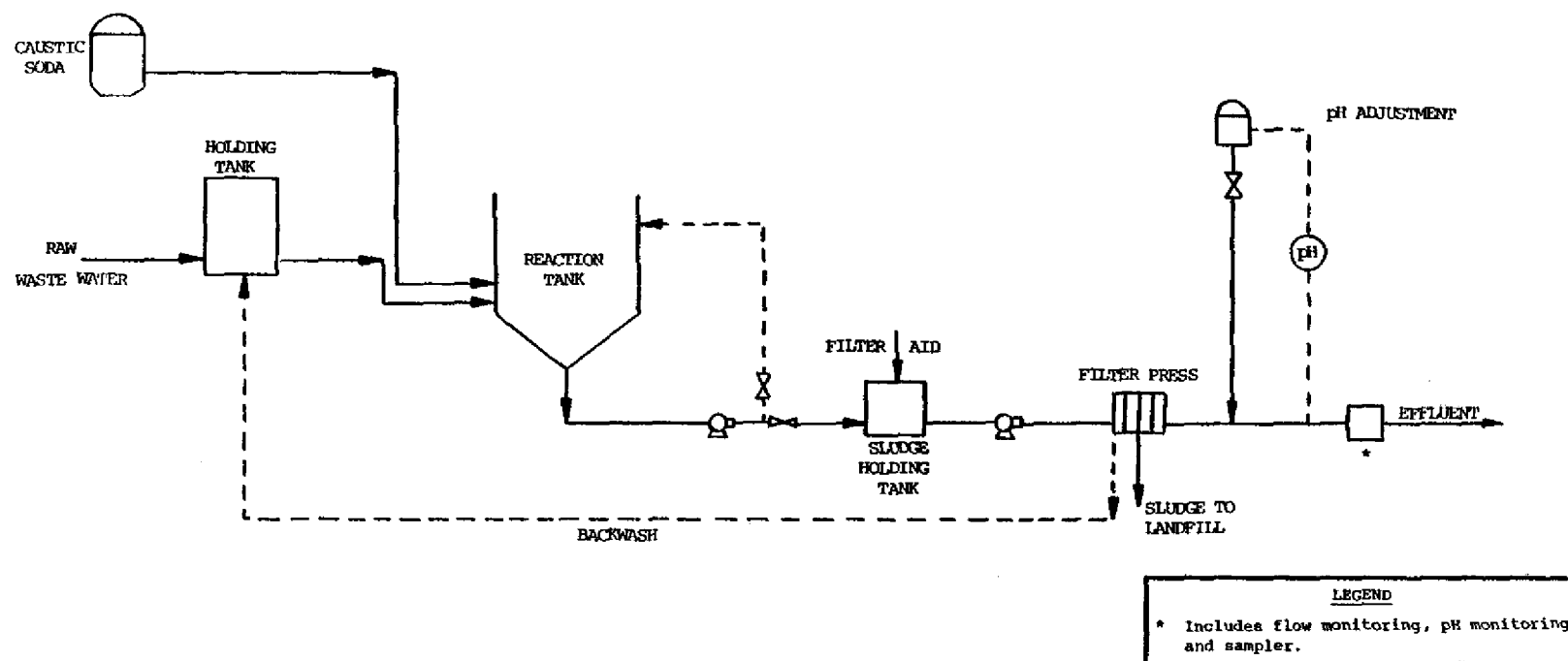


Figure 22-6. Level 1 waste water treatment for the nickel sulfate subcategory -- low and medium production models -- batch process.

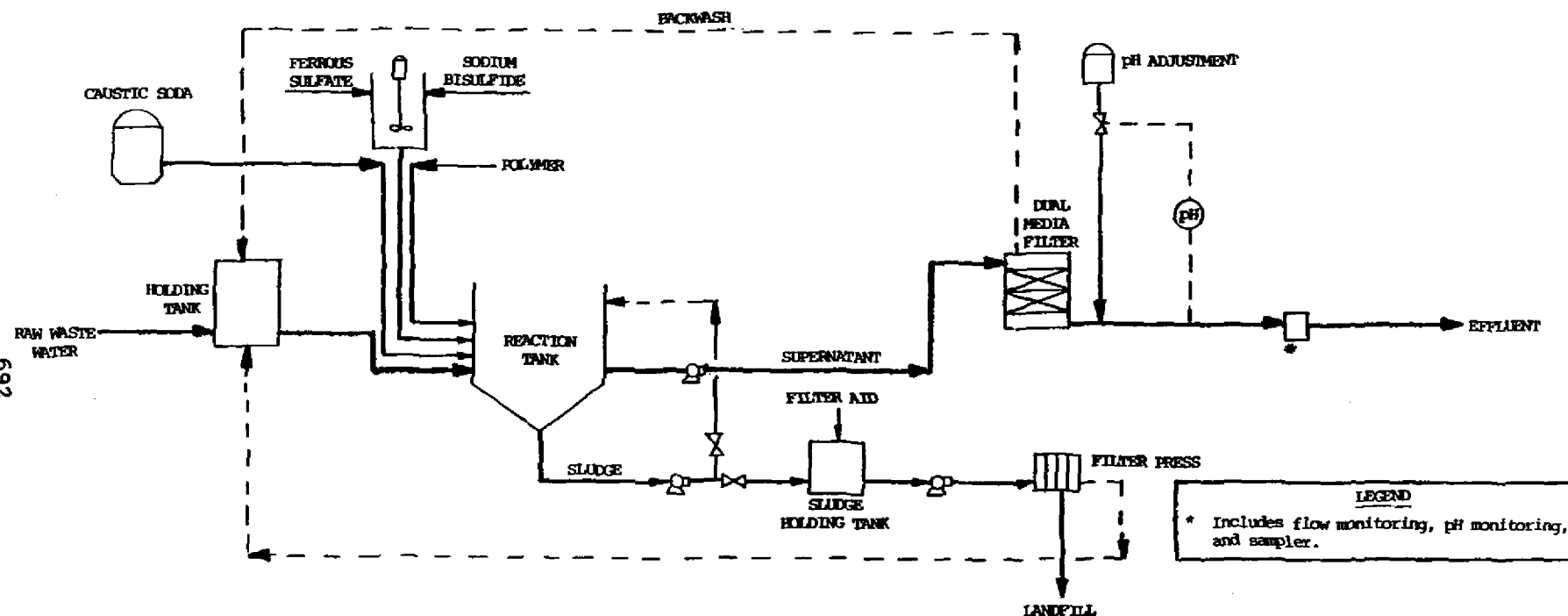


Figure 22-7. Level 2 waste water treatment for nickel sulfate subcategory -- high production model -- batch process.

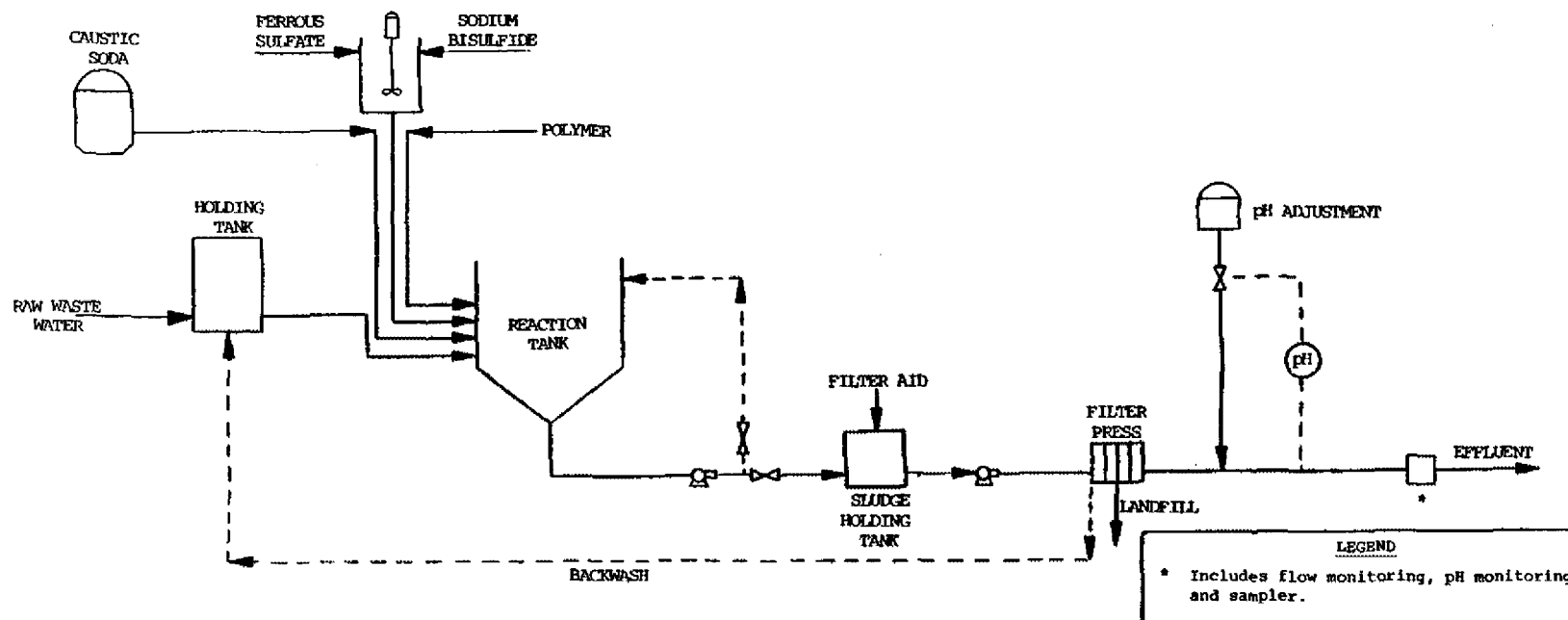


Figure 22-8. Level 2 waste water treatment for nickel sulfate -- low and medium production models -- batch process.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed for Level 1 technology as follows:

A. Wastewater Flow

Table 22-3 shows the wastewater discharged to treatment for five plants. The unit wastewater flow for the two single waste source plants ranged from 0.42 m³/kgg of NiSO₄ to 0.72 m³/kgg of NiSO₄. For the model plant cost estimates, a production-weighted average of 0.68 m³/kgg for the two plants was used. This was accomplished by multiplying the unit flow of each plant by its daily production, adding the resultant values and dividing by the total production of the two plants, which results in these values being representative of the different production level plants.

B. Production

Nickel sulfate production ranges from 45 kkg/yr to 5,900 kkg/yr in the plants for which the 308-Questionnaires were available. The average production for these six plants was 2,100 kkg/yr, the median was 1,600 kkg/yr. For wastewater treatment cost estimates, three production levels were selected as model plants. These are 900 kkg/yr, 4,000 kkg/yr, and 7,000 kkg/yr. The mode of operation at all nickel sulfate plants is the batch process and, for the model plant, is assumed to operate for 250 days/year.

C. Solid Waste Generation

Solid wastes are generated from the filtration and settling of metals from the nickel sulfate solution. The solids can be recycled to the process for reuse when pure raw materials are used. If the solids are not recycled, they are disposed of in an industrial landfill. The quantity of solids generated is 0.39 kg/kgg of nickel sulfate.

D. Treatment Chemicals

Caustic is required for neutralization to precipitate the metals as their hydroxides. Acid is needed for pH adjustment before final discharge. For the model plant, these practices were estimated to use 0.016 kg/kgg and 0.00010 kg/kgg, respectively.

Model Plant Control Costs

The cost estimates for three models having different production levels are presented in Tables 22-6, 22-7, and 22-8.

Table 22-9 gives a summary of the unit cost distribution between amortization and operation and maintenance cost components at various production rates and levels of treatment.

Cost estimates developed for the first level of treatment (BPT, BAT, NSPS) indicate that at low production levels, labor cost has a significant impact on the total annual costs. At a medium production level, amortization, operation, and maintenance costs are the important factors in the annual costs. At a high production level, amortization cost is the significant factor in the annual costs.

Basis for Regulations

Evaluation of BPT Treatment Practices

Nickel sulfate can be manufactured using pure nickel as the raw material or an impure nickel raw material. Waste loads emanating from the two sources differ in that total recycle of process wastes can be accomplished at plants using a pure nickel source, while at plants using an impure raw material, waste streams need to be purged periodically to avoid build-up of contaminants in the process.

A. Pollutant Removal with BPT Treatment

BPT technology for nickel sulfate plants utilizing impure raw materials is equivalent to treatment Level 1. Table 22-10 presents the toxic pollutant treated effluent data for both Plants #369 and #120 in a similar manner as Table 22-5 presented the raw waste data. In evaluating BPT treatment the data from Plant #120 was used, rather than Plant #369, or overall average data. This is because the treatment at Plant #120 represents a typical BPT system, while Plant #369 has no filtration before discharge to a POTW. Long-term effluent monitoring data for Plant #120 can be found in Tables A-15a through A-15d. The data is for nickel only and is presented in concentration and daily loading units for both daily and monthly measurements.

In comparing raw waste and effluent data (Tables 22-4, 22-5, and 22-10), BPT treatment gave a suspended solids removal of over 93 percent, while the toxic metals nickel and copper had over 98 percent removal. All of the toxic pollutant concentration were below the lower limit of treatability-based achievable concentrations. Many of the toxic metals from the effluent of Plant #369 were below BPT based achievable levels, with only hydroxide precipitation and settling.

Basis for BPT Effluent Limitations

BPT regulations for the Nickel Sulfate Subcategory are presently in effect, 40 CFR 415.472 (See Table 22-2). The technology basis for the existing BPT is alkaline precipitation plus dual-media filtration and final pH adjustment before discharge. Most direct dischargers in this subcategory have installed BPT technology or equivalent.

TABLE 22-6. MODEL PLANT TREATMENT COSTS

Subcategory	Nickel Sulfate Production 900 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	1,200	0
Equipment	35,000	0
Monitoring equipment	20,000	0
Subtotal	56,200	0
Contractor's O & P ^b	8,430	0
Subtotal	64,630	0
Engineering	12,926	0
Subtotal	77,556	0
Contingencies	7,756	0
Subtotal	85,312	0
Land	1,200	0
TOTAL INVESTMENT COST	86,512	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	8,000	0
Energy	30	0
Chemicals	200	0
Maintenance	8,531	0
Taxes and insurance	2,595	0
Residual waste disposal	100	0
Monitoring, analysis and reporting	5,000	0
TOTAL OPERATION AND MAINTENANCE COST	24,457	0
C. AMORTIZATION OF INVESTMENT COST	13,880	0
TOTAL ANNUAL COST	38,337	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 22-7. MODEL PLANT TREATMENT COSTS

Subcategory	Nickel Sulfate	
Production	4,000 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	1,800	0
Equipment	70,500	0
Monitoring equipment	20,000	0
Subtotal	92,300	0
Contractor's O & P ^b	13,845	0
Subtotal	106,145	0
Engineering	21,229	0
Subtotal	127,374	0
Contingencies	12,737	0
Subtotal	140,111	0
Land	1,800	0
TOTAL INVESTMENT COST	141,911	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	8,000	0
Energy	40	0
Chemicals	900	0
Maintenance	14,011	0
Taxes and insurance	4,257	0
Residual waste disposal	100	0
Monitoring, analysis and reporting	5,000	0
TOTAL OPERATION AND MAINTENANCE COST	32,308	0
C. AMORTIZATION OF INVESTMENT COST	22,796	0
TOTAL ANNUAL COST	55,105	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 22-8. MODEL PLANT TREATMENT COSTS

Subcategory Production	Nickel Sulfate 7,000 metric tons per year	(\$)	
A. INVESTMENT COST	BPT	BAT ^a	
Site development	3,000	0	
Equipment	106,500	0	
Monitoring equipment	20,000	0	
Subtotal	129,500	0	
Contractor's O & P ^b	19,425	0	
Subtotal	148,925	0	
Engineering	29,785	0	
Subtotal	178,710	0	
Contingencies	17,871	0	
Subtotal	196,581	0	
Land	3,000	0	
TOTAL INVESTMENT COST	199,581	0	
B. OPERATION AND MAINTENANCE COST			
Labor and supervision	8,000	0	
Energy	50	0	
Chemicals	1,500	0	
Maintenance	19,658	0	
Taxes and insurance	5,987	0	
Residual waste disposal	200	0	
Monitoring, analysis and reporting	5,000	0	
TOTAL OPERATION AND MAINTENANCE COST	40,396	0	
C. AMORTIZATION OF INVESTMENT COST	31,984	0	
TOTAL ANNUAL COST	72,379	0	

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 22-9 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Nickel Sulfate

Annual Treatment Costs (\$/kg)

LEVEL OF TREATMENT

COST ITEM	PRODUCTION (kg/yr)	BPT	BAT*	NSPS
Annual Operation and Maintenance	900	27.17	NA	NA
	4,000	8.08	NA	NA
	7,000	5.77	NA	NA
Annual Amortization	900	15.42	NA	NA
	4,000	5.70	NA	NA
	7,000	4.57	NA	NA
Total Annual Cost	900	42.60	NA	NA
	4,000	13.78	NA	NA
	7,000	10.34	NA	NA

*Represents the incremental cost above BPT

A. Conventional Parameters

For pH the treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

In the existing BPT regulations, EPA has different limitations for pure and impure raw materials processes. EPA is not establishing different limits for these processes in the BPT, BAT, BCT, NSPS, PSES, and PSNS regulations. This is because both processes are adequately covered by the one regulation since the pure raw materials process can, with proper design, comply without end of the pipe treatment. Only nickel, TSS and pH are regulated because these are the only three parameters limited in the existing BPT regulation.

Basis for BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Effluent Limitations

A. Technology Basis

For BAT, the Agency is establishing limitations based on BPT technology which is alkaline precipitation followed by dual-media filtration. The Agency considered treatment Level 2 (sulfide precipitation), but rejected it because the treatment removed only small additional amounts of toxic metals in this subcategory.

B. Flow Basis

The model plant BAT treatment system is based on an inflow rate of 0.68 m³/kkg for effluent limitation purposes. The rationale for the flow is the same as that used for the model plant for cost estimating as described in this section.

TABLE 22-10. TOXIC POLLUTANT TREATED EFFLUENT DATA

SUBCATEGORY: Nickel Sulfate

Average Daily Pollutant Concentrations and Loadings at Plants Sampled⁽¹⁾

Pollutant	$\frac{(\text{mg/l})}{(\text{Kkg of NiSO}_4 \cdot 7\text{H}_2\text{O})}$		Overall ⁽²⁾ Average
	#369 (S)	#120 (V)	
Antimony	0.2 0.000083	*	0.2 0.000083
Arsenic	0.26 0.00011	<0.010 <0.0000072	< 0.13 < 0.000059
Cadmium	< 0.001 < 0.00000042	0.00013 0.000000094	< 0.00056 < 0.00000026
Chromium	0.45 0.00019	0.057 0.000041	0.25 0.00012
Copper	18.0 0.0075	<0.043 <0.000031	9.02 < 0.0038
Lead	0.001 0.00000042	0.003 0.0000022	0.002 0.0000013
Nickel	1.4 0.00058	0.20 0.00014	0.8 0.00036
Selenium	0.012 0.000005	<0.008 <0.0000058	0.01 0.0000054
Thallium	0.029 0.000012	0.00033 0.00000024	0.015 0.0000061
Zinc	0.17 0.000071	0.058 0.000042	0.11 0.000056

(S) - Screening data from one grab composite sample of treated effluent.

(V) - Verification data from three 24-hour composite samples, averaged.

(1) - The effluent data presented here corresponds to the raw waste data shown in Table 12-5 excluding Plant #572. The methodology of the sampling program is described in Section 5.1.2, and the scope of sampling in the Nickel Sulfate industry is described in Section 22.3.3.

(2) - When averaging values indicated as "less than" (<), the absolute value was used and the resulting average was indicated as a "less than" value.

* - Concentration below significant level.

C. Selection Basis for Pollutants to be Regulated

The selection of pollutants for which numerical effluent limitations were proposed was based on an evaluation of raw waste data from the screening and verification sampling program. The two major factors considered were: 1) individual sampling raw waste concentrations, and 2) the total subcategory raw waste loadings.

1. Raw Waste Pollutant Concentrations

A tabular summary of maximum raw waste concentrations found in sampling is presented above. Data from the plants sampled in screening and verification are shown for comparison. For each pollutant, the maximum concentration observed gave a preliminary indication of its potential significance in the subcategory. On this basis, the preliminary selection of nickel, copper, chromium, and to a lesser extent, lead, antimony, and zinc were included as candidates for regulation. These pollutants were observed at least once during screening at concentrations considered treatable in this industry using one of the available treatment technology options. The other toxic metals (mercury, cadmium, and selenium) were found to have maximum concentrations that were lower than the minimum levels achievable by treatment.

2. Total Subcategory Raw Waste Pollutant Loadings

Pollutant raw waste loading data were used to evaluate the overall magnitude of the pollution potential. Data from the plants sampled are summarized in Table 22-5. This information, coupled with the estimated total nickel sulfate production rate of 6,350 kkg/year found in Table 22-1, yielded the approximate total annual pollutant loading rates for the subcategory shown in this section. This method of ranking the pollution potential of the observed toxic metals confirms the maximum concentration-based ranking and indicated that nickel, copper, chromium, antimony, zinc, and lead were the six dominant toxic metals in terms of both total mass loading and treatable raw waste concentrations.

3. Final Selection of Pollutants to be Regulated

Originally, limitations were proposed for all the aforementioned dominant toxic pollutants. The Agency has decided, however, to promulgate regulations on copper and nickel only. Copper and nickel are by far the most prominent toxic metals in this subcategory's waste. The nature of the treatment technology employed in this industry is such that control of certain key parameters ensures control of all the toxic metals of concern. Elaboration on this topic may be found in Section 8 of this document.

Section 8 (See Table 8-14) indicates that toxic metals can be divided into two groups for pH optimization of alkaline precipitation, and that control of one or more of the metals in each of these groups will ensure control of others in that group. In controlling copper and nickel, both of these groups are covered. Therefore, since these two metals are the major toxic pollutants in the raw waste, control of these parameters will ensure control of all metals previously considered for limitations. This is supported by sampling data from Plant #120.

Optimization of treatment conditions for nickel and copper removal may cause less efficient performance in chromium control, but in light of the relatively low incoming chromium concentrations, control should be adequate. Table 8-14 and Figure 7-1 indicate a pH in the neighborhood of 10 would be optimum for control of pollutants in this subcategory.

D. Basis of Pollutant Limitations

1. Toxic Pollutants

The effluent limitations for the selected toxic pollutant control parameters are derived from estimated industry achievable long-term averages (Table 8-13), and literature-based treatability estimates (Table 8-11). This is because plant performance data from sampling at Plant #120 (Table 22-10) show effluent concentrations below the lower limit of treatability estimates for all of the toxic metals except nickel.

BAT effluent limitations for copper and nickel are shown in Table 22-11 along with corresponding concentration bases. Also indicated are recommended concentration bases for other toxic metals detected at treatable levels. Those are included for those cases where control of one or more of the unregulated metals is deemed necessary.

Concentration bases for copper, nickel, and chromium are derived from estimated achievable long-term averages (Table 8-13), while those for the other metals of concern were derived from the lowest applicable treatability level (Table 8-11). This approach results in the setting of achievable limitations, and provides for variations in the influent quality that may be associated with different nickel or nickel solution impurity levels or other process variables.

The basis for proposed BAT limitations on each of the selected metals is given below. Calculations of maximum 30-day average and daily maximum concentrations from long-term averages are based on variability factors of 1.2

and 3.6, respectively. This gives a variability factor ratio of:

$$\frac{3.6}{1.2} = 3.0$$

These values were determined by statistical analysis of data presented in the Treatability Study (61) for the nickel and copper sulfate subcategories.

a. Nickel

Table 8-13 indicates an estimated achievable long-term average for nickel of 0.30 mg/l which is supported by the Treatability Study (61). This reflects industry performance using BAT technology and is above effluent levels indicated during sampling at Plant #120. Therefore, using this value and the 30-day variability factor of 1.2 the 30-day concentration basis becomes:

$$(0.30 \text{ mg/l}) (1.2) = 0.36 \text{ mg/l}$$

Multiplying by a VFR of 3.0, the daily maximum concentration is:

$$(0.36 \text{ mg/l}) (3.0) = 1.1 \text{ mg/l}$$

The effluent limitations for nickel are determined using a model flow of 0.68 m³/kkg NiSO₄, with the maximum 30-day average limitations calculated as follows:

$$(0.36 \text{ mg/l})(0.68 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.00024 \text{ kg/kkg}$$

The 24-hour maximum limitation is:

$$(3.6)(0.3 \text{ mg/l})(0.68 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.00074 \text{ kg/kkg}$$

These values are considerably lower than the BPT limits presented in Table 22-2. This is because the information on treatment system performance based on information collected to support this regulation showed better performance than that expected when the existing BPT regulation was developed.

b. Copper

Because the effluent concentration of copper observed at Plant #120 was below treatability estimates, the estimated long-term average (Table 8-13) of 0.30 mg/l

TABLE 22-11. EFFLUENT LIMITATIONS
Nickel Sulfate
Best Available Technology ⁽¹⁾
Waste Water Flow: 0.68 m³/kgg of NiSO₄

Pollutant	Subcategory Performance (mg/l)	VFR ⁽²⁾	Concentration Basis (mg/l)		Effluent Limit (kg/kgg of NiSO ₄)	
			Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
Antimony	0.40 ⁽³⁾	3.6/1.2	0.48	1.4	-- ⁽⁵⁾	-- ⁽⁵⁾
Cadmium	0.05 ⁽³⁾	3.6/1.2	0.060	0.18	-- ⁽⁵⁾	-- ⁽⁵⁾
Chromium	0.20 ⁽⁴⁾	3.6/1.2	0.24	0.72	-- ⁽⁵⁾	-- ⁽⁵⁾
Copper	0.30 ⁽⁴⁾	3.6/1.2	0.36	1.1	0.00024	0.00074
Lead	0.050 ⁽³⁾	3.6/1.2	0.060	0.18	-- ⁽⁵⁾	-- ⁽⁵⁾
Nickel	0.30 ⁽⁶⁾	3.6/1.2	0.36	1.1	0.00024	0.00074
Selenium	0.10 ⁽³⁾	3.6/1.2	0.12	0.36	-- ⁽⁵⁾	-- ⁽⁵⁾
Zinc	0.20 ⁽⁴⁾	3.6/1.2	0.24	0.72	-- ⁽⁵⁾	-- ⁽⁵⁾

(1) Also applies to NSPS.

(2) Variability factor ratio: Ratio of the daily variability factor to monthly based on statistical analyses of treatability study data for nickel and copper sulfate (61).

(3) Lower limit of treatability (Table 8-11) used as long-term average.

(4) Industry long-term average (Table 8-13).

(5) Indicates no effluent limitation established.

(6) Treatability study estimate.

was chosen to determine the concentration bases for copper. Again, the 30-day average variability factor of 1.2 and the VFR of 3.0 apply. Calculation of the maximum 30-day average concentration basis is:

$$(0.30 \text{ mg/l}) (1.2) = 0.36 \text{ mg/l}$$

and the 24-hour maximum is:

$$(3.0) (0.36 \text{ mg/l}) = 1.1 \text{ mg/l}$$

The maximum 30-day average effluent limitation based on a $0.68 \text{ m}^3/\text{kg}$ flow is:

$$(0.36 \text{ mg/l}) (0.68 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.00024 \text{ kg/kg}$$

and the 24-hour maximum is:

$$(3.6) (0.30 \text{ mg/l}) (0.68 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.000074 \text{ kg/kg}$$

c. Chromium

Effluent concentration for chromium at Plant #120 was near the lower limit of treatability, however, to account for variations in raw waste loading the long-term average estimate (Table 8-13) is used. The 30-day average variability factor of 1.2 and VFR of 3.0 apply. The maximum 30-day average concentration basis is:

$$(0.20 \text{ mg/l}) (1.2) = 0.24 \text{ mg/l}$$

and the 24-hour maximum is:

$$(3.0) (0.24 \text{ mg/l}) = 0.72 \text{ mg/l}$$

d. Antimony

The lower limit of treatability (Table 8-11) of 0.40 mg/l is chosen as the long-term average. Effluent concentrations at Plant #120 were well below this value. The 30-day variability factor of 1.2 and VFR of 3.0 are used. The maximum 30-day average concentration basis is:

$$(0.40 \text{ mg/l}) (1.2) = 0.48 \text{ mg/l}$$

and the 24-hour maximum is:

$$(3.0) (0.48 \text{ mg/l}) = 1.4 \text{ mg/l}$$

e. Lead

By the same rationale applied to antimony, the long-term average for lead is set to the lower limit of treatability which is 0.050 mg/l. The same variability factors apply. The maximum 30-day average concentrations basis is:

$$(0.050 \text{ mg/l}) (1.2) = 0.60 \text{ mg/l}$$

and the 24-hour maximum is:

$$(3.0) (0.060 \text{ mg/l}) = 0.18 \text{ mg/l}$$

f. Zinc

Again, the lower limit of treatability is used as a long-term average by the rationale mentioned above. This value is 0.20 mg/l, therefore, by applying the same variability factors, the maximum 30-day average concentration basis is:

$$(0.20 \text{ mg/l}) (1.2) = 0.24 \text{ mg/l}$$

and the 24-hour maximum is:

$$(3.0) (0.24 \text{ mg/l}) = 0.72 \text{ mg/l}$$

g. Cadmium

Using the lower limit of treatability, which is 0.05 mg/l, as a long-term average and applying the same variability factors, the maximum 30-day average concentration basis for cadmium is:

$$(0.05 \text{ mg/l}) (1.2) = 0.060 \text{ mg/l}$$

and the 24-hour maximum is:

$$(3.0) (0.060 \text{ mg/l}) = 0.18 \text{ mg/l}$$

h. Selenium

The lower limit of treatability applies for selenium. This value is 0.10 mg/l, therefore, by applying the same variability factors, the maximum 30-day average concentration basis is:

$$(0.10 \text{ mg/l}) (1.2) = 0.12 \text{ mg/l}$$

and the 24-hour maximum is:

$$(3.0) (0.12 \text{ mg/l}) = 0.36 \text{ mg/l}$$

New Source Performance Standards

After examination of the effectiveness of the two treatment technologies applicable to nickel sulfate wastes, it has been determined that BAT technology be the basis for NSPS. The effluent limits for toxic metals are the same as for BAT shown in Table 22-11, and the TSS is being limited at the same effluent level as in the existing BPT regulation presented in Table 22-2. Also, pH is limited to the range 6 to 9 as based on data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

Basis for Pretreatment Standards

All five of the direct dischargers and four of the six indirect dischargers in the Nickel Sulfate Subcategory have BPT/BAT treatment installed.

There is an existing PSES regulation, 40 CFR 415.474. The Agency is amending that section of these regulations based on new treatment system performance data and the PSES limitations are the same as those presented for BAT in Table 22-11. EPA is also setting PSNS limitations equal to the BAT limits presented in Table 22-11. The pollutants limited by the final PSES and PSNS regulations are nickel and copper. Pretreatment is necessary because BAT provides better removal of toxic metals than is achieved by a well-operated POTW with secondary treatment installed, and therefore these pollutants would pass through a POTW in the absence of pretreatment.

SECTION 23

SILVER NITRATE INDUSTRY

Summary of Determinations

Action on this subcategory has been deferred, and a new subcategory including all silver compounds will be reviewed under Phase II BAT review, because the logical sequence of guideline promulgation was to start the guideline process with nonferrous metals to be followed later by a regulation on silver compounds.

Assessment of the Water Pollution Potential

Production Processes and Effluents

Most of the silver nitrate produced is for captive use in the photographic industry. It is also used in the manufacture of silver salts, mirrors, for silver plating, coloring porcelain and as a chemical reagent.

The industry profile data is given in Table 23-1.

Toxic pollutants found at significant levels during sampling at one plant were:

<u>Pollutant</u>	<u>Concentration (μg/l)</u>	
	<u>Screening</u>	<u>Verification</u>
Silver	164	65
Cyanide	580	470

Silver was not found at a significant concentration during verification sampling of the same plant. However, a significant level of cyanide was found again. The source of cyanide was found to be from a soaking solution which is used to remove silver nitrate stains from workers' clothes. The solution is sent to the silver recovery treatment system. When plant personnel discontinued this practice, cyanides disappeared from the effluent.

Status of Regulations

BPT limitations for this subcategory (Subpart BA) were promulgated on May 22, 1975, (40 FR 22421) and PSES were promulgated on July 20, 1977, (42 FR 37301). Both the BPT limitations and PSES are still in effect (40 CFR Part 415.530, 415.531, and 415.534).

TABLE 23-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY

SILVER NITRATE

Total subcategory capacity rate	
Total subcategory production rate	35,000 kkg/year
Number of plants in this subcategory	7
308 Data on file for	2
With total capacity of	6,507 kkg/year
With total production of	3,256 kkg/year
Representing capacity	NA
Representing production	9 percent
Plant production range:	
Minimum	50 kkg/year
Maximum	3,206 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	20 years
Maximum	64 years
Waste water flow range:	
Minimum	<1 cubic meters/day
Maximum	38 cubic meters/day
Volume per unit product:	
Minimum	1 cubic meter/kkg
Maximum	4 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

NA = Not Available

SECTION 24

SODIUM BISULFITE INDUSTRY

Industry Profile

General Description

Sodium bisulfite (NaHSO_3) is manufactured both in liquid and powdered form. Captive use is very small. Sodium bisulfite is used in the manufacture of photographic chemicals, textiles, and in food processing. It is also used in the tanning industry and in the sulfite process for the manufacture of paper products.

The industry profile data are given in Table 24-1, while the status of regulations prior to promulgation of this regulation is summarized in Table 24-2.

Subcategorization

The method of primary subcategorization chosen for the inorganic chemicals point source category was subdivision by dominant product. Other factors taken into consideration for subcategorization included: raw materials used, manufacturing process employed, geographical location, size and age of equipment and facility involved, non-water-quality aspects of waste characteristics, water pollution control technology, treatment costs, energy requirements and solid waste disposal. A detailed discussion of these factors is given in Section 4. No further subcategorization of the sodium bisulfite industry, besides dominant product, was required.

General Process Description and Raw Materials

Sodium bisulfite is produced by reacting sodium carbonate (soda ash) with sulfur dioxide and water. The reaction is:



This reaction produces a slurry of sodium bisulfite crystals which can be sold, but which is usually processed to form anhydrous sodium metabisulfite. This requires thickening, centrifuging, drying, and packaging operations.

Water Use and Waste Source Characteristics

Water Use

Direct process contact water is used to slurry the sodium carbonate for the reaction. Noncontact cooling water is another water use at one plant. Water is also used for pump seals, maintenance and washdowns. Table 24-3 gives a summary of water usage at the plants for which 308-Questionnaires were available.

TABLE 24-1. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY Sodium Bisulfite

Total subcategory capacity rate	
Total subcategory production rate	98,000 kkg/year (1)
Number of plants in this subcategory	7
308 Date on file for	2
With total capacity of	46,000 kkg/year
With total production of	28,300 kkg/year
Representing production	
Plant production range:	
Minimum	4,700 kkg/year
Maximum	23,600 kkg/year
Average production	17,800 kkg/year
Median production	16,900 kkg/year
Average capacity utilization	62 percent
Plant age range:	
Minimum	4 years
Maximum	19 years
Waste water flow range:	
Minimum	3 cubic meters/day
Maximum	100 cubic meters/day
Volume per unit product:	
Minimum	< 1 cubic meters/kkg
Maximum	< 1 cubic meters/kkg

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry."

- (1) "Energy and Environmental Analysis, Inc.; Economic Analysis of Proposed Revised Effluent Guidelines And Standards for the Inorganic Chemicals Industry," March 1980.

TABLE 24-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY Sodium Bisulfite
 SUBPART BB (40 CFR 415.540, 5/22/75)

STANDARDS

Product Process	Para- meters	BPCTCA		BATEA		NSPS	
		Max. ¹ kg/kg (mg/l)	Avg. ² kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)	Max. kg/kg (mg/l)	Avg. kg/kg (mg/l)
Sodium Bisulfite	Reserved	Reserved	Reserved	Reserved	Reserved	Reserved	Reserved

¹Max = Maximum of any one day.

²Avg = Average of daily values for thirty consecutive days shall not exceed.

Waste Sources

Noncontact cooling water for the centrifuge is a source of waste at one plant. However, direct process contact water is the main source of wastewater which must be treated, together with miscellaneous wastes such as water used for maintenance purposes, washdowns, and spill cleanup.

Table 24-4 summarizes the wastewater unit flows from the major waste source for plants #987 and #282. Plant #987 has two facilities that produce sodium bisulfite which are designated A and B.

There is little solid waste generation in the production of sodium bisulfite and process waste treatment. There are minor quantities which are precipitated as metal hydroxides resulting in insignificant amounts of filter cake requiring disposal. Generation of solid waste is therefore assumed negligible.

Description of Plants Visited and Sampled

Screening

Plant #282 was visited in the screening phase of the program. The bisulfite waste is treated on a batch basis every two or three days. Sodium hypochlorite is added to the waste to oxidize the sulfite waste, which is then mixed with wastes from an organic chemical plant and neutralized. The combined wastes are then discharged to a sewer. Table 24-5 shows the flow data and pollutant discharges, while Figure 24-1 gives the process flow diagram and shows the sampling points used in screening.

Verification

In verification, two plants were visited, Plants #586 and #987. At Plant #586 the sodium bisulfite wastes are combined with many other process wastes and all treated together. Figure 24-2 shows the flowsheet and the points sampled. Table 24-6 gives the pollutant emissions and flow data for the waste streams. The filter wash is the main process waste at Plant #987. This waste is neutralized with caustic soda to pH 9 - 10 to convert the bisulfite waste to sulfite. The sulfite is then oxidized with air to sulfate. The treated waste, including solids, is discharged to a river. Table 24-7 shows the pollutant emissions and flow data for the waste streams sampled. Figure 24-3 shows the process flow diagram and sampling points at Plant #987.

Toxic Pollutant Analytical Results

The following table is a tabulation of the toxic pollutants identified at detectable concentrations in the raw process waste during screening and verification. The concentrations presented under verification represent the highest observed in the raw process waste during

TABLE 24-3. WATER USAGE IN THE SODIUM BISULFITE SUBCATEGORY

Plant	Direct Contact Process (m ³ /kkg)	Noncontact Cooling (m ³ /kkg)	Maintenance Washdowns, etc. (m ³ /kkg)
# 282	0.14	3.85	1.00
# 586	NA	NA	NA
# 987	1.15	0	0.38

NA = Not Available

TABLE 24-4. WASTE WATER FLOW AT PLANTS #987 AND #282
FOR SODIUM BISULFITE SUBCATEGORY

SUBCATEGORY		SODIUM BISULFITE		
Source	Flow Rate Per Unit of Production(m ³ /kkg) ⁽¹⁾			
	#987A	#987B	#282	
Direct Process ⁽³⁾ Contact	0.018	0.018	0.14	
Indirect Process Contact	1.50	1.17	0.030	
Miscellaneous Washdown	0.31	0.42	1.00 ⁽²⁾	
Total	1.83	1.61	1.17	
Average	1.50			

(1) - Plant #987 contains two separate facilities labeled A and B for the purpose of comparison.

(2) - Includes steam condensate which is currently treated prior to discharge.

(3) - Mother liquor filter wash.

TABLE 24-5. FLOW AND POLLUTANT LOAD DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #282 PRODUCING SODIUM BISULFITE⁽¹⁾

Waste Stream	Flow (m ³ /kkg)	TSS (kg/kkg)	COD (kg/kkg)
Untreated waste	2.67	UTD ⁽²⁾	4.04
Treated waste	2.67	0.424	2.61

(1) - Data based on screening sampling which involves one 72 hour composite sample.

(2) - Unable to determine.

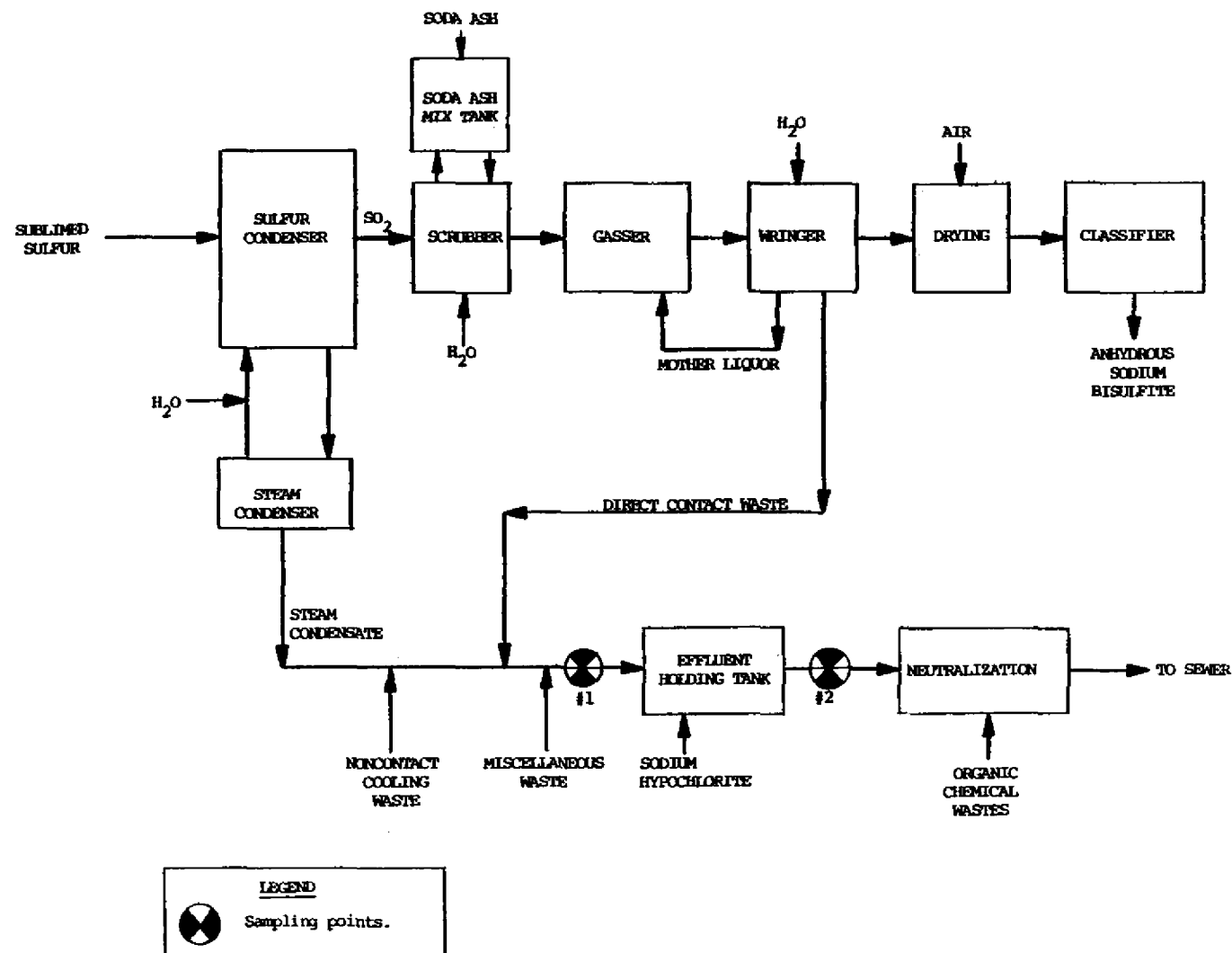


Figure 24-1. General process flow diagram at plant #282 showing the sampling points. Sodium bisulfite manufacture.

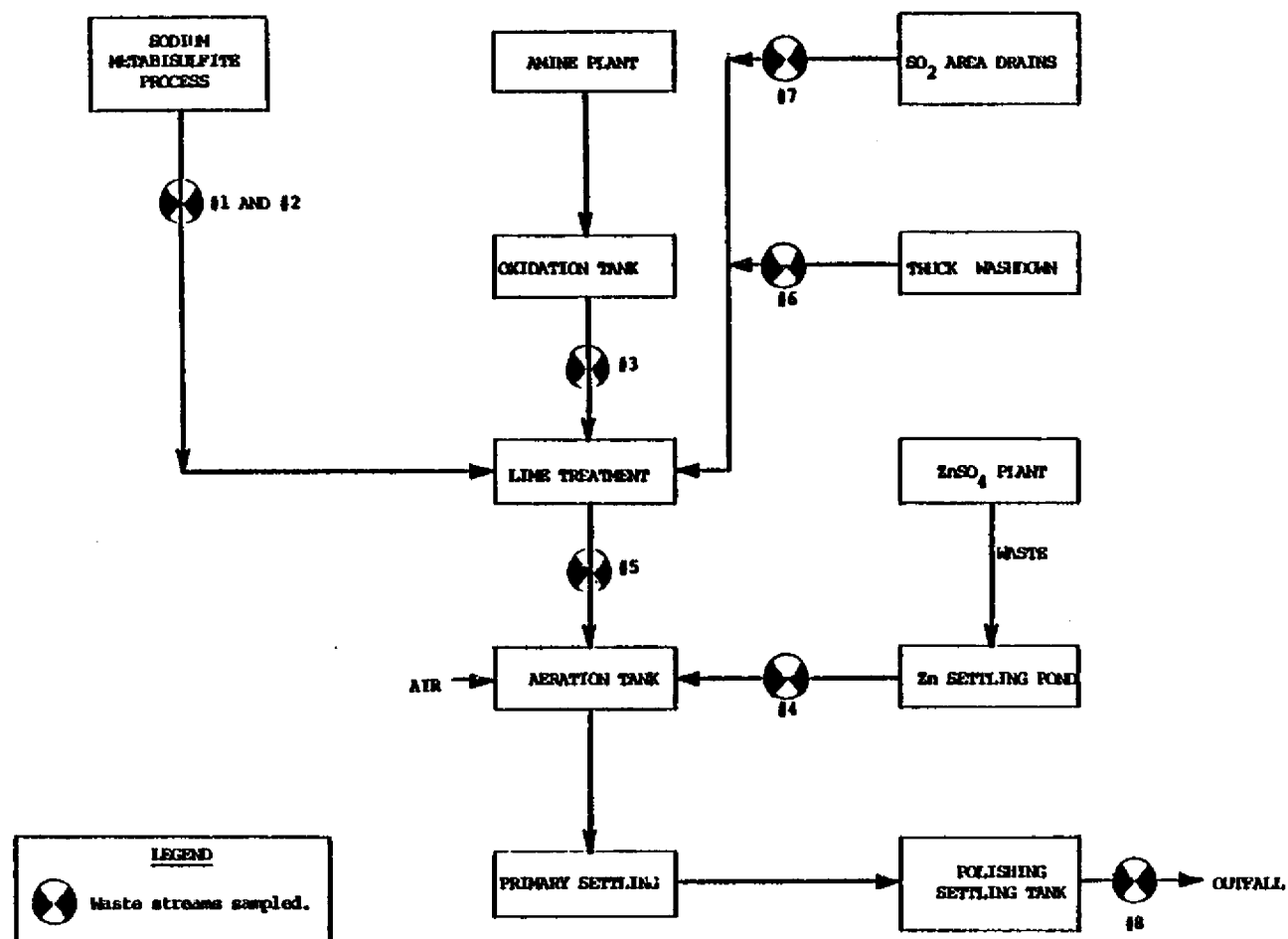


Figure 24-2. General flow diagram at plant #586 showing the sampling points. Sodium bisulfite manufacture.

TABLE 24-6. FLOW AND POLLUTANT LOAD DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #586⁽¹⁾

Stream Number	Waste Stream Description	Flow (m ³ /kkg)	TSS (kg/kkg)	COD (kg/kkg)
1	MBS Sump #1	9.68 ⁽²⁾	0.19	1.1
2	MBS Sump #2	9.68 ⁽²⁾	0.051	0.46
	Total loads (1,2)	19.4	0.24	1.6
3	Amine Oxidation Pond	2.77 ⁽³⁾	2.4	2.3
4	ZnSO ₄ Pond Effluent	78.5 ⁽³⁾	12	0.76
5	Lime Treatment Effluent	110 ⁽³⁾	11	29
6	Truck Washdown	0.134 ⁽³⁾	0.012	0.098
7	SO ₂ Wastes	85.9 ⁽³⁾	2.0	53
8	Treated Effluent	188 ⁽⁴⁾	4.3	22
	Total loads (1,2,3,4,6,7)	187	17	57

- (1) - Data based on verification sampling which involves three 24 hour composite samples.
- (2) - Includes noncontact process water that does not contribute to the pollutant load.
- (3) - Raw process waste flows that are not directly related to the sodium bisulfite industry, but are currently treated in combination with raw process waste that is related.
- (4) - Treated effluent from combined treatment of a number of different raw process waste streams not all related to sodium sulfite production.

TABLE 24-7. FLOW AND POLLUTANT LOAD DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #987(1)

Stream Number	Waste Stream Description	Flow (m ³ /kkg)	TSS (kg/kkg)	COD (kg/kkg)
1	No. 1 Filter Wash	0.055	0.11	1.4
2	Floor wash, spill, etc.	0.013	0.046	0.30
3	No. 2 Filter Wash	0.041	0.0052	0.91
4	Raw Process Waste (Streams 1+2+3)	0.11	0.32	3.5
5	54 Hour Aeration	0.14	0.38	1.2
6	Treated Effluent	0.14	0.0031	1.0

(1) - Data based on verification sampling which involves three 24-hour composite samples.

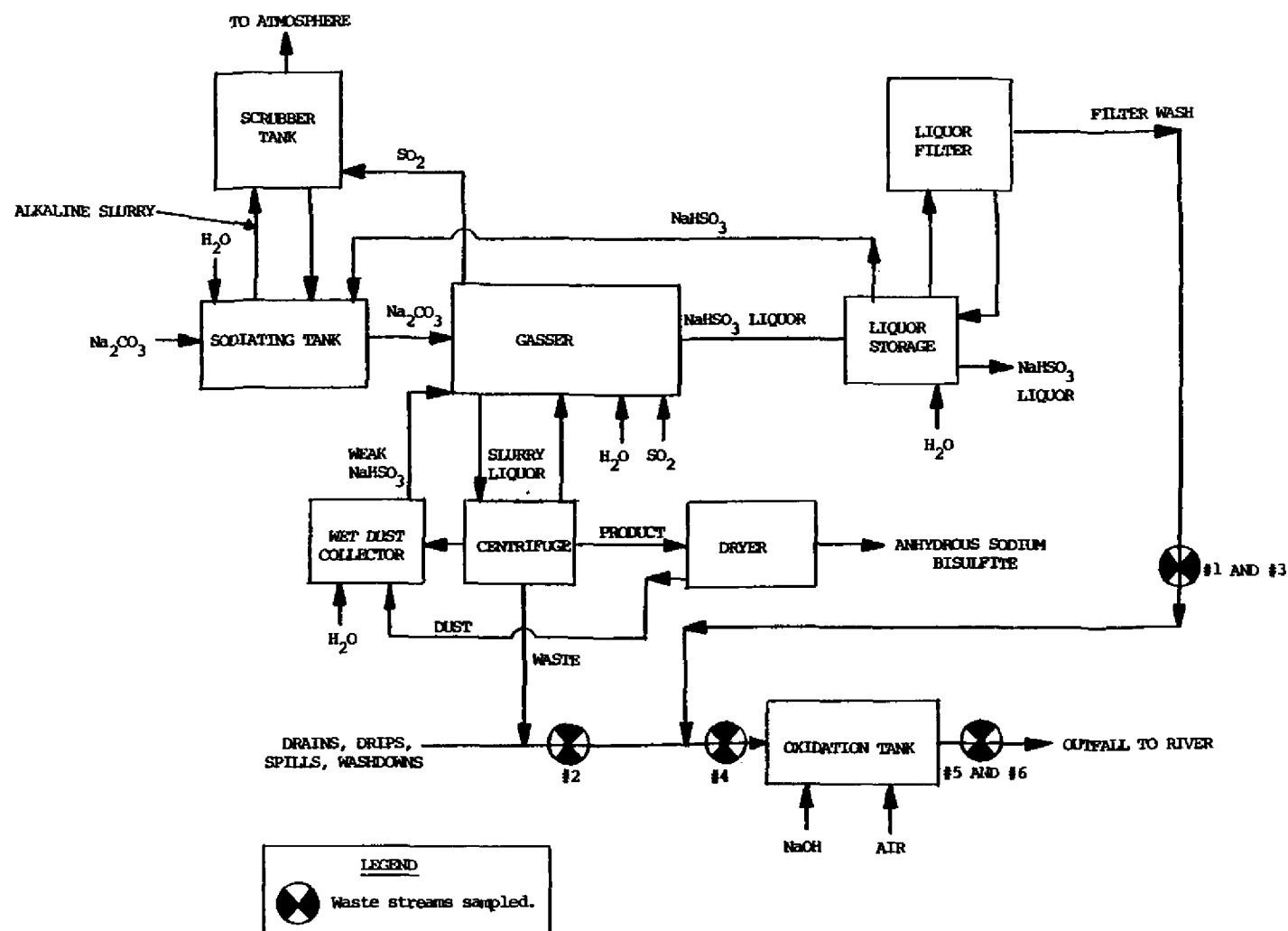


Figure 24-3. General process flow diagram at plant #987 showing the sampling points. Sodium bisulfite manufacture.

sampling. No organic toxic pollutants were found at detectable levels.

Maximum Raw Waste Concentration Observed
($\mu\text{g/l}$)

<u>Pollutant</u>	<u>Screening Plant #282</u>	<u>Verification Plant #586 and #987</u>
Arsenic	12	67
Copper	380	930
Zinc	2500	3600
Cadmium	6	41
Chromium	0	3400
Antimony	30	650
Lead	8	1100
Mercury	3	17
Nickel	250	460
Silver	2	15
Thallium	8	8

Section 5 of this report describes the methodology of the screening and verification sampling program. In the Sodium Bisulfite subcategory a total of seven days of sampling were conducted at Plants #282, #586, and #987. Sixteen different sampling points were identified for the various waste streams at these three plants. The evaluation of toxic metal content of these waste streams was based on 429 analytical data points and an additional 516 points for the toxic organic pollutants sampled during screening.

The daily raw waste loads were calculated from the waste stream flow rates measured or estimated at the time of sampling and the measured pollutant concentration.

That is,

$$\text{Daily loading (as kg of pollutant per day)} = \frac{(C)(Q)}{1000}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: $\text{kg/m}^3 = 1000 \text{ mg/l}$), and

Q is the waste steam flow rate expressed in units of m^3/day . (m^3 , a cubic meter, is equal to 264.2 U.S. gallons).

Similarly, the unit loadings were calculated from the reported sodium bisulfite production rate, the waste stream flow rate, and the measured pollutant concentration.

$$\text{Unit loading (as kg of pollutant per kkg of NaHSO}_3\text{)} = \frac{(C)(Q)}{1000P}$$

where C and Q are the same as described above, and P is the sodium bisulfite production rate expressed in units of kkg/day. (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs.)

Table 24-8 presents the toxic pollutant unit loading and concentration at the three plants sampled. Each concentration represents the average of three composite samples for verification and a single composite sample during screening.

In Table 24-9, the toxic pollutant raw waste data are presented as the minimum, average, and maximum unit loadings based on the results summarized for each plant in Table 24-9. The average unit loading is based on the average obtained at the three plants sampled.

Based on the total annual production of this subcategory and the average waste load generated per unit product, the estimated toxic pollutant raw waste loads generated each year for this subcategory are as follows:

Total Annual Pollutant Load

<u>Pollutant</u>	<u>Raw Waste Load (kg/year)</u>
Antimony	5.0
Cadmium	1.0
Chromium	1100.0
Copper	45
Lead	9.0
Mercury	0.60
Nickel	30
Zinc	520
Silver	6.2
Arsenic	2.3
Thallium	22

Table 24-10 presents the average toxic pollutant concentration observed in the treated effluent during verification sampling.

Pollution Abatement Options

Toxic Pollutants of Concern

It is reported that some sources of sodium carbonate contain zinc and other trace metals in measurable amounts. The screening and verification sampling program revealed zinc, chromium, copper, lead, nickel, and antimony were at significant concentration levels which may require regulation. Zinc may enter the waste stream by corrosion of galvanized metals by coproduct operations or from nonprocess zinc compounds used by the industry. Cadmium, arsenic, thallium, mercury, and silver though detected in the raw waste are not at treatable

TABLE 24-8. TOXIC POLLUTANT RAW WASTE LOADS

SUBCATEGORY		SODIUM BISULFITE				
POLLUTANT	PLANT AND SAMPLING PHASE					
	Screening ⁽¹⁾ #282		Verification ⁽²⁾			
			#987		#586	
	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)
Arsenic	0.012	0.000030	0.067	0.000010	0.0020	0.000030
Copper	0.38	0.0010	0.74	0.000070	0.018	0.00030
Zinc	2.5	0.0070	2.4	0.00020	0.52	0.0088
Cadmium	0.0060	0.000017	0.040	0.000004	0.00050	0.000010
Chromium			2.6	0.00030	1.3	0.022
Lead	0.0025	0.000007	0.60	0.000070	0.012	0.00020
Mercury	0.0030	0.000007	0.012	0.000001	0.00060	0.000010
Nickel	0.25	0.00070	0.46	0.000050	0.010	0.00017
Antimony	0.030	0.000070	0.65	0.000070	0.0050	0.000080
Thallium	0.0080	0.000020	<0.050	<0.000004	0.025	0.00042
Silver	0.0060	0.000017	<0.030	<0.000003	0.010	0.00017

(1) - One 72-hour composite sample

(2) - Average of three 24-hour composite samples

TABLE 24-9. SUMMARY OF RAW WASTE LOADINGS FOUND IN SCREENING AND VERIFICATION SAMPLING

SUBCATEGORY SODIUM BISULFITE						
Pollutant	Loading Range (kg/day)		Unit Loading (kg/kg)			No. of Plants
	Minimum	Maximum	Minimum	Average	Maximum	
<u>Priority</u>						
Antimony	0.00045	0.0041	0.000007	0.000052	0.000080	2
Cadmium	0.00023	0.00041	0.000004	0.000010	0.000017	3
Chromium	0.018	1.1	0.00030	0.011	0.022	2
Copper	0.0050	0.015	0.000070	0.00046	0.0010	2
Lead	0.000091	0.0095	0.000007	0.000092	0.00020	3
Mercury	0.000091	0.00045	0.000001	0.000006	0.000010	2
Nickel	0.0032	0.0091	0.000050	0.00031	0.00070	3
Zinc	0.016	0.42	0.00020	0.0053	0.0088	3
Silver	<0.00020	0.0080	<0.000003	0.000060	0.00017	3
Arsenic	0.00040	0.0014	0.000010	0.000023	0.000030	3
Thallium	<0.000052	0.020	<0.000004	0.00015	0.00042	3
<u>Conventional</u>						
Total Suspended Solids (TSS)						
	3.20	25.4	0.21	0.27	0.38	3
Chemical Oxygen Demand (COD)						
	54.4	234	1.33	2.94	4.04	3

(1) - Average of values obtained in Table 24-8 for those plants where the toxic pollutant was detected.

TABLE 24-10. TOXIC POLLUTANT CONCENTRATIONS OBSERVED IN TREATED EFFLUENT DURING VERIFICATION SAMPLING

Pollutant	#987 (mg/l)	Plant	#586 (mg/l)
Arsenic	ND		ND
Copper	0.27		ND
Zinc	0.010		ND
Cadmium	ND		ND
Chromium	0.11		ND
Lead	0.15		ND
Mercury	ND		0.010
Nickel	ND		0.050
Antimony	ND		0.020
Thallium	ND		ND
Silver	ND		ND

ND - Not Detected

concentrations and thus are not considered toxic pollutants of concern.

Prevailing Control and Treatment Practices

Plant #987 adds 50 percent caustic solution to the oxidation tank to raise the pH to approximately 9.5 and blows air through while mechanically agitating. The waste is discharged to a river following a 17-hour retention period.

Plant #282 uses caustic soda or sodium carbonate for pH control followed by sodium hypochlorite addition to oxidize sulfite and other reduced sulfur species. The waste is then neutralized and discharged to a County sewer.

Plant #586 mixes the bisulfite waste, amine plant waste, and truck wash waste. Lime is added to the combined wastes which are then passed through an aeration tank with eight-hour's retention time where zinc sulfate production wastes are added. The treated waste goes through primary and secondary settling before final discharge.

Advanced Treatment Technologies

Toxic metals may be precipitated at alkaline pH values, when reacted with sulfides in various forms, in some cases by ion exchange resins, and the Xanthate process. Sulfide precipitation from cleared solutions could be used to provide additional removal of zinc, lead, nickel, copper, and to a lesser extent, antimony.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1 (BPT/BAT)

Neutralization with caustic soda to a pH of 9.5 followed by aeration and settling was chosen as the most cost-effective method of lowering the COD associated with the primary pollutant, sodium bisulfite. Toxic metals in the waste form metal hydroxide precipitates which are removed from the wastewater by settling. The flow diagram is shown in Figure 24-4.

B. Level 2

Aerated effluent from the BPT system is chlorinated to complete COD removal, and is then filtered to remove finely divided suspended matter carried through or produced in the BPT system, particularly if toxic metals are present in the incoming wastes. The flow diagram is shown in Figure 24-5. Cost estimates for this level of treatment are given in the proposed Development Document (60).

C. Level 3

Ferrous sulfide is applied ahead of the Level 2 filter, to precipitate any residual metals by the more effective sulfide process. The flow diagram is shown in Figure 24-6. Cost estimates for this level of treatment are given in the proposed Development Document (60).

Equipment for Different Treatment Levels

A. Equipment Functions

In Level 1, the raw wastes are received in one of two similar holding/reaction tanks (sized for one day's flow), recirculated and automatically adjusted to pH 9.5. During the second working day, while the contents of the first tank are jet aerated and allowed to settle, the daily raw wastes are received, recirculated and pH adjusted in the second tank. At Level 1, the aerated and settled effluent is discharged directly from the alternate holding/reaction tanks. Sludge is drawn off the tanks at suitable intervals and disposed of. At Levels 2 and 3, the aerated and settled effluent is pumped through a multi-media filter on a schedule which will leave its tank empty and ready for the next working day's influent. At Levels 2 and 3, supplemental chlorination equipment is provided. At Level 3, residual heavy metals which may have escaped prior treatment, or may have been released by pH change during chlorination, will be converted to metallic sulfides by addition of ferrous sulfide ahead of the Level 2 filter. Should COD and toxic metals be very low in specific instances, the chlorination and ferrous sulfide steps could be eliminated.

B. Chemicals and Handling

Caustic soda solution, chlorine, and ferrous sulfide are used in the treatment processes. Caustic soda and chlorine are common industrial chemicals which are fed by conventional equipment designed to minimize leaks, spills, and hazards to personnel. Ferrous sulfide is prepared by mixing ferrous sulfate with sodium bisulfide under well ventilated conditions. When the usual precautions are taken in the proper handling of corrosive and toxic chemicals, there should be no special problems in applying the proposed technologies.

C. Separation and Removal of Solids

No solids are formed in the proposed treatment, with the possible exception of small amounts of metal hydroxides and sulfides if metals should be present in the raw wastes. In that event, the precipitated solids, which are formed in the holding/reaction tank or which are returned to the holding/reaction tank during backwashing, will settle in the hopper bottom of the reaction

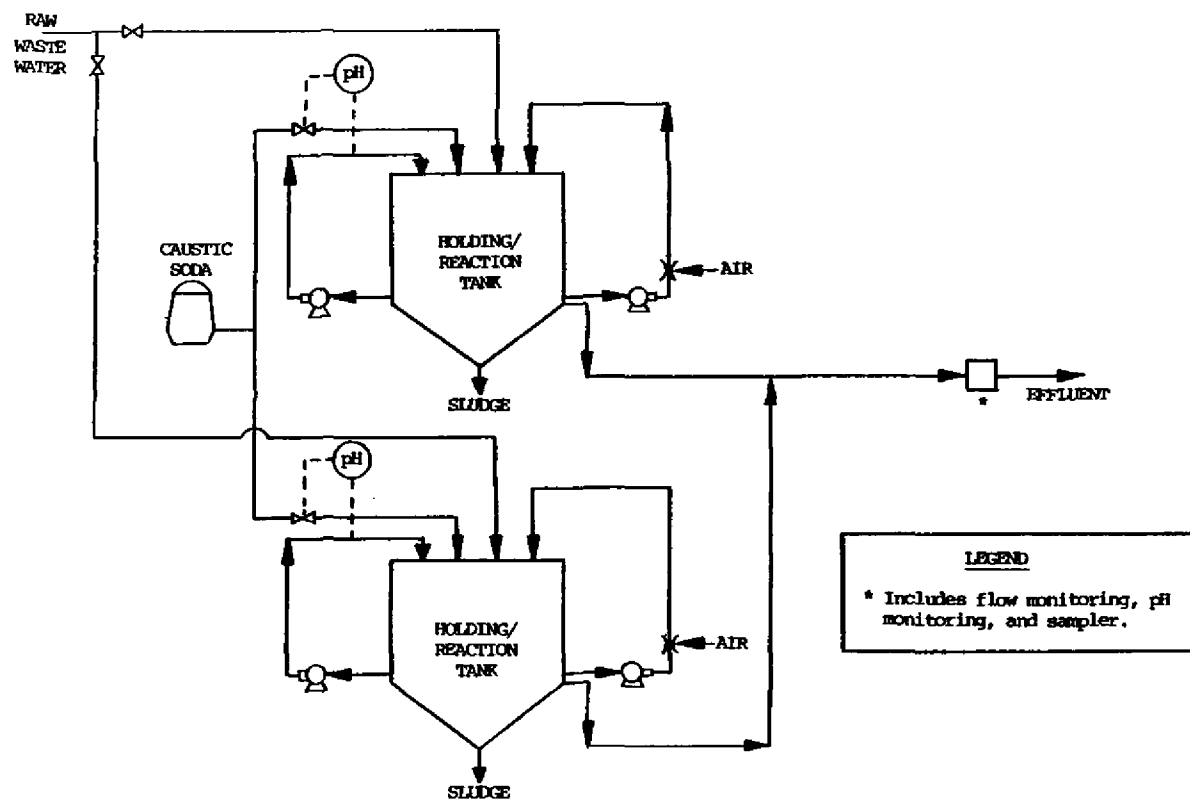


Figure 24-4. Level 1 waste treatment for the sodium bisulfite subcategory -- batch process.

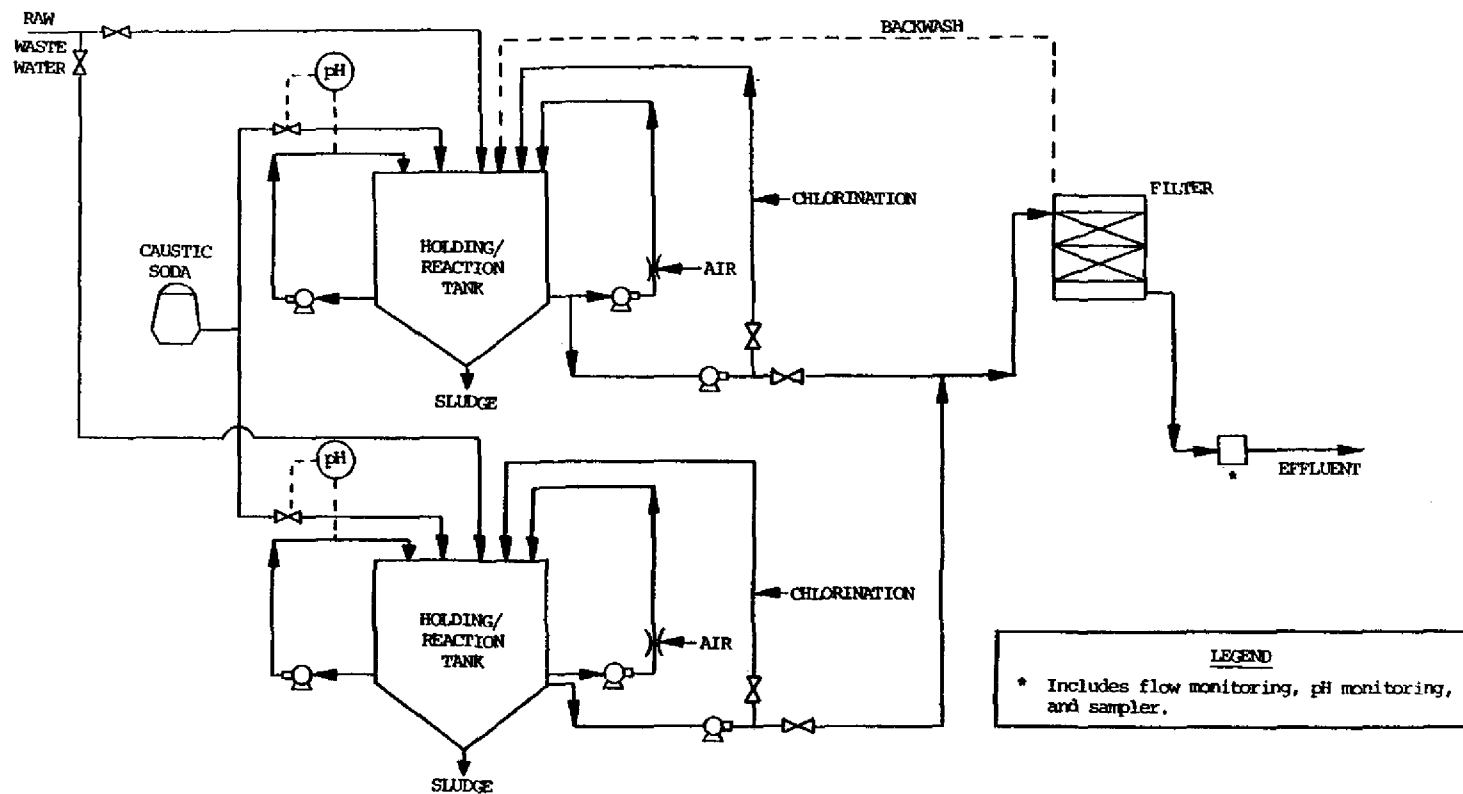


Figure 24-5. Level 2 waste water treatment for the sodium bisulfite subcategory -- batch process.

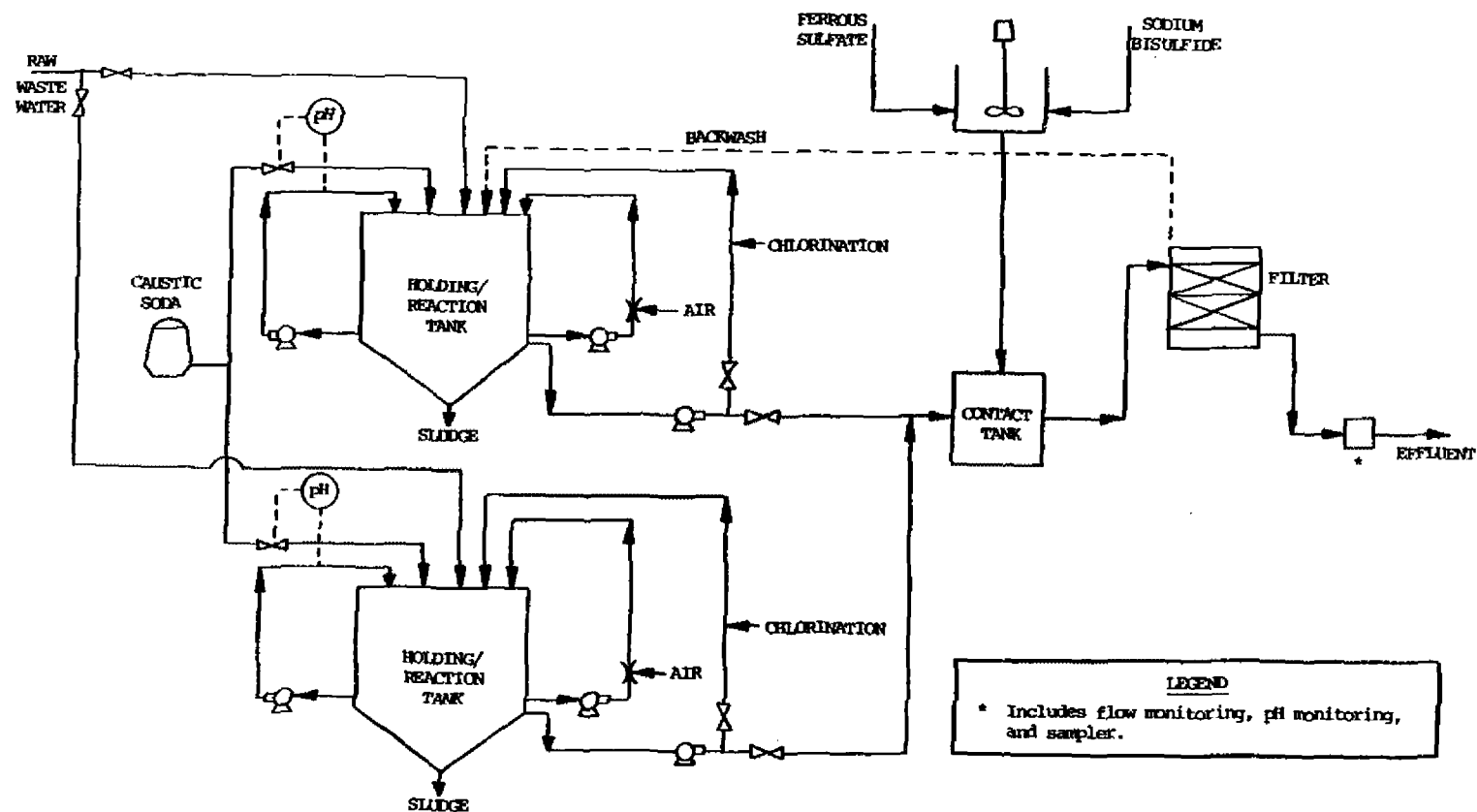


Figure 24-6. Level 3 waste water treatment for the sodium bisulfite subcategory -- batch process.

tank. As necessary, these solids can be drawn off and disposed of in an appropriate manner.

D. Monitoring Requirements

Internal process monitoring will be done with standard field equipment measuring pH, dissolved oxygen, and chlorine. If metals are present in the raw materials a periodic laboratory analysis for metals should be made on the final effluent. Monitoring for dissolved sulfide should not be necessary, since the ferrous sulfide applied in Level 3 is rather insoluble.

Treatment Cost Estimates

General Discussion

To prepare treatment cost estimates, a model plant concept was developed for a single level of technology as follows:

A. Wastewater Flow

The sources of wastewater include wet air scrubbers, filter backwash, floor washings, leaks, and spills. The unit flow rates ranged from 1.8 m³/kkg to 1.2 m³/kkg of product at the three facilities for which information was available. The average was approximately 1.5 m³/kkg and this was used for the model plant (Table 24-4).

B. Production

Sodium bisulfite production ranges from 4770 kkg/yr to 31,800 kkg/yr at the three plants for which data was available. The average production is 17,800 kkg/yr. The production rates at the three plants were used as the model plant production rates. The operational mode is continuous and is assumed to run 350 days per year.

C. Solid Wastes

In the production of sodium bisulfite and process waste treatment there is little solid waste generation, although precipitation of metal hydroxides may result in small quantities of solids requiring disposal. The model plants assumed no significant solid waste production.

D. Treatment Chemicals

Caustic soda is needed to adjust the pH to 9.5. The only other requirement is air to oxidize the waste. For the model plant, the caustic soda dosage was assumed to be 0.195 kg/kkg.

Cost Estimates

The cost estimates of three models having different production level are presented in Tables 24-11, 24-12 and 24-13.

Table 24-14 gives a summary of the unit cost distribution between amortization, operation and maintenance. Cost components at various production levels are also shown.

Basis for Regulations

Evaluation of BPT Treatment Practices

All seven plants in this subcategory have installed BPT or equivalent technology. Plant performance was estimated on the basis of verification sampling results for Plant #987. Plant #282 was excluded from the evaluation since the treatment technology applied at the particular point of treated effluent sampling does not represent the appropriate level of treatment. Plant #586 was excluded from consideration, since the combined treatment of the sodium bisulfite process waste with wastes from other unrelated processes, has made an evaluation of the plant performance data too speculative.

Table 24-15 is a comparison of the maximum raw waste concentrations from screening and verification sampling with treatability data from Plant #987, literature-based estimates, and industrial wastewater treatment system performance. The data used in this table are from the screening and verification results, Table 8-11, Table 8-12, Table 8-13 and the Treatability Study (61).

Basis for BPT Effluent Limitations

A. Technology Basis

The Agency is setting limitations based upon hydroxide precipitation of toxic metals with caustic soda plus batch aeration and settling for BPT. The flow schematic for BPT is shown in Figure 24-4 in Section 24 as Level 1 treatment. The Agency has selected Level 1 treatment as the basis for BPT because it reflects current industry practice.

B. Flow Basis

The basis of flow for BPT limitations is estimated from data provided in the Section 308-Questionnaires for two of the three complete plant responses, including Plant #987 and #282. Plant #586 was omitted in view of the lack of adequate information to identify the wastewater streams contributed by the sodium bisulfite process alone.

The three major raw process wastewater streams include direct and indirect process contact waste and miscellaneous floor and tank washdown wastewater.

TABLE 24-11. MODEL PLANT TREATMENT COSTS

Subcategory	Sodium Bisulfite	
Production	4,770 metric tons per year	
		($\text{\$}$)
A. INVESTMENT COST	BPT	BAT ^a
Site development	3,000	0
Equipment	70,000	0
Monitoring equipment	20,000	0
Subtotal	93,000	0
Contractor's O & P ^b	13,950	0
Subtotal	106,950	0
Engineering	21,390	0
Subtotal	128,340	0
Contingencies	12,834	0
Subtotal	141,174	0
Land	3,000	0
TOTAL INVESTMENT COST	144,174	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	0
Energy	2,100	0
Chemicals	2,900	0
Maintenance	14,117	0
Taxes and insurance	4,325	0
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	94,443	0
C. AMORTIZATION OF INVESTMENT COST	22,969	0
TOTAL ANNUAL COST	117,412	0

^a Represents the incremental cost above that for BPT treatment

^b Overhead and Profit

TABLE 24-12. MODEL PLANT TREATMENT COSTS

Subcategory Sodium Bisulfite Production 16,900 metric tons per year		(\$)	
A. INVESTMENT COST		BPT	BAT ^a
Site development	3,000		0
Equipment	117,000		0
Monitoring equipment	20,000		0
Subtotal	140,000		0
Contractor's O & P ^b	21,000		0
Subtotal	161,000		0
Engineering	32,200		0
Subtotal	193,200		0
Contingencies	19,320		0
Subtotal	212,520		0
Land	3,000		0
TOTAL INVESTMENT COST	215,520		0
B. OPERATION AND MAINTENANCE COST			
Labor and supervision	56,000		0
Energy	2,900		0
Chemicals	9,800		0
Maintenance	21,252		0
Taxes and insurance	6,466		0
Residual waste disposal	0		0
Monitoring, analysis and reporting	15,000		0
TOTAL OPERATION AND MAINTENANCE COST	111,418		0
C. AMORTIZATION OF INVESTMENT COST	34,577		0
TOTAL ANNUAL COST	145,995		0

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 24-13. MODEL PLANT TREATMENT COSTS

Subcategory	Sodium Bisulfite	
Production	31,800 metric tons per year	
	(\$)	
A. INVESTMENT COST	BPT	BAT ^a
Site development	6,000	0
Equipment	195,000	0
Monitoring equipment	20,000	0
Subtotal	221,000	0
Contractor's O & P ^b	33,150	0
Subtotal	254,150	0
Engineering	50,830	0
Subtotal	304,980	0
Contingencies	30,498	0
Subtotal	335,478	0
Land	6,000	0
TOTAL INVESTMENT COST	341,478	0
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	56,000	0
Energy	3,800	0
Chemicals	19,000	0
Maintenance	33,548	0
Taxes and insurance	10,244	0
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	0
TOTAL OPERATION AND MAINTENANCE COST	137,592	0
C. AMORTIZATION OF INVESTMENT COST	54,582	0
TOTAL ANNUAL COST	192,174	0

^a Represents the incremental cost above that for BPT treatment
^b Overhead and Profit

TABLE 24-14 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Sodium Bisulfite

Annual Treatment Costs (\$/kkg)

LEVEL OF TREATMENT

COST ITEM	PRODUCTION (kkg/yr)	BPT
Annual Operation and Maintenance	4,770	19.80
	16,900	6.59
	31,800	4.33
Annual Amortization	4,770	4.82
	16,900	2.05
	31,800	1.72
Total Annual Cost	4,770	24.61
	16,900	8.64
	31,800	6.04

TABLE 24-15. COMPARISON OF MAXIMUM RAW WASTE CONCENTRATIONS WITH TREATABILITY

Pollutant	Maximum Avg. Raw Waste Concentration During Screening and Verification (mg/l)	Treated Effluent Concentration From Plant #987 Verification Sampling (mg/l)	Literature-Based Treatability Estimates from Table 8-11 for Lime/Settling (mg/l)	Industrial Waste Water Treatment System Performance for Lime/Settling (mg/l)
TSS	2,250	22	--	38 ⁽¹⁾
COD	24,700	7,300	--	450 ⁽²⁾
Arsenic	0.067	ND	0.50	0.080 ⁽³⁾
Copper	0.74	0.27	0.50	0.40 ⁽⁴⁾
Zinc	2.5	0.010	0.50	0.80 ⁽⁴⁾
Cadmium	0.0060	ND	0.10	0.10 ⁽⁴⁾
Chromium	2.6	0.11	0.10	0.32 ⁽⁴⁾
Lead	0.60	0.15	0.30	0.15 ⁽⁴⁾
Mercury	0.012	ND	--	--
Nickel	0.46	ND	0.20	0.40 ⁽⁴⁾
Antimony	0.65	ND	0.80	0.18 ⁽³⁾
Thallium	0.050	ND	0.20	--
Silver	0.030	ND	0.40	--

ND = Not Detected

- (1) Data from Treatability Study (61) on lime/settling in nickel sulfate and sodium dichromate industries.
- (2) Average of extended aeration tests from Treatability Study (61).
- (3) Data from Table 8-12.
- (4) Estimated achievable long-term average concentrations from Table 8-13.

Table 24-4 summarizes the unit flows reported for each of the three sources at each facility. Plant #987 has two facilities which manufacture sodium bisulfite and are designated as A and B. The basis of model plant flow for the sodium bisulfite industry is estimated as the average total raw wastewater flow for the three plants, and is used to estimate pollutant discharge loadings for the purpose of regulation. The average total flow for the three facilities considered is 1.5 m³/kgg of product.

C. Selection Basis for Pollutants to be Regulated

The selection of pollutants for which specific numerical effluent limitations are promulgated was based on an evaluation of raw waste data from the screening and verification sampling program. Pollutant data from the plant sampled during screening was used to determine the need for verification sampling. Verification sampling at Plants #586 and #987 provided additional pollutant raw waste concentration data needed to assess the performance of treatment technology.

Results of the screening and verification sampling are tabulated in Table 24-15 for the raw process waste streams.

Toxic pollutants are listed based on their presence, during sampling, at detectable concentration levels. Pollutants from this list were considered as candidates for regulation if their concentration appeared at least to equal or exceed the lowest level estimated as treatable using any available technology appropriate for their removal (Table 8-11).

The relative significance of the candidate toxic pollutants was estimated based on the total annual raw waste load for each pollutant which appears in a Table above. The total annual load is based on the average concentration observed during screening and verification, which is tabulated in Table 24-9, in addition to the estimated annual production of 98,000 kkg of product for the industry.

On the basis of concentration and total annual raw waste loads determined during sampling, COD, TSS, chromium, zinc, copper, nickel, lead, and antimony have been identified at significant concentration levels in the raw waste stream and are candidates for regulation. These pollutants are listed in order of their relative significance with regard to decreasing raw waste concentration.

In view of the treatment technology currently practiced and the related nature of the candidate toxic pollutants (see Section 8), control of the more significant toxic pollutants will ensure adequate control of those metals which may occasionally appear at treatable levels. Therefore, only chromium and zinc will have effluent limitations. Concentration values for the other metals are intended for guidance only.

The Agency conducted treatability studies (61) using Level 1 (BPT) technology (without settling) on typical raw wastewater from the sodium bisulfite industry. In the tests the average COD level was reduced from 950 mg/l to 450 mg/l. Use of the standard iodide-iodate test for sulfite indicated the tests reduced the average iodate demand as oxygen from 800 mg/l to 25 mg/l. The Agency is evaluating the standard iodide-iodate test for sulfite for possible application in effluent monitoring but will continue to set effluent limitations using the conventional COD test.

D. Basis of Pollutant Limitations

BPT limitations are presented in Table 24-16.

1. Conventional and Nonconventional Parameters

a. pH

The treated effluent is to be controlled within the range of 6.0 to 9.0. This limitation is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS

The BPT limitations for TSS are based on data from the Treatability Study (61) using lime/settling from the nickel sulfate and sodium dichromate industries. The long-term average is 38 mg/l. The daily and 30-day variability factors are 5.6 and 1.4, respectively.

The 24-hour maximum concentration is:

$$(38 \text{ mg/l}) (5.6) = 210 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(38 \text{ mg/l}) (1.4) = 53 \text{ mg/l}$$

The load limitations for TSS (kg/kkg) are calculated based on the unit flow rate of 1.5 m³/kkg, thus:

$$(210 \text{ mg/l}) (1.5 \text{ m}^3/\text{kkg}) \frac{(\text{kg/m}^3)}{(1000 \text{ mg/l})} = 0.32 \text{ kg/kkg}$$

for the 24-hour maximum limit. The maximum 30-day average is calculated similarly, i.e.:

$$(53 \text{ mg/l}) (1.5 \text{ m}^3/\text{kkg}) \frac{(\text{kg/m}^3)}{(1000 \text{ mg/l})} = 0.080 \text{ kg/kkg}$$

TABLE 24-16. EFFLUENT LIMITATIONS
SODIUM BISULFITE
Best Practicable Control Technology Currently Available
Wastewater Flow: 1.5 m³/kkq

Pollutant	Subcategory Performance (mg/l)	Daily Variability Factor 30-day Variability Factor	Concentration Basis (mg/l)		Effluent Limit (kg/kkg)	
			Max. 30-day Avg.	24-hr. Max.	Max. 30-day Avg.	24-hr. Max.
<u>Conventional/ Nonconventional Pollutants:</u>						
Total Suspended Solids, TSS ⁽⁶⁾	38 ⁽¹⁾	5.6/1.4	53	210	0.080	0.32
Chemical Oxygen Demand, COD ⁽⁷⁾	450 ⁽²⁾	5.6/1.4	630	2500	0.95	3.8
<u>Toxic Pollutants:</u>						
Chromium ^{(7),(9)}	0.32 ⁽³⁾	4.2/1.3	0.42	1.3	0.00063	0.0020
Zinc ⁽⁷⁾	0.80 ⁽³⁾	4.2/1.3	1.0	3.4	0.0015	0.0051
Copper	0.40 ⁽³⁾	4.2/1.3	0.52	1.7	--(8)	--(8)
Lead	0.15 ⁽³⁾	4.2/1.3	0.20	0.63	--(8)	--(8)
Nickel	0.40 ⁽³⁾	4.2/1.3	0.52	1.7	--(8)	--(8)
Antimony	0.80 ⁽⁵⁾	4.2/1.3	1.0	3.4	--(8)	--(8)

- (1) Data from Treatability Study (61) on lime/settling in nickel sulfate and sodium dichromate industries.
- (2) Based on data from Treatability Study (61).
- (3) Based on estimated achievable long-term average concentrations from Table 8-11.
- (4) Maximum untreated effluent concentration from screening and verification sampling data.
- (5) Based on lower limit of literature-based treatability estimate from Table 8-11.
- (6) Also applicable to NSPS regulations.
- (7) Also applicable to NSPS, and BAT regulations.
- (8) No effluent limitation.
- (9) Also applicable to PSNS regulations.

c. COD

The BPT limitations for COD are based on data from the Treatability Study (61) on the aeration of sodium bisulfite waste. The average concentration of the treated effluent from the tests, 450 mg/l, is used as a long-term average. The daily and 30-day average variability factors used for TSS above are employed again.

The 24-hour maximum concentration is:

$$(450 \text{ mg/l}) (5.6) = 2500 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(450 \text{ mg/l}) (1.4) = 630 \text{ mg/l}$$

The load limitations for COD (kg/kkg) are calculated based on the unit flow rate of 1.5 m³/kkg, thus:

$$(2500 \text{ mg/l}) (1.5 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 3.8 \text{ kg/kkg}$$

for the 24-hour maximum limit. The 30-day average limit is calculated similarly, i.e.:

$$(630 \text{ mg/l}) (1.5 \text{ m}^3/\text{kkg}) \left(\frac{\text{kg/m}^3}{1000 \text{ mg/l}} \right) = 0.95 \text{ kg/kkg}$$

2. Toxic Pollutants

No long-term sodium bisulfite industry data is available to establish limitations and guidelines for the selected toxic pollutants. The effluent limitations and guidelines are based on four information sources including: (1) estimated achievable long-term average concentrations from Table 8-13, (2) industrial wastewater treatment system performance data from Table 8-12, (3) screening and verification data, and (4) literature-based treatability estimates.

a. Chromium

The limitations for chromium are based on the estimated achievable long-term average concentration of 0.32 mg/l from Table 8-13. The daily and 30-day average variability factors of 4.2 and 1.3, respectively, are obtained from data in the Treatability Study (61) on chromium removal using lime/settling from the chlor-alkali, titanium dioxide, sodium dichromate and chrome pigments industries.

The 24-hour maximum concentration is:

$$(0.32 \text{ mg/l}) (4.2) = 1.3 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.32 \text{ mg/l}) (1.3) = 0.42 \text{ mg/l}$$

The load limitations for chromium (kg/kg) are calculated based on the unit flow rate of $1.5 \text{ m}^3/\text{kg}$, thus:

$$(1.3 \text{ mg/l}) (1.5 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0020 \text{ kg/kg}$$

for the 24-hour maximum limit. The maximum 30-day average is calculated similarly, i.e.:

$$(0.42 \text{ mg/l}) (1.5 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.00063 \text{ kg/kg}$$

b. Zinc

The limitations for zinc are based on the estimated achievable long-term average concentration of 0.80 mg/l from Table 8-13. The daily and 30-day average variability factors used for chromium are employed again.

The 24-hour maximum concentration is:

$$(0.80 \text{ mg/l}) (4.2) = 3.4 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.80 \text{ mg/l}) (1.3) = 1.0 \text{ mg/l}$$

The load limitations for zinc (kg/kg) are calculated based on the unit flow rate of $1.5 \text{ m}^3/\text{kg}$, thus:

$$(3.4 \text{ mg/l}) (1.5 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0051 \text{ kg/kg}$$

for the 24-hour maximum limit. The maximum 30-day average is calculated similarly, i.e.:

$$(1.0 \text{ mg/l}) (1.5 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0015 \text{ kg/kg}$$

c. Copper

The guidance for copper is based on the estimated achievable long-term average concentration of 0.40 mg/l from Table 8-13. The daily and 30-day average variability factors used for chromium are employed again.

The 24-hour maximum concentration is:

$$(0.40 \text{ mg/l}) (4.2) = 1.7 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.40 \text{ mg/l}) (1.3) = 0.52 \text{ mg/l}$$

d. Lead

The guidance for lead is based on the estimated achievable long-term average concentration of 0.15 mg/l from Table 8-13. The daily and 30-day average variability factors used for chromium are employed again.

The 24-hour maximum concentration is:

$$(0.15 \text{ mg/l}) (4.2) = 0.63 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.15 \text{ mg/l}) (1.3) = 0.20 \text{ mg/l}$$

e. Nickel

The guidance for nickel is based on the estimated achievable long-term average concentration of 0.40 mg/l from Table 8-13. The variability factors used for chromium are employed again.

The 24-hour maximum concentration is:

$$(0.40 \text{ mg/l}) (4.2) = 1.7 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.40 \text{ mg/l}) (1.3) = 5.2 \text{ mg/l}$$

f. Antimony

The guidance for antimony is based on the literature-based treatability estimate in Table 8-11 which is higher than the industrial wastewater treatment system performance data from Table 8-12. The

value of 0.80 mg/l for the lime/settling technology is used as a long-term average. The variability factors used for chromium are employed again.

The 24-hour maximum concentration is:

$$(0.80 \text{ mg/l}) (4.2) = 3.4 \text{ mg/l}$$

The maximum 30-day average concentration is:

$$(0.80 \text{ mg/l}) (1.3) = 1.0 \text{ mg/l}$$

Basis for BCT Effluent Limitations

While EPA has not yet proposed or promulgated a revised BCT methodology in response to the American Paper Institute v. EPA decision mentioned in Section 3, EPA is promulgating BCT limitations for this subcategory. These limits are identical to those for BPT. EPA is not promulgating any more stringent limitations since we have identified no technology option which would remove significant additional amounts of conventional pollutants. As BPT is the minimal level of control required by law, no possible application of the BCT cost tests could result in BCT limitations lower than those promulgated in this regulation. Accordingly, there is no need to wait until EPA revises the BCT methodology before promulgating BCT limitations.

Basis for BAT Effluent Limitations

A. The Application of Advanced Level Treatment

The Agency has analyzed the cost effectiveness of the base level systems (BPT) and the various advanced level options for conventional and toxic pollutant removal based on the cost estimates presented in this report and the proposed Development Document (60). The regulations being promulgated for BAT consist of Level 1 or BPT treatment. The removal of additional pollutants by Levels 2 and 3 treatment systems is not sufficient to offset the additional cost to install and operate these advanced treatment systems.

B. Technology Basis

The BAT treatment system is the same as that described above for BPT.

C. Flow Basis

The model plant flow developed for BPT treatment applies also to BAT in the development of the regulations. Therefore the value of 1.5 m³/kgg of product is used for the unit flow.

D. Selection of Pollutants to be Regulated

For the BAT regulations, the Agency is setting the regulation of COD and the same two toxic metals considered for BPT limitations listed in Table 24-16. Concentration values for the other metals are intended for guidance only.

E. Basis of Pollutant Limitations

1. Nonconventional Pollutants

The only nonconventional pollutant is COD in the sodium bisulfite subcategory. Since BAT has been set equal to BPT by the Agency, the limitation is then identical to BPT for COD. Refer to Table 24-16 for the BAT regulation.

2. Toxic Pollutants

The Agency is setting limitations on chromium and zinc which equal those for BPT. See above for the development of these limitations.

Basis for New Source Performance Standards

The NSPS limitations (applicable to pH, TSS, COD and two toxic metals) are set equal to BAT for toxic and nonconventional pollutants and BPT for conventional pollutants. Table 24-16 for the BPT and BAT limitations would be identical in all respects with NSPS limitations. See above for the development of the regulations.

Basis for Pretreatment Standards

Pretreatment standards are necessary because NSPS provides better removal of chromium than is achieved by a well-operated POTW with secondary treatment installed and therefore chromium would pass through a POTW in the absence of pretreatment. Based on the average raw waste loads given in Table 24-9 and the long-term average subcategory performance given in Table 24-16, NSPS treatment reduces COD by 76% and zinc by 77%. A POTW will reduce COD by 80% and zinc by 76% (See Fate of Priority Pollutants in Publicly Owned Treatment Works - Interim Report, EPA-440/1-80-301, October 1980). A POTW therefore achieves a percent removal equal to or greater than that achieved by NSPS for COD and Zinc, and therefore there is no pass through of those two pollutants in this subcategory.

A. Existing Sources

The Agency is excluding this subcategory from Pretreatment Standards for Existing Sources (PSES) under the provisions of paragraph 8(b)(ii) of the Settlement Agreement. The total toxic metal discharge from the one existing indirect discharger to POTW is 120 pounds per year, which is so insignificant as not to justify developing a national standard.

B. New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is promulgating limitations based on NSPS. The pollutant limited is chromium.

SECTION 25

SODIUM HYDROSULFITE (FORMATE PROCESS) INDUSTRY (Excluded)

Summary of Determinations

We proposed BPT, BCT, and BAT limitations and NSPS, PSES, and PSNS for this subcategory. The proposed regulation basically added control of selected toxic metal pollutants to existing treatment practiced in the industry. We have reviewed the basis for the proposed regulation and we concluded that the total current treated discharge load of only 0.42 pounds per day total toxic metals from all plants in the subcategory is too insignificant to justify developing a national regulation. Accordingly, we have excluded this subcategory from national regulation development under paragraph 8(a)(iv) of the Settlement Agreement.

The information presented in the remainder of this Section is provided as guidance for use by permit writers.

Industry Profile

General Description

Most of the sodium hydrosulfite produced in the U.S. is sold in the merchant market. Sodium hydrosulfite is used extensively in dyeing cotton and in the printing industry. It is a powerful reducing agent and is used in wood pulp bleaching, and stripping operations in the food, vegetable oil, and soap industries.

The industry profile data are presented in Table 25-1, while status of regulations are summarized in Table 25-2.

Subcategorization

A detailed summary of factors considered in subcategorization is presented in Section 4. Sodium hydrosulfite is produced by three processes including the Werbs, formate, and zinc processes. The zinc and Werbs processes are deferred to Phase II of the inorganic chemicals regulation development effort. This section concerns the formate process only.

General Process Description and Raw Materials

In the formate process, sodium hydrosulfite is produced by reacting sodium formate solution, sodium hydroxide solution, and liquid sulfur dioxide in the presence of a recycled stream of methanol solvent. The general reaction is:



TABLE 25-1. SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	SODIUM HYDROSULFITE (FORMATE PROCESS)
Total subcategory capacity rate	40,340 kkg/year
Total subcategory production rate	39,940 kkg/year
Number of plants in this subcategory	2
308 Data on file for	1
With total capacity of	20,450 kkg/year
With total production of	20,450 kkg/year
Representing capacity	50 percent
Representing production	51 percent
Plant production range:	
Minimum	NA
Maximum	NA
Average production	NA
Median production	NA
Average capacity utilization	100 percent
Plant age range:	
Minimum	NA
Maximum	NA
Wastewater flow range:	273 cubic meters/day
Minimum	NA
Maximum	NA
Volume per unit product:	4.68 cubic meters/kkg
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

NA = Not Available

TABLE 25-2. STATUS OF REGULATIONS - EFFLUENT LIMITATION GUIDELINES

SUBCATEGORY Sodium Hydrosulfite

SUBPART BE (40 CFR 415.570, 5/22/75)

STANDARDS							
Product Process	Para- meters	BPCTCA		BATEA		NSPS	
		Max. ¹	Avg. ²	Max.	Avg.	Max.	Avg.
		kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)	kg/kg (mg/l)
Sodium Hydro- Sulfite	Reserved	Reserved	Reserved	Reserved	Reserved	Reserved	Reserved

¹Max. = Maximum of any one day.

²Avg. = Average of daily values for thirty consecutive days.

The operation occurs in several steps:

An aqueous solution of sodium formate is prepared and introduced into the reactor.

The recycled stream of methanol containing sulfur dioxide is introduced into the reactor.

The sodium hydroxide and sodium formate solutions, liquid sulfur dioxide, and recycled methanol are then contacted under pressure at slightly elevated temperatures.

Sodium hydrosulfite then precipitates and forms a slurry in the reactor. The by-product, sodium sulfite, and sodium bicarbonate and carbon monoxide gas are formed.

There is a small amount of methyl formate produced in the reactor as a side reaction between the sodium formate and methanol:



This side reaction product remains in the recycling methanol during the entire process. As a result, some of the methanol must be periodically purged from the recycle system to avoid excessive buildup of this impurity.

The resulting slurry of sodium hydrosulfite in the solution of methanol, methyl formate, and by-products is sent to a pressurized filter operation which recovers the crystals of sodium hydrosulfite. The crystals are dried in a steam heated rotary drier, recovered and packaged. The filtrate and backwash liquors from the filter operation are sent to the solvent recovery system as is the vaporized methanol from the drying operation. The drying of the sodium hydrosulfite filter cake must be done very carefully as it is heat sensitive and tends to decompose to sulfite.

A general process flow diagram for Plant #672 can be found in Figure 25-1, as it is typical for this subcategory.

Water Use and Waste Source Characteristics

Water Use

Water is used in the process as make up for the reaction solutions and for steam generation in the rotary dryers. Water is also used for noncontact cooling in the reactor gas vent scrubbers and dryers, as well as pump seals and washdowns, and as dilution water in the wastewater treatment system to assist in biological oxidation of organic materials.

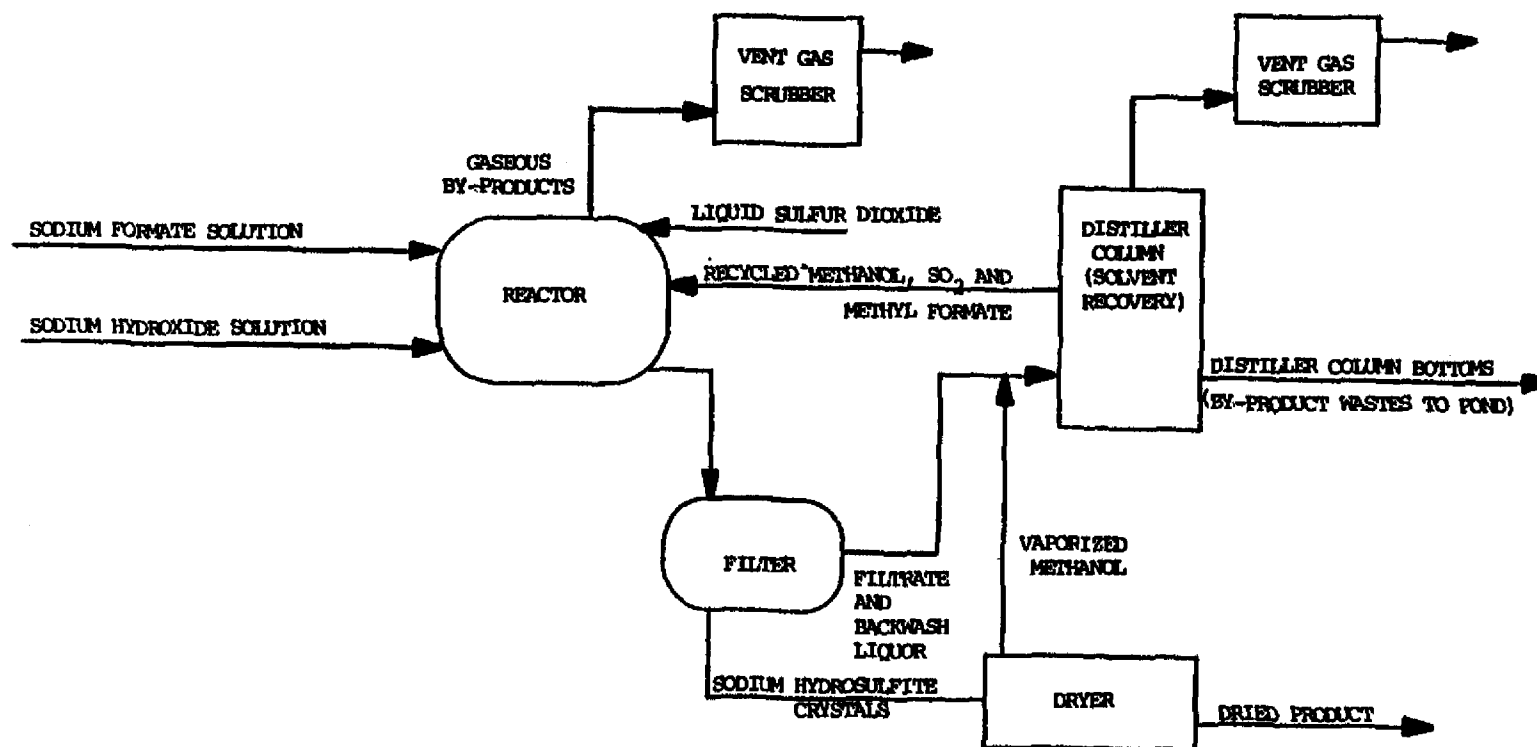


Figure 25-1. General process flow diagram at plant #672.
(Sodium hydrosulfite manufacture.)

Waste Sources

The strongest process waste is the aqueous residue from the distillation column bottoms (solvent recovery system). This waste contains concentrated reaction by-products and is purged from the system at a rate of approximately 14,000 gallons per day. At Plant #672, this waste is sent to a by-product pond where it is held and either sold to the pulp and paper industry or bled into the treatment system.

The dilute wastes from the process are contributed by leaks, spills, washdowns, and tank car washing. At Plant #672, this is collected in a sump and then sent to the biological treatment system.

Cooling tower and boiler blowdown constitute a noncontaminated wastewater source. This is sent to the final compartment of the chlorine contact tank without treatment, for discharge with the combined effluent of the treatment plant.

The vent gas scrubbers create a wastewater source which is sent to the methanol recovery stills for recycle. At Plant #672, this waste eventually goes to the by-product pond with the distillation column bottoms.

Table 25-3 presents the unit flows for the three primary sources of process wastewater which contribute to the pollutant load.

Solid wastes currently are generated in the activated sludge waste treatment system. An estimated 2,400 gallons of biological sludge are discharged per day to an on-site drying bed. Application of more stringent waste treatment of toxic pollutants is estimated to generate an additional 6 kg/kg of product of solid waste which must be disposed of at an approved site.

Description of Plants Visited and Sampled

Screening and Verification

The only plant visited during the sampling program was Plant #672, where verification sampling procedures were used. Plant #672 is one of two plants that currently utilize the formate process in the sodium hydrosulfite subcategory. An evaluation of plants that currently utilize the zinc process for sodium hydrosulfite manufacture has been deferred to a later phase of regulation development by the Agency.

Data from Plant #672 can be considered representative of this process for both plants, since the other plant in this subcategory has an identical, though slightly smaller, production process. However, the second plant has a different waste treatment system. It also receives large loadings of waste from several other products. Because of this the plant is considered nonrepresentative of the hydrosulfite process and visits were limited to Plant #672 for this reason.

TABLE 25-3. WASTE SOURCE DATA AT PLANT #672

WASTE SOURCE	FLOW (m ³ /kg)
Dilute Waste (spills, etc.)	1.95
Dilution Water (contact)	1.75
By-product Waste	0.95
Total	4.65
(Basis of flow for model plant and regulation development)	

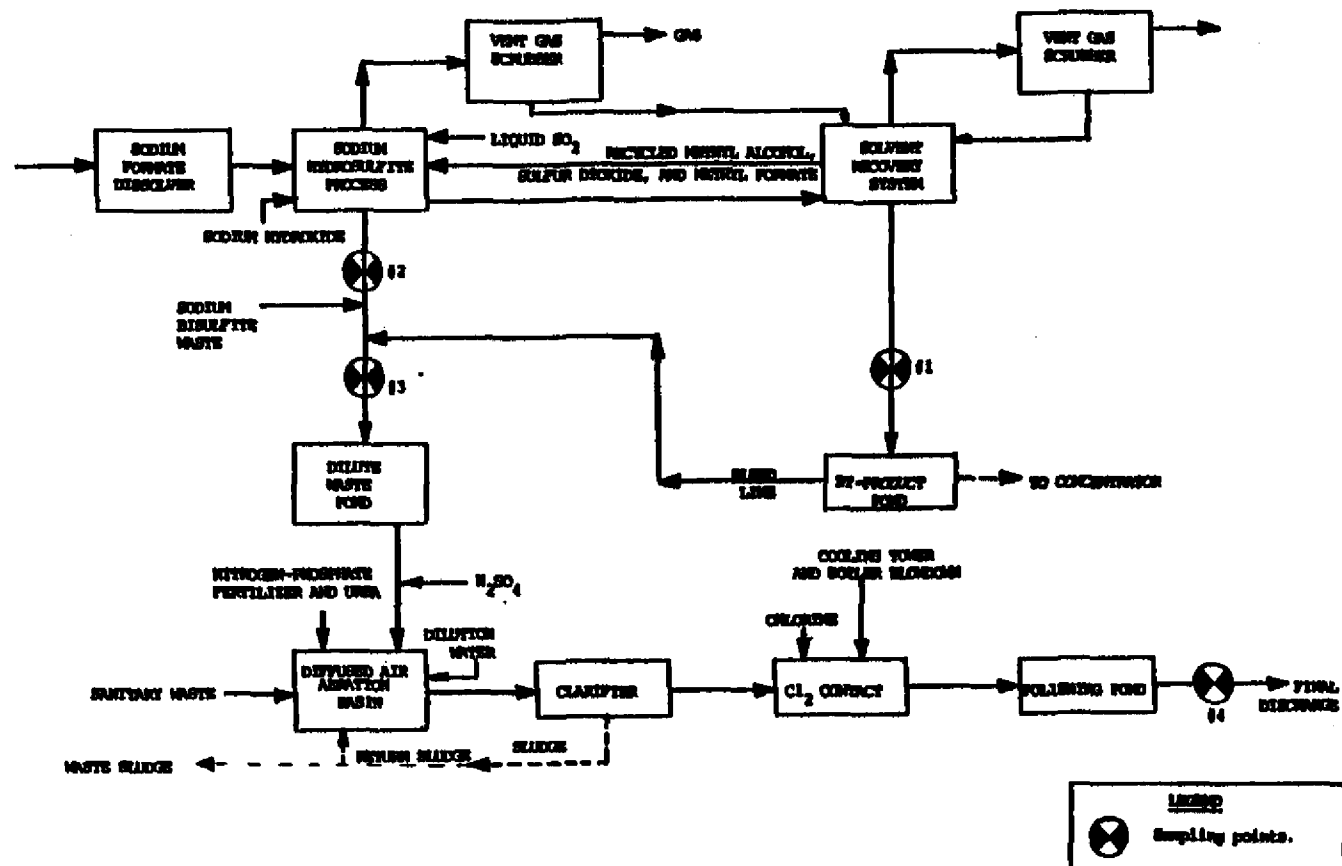


Figure 25-2. General process flow diagram at plant #672 showing the sampling points. (Sodium hydrosulfite manufacture.)

A general flow diagram of Plant # 672 showing process waste sources and sampling points is shown in Figure 25-2. The sources of wastewater for each sampling point are as follows:

By-product pond.

Dilute waste from sodium hydrosulfite process area and sumps.

Combined influent to treatment. This point collects waste from points 1 and 2, plus the sodium bisulfite waste stream.

Treated effluent at the outfall.

At the time screening sampling was conducted at Plant #672, none of the by-product wastewater was being sent to the biological treatment system. As a result, the sodium hydrosulfite process waste being treated was from the dilute waste area only.

Table 25-4 presents the results of the conventional and nonconventional pollutant concentrations and unit loads for each of the streams sampled. The results are based on three 24-hour composite samples. It should be noted that sampling was done during a time when no by-product waste was entering streams 3 and 4. The unit flow indicated is the estimated flow observed during sampling.

Toxic Pollutant Concentrations

Toxic pollutants were identified in the raw process waste stream at Plant #672. The following toxic pollutants were found at detectable concentration levels.

Maximum Raw Waste Concentrations Observed ($\mu\text{g/l}$)

<u>Pollutant</u>	<u>Verification Plant #672</u>
Arsenic	79
Cadmium	43
Chromium	9300
Copper	1500
Lead	1300
Nickel	1700
Silver	130
Zinc	27000
Pentachlorophenol	580
Phenol	170
Cyanide	100
Mercury	28
Selenium	34

Two toxic organic pollutants, pentachlorophenol and phenol, were identified at low, but detectable, concentration levels. The raw process materials, including sodium formate and methanol, are likely sources. The sodium formate currently used in the process is a

TABLE 25-4. FLOW, POLLUTANT CONCENTRATION, AND LOAD DATA OF THE SAMPLED WASTE STREAMS FOR PLANT #672 PRODUCING SODIUM HYDROSULFITE

Stream Designation	Description	Flow	TSS		COD	
		(m ³ /kkg)	(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)
1	By-product	0.95	61	0.058	78,000	74
2	Dilute Waste	1.95	260	0.51	15,000	29
3	Dilute Waste and SBS Waste	2.05	840	1.7	16,000 ⁽¹⁾	32
4	Final Discharge	4.87	25	0.12	740 ⁽¹⁾	3.6

(1) Value is that observed during sampling which may differ significantly if the by-product stream is contributing.

by-product from an unrelated organic chemicals process which may contain the organic impurities. Methanol is also a suspect source of organic impurities in view of the difficulty involved with its purification and high degree of solubility with pentachlorophenol. Also possible is coincidental formation of pentachlorophenol in the process due to the presence of specific chlorinated hydrocarbons under conditions conducive to its development.

Section 5 of this report describes the methodology of the screening and verification sampling program. In the sodium hydrosulfite industry, a total of three days of sampling were conducted at Plant #672. Three 24-hour composite samples were taken at four different sampling points. The sampling involved 169 analytical data points for the toxic inorganic pollutants and 387 additional points for the toxic organic pollutants. The daily raw waste loads were calculated from the waste stream flow rates measured or estimated at the time of sampling and the measured pollutant concentration.

That is,

$$\text{Daily loading (as kg of pollutant per day)} = \frac{(C)(Q)}{(1000)}$$

where:

C is the concentration of the pollutant expressed in units of mg/l (Note: $\text{kg/m}^3 = 1000 \text{ mg/l}$), and

Q is the waste stream flow rate expressed in units of m^3/day . (m^3 , a cubic meter, is equal to 264.2 U.S. gallons.)

Similarly, the unit loadings were calculated from the reported sodium hydrosulfite production rate, the waste stream flow rate, and the measured pollutant concentration.

$$\text{Unit loading (as kg of pollutant per kkg of sodium hydrosulfite)} = \frac{(C)(Q)}{1000P}$$

where C and Q are the same as described above, and P is the sodium hydrosulfite production rate expressed in units of kkg/day. (kkg is 1000 kg, a metric ton, which is equal to 2205 lbs.)

Table 25-5 presents the average toxic pollutant concentrations observed during sampling for the raw and treated wastewaters at Plant #672. The concentration indicated is based on three 24-hour composite samples. Table 25-6 is a tabulation of the unit loadings for each of the toxic pollutants found at detectable levels in the raw waste water.

The estimated total toxic pollutant raw waste loads generated each year for this subcategory were based on the total estimated annual production of sodium hydrosulfite. The loads are as follows:

<u>Pollutant</u>	<u>Waste Load (kg/year)</u>
Arsenic	4.8
Cadmium	1.3
Chromium	22
Copper	7.6
Lead	40
Nickel	64
Silver	6.4
Zinc	960
Pentachlorophenol	33
Phenol	6.0
Cyanide	1.56
Mercury	0.80
Selenium	1.2

Pollution Abatement Options

Toxic Pollutants of Concern

Although sodium hydrosulfite is being manufactured by both the zinc process and the formate process, the trend is away from the zinc process for environmental reasons. This discussion concerns only the formate process, using a sodium formate feed stock from a source which appears to contain heavy metal impurities (chromium, zinc, nickel, lead, and copper) as well as trace amounts of cyanide. A predominant characteristic of sodium hydrosulfite wastes is their high chemical oxygen demand resulting from various forms of sulfite, from methyl formate, and from residual methanol after a solvent recovery process. Low levels of phenolic compounds are also found in the raw wastes.

Prevailing Control and Treatment Practices

Due to the nature of the two primary raw waste streams, each one is handled differently. The dilute waste is first sent to a holding pond where the flow is equalized and the waste mechanically aerated. This pond also contains approximately 1500 gallons per day of waste from a sodium bisulfite process. The pond effluent is pH adjusted with sulfuric acid and sent to an aeration basin. A nitrogen-phosphate fertilizer and urea are added to provide nutrients. Approximately 3500 gallons per day of sanitary waste and up to 25,900 gallons per day of clean dilution water are also added to the aeration basin. This basin formerly had mechanical aerators, but now has air diffusers which allow better temperature control for biological oxidation. The effluent from aeration goes to a clarifier. Approximately 14,000 gallons per day of settled sludge is returned to the aeration basin and 2,400 gallons per day is sent to drying piles on site. More dilution water is added to the clarifier when needed for Total Dissolved Solids control. The overflow from the clarifier goes to a chlorine contact tank because of the sanitary waste. The blowdown water from the cooling tower and boilers is added to the final chamber of the chlorine contact tank. The effluent from this unit is sent to a final polishing pond for settling and equalization before discharge.

The by-product waste from the distillation column bottoms is sent to a lined by-product pond at a rate of 14,000 gallons per day and held for one of two possible disposal methods. When there is a market for the by-products, the waste is concentrated and sold to the pulp and paper industry. At times when this is not possible, and the pond nears capacity, the waste is bled into the treatment system described above through the dilute waste holding pond.

Advanced Treatment Technologies

Practical technologies for controlling COD include various forms of mechanical and biological oxidation. For the relatively simple chemical oxidation of hydrosulfite to sulfate, intimate contact with atmospheric oxygen is effective, using submerged air diffusers, induced air in a circulating system, or mechanical surface aeration. For biochemical oxidation of resistant organics such as formates, phenols, chlorinated hydrocarbons, and methanol, the use of trickling filtration, rotating biological discs, or variations of the activated sludge process can provide intimate contact between organic pollutants and the microbiological organisms which use them as food.

Technologies for controlling heavy metals include alkaline precipitation, which is effective for the common heavy metals, and sulfide treatment, which precipitates nickel, zinc, and copper, but does not increase control of chromium. Other less appropriate metal removal techniques have been discussed in Section 8.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1

Treatment system pH adjustment, biological oxidation, settling, and chlorination are used to reduce COD and coliform organisms in the combined wastes, in accordance with existing plant practice. The flow diagram is shown in Figure 25-3.

B. Level 2

The by-product wastes are treated separately by alkaline precipitation to remove the toxic metals and then are combined with the product wastes for biological oxidation treatment and chlorination, as in Level 1.

If an acetal formate process plant employs metal-free sodium formate in its process there is no reason to expect heavy metals in the process wastes and Level 2 treatment should not be necessary. The flow diagram is shown in Figure 25-4.

Equipment for Different Treatment Levels

A. Equipment Functions

Product waste and by-product wastes are received in a mixed and aerated equalizing basin, adjusted to a neutral pH, and aerated in a four-day aeration lagoon, including 50 percent return of underflow to the influent. Plant sewage, nutrients, and diluting water are added to the lagoon to promote biological oxidation of organics and other COD. Lagoon effluent is clarified, chlorinated, and sent to a polishing pond before discharge through effluent monitoring facilities. Cooling tower and boiler blowdown wastes enter the system after chlorination, since they require no treatment except settling of scale and inert debris in the polishing pond. Floating aerators are used in the equalization basin and compressed air is diffused in the aerated lagoon, for mixing and introduction of dissolved oxygen into the mixed liquor.

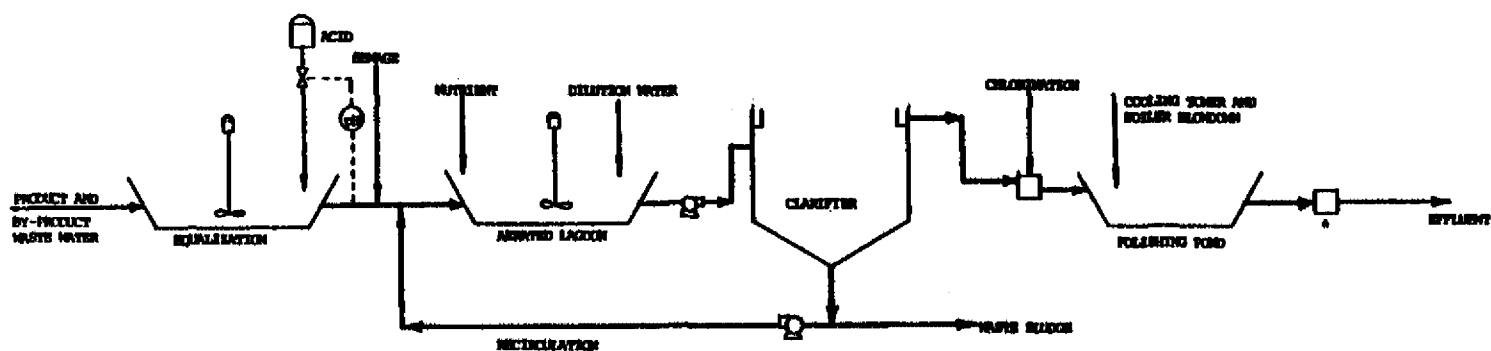
In Level 2 treatment, by-product wastes are received in a separate 18-hour aerated and recirculated holding tank, which is pumped at average daily flow to a gravity clarifier, adding sufficient lime to reach a pH of 10.5. The clarifier overflow joins the product waste stream in the equalization basin of the Level 1 system. All features of the Level 1 system remain the same, since it was originally sized to handle the combined wastes.

B. Chemicals and Handling

Sulfuric acid, lime, filter aid, and chlorine are chemicals commonly used in waste treatment. When handled in corrosion resistant equipment designed for their use, no unusual hazards are expected. Raw sewage and 10-10-10 liquid fertilizer introduced into the aerated lagoon become thoroughly mixed and are eventually consumed in the biological oxidation process, constituting no threat to operating personnel. Chlorine, used for control of coliform bacteria, is received in ton containers and applied as a chlorine water solution using standard solution feed chlorination equipment. There are no unusual chemical handling problems in treating these wastes, provided the waste streams are kept at a neutral or alkaline pH.

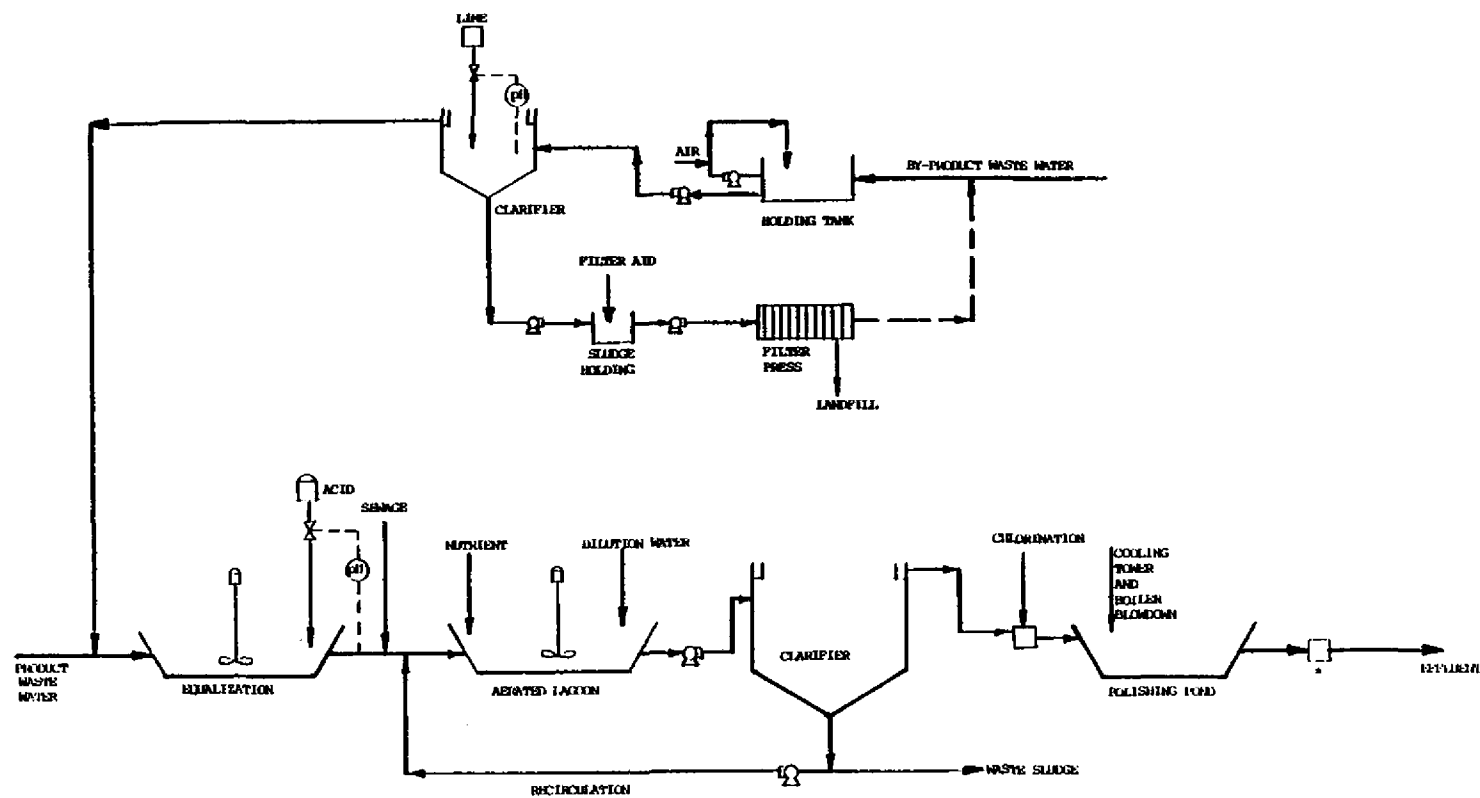
C. Separation and Disposal of Solids

In the Level 1 system, waste activated sludge solids are assumed to be dried in sludge beds at the site, to be used as fertilizer for plant landscaping. Clarifier underflow from alkaline precipitation of by-product waste in Level 2 is assumed to be sent to a sludge holding tank and dewatered at suitable intervals in a filter press, followed by hauling of solids to a chemical landfill. Filter press filtrate is returned to the holding tank for retreatment.



* Includes flow monitoring, pH monitoring and sampler.

Figure 25-3. Level 1 waste water treatment for sodium hydrosulfite subcategory.



* Includes flow monitoring, pH monitoring and sampler.

Figure 25-4. Level 2 waste water treatment for sodium hydrosulfite subcategory.

D. Monitoring Requirements

Internal monitoring should include simple field tests for pH, chlorine residual, and settleable solids. Maintenance of the by-product stream clarifier at a pH of 10.5 is expected to provide control of toxic metals without need for routine metal analyses. Periodically, effluent samples should be analyzed for chromium, zinc, copper, nickel, and lead by atomic absorption in addition to routine COD tests for general evaluation of the treatment.

Treatment Cost Estimates

General Discussion

A model plant concept was prepared for the purpose of the cost estimates. The specifications of the waste input parameters and the design of the model plant Level 1 treatment system are based on the information presented for Plant #672.

In this subcategory, commercial fertilizer and urea are added to stimulate growth of the biomass employed in biological treatment, and not for direct reaction with a residual pollutant. Therefore, the chemicals used do not bear a fixed relationship to the plant production in units of sodium hydrosulfite.

Organic solids generated in the model treatment system are assumed to be disposed of on land at the site, without a separate cost for sludge disposal.

Cost Estimates

The model plant cost estimate for two levels of treatment applied to the same level of production is presented in Table 25-7. Table 25-8 gives a summary of the unit cost distribution between amortization, operation and maintenance cost components at two levels of treatment.

Cost estimates developed for the first and the second level of treatment indicate that labor and supervision costs constitute a major portion of the annual cost. This reflects the manpower requirements for operating the treatment systems on a 24-hour basis.

Basis for Guidance

Evaluation of Level 1 Treatment Practices

There are two plants producing sodium hydrosulfite by the formate process, both of which have Level 1 equipment in place and both are in compliance with their NPDES permits.

Level 1 technology has been specified as the technology presently in use at Plant #672. Design and cost estimates are based on inclusion of by-product wastes.

TABLE 25-7. MODEL PLANT TREATMENT COSTS

Subcategory	Sodium Hydrosulfite - Formate process	
Production	20,450 metric tons per year	
	(\$)	
A. INVESTMENT COST	Level 1	Level 2
Site development	23,000	0
Equipment	138,500	121,000
Monitoring equipment	20,000	0
Subtotal	181,500	121,000
Contractor's O & P ^b	27,225	18,150
Subtotal	208,725	139,150
Engineering	41,745	27,830
Subtotal	250,470	166,980
Contingencies	25,047	16,698
Subtotal	275,517	183,678
Land	12,000	3,000
TOTAL INVESTMENT COST	287,517	186,678
B. OPERATION AND MAINTENANCE COST		
Labor and supervision	168,000	84,000
Energy	12,000	1,200
Chemicals	3,500	18,500
Maintenance	27,552	18,368
Taxes and insurance	8,626	5,600
Residual waste disposal	0	0
Monitoring, analysis and reporting	15,000	7,500
TOTAL OPERATION AND MAINTENANCE COST	234,677	135,168
C. AMORTIZATION OF INVESTMENT COST	44,827	29,884
TOTAL ANNUAL COST	279,504	165,053

^a Represents the incremental cost above that for Level 1 treatment

^b Overhead and Profit

TABLE 25-8 MODEL PLANT UNIT TREATMENT COSTS

Subcategory Sodium Hydrosulfite -Formate process

COST ITEM	PRODUCTION (kgg/yr)	Annual Treatment Costs (\$/kgg)	
		LEVEL OF TREATMENT	
		Level 1	Level 2
Annual Operation and Maintenance	20,450	11.48	6.61
Annual Amortization	20,450	2.19	1.46
Total Annual Cost	20,450	13.67	8.07

*Represents the incremental cost above Level 1.

An evaluation of treatment practices was performed at Plant #672 based on the pollutant sampling, since long-term monitoring data was not available for the pollutants of concern. Details concerning the performance evaluation calculations and assumptions are discussed below for the pollutants of concern.

A. Conventional and Nonconventional Pollutants

1. Chemical Oxygen Demand (COD)

At the time of sampling, the by-product waste (stream #1, Figure 25-2) was not flowing into the wastewater treatment system (Stream #3, Figure 25-2).

Review of Table 25-4 indicates that a majority of the COD load is contributed by the by-product waste stream. The other major source of COD is contributed by the dilute waste stream #2. Estimates of subcategory performance are made for COD based on the following assumptions:

a. Assumption 1

The COD load for the by-product stream must be included in the evaluation of the treatment system performance, since its contribution to the final COD load will have a significant influence. Therefore, it is assumed that the percent COD removed in the treatment system would be the same percent COD removed for the by-product waste stream as if it had received treatment. This assumption is necessary since plant performance information is available only for the dilute waste stream.

b. Assumption 2

In order to estimate the COD removed during treatment in the dilute waste stream, two minor assumptions must also be made to account for COD contributions from the sodium bisulfite (SBS) and sanitary streams which are not considered sodium hydrosulfite process-related. It is assumed that the final COD concentration for the treated sodium bisulfite waste stream is 680 mg/l (from Table 24-16) and 60 mg/l which is a conservative estimate for treated sanitary wastes. These assumptions are not critical since the total combined waste flow from these two waste sources is only 0.30 m³/kkg compared with 2.9 m³/kkg of other process related wastes.

Table 25-9 is a summary of the subcategory performance evaluation of TSS and COD for Plant #672. The COD evaluation is developed in the table on the bases of

the assumptions above and sampling information in Table 25-4.

A determination of achievable effluent COD load is shown in the following steps beginning with an estimation of the COD removal efficiency in the waste treatment system.

The observed effluent COD load is 3.6 kg/kkg from Table 25-4 which includes contributions from the sodium bisulfite (SBS) and sanitary waste streams which are not process related. These loads are determined as follows:

$$\text{SBS load} = (680 \text{ mg/l}) (0.10 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.068 \text{ kg/kkg}$$

(0.10 m³/kkg from Table 25-9; 680 mg/l from Assumption 2 above)

Sanitary waste COD load =

$$(60 \text{ mg/l})(0.24 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.014 \text{ kg/kkg}$$

(0.24 m³/kkg from Table 25-9; 60 mg/l from Assumption 2 above).

The effluent COD load contributed by the SBS and sanitary waste streams are subtracted from the observed load of 3.6 kg/kkg to obtain the actual COD load contributed by the process related dilute waste as follows:

$$3.6 \text{ kg/kkg} - (0.068 \text{ kg/kkg} + 0.014 \text{ kg/kkg}) = 3.5 \text{ kg/kkg}$$

The effluent COD load is 3.5 kg/kkg which when expressed as a ratio with the raw COD waste load (Assumption 1) can be used to estimate the additional COD contributed by the by-product waste as follows:

Raw COD load contributed = 29 kg/kkg from Table 25-4 by dilute waste

Raw COD load contributed = 74 kg/kkg from Table 25-4 by by-product waste

$$\begin{aligned} \text{Effluent COD load of} &= \frac{(74 \text{ kg/kkg}) (3.5 \text{ kg/kkg})}{(29 \text{ kg/kkg})} \\ &= 8.9 \text{ kg/kkg} \end{aligned}$$

TABLE 25-9. SUBCATEGORY PERFORMANCE EVALUATION SUMMARY AT PLANT #672 FOR CONVENTIONAL AND NONCONVENTIONAL POLLUTANTS IN THE EFFLUENTS

Effluent Waste Description	Flow (m ³ /kkg)	TSS ⁽²⁾		COD ⁽²⁾	
		(mg/l)	(kg/kkg)	(mg/l)	(kg/kkg)
A - Dilute Waste	1.95	260	0.51	1800	3.5
B - Sodium Bisulfite Waste	0.10	NA ⁽¹⁾	NA	680 ⁽³⁾	0.068
C - Sanitary Waste	0.24	NA	NA	60 ⁽³⁾	0.014
D - Dilution Water	1.75	NA	NA	0	0
E - Boiler Blowdown	0.83	NA	NA	0	0
F - By-product	0.95	61	0.058	9600	9.2
Total Load (A+D+F)		NA	NA	NA	13
Effluent Concentration	4.87	25	NA	NA	NA
Model Plant Flow (A+D+F)	4.65	NA	NA	NA	NA
Concentration At Model Plant Flow	4.65	26	NA	2700	NA
BASIS OF LIMITATION	4.65	25	NA	NA	12

(1) - NA Not applicable to evaluation.

(2) - Data based on average of three 24-hour composite samples.

(3) - Assumed value discussed in Section 25.7.1 under Chemical Oxygen Demand.

Total effluent COD load contributed by both the dilute and by-product waste =

$$3.5 \text{ kg/kg} + 8.9 \text{ kg/kg} = 12 \text{ kg/kg}$$

The effluent load for COD is 12 kg/kg based on the plant performance evaluation and sampling data.

2. Total Suspended Solids (TSS)

The removal of TSS from the raw wastewater is much more complex on a load basis. TSS removal must therefore be estimated on a concentration basis as indicated in Table 25-9. A TSS concentration of 25 mg/l was observed in the treated effluent during sampling (Table 25-4) which is used as the long-term average in developing the TSS guidance.

B. Toxic Pollutants

The removal of toxic pollutants in the treatment system at Plant #672 during sampling is indicated in Table 25-5 for the purpose of evaluating plant performance.

Basis for Level 1 Treatment Performance

A. Technology Basis

The technology basis is, or is equivalent to, equalization, pH adjustment, aeration in a biological oxidation system, clarification, and chlorination before discharge of the treated effluent.

B. Flow Basis

The basis of flow used for the cost estimates, and as a basis to estimate pollutant discharge loadings for the purpose of guidance development, was derived from plant information received at Plant #672. Table 25-3 presents the unit flows from the three primary waste sources identified in the industry. The dilute and by-product wastewaters are primarily process related, whereas the dilution water is required for proper operation of the biological waste treatment system.

There are only two plants which currently use the formate process for the manufacture of sodium hydrosulfite. The model plant flow is 4.7 m³/kg of product for the sodium hydrosulfite subcategory as presented in Table 25-3 and is based on Plant #672 data. Plant #672 was chosen for evaluation because it is not complicated by other unrelated manufacturing processes.

C. Selection of Pollutants to be Controlled

The Level 1 treatment technology is directed primarily toward removal of TSS and COD. In addition to these conventional and nonconventional pollutants, toxic organic pollutants were identified in small quantities. These toxic organic pollutants include pentachlorophenol, phenol, and other trace organics. The presence of these toxic pollutants is currently under investigation by the plant to: 1) determine the source of the pollutants and identify whether they are process related, and 2) determine whether process modifications or best management practices might be available to eliminate their presence if they are discovered to be process related.

D. Basis of Pollutant Control Guidance

1. Conventional and Nonconventional Parameters

a. pH

The treated effluent is to be controlled within the range of 6.0 to 9.0. This is based on the data presented in Appendix B of the proposed Development Document (60) and the JRB Study (52).

b. TSS and COD

The data presented in Table 25-9 was used for the development of TSS and COD control guidance. The data presented is for Plant #672 which is the only plant in the subcategory where the treatment performance can be observed clearly.

No long-term monitoring data is currently available for a statistical estimation of the variability factors in the Sodium Hydrosulfite Subcategory.

Therefore, the 30-day average and daily variability factors are estimated from the treatability study (61) for COD removal. The study indicates a 30-day average variability factor of 1.2 and daily variability factor of 4.0.

The maximum 30-day average COD level is estimated from plant performance data in Table 25-9 to be 12 kg/kkg. The maximum 30-day average concentration is determined as follows:

$$\frac{(12 \text{ kg/kkg})}{(4.7 \text{ m}^3/\text{kkg})} \frac{(1000 \text{ mg/l})}{(\text{kg/m}^3)} = 2600 \text{ mg/l}$$

The long-term average COD concentration is determined using the 30-day average variability factor of 1.2 as follows:

$$\frac{2600 \text{ mg/l}}{1.2} = 2200 \text{ mg/l}$$

The 24-hour maximum concentration is determined using the daily variability factor as follows:

$$(2200 \text{ mg/l}) (4.0) = 8800 \text{ mg/l}$$

The 24-hour maximum loading for COD is then:

$$(8800 \text{ mg/l}) (4.7 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 41 \text{ kg/kg}$$

The long term average TSS concentration is 25 mg/l from plant performance information in Table 25-9. The TSS control guidance is based on this long-term average and the variability factors used for COD. The 30-day average variability factor of 1.2 is used to determine the TSS maximum 30-day average concentration as follows:

$$(25 \text{ mg/l}) (1.2) = 30 \text{ mg/l}$$

The 24-hour maximum concentration is determined similarly as follows:

$$(30 \text{ mg/l}) (4.0) = 100 \text{ mg/l}$$

The maximum 30-day average loading is determined as follows:

$$(30 \text{ mg/l}) (4.7 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.14 \text{ kg/kg}$$

The 24-hour maximum loading is:

$$(100 \text{ mg/l}) (4.7 \text{ m}^3/\text{kg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.47 \text{ kg/kg}$$

Guidance for effluent control is presented in Table 25-10.

2. Toxic Organic Pollutants

The verification sampling results presented in Table 25-5 for pentachlorophenol and phenol indicate that both of these toxic organic pollutants are currently removed by the existing treatment system to the analytical detection limit and are therefore excluded from further consideration.

TABLE 25-10. GUIDANCE FOR EFFLUENT CONTROL
Sodium Hydrosulfite
Level 1 Performance
Waste Water Flow: 4.7 m³/kkg

Pollutant	Subcategory Performance (mg/l)	VFR ⁽¹⁾	Concentration Basis (mg/l)		Effluent Loading (kg/kkg)	
			Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
<u>Conventional and nonconventional pollutants:</u>						
Total Suspended Solids, TSS	25 ⁽²⁾	4.0/1.2 ⁽³⁾	30	100	0.14	0.47
Chemical Oxygen Demand, COD	2200	4.0/1.2 ⁽³⁾	2600	8800	12 ⁽²⁾	41

(1) - VFR: ratio of the 24-hour variability factor to the 30-day average variability factor.

(2) - Based on subcategory performance estimates utilizing three 24-hour composite samples.

(3) - Based on treatability study (61) for the removal of COD.

(4) - No effluent limitation has been established.

3. Toxic Metal Pollutants

The Level 1 treatment technology is not amenable to the removal of toxic metal pollutants although, as shown in Table 25-5, considerable incidental removal can occur. Level 1 technology can not reasonably ensure the removal of toxic metals on a consistent basis.

Basis for Level 2 Treatment Performance

A. The Application of Advanced Level Treatment

The Agency has analyzed the cost effectiveness of the base level systems and the various advanced level options for the removal of pollutants based on cost estimates presented in this report. No plant has this additional technology installed.

B. Technology Basis

Level 2 is based on treatment that provides more stringent removal of toxic pollutants in the by-product waste stream by introducing alkaline precipitation with lime and settling prior to base level treatment. The by-product waste stream was the primary source of toxic metal pollutants observed during sampling.

C. Flow Basis

The unit flow used for the treatment performance estimates is based on 4.7 m³/kgg of product. The estimated flow does not change for Level 1 and Level 2 treatment.

D. Selection of Pollutants to be Controlled

Selection of pollutants is based on an evaluation of verification sampling data at Plant #672. Results of the sampling program are presented in this section. On the basis of concentration and total annual raw waste loads, zinc, nickel, lead, chromium, and copper have been identified at treatable levels and were considered as candidates for control in addition to TSS and COD.

Review of Section 8 indicates that not all toxic pollutants present in raw waste effluents need to be specified for alkaline precipitation. In fact, two primary groups of heavy metals appear to reach a minimum solubility at slightly different pH levels. Zinc is the major toxic pollutant determined at Plant #672 which represents one of these primary groups of metals and nickel, also identified at treatable levels, represents the other group that achieves optimum removal at slightly higher pH values. Adequate control of zinc and nickel can be achieved in a single step alkaline precipitation system operated in an intermediate pH range of approximately 9.5 to 10.5. The basis for this is presented in Section 8 of this report. Control of zinc and

nickel will also ensure removal of lead, chromium, and copper which may occasionally occur at treatable concentrations in the raw waste.

E. Basis of Pollutant Control Guidance

1. Nonconventional Pollutants

The only nonconventional pollutant selected for limitation is COD. In view of the proposed technology for Level 2, no additional removal of COD is anticipated beyond what is already estimated for Level 1. That section discusses the development of the COD control guidance.

The maximum 30-day average COD effluent loading is 12 kg/kkg and the 24-hour maximum is 41 kg/kkg presented in Table 25-11.

2. Toxic Pollutants

Alkaline precipitation and settling of the by-product waste is expected to remove the five candidate toxic metal pollutants to within the limits of treatability. Review of Table 25-5 indicates that the existing Level 1 treatment system is providing incidental removal of the toxic metals. Table 8-12 presents the estimated levels achievable for the toxic metal pollutants based on literature treatability which was used for the purpose of establishing the long-term average concentration used for guidance control.

No long-term pollutant monitoring data were available to develop the variability factors. However, treatability studies (61) were performed that estimate the 30-day average and 24-hour maximum variability factors for a number of toxic pollutants. Variability factors for zinc were estimated as the average of values obtained in the nickel and copper sulfate industries. The 30-day average and daily variability factors are 1.2 and 4.1, respectively, and are used for guidance development.

a. Zinc

Review of the zinc concentration in the raw by-product waste stream indicates levels as high as 27 mg/l and an average of 24 mg/l from three 24-hour composite samples (Table 25-6). Literature treatability presented in Table 8-12 indicates an achievable long-term average concentration of 0.80 mg/l for alkaline precipitation and settling of zinc. The maximum 30-day average concentration is developed as follows:

$$(0.80 \text{ mg/l}) (1.2) = 0.96 \text{ mg/l}$$

TABLE 25-11. GUIDANCE FOR EFFLUENT CONTROL

Sodium Hydrosulfite
 Level 2 Performance
 Waste Water Flow: 4.7 m³/kkg

Pollutant	Subcategory Performance (mg/l)	VFR (1)	Concentration Basis (mg/l)		Effluent Loading (kg/kkg)	
			Max 30-day Avg	24-hr Max	Max 30-day Avg	24-hr Max
<u>Conventional and nonconventional pollutants:</u>						
Chemical Oxygen Demand, COD	2200	4.0/1.2 ⁽⁵⁾	2600	8800	12 ⁽²⁾	41
<u>Toxic pollutants:</u>						
Zinc ⁽⁶⁾	0.80 ⁽³⁾	4.1/1.2 ⁽⁵⁾	0.96	3.3	0.0045	0.016
Nickel ⁽⁶⁾	0.40 ⁽³⁾	4.1/1.2 ⁽⁵⁾	0.48	1.6	0.0023	0.0075
Lead ⁽⁶⁾	0.15 ⁽³⁾	4.1/1.2 ⁽⁵⁾	0.18	0.62	-- ⁽⁴⁾	-- ⁽⁴⁾
Chromium ⁽⁶⁾	0.32 ⁽³⁾	4.1/1.2 ⁽⁵⁾	0.38	1.3	-- ⁽⁴⁾	-- ⁽⁴⁾
Copper ⁽⁶⁾	0.40 ⁽³⁾	4.1/1.2 ⁽⁵⁾	0.48	1.6	-- ⁽⁴⁾	-- ⁽⁴⁾

(1) - VFR: ratio of the 24-hour variability factor to the 30-day average variability factor.

(2) - Based on subcategory performance estimates utilizing three 24-hour composite samples.

(3) - The long-term average concentration estimate from Table 8-12 is used.

(4) - No control specification is needed.

(5) - Based on treatability study (61) for nickel and copper sulfate subcategories.

(6) - Also applicable for pretreatment.

The 24-hour maximum concentration is similarly developed as follows:

$$(0.80 \text{ mg/l}) (4.1) = 3.3 \text{ mg/l}$$

The maximum 30-day average effluent loading for zinc is:

$$(0.96 \text{ mg/l})(4.7 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0045 \text{ kg/kkg}$$

The 24-hour maximum loading for zinc is:

$$(3.3 \text{ mg/l})(4.7 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.016 \text{ kg/kkg}$$

Guidance for effluent control is presented in Table 25-11.

b. Nickel

The concentration of nickel was observed as high as 1.7 mg/l in the raw by-product waste stream and averaged 1.1 mg/l in the three 24-hour composite samples (Table 25-6). Literature treatability presented in Table 8-12 indicates an estimated achievable long-term average concentration of 0.40 mg/l. The maximum 30-day average concentration is as follows:

$$(0.40 \text{ mg/l}) (1.2) = 0.48 \text{ mg/l}$$

The 24-hour maximum concentration is similarly developed as follows:

$$(0.40 \text{ mg/l}) (4.1) = 1.6 \text{ mg/l}$$

The maximum 30-day average loading for nickel is:

$$(0.48 \text{ mg/l})(4.7 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0075 \text{ kg/kkg}$$

The 24-hour maximum loading for nickel is:

$$(1.6 \text{ mg/l}) (4.7 \text{ m}^3/\text{kkg}) \frac{(\text{kg}/\text{m}^3)}{(1000 \text{ mg/l})} = 0.0075 \text{ kg/kkg}$$

Guidance for effluent control is summarized in Table 25-11 for Level 2 treatment.

3. Other Pollutants

The concentration basis for lead, chromium, and copper are also presented in Table 25-11. These

concentrations are intended to serve as guidance in cases where these toxic pollutants are found to be of serious concern.

100

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

126

127

128

129

130

131

132

133

134

135

136

137

138

139

140

141

142

143

144

145

146

147

148

149

150

151

152

153

154

155

156

157

158

159

160

161

162

163

164

165

166

167

168

169

170

171

172

173

174

175

176

177

178

179

180

181

182

183

184

185

186

187

188

189

190

191

192

193

194

195

196

197

198

199

200

SECTION 26

EXCLUDED SUBCATEGORIES

Aluminum Sulfate

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT or NSPS for this subcategory. The basis for this recommendation is that there is a zero discharge regulation in effect for BAT and NSPS and it controls toxic pollutants.

Production Process and Effluents

Aluminum sulfate is produced by the reaction of bauxite ore with concentrated sulfuric acid. Ground ore and acid are reacted in a digester yielding aluminum sulfate in solution plus muds and insoluble wastes. The aluminum sulfate is sold as a solution or evaporated to produce a solid product. Waste muds are ponded to allow settling and the clear liquor is returned to the process. Wastes from washing and leaks are directed to the pond and also returned to the process. Toxic pollutants in the pond include zinc, copper, chromium and cadmium.

Plants

There are 82 aluminum sulfate producing facilities in the industry.

BPT Limitations

BPT limitations were promulgated March 12, 1974 (40 CFR 415.20). The limitations provide for zero discharge of process wastewater except that if the pond has sufficient volume to hold a 10-year, 24-hour storm, the amount of water equal to the precipitation less the evaporation may be discharged. The water must have a pH of 6.0 to 9.0 and average less than 25 mg/l of suspended solids.

BAT, Pretreatment and NSPS Limitations

BAT and NSPS limitations were promulgated on March 12, 1974 (40 CFR 415.23 and 415.25). The limitations provide for zero discharge of process wastewater except that if the pond has sufficient volume to hold a 25-year, 24-hour storm, the volume of precipitation that falls within the pond in excess of a 25-year, 24-hour storm may be discharged. These zero discharge limitations adequately control the toxic pollutants. Development of Pretreatment Standards has been deferred to Phase II.

Ammonium Chloride

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT, NSPS, or Pretreatment regulations and the subcategory is excluded under Paragraph 8 of the Settlement Agreement. The bases for this determination are: 1) Only one of the major producers of ammonium chloride uses the Solvay Process. Ammonium chloride is recovered as a by-product. 2) No toxic pollutants were found at significant concentrations in the waste during screening of one ammonium chloride plant.

Production Process and Effluents

Ammonium chloride is used in the manufacture of dry cell batteries, explosives, dyes, washing powder, soldering flux, chemical reagent, and as a medicinal additive to livestock feed. It is also used in pharmaceutical preparations and freezing mixtures.

Ammonium chloride is produced by three methods. A major portion is a by-product in the manufacture of sodium carbonate by the Solvay process. The wastes produced are associated with the sodium carbonate subcategory. A second process produces ammonium chloride by the reaction of hydrogen chloride with ammonia. Discharges from this process come from crystallization and wet scrubber operations.

The industry profile data for this subcategory are given in Table 26.2-1.

Toxic Pollutants

Data have been received on about 50 percent of the industry as a result of Section 308 letters. In addition, a sampling survey for toxic pollutants was made at one plant. The results of the 308 letters and the sampling survey indicate that no toxic pollutants are being discharged in significant quantities. Ammonia was found to be the only pollutant of significance. Since ammonia is adequately controlled by the existing BPT regulation 40 CFR 415.242, this subcategory is being excluded under Paragraph 8 of the Settlement Agreement.

Pollutants found during sampling at one plant are:

<u>Pollutant</u>	<u>Concentration</u>
Chromium	29 µg/l (max.)
Nickel	25 µg/l (max.)
Zinc	29 µg/l (max.)
Ammonia	104 mg/l (avg.)

TABLE 26.2 - 1 SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY AMMONIUM CHLORIDE

Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	6
308 Data on file for	3
With total capacity of	52,400 kkg/year
With total production of	29,800 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	4,600 kkg/year
Maximum	13,400 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	17 years
Maximum	43 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA= Not Available

Status of Regulations

BPT regulations (40 CFR 415.242) are in effect for this subcategory.

Ammonium Hydroxide

Summary of Determinations

It has been determined that no further effort be given to developing BPT, BAT, NSPS, and Pretreatment regulations for the Ammonium Hydroxide Subcategory. The bases for this determination are: 1) the process has no toxic pollutants as reactants, and 2) no direct process waters are discharged from manufacturing operations. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Ammonium hydroxide is used predominately as a chemical intermediary and reagent. It is also used in the dyeing and bleaching of fabrics, the production of ammonium salts and aniline dyes, and the extraction of alkaloids from plants.

The most common method of ammonium hydroxide production is the modified Haber-Bosch process, wherein hydrogen and nitrogen are reacted directly over a catalyst surface to form ammonia. The hydroxide is formed by adding water. The only process wastewater source is derived from equipment washing.

The industry profile for this subcategory is given in Table 26.3-1.

Toxic Pollutants

Data was received on six of seven plants as a result of 308 letters. In addition, a sampling survey was made at one plant which had a potential for discharge. However, no process water discharge was found at the facility. There are low volume discharges as a result of spills and washdowns. The amount discharged was such that a sample could not be obtained for analysis.

Status of Regulations

Because no significant quantities of toxic pollutants are present, no further effort will be given to development of pretreatment regulations for this subcategory. Subpart Y has been reserved for this subcategory.

Barium Carbonate

Summary of Determinations

It has been determined that no further effort be given to developing or revising BPT, BAT, NSPS, and Pretreatment regulations for the Barium Carbonate Subcategory. The basis for this determination is

TABLE 26.3-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY AMMONIUM HYDROXIDE

Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	6
308 Data on file for	
With total capacity of	41,800 kkg/year
With total production of	17,000 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	206 kkg/year
Maximum	9,500 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	10 years
Maximum	26 years
Waste Water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA= Not Available

that the small quantities of toxic pollutants found during screening are far below accepted treatability levels.

Production Processes and Effluents

Barium carbonate is used in glass manufacturing, as a flux in ceramics and enamelling, as an intermediate in the production of barium oxide and hydroxide, and as a coating for photographic paper. It is also used in the synthetic dyestuff industry and for the removal of soluble sulfate in brick manufacturing.

Barium sulfide solution is reacted with soda ash to precipitate barium carbonate. The reacted solution is filtered. The filter cake is washed, dried, and calcined. Wastewater results from filter cake washing, leaks and spills. The industry profile data for this subcategory are given in Table 26.4-1.

Toxic Pollutants

Data has been received on about 70 percent of the industry as a result of Section 308 letters. In addition, a sampling survey for toxic pollutants was made at one plant. The results of the 308 letters and the sampling survey indicate that no toxic pollutants are being discharged in significant quantities.

The maximum concentration found the raw waste load in sampling for this subcategory were:

<u>Pollutant</u>	<u>Concentration. (μg/l)</u>
Nickel	21
Zinc	68

Status of Regulations

Subpart Z has been reserved for this subcategory.

Borax

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT and NSPS regulations for the Borax Subcategory. The basis for this determination is that existing BPT regulations specify zero discharge of process wastewater pollutants to navigable waters. Development of pretreatment regulations is deferred to Phase II.

Production Processes and Effluents

Borax is produced by dissolving sodium borate ores in recycled mother liquors and water. The insolubles settle out in ponds or are removed

TABLE 26.4-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY BARIUM CARBONATE

Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	7
308 Data on file for	5
With total capacity of	57,000 kkg/year
With total production of	48,745 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	158 kkg/year
Maximum	26,190 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	9 years
Maximum	24 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA= Not Available

by thickeners, and the clarified borax solution (mother liquor) is fed to crystallizers where a slurry of borax crystals is formed. The borax is separated from the water by centrifugation, dried, screened and packaged. Process effluents are recycled with excess going to evaporation ponds or returned to source.

Plants

Three plants produce borax in the United States. All three practice total recycle of wastewater.

BPT Limitations

BPT limitations were promulgated on May 22, 1975 (40 CFR 415.272), and require no discharge of wastewater pollutants to navigable waters.

BAT and NSPS Limitations

BAT and NSPS limitations were proposed on May 22, 1975. They were never promulgated. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

Boric Acid

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT, NSPS, or Pretreatment regulations for the boric acid industry. The basis for this determination is that there is only one plant which manufactures boric acid from mined ore. There is an indication that this plant will discontinue operation. All other plants manufacture boric acid using the Trona process and have zero discharge. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Boric acid is manufactured by acidification of borax. It is used in the manufacture of chromic oxide, glazes, enamels, textiles, fiberglass, and heat resistant glass. It is also used medicinally as a mild antiseptic and in atomic power plants as a nuclear moderator. Process wastes may consist of excess boric acid liquor, waste sodium sulfate by-product liquor and filtration impurities.

The industry profile data is given in Table 26.6-1.

Toxic Pollutants

Toxic pollutants found at significant concentrations during screening of one plant were:

<u>Pollutant</u>	<u>Concentration ($\mu\text{g/l}$)</u>
Copper	340
Thallium	140
Zinc	1200
Bis(2-ethylhexyl) phthalate	530
Mercury	1.6

There is an indication that this plant will discontinue manufacture of boric acid. All other plants have zero discharge because of the use of a different process.

Status of Regulations

BPT limitations were promulgated on May 22, 1975 (40 CFR 415-272) for this subcategory.

Bromine

Summary of Determinations

It has been determined that no further effort will be given to developing or revising BAT and NSPS regulations for the Bromine Subcategory. The basis for this recommendation is that existing BPT regulations specify zero discharge of process wastewater to navigable waters. Development of pretreatment is deferred to Phase II.

Production Processes and Effluents

Most bromine is produced from brines pumped from brine wells. A small amount (1 percent) is produced from brines from Searles Lake near Trona, California. This is not a navigable water in that it is 35 percent solids. The brine, after appropriate dilution and degassing is extracted by debromination with chlorine and steam. The steam and bromine is condensed, separated and distilled to obtain bromine. The raw waste load from the process is the residual brine and the chloride salts formed when the chlorine replaces the bromine. The raw wastes are returned to the brine well or brine source.

Plants

There are nine plants producing bromine in the United States, all of which return their wastes to the brine source.

BPT Limitations

Regulations were promulgated on May 22, 1975, (40 CFR 415.292) requiring zero discharge of process wastewater pollutants to navigable

TABLE 26.6-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY

BORIC ACID

Total subcategory capacity rate	NA
Total subcategory production rate	122,600 kkg/year
Number of plants in this subcategory	3
308 Data on file for	2
With total capacity of	97,500 kkg/year
With total production of	93,850 kkg/year
Representing capacity	NA
Representing production	77 percent
Plant production range:	
Minimum	30,156 kkg/year
Maximum	63,694 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	30 years
Maximum	83 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA= Not Available

waters except that residual brine depleted liquor may be returned to the body of water from which the brine solution was originally withdrawn. In no case is the brine source a navigable water. The source is wells except for a small portion that comes from a "lake" having 35 percent dissolved solids.

BAT and NSPS Limitations

BAT and NSPS were proposed on May 22, 1975, but never finalized. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

Calcium Carbide

Summary of Recommendations

It has been determined that no additional effort be given to developing revised BAT and NSPS regulations for this subcategory. The basis for this recommendation is that BPT, BAT and NSPS regulations specify zero discharge of process wastewater pollutants. Pretreatment standards will be developed under Phase II.

Production Processes and Effluents

Calcium carbide is manufactured by reaction of calcium oxide and coke. Calcium oxide and dried coke are reacted in a furnace and the product is cooled, crushed, screened, packaged and shipped. There are generally no process related wastewaters except that one plant had a wet scrubber discharge.

Plant

There are five plants producing calcium carbide.

BPT, BAT and NSPS Limitations

BPT, BAT and NSPS regulations were promulgated on March 12, 1974 (40 CFR 415.32, 415.33 and 415.35). All subparts require zero discharge of process wastewater pollutants. It has been determined that the calcium carbide subcategory will be excluded from development of revised BAT and NSPS limitations because the operations are now subject to zero discharge regulations.

Calcium Carbonate

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT, NSPS, and Pretreatment regulations for the Calcium Carbonate Subcategory. The bases for this determination are: 1) there are only four plants manufacturing calcium carbonate, and 2) the small quantities of pollutants found during screening were at or very

near detectable levels of analysis. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Calcium carbonate is manufactured both in pure and impure form and is used extensively in many industries. In the pure form, it is used in the rubber, paint, cement, paper and pharmaceutical industries.

In one process, slaked lime is reacted in slurry form with carbon dioxide. The slurry is then screened and filtered. The recovered product is dried, milled and packaged for sale. The waste liquor from the filtration step is recycled or discharged, depending on requirements. The coarse materials recovered from the screening step are discharged.

The second process is based on waste streams from the Solvay Process. A solution of sodium carbonate and sodium bicarbonate from the soda ash plant is reacted with waste calcium chloride liquor which has been treated through a settler. The calcium carbonate produced together with by-product sodium chloride and unreacted calcium chloride is pumped to a thickener. The overflow from the thickener is collected with plant drainage streams in a sump to which soda ash finishing wastewater is added, precipitating calcium carbonate. This mixed stream then goes to waste collection. The calcium carbonate underflow is filtered, washed, atomized with steam, dried in a spray dryer, collected in a particle collector and packaged for sale.

An ultrafine grade of calcium carbonate is produced in a similar manner to that described above with some additional polish filtering, tunnel drying and milling. At each plant, the neutralized brine and process wastewater are returned to the brine cavity. No process wastewater is discharged.

The industry profile for this subcategory is given in Table 26.9-1.

Toxic Pollutants

There are four plants producing calcium carbonate in the United States. One discharges to a POTW. Data has been received on three plants as a result of Section 308 letters. In addition, a sampling survey for toxic pollutants was made at one plant which represents approximately 50 percent of total industry capacity. The results of the 308 letters and the sampling survey indicate that no toxic pollutants are being discharged. The sampling survey results found pollutant levels below treatability levels.

Maximum concentration of toxic pollutants found in raw waste were:

<u>Pollutant</u>	<u>Concentration (μg/l)</u>
Nickel	21
Zinc	68

Status of Regulations

Interim final regulations (40 CFR 415.302) were promulgated on May 22, 1975. These regulations require control of pH and suspended solids for both the Solvay and lime process. No change in the regulations is needed.

BAT and NSPS regulations (40 CFR 415.303) were proposed on May 22, 1975. These regulations were never finalized. It has been determined that the Calcium Carbonate Subcategory be excluded from the development of BAT and NSPS limitations under Paragraph 8 of the Settlement Agreement for the following reasons: There are only four plants manufacturing calcium carbonate and the 308 letters and sampling survey indicate that no toxic pollutants are being discharged in significant quantities.

Because no significant quantities of toxic pollutants are present, no further effort will be given to development of pretreatment regulations for this subcategory.

Calcium Chloride

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT or NSPS for the Calcium Chloride Subcategory. The bases for this determination are: 1) there are existing BAT and NSPS regulations that prohibit discharge of process wastewater pollutants from the brine extraction process, and 2) there is only one Solvay process plant in the United States where calcium chloride is recovered as a by-product.

Production Processes and Effluents

There are two processes for the manufacture of calcium chloride. In the first and major production process, calcium chloride is extracted from natural brines. The salts are solution mined and the resulting brines first are concentrated to remove sodium chloride by precipitation and then purified by the addition of other materials to precipitate sodium, potassium, and magnesium salts. The purified calcium chloride brine is then evaporated to yield a wet solid which is flaked and calcined to a dry solid product. The second process is the Solvay Process, which is primarily used for the manufacture of soda ash. In the Solvay Process, calcium chloride is recovered as a by-product. All the wastes from the process are associated with the sodium carbonate subcategory.

TABLE 26.9-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY CALCIUM CARBONATE

Total subcategory capacity rate	NA
Total subcategory production rate	129,600 kkg/year
Number of plants in this subcategory	NA
308 Data on file for	3
With total capacity of	81,300 kkg/year
With total production of	72,400 kkg/year
Representing capacity	NA
Representing production	56 percent
Plant production range:	
Minimum	555 kkg/year
Maximum	49,800 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	25 years
Maximum	50 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA= Not Available

Plants

There are 11 plants producing calcium chloride in the United States, one of which recovers it as a by-product from the Solvay Process.

Status of Regulations

Existing regulations for calcium chloride (40 CFR 415.4) include regulations for BAT and NSPS that prohibit discharge of wastewater pollutants from the brine process.

Calcium Hydroxide

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT or NSPS for the Calcium Hydroxide Subcategory. The basis for this determination is that an existing BPT regulation provides for zero discharge of process wastewater pollutants (40 CFR 415.312). Pretreatment regulations will be developed in Phase II.

Production Processes and Effluents

Calcium hydroxide is produced by adding water to calcium oxide in a pug mill premixer. The reacted mixture goes to an agitated hydrator where more water is added, resulting in an exothermic reaction. No wastewater is produced and therefore, there is zero discharge to navigable waters.

Plants

There are approximately fifteen plants producing calcium hydroxide in the United States.

Chromic Acid

Summary of Recommendations

It has been determined that no additional effort will be given to developing revised BAT, and NSPS regulations for this subcategory. The basis for this determination is that the existing interim final BPT regulation is zero discharge. Pretreatment standards will be developed in Phase II.

Production Process and Effluents

Sodium dichromate liquor from the dichromate manufacturing operation is reacted with sulfuric acid and filtered to recover impure chromic acid as a solid. The mother liquor is returned to the dichromate process for reuse. The recovered chromic acid is fed to a melter in which the sodium bisulfate liquifies and is separated from the chromic acid. The bisulfate is returned to the dichromate operation. The

chromic acid is resolidified, flaked and packaged for sale. Wastes are returned to the dichromate process for reuse.

Plants

There are five plants producing chromic acid.

BPT Limitations

Regulations for BPT were promulgated on May 22, 1975 (40 CFR 415.352). It has been determined that this subcategory will be excluded from development of BAT and NSPS regulations under Paragraph 8 of the Settlement Agreement because the operations are subject to zero discharge regulations for BPT.

Cuprous Oxide

Summary of Determinations

It has been determined that no further effort be given to developing BPT, BAT, NSPS, and Pretreatment regulations for the Cuprous Oxide Subcategory. The basis for this determination is that there is only one plant manufacturing cuprous oxide. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Cuprous oxide is manufactured by reducing cupric oxide by thermal decomposition in an oxygen-free environment. The reaction occurs at high temperature aided by a proprietary catalyst. There is no process related wastewater.

Cuprous oxide is used in the manufacture of glass, ceramics, marine paints, and photoelectric cells. It is also used in agriculture as a seed fungicide, as an antiseptic and as a catalyst.

Status of Regulations

Subpart AK has been reserved for this subcategory (Table 26.13-2).

Ferric Chloride

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT or NSPS regulations for this industry. The basis for this determination is that the existing regulation for BPT is zero discharge. Pretreatment will be developed in Phase II.

Production Processes and Effluents

Ferric chloride is produced from waste pickle liquor. The pickle liquor is reacted with iron, chlorine and hydrochloric acid. The

solution is filtered and sold as a solution or evaporated to dryness to produce a solid product. Wastewater from filter washes, equipment washing and leaks and spills is returned to the process.

Plants

There are 21 plants producing ferric chloride. Two plants are known to discharge to POTW.

Toxic Pollutants

The source of toxic pollutants is the pickle liquor feed. Toxic pollutants involved are chromium, copper, lead, nickel and zinc.

BPT Limitations

Regulations for BPT were promulgated on May 22, 1975 (40 CFR 415.382), which require zero discharge of process wastewater pollutants. The regulations have not been challenged.

BAT and NSPS Limitations

Zero discharge regulations were proposed May 22, 1975 for BAT and NSPS. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

Ferrous Sulfate

Summary of Determinations

It has been determined that no further effort be given to developing BAT, NSPS, or Pretreatment regulations for the Ferrous Sulfate Subcategory. The basis for this determination is that ferrous sulfate is recovered as a by-product and in each of the two processes, the wastes are attributable to the primary process. Recovery of ferrous sulfate actually reduces the waste load of both the primary operations. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Ferrous sulfate is made using two processes. In the first case, it is recovered from the waste sulfuric acid pickle liquor containing ferrous sulfate, ferric sulfate, and unreacted sulfuric acid. The solution is reacted with iron to reduce ferric ions to ferrous ions. The process is a by-product recovery from a waste solution rather than a direct manufacturing process. In the second process, the sulfate process, ferrous sulfate is obtained as a by-product during the manufacture of titanium dioxide. In the sulfate process, titanium dioxide-bearing ores are dissolved in sulfuric acid at a high temperature to produce iron (ferrous sulfate) and titanium sulfate. Iron sulfate is removed by crystallization and titanium sulfate is hydrolyzed and then calcined to produce the final titanium dioxide

product. All the wastes from the second process are associated with the titanium dioxide production.

Process wastewater is derived principally from gas scrubbers.

Plants

There are 13 producers recovering ferrous sulfate from titanium dioxide manufacture as a by-product or from the waste pickle liquor. Four of the 13 producers recover ferrous sulfate as a by-product from the sulfate process. The ferrous sulfate subcategory is excluded under Paragraph 8 of the Settlement Agreement because there is no direct method used for its manufacture and it is either recovered from the waste pickle liquor or as a by-product from the titanium dioxide manufacture and contributes no wastewater discharge of its own.

Fluorine

Summary of Determinations

It has been determined that no additional effort be given to developing revised BAT or NSPS regulations for this subcategory. The basis for this recommendation is that the existing interim final BPT regulations is zero discharge. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Fluorine is produced by electrolysis of liquid hydrogen fluoride. Fluorine is formed at one electrode and hydrogen at the other. The fluorine is compressed and packaged in cylinders. There is no process wastewater from this process.

Plants

There are 3 plants producing fluorine.

BPT Limitations

Regulations for BPT were promulgated on May 22, 1975, (40 CFR 415.402) and require zero discharge of process wastewater pollutants. The regulations have not been challenged.

BAT and NSPS Limitations

Zero discharge regulations were proposed for BAT and NSPS but never promulgated. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

Hydrochloric Acid

Summary of Determinations

It has been determined that no further effort be given to developing regulations for BPT, BAT, NSPS, or Pretreatment for the Hydrochloric Acid Subcategory. The basis for this determinations is: the small quantities of toxic pollutants found during screening are far below levels treatable by demonstrated treatment technology. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Most of the hydrochloric acid is produced as a by-product in the manufacture of chlorinated organic compounds. It is used in oil well activations, pickling of steel, metal cleaning, in monosodium glutamate manufacture and starch hydrolysis. It is also used as an acid reagent in several chemical manufacturing processes.

The industry profile data for this subcategory is given in Table 26.17-1. The data given and coverage of this subcategory applies only to the manufacture of hydrochloric acid by the thermal combination of chlorine and hydrogen. Wastes from this process come from combustion chamber condensate and from a fume scrubber.

While most of the hydrochloric acid is produced as a by-product in the manufacture of chlorinated organic compounds, the wastes are attributable to the organic compounds involved. This by-product production is not covered in this subcategory.

Toxic Pollutants

Data has been received on about 25 percent of the industry as a result of Section 308 letters. In addition, a sampling survey for toxic pollutants was made at one plant. The results of the 308 letters and the sampling survey showed concentrations close to the limits of detectability.

The maximum concentrations of priority pollutants found were:

<u>Pollutant</u>	<u>Maximum Concentration Observed (μg/l)</u>
Lead	3.5
Mercury	2
Nickel	5.5

Status of Regulations

BPT, BAT, NSPS and PSNS regulations (40 CFR 415.72) requiring zero discharge were promulgated on March 12, 1974. These regulations have since been remanded by the court and are not in effect.

Hydrogen

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT or NSPS regulations for this subcategory. The basis for this recommendation is that the existing BPT regulation is zero discharge of process wastewaters to navigable waters. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Hydrogen is made chiefly from two sources: purification of petroleum refinery by-product gases and as a co-product in the manufacture of carbon monoxide. In the latter case, the wastes are attributed to the carbon monoxide subcategory. Only the production of hydrogen from refinery by-product gases will be discussed.

Crude hydrogen as a refinery by-product is passed through a catalytic bed to remove oxygen and a drier to remove the water formed by the catalytic reaction. The gas is then cooled, purified and passed through a converter to change ortho-hydrogen to the para-form. Hydrogen is usually cooled to a liquid form for storage or shipping. No contact process water is used during the manufacture.

Plants

There are approximately 137 plants producing hydrogen. None are known to have discharges.

BPT Limitations

Regulations were promulgated on May 22, 1975, (40 CFR 415.412) requiring zero discharge of process wastewater pollutants to navigable waters. Only contaminated non-process water is allowed. This includes rain water, waters which come in contact with accidental spills and leaks, and discharges for personal safety. All reasonable measures must have been made to prevent, reduce, and control each contact and to mitigate the effects.

BAT and NSPS Limitations

BAT and NSPS were proposed on May 22, 1975, requiring zero discharge of process wastewater to navigable waters. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

TABLE 26.17-1 -- SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY HYDROCHLORIC ACID

Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	NA
308 Data on file for	6
With total capacity of	163,000 kkg/year
With total production of	119,000 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	NA
Maximum	NA
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	4 years
Minimum	20 years
Maximum	NA
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

Iodine

Summary of Determinations

It has been determined that no additional effort will be given to developing revised BAT or NSPS regulations. The basis for this determination is that the existing regulation for BPT is zero discharge. Pretreatment standards will be developed in Phase II.

Production Process and Effluents

Iodine is produced from brine solutions containing iodine. The brine is acidified and chlorinated liberating free iodine. The free iodine is stripped from the brine and treated again with chlorine yielding solid iodine. The slurry is filtered, treated with sulfuric acid and refiltered. The product is then crushed and packaged for sale. The wastes from this process are spent brine solutions which are returned to the well from which the brine was initially obtained.

Plants

There are 4 plants producing iodine.

BPT Limitations

Regulations for BPT were promulgated on May 22, 1975, (40 CFR 415.432) and require zero discharge of process wastewater pollutants. The regulations have not been challenged.

BAT and NSPS Limitations

Zero discharge regulations were proposed for BAT and NSPS on May 22, 1975. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

Lead Monoxide

Summary of Determinations

It has been determined that no further effort will be given to developing BAT or NSPS regulations for this subcategory. The basis for this recommendation is that the existing BPT regulation requires zero discharge. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Lead monoxide is produced by the thermal oxidation of lead. There are no process wastewater streams generated by lead monoxide production. Dust control is the problem in this subcategory. Use of dry collection systems rather than a water collection system is the control technology for meeting the regulation.

Plants

There are 15 plants producing lead monoxide in the United States. Ten plants are known to use dry bag collection systems and have no discharge of wastewater. Others are subject to existing zero discharge regulations.

BPT Limitations

BPT limitations were promulgated on May 22, 1975 (40 CFR 415.442). The limitations require zero discharge of process wastewater pollutants into navigable waters.

BAT and NSPS Limitations

On May 22, 1975, zero discharge regulations were proposed but never promulgated for BAT and NSPS. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

Lithium Carbonate

Summary of Determinations

It has been determined that no further efforts be given to developing or revising regulations for BPT, BAT, NSPS, or Pretreatment for the Lithium Carbonate Subcategory. The bases for this determination are: 1) there is only one plant in this subcategory using the spodumene ore process and discharging process wastewater, and 2) there is an existing zero discharge regulation for the brine process. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Lithium carbonate is produced by two processes. In one process, spodumene ore is heated at a high temperature to render it highly reactive. It is then cooled, ball-milled, and mixed with concentrated sulfuric acid. The acid-roasted ore is leached with water, and the excess acid is neutralized with ground limestone. This mixture is filtered and further treated with lime and soda ash. Further processing precipitates lithium carbonate. Wet scrubbers are the sources of wastewater. Significant quantities of toxic pollutants are not found in the wastewater.

In the other process, lithium carbonate is produced by the reaction of lime with concentrated brine, and lithium carbonate is precipitated by filtration. Process wastewater consists of spent brines, which are sent to on-site evaporation ponds. There is no process wastewater discharge from this process.

Status of Regulations

There is an existing BPT regulation for this subcategory (40 CFR 415.452).

Manganese Sulfate

Summary of Determinations

It has been determined that no further effort be given to developing or revising BPT, BAT, NSPS, or Pretreatment regulations for the Manganese Sulfate Subcategory. The bases for this determination are: 1) there is only one plant making commercial grade manganese sulfate that has a wastewater discharge, and 2) the amount of wastewater produced by that plant is low. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

There are two processes for the manufacture of manganese sulfate; the hydroquinone process and the coke and ore process. In the hydroquinone process, manganese ore, aniline and sulfuric acid are reacted to produce manganese sulfate, quinone and ammonium sulfate. The reacted mixture is steam distilled to remove quinone which is further processed to hydroquinone. The mixture of manganese and ammonium sulfate is filtered, evaporated, and crystallized. Manganese sulfate is recovered as crystals, and the spent liquor contains ammonium sulfate. In the second process, manganese ore and coke are reacted in a kiln and the product is leached with sulfuric acid. The resulting slurry is evaporated to dryness to recover a 30 percent product for agricultural purposes. The amount of wastewater produced from the hydroquinone process is small and the other process produces no waterborne waste.

Plants

Four plants are manufacturing manganese sulfate. Two of the producers use it for fertilizer production and they generate no waterborne wastes. One plant produces reagent grade product and the total production is very low. Only one other plants manufactures manganese sulfate (commercial grade) and has a significant wastewater flow.

Status of Regulations

Since only one manganese sulfate plant discharges waste to navigable waters, the subcategory is excluded from federal discharge regulation for BPT, BAT, NSPS, and Pretreatment standards under Paragraph 8 of the Settlement Agreement.

Nitric Acid

Summary of Determinations

The existing nitric acid regulation in the fertilizer category (40 CFR 418.5) is applicable to all nitric acid plants captive to a fertilizer production facility. In addition, sampling has shown that there are no significant quantities of toxic pollutants in the process wastewaters from stand alone nitric acid plants. Further BPT, BAT, NSPS or Pretreatment regulations will not be developed for this subcategory.

Production Processes and Effluents

Most of the nitric acid produced is used in the manufacture of ammonium nitrate and other nitrogen fertilizers. On site captive use is extensively practiced. It is also used in the manufacture of explosives, plastics and other organic products. Other uses are as an acidic and pickling agent. The source of process wastewater is equipment washing operations.

The industry profile data for this subcategory are given in Table 26.23-1.

Toxic pollutants found in raw wastes during sampling were as follows:

Maximum Concentration Observed ($\mu\text{g/l}$)

<u>Pollutant</u>	<u>Screening (2 Plants)</u>	<u>Verification (1 Plant)</u>
Chromium	110	100
Zinc	120	791
Lead	29	< 10
Mercury	0.47	4.5
Silver	0.5	< 15
2,4-Dinitrophenol	215	Not Analyzed
Nickel	170	85
Cyanide	< 0.04	< 0.02

The 2,4-Dinitrophenol is caused by contamination from organic products manufactured at the plant and will be addressed in that guideline. The chromium and zinc are ingredients of cooling water conditioners present in the blowdown which is mixed with process streams. Appropriate control is by best management practice not end-of-pipe treatment via national regulation. Other metals are below the limit of treatability.

Status of Regulations

BPT, BAT, NSPS, and PSNS regulations (40 CFR 415.100) requiring zero discharge were promulgated on March 12, 1974. These regulations have since been remanded by the court and are not in effect.

Oxygen and Nitrogen

Summary of Determinations

It has been determined that no further effort be given to developing or revising regulations for BAT, NSPS, or Pretreatment for the Oxygen and Nitrogen Subcategory. The bases for this determination are: 1) the wastewater discharge mainly consists of compressor water, and 2) the only toxic pollutant detected at or above treatability level was copper which is at the level of treatability. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Oxygen and nitrogen are produced from air by distillation of liquified air. Oxygen is used in the production of steel, gas welding, medicine, jet fuel, in sewage treatment plants and in the manufacture of ethylene and acetylene. In rocket propulsion, liquid oxygen is often used as a cryogenic liquid oxidizer.

The greatest use of nitrogen is in the manufacture of ammonia by the Haber process. It is also used in cryosurgery. As an inert gas, it is used to prevent oxidation by air. In the liquid form, it is used for low temperature refrigeration.

The wastewater discharge mainly consists of compressor cooling water. Other wastewaters are small quantities of boiler blowdown, intake air scrubber waters, and compressor condensate.

The industry profile for this subcategory is given in Table 26.24-1.

Toxic Pollutants

Data has been received on 10 plants as a result of Section 308 letters. There are at least 230 plants in the United States. However, all operate using the same basic process. One plant was sampled during the screening program. Toxic pollutants found in the raw waste loading during sampling were:

TABLE 26.23-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	NITRIC ACID
Total subcategory capacity rate	9,177,000 kkg/year
Total subcategory production rate	7,171,000 kkg/year
Number of plants in this subcategory	87
308 Data on file for	11
With total capacity of	1,106,000 kkg/year
With total production of	774,400 kkg/year
Representing capacity	12 percent
Representing production	11 percent
Plant production range:	
Minimum	NA
Maximum	NA
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	4 years
Maximum	83 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

<u>Pollutant</u>	<u>Concentration ($\mu\text{g/l}$)</u>
Chromium	26
Copper	590
Lead	51
Nickel	79
Zinc	170

The likely sources of copper are corrosion and bearing wear, and concentration in boiler and cooling tower blowdowns. The copper levels are at the accepted levels of treatment, therefore further reduction is not practical.

Status of Regulations

Interim Final BPT regulations (40 CFR 415.492) were promulgated on May 22, 1975. These regulations require limitations on pH and oil and grease. These regulations remain in effect and no change is needed.

BAT and NSPS regulations (40 CFR 415.494) were proposed on May 22, 1975. These regulations were never finalized. It has been determined that the Oxygen and Nitrogen Subcategory be excluded from the development of BAT and NSPS limitations under Paragraph 8 of the Settlement Agreement for the following reasons: The discharge consists of compressor water wherein the only toxic pollutant found is copper which is at the level of treatability.

Potassium Chloride

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT or NSPS regulations for the potassium chloride subcategory. The basis for this determination is that existing BPT regulations specify zero discharge of process waters. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Potassium chloride is produced in the United States by two principal processes: extraction from sylvite ore and extraction from lake brine (Trona Process). Sylvite ore is a combination of potassium chloride and sodium chloride. The ore is crushed, screened, and wet-ground in brine. The ore is then separated from clay impurities in a desliming process. The clay impurities are fed to a gravity separator which removes some of the sodium chloride precipitated from the leach brine and insolubles for disposal as waste. After desliming, the ore is chemically treated and the potassium chloride is separated from the sodium chloride in a flotation process. The tailings from flotation

TABLE 26.24-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	OXYGEN AND NITROGEN
Total subcategory capacity rate	35,526,000 kkg/year
Total subcategory production rate	NA
Number of plants in this subcategory	113
308 Data on file for	9
With total capacity of	1,588,000 kkg/year
With total production of	1,473,000 kkg/year
Representing capacity	4.5 percent
Representing production	NA
Plant production range:	
Minimum	2,400 kkg/year
Maximum	378,000 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	4 years
Maximum	36 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1979, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

are wasted and the resulting potassium chloride slurries are centrifuged to recover the potassium chloride. The product is then dried, screened, and packaged. The centrifuge liquors are recycled to the flotation circuit.

The Trona Process uses a cyclic evaporation-crystallization system in which saline brine is evaporated to nominal dryness. The brine and recycle liquor is concentrated in triple effect evaporators to produce a hot liquor high in potassium chloride and borax. Large quantities of sodium chloride and burkeite ($\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$) are crystallized and separated during evaporation. The sodium chloride is returned to the brine source, and the burkeite is transported to other processes for separation and refining. The hot liquor is then cooled rapidly in vacuum crystallizers and the potassium chloride is filtered from the slurry. The potassium chloride is then dried and packaged. A small portion may be refined further and/or converted to potassium sulfate. The cool liquor remaining is then allowed to crystallize the remaining borax which is then refined further using recrystallization and other processes. The remaining liquor is recycled back to the evaporation-crystallization step.

Plant

There are thirteen plants producing potassium chloride, two of which use the Trona Process.

BPT Regulations

BPT regulations were promulgated on May 22, 1975 (40 CFR 415.502) requiring zero discharge of process wastewater pollutants to navigable waters, except that residual brine and depleted liquor may be returned to the body of water from which the brine solution was withdrawn. There are no instances where the brine source is a navigable water.

BAT and NSPS Limitations

BAT and NSPS were proposed on May 22, 1975, requiring zero discharge of process wastewater to navigable waters. It has been determined that the potassium chloride subcategory will be excluded from the development of revised BAT and NSPS limitations under Paragraph 8 of the Settlement Agreement since a zero discharge regulation is in effect. In the absence of BAT and NSPS regulations, permits will be based on BPT.

Potassium Dichromate

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT and NSPS regulation for the Potassium Dichromate Subcategory. The basis for this determination is that existing BPT, BAT and NSPS regulations specify zero discharge of

process wastewater pollutants to navigable waters. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Potassium dichromate is made by reacting a sodium dichromate dihydrate solution with potassium chloride. The potassium dichromate is crystallized from solution requiring only removal of water prior to sizing and packaging. The process water is recycled back to the initial reaction tank.

BPT, BAT and NSPS Limitations

BPT, BAT and NSPS limitations were promulgated March 12, 1974 (40 CFR 415.122, 415.123 and 415.125). All subparts require zero discharge of process wastewater pollutants to navigable waters.

It has been determined that the potassium dichromate subcategory will be excluded from the development of revised BAT and NSPS limitations under Paragraph 8 of the Settlement Agreement. The basis for this determination is that by maintaining existing BPT, BAT and NSPS limitations, no discharge of wastewater pollutants to navigable waters will occur.

Potassium Iodide

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT, NSPS, and Pretreatment regulations for the Potassium Iodide Subcategory. The bases for this determination are: 1) because the wastewater discharge is less than 100 gallons per day, the quantity of pollutants discharged is very low; and 2) the concentrations of the toxic pollutants are at or below accepted treatment levels. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Potassium iodide is used in photographic emulsions, in animal and poultry feeds, table salts and analytical chemistry. It also has a number of medical uses.

One manufacturing process is known as the iron carbonate process. This involves the reaction of iron powder with iodine in aqueous solution. An intermediate compound, ferrosferricyanide, is formed which is subsequently reacted with potassium carbonate to yield potassium iodide. The raw product is purified, concentrated by evaporation and cooled to promote crystallization. Water used directly in the process is lost by evaporation. The only source of process wastewater is from equipment wash down operations.

The industry profile for this subcategory is given in Table 26.27-1.

Toxic Pollutants

Data has been received for approximately 50 percent of the industry as a result of Section 308 letters. In addition, a sampling survey was made at one plant. The following toxic pollutants were identified in the plant wastes:

<u>Pollutant</u>	<u>Concentration (μg/l)</u>
Antimony	48
Chromium	22
Copper	1040
Lead	26
Silver	34
Zinc	30

However, the levels of these pollutants are at or below accepted level of treatability. In addition, the flows are less than 100 gallons per day. At the one plant sampled, there was no process wastewater discharged since the wash water was sent to an evaporation pond.

Status of Regulations

A. BPT Limitations

BPT regulations (40 CFR 415.511) were promulgated on May 22, 1975. These regulations require limitations on pH, TSS, sulfide, iron and barium. These regulations are adequate for the control of conventional and nonconventional pollutants.

B. BAT and NSPS Regulations

NSPS and BAT limitations were proposed in May 22, 1975, but never finalized. It has now been determined that the Potassium Iodide Subcategory be excluded from the development of BAT and NSPS limitations under Paragraph 8 of the Settlement Agreement for the following reasons: 1) very small quantities of toxic pollutants are discharged from this industry, and 2) those pollutants discharged are at or below accepted treatability levels.

C. Pretreatment Limitations

Because no significant quantities of toxic pollutants are present, no further effort will be given to development of pretreatment regulations for this subcategory.

Potassium Metal

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT or NSPS regulations for the Potassium Metal Subcategory. These bases for this recommendation are: 1) existing

BPT, BAT and NSPS regulations specify zero discharge of process wastewaters; and 2) there is only one plant producing potassium in the U.S. and that plant uses a dry process. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Potassium metal is prepared by melting potassium chloride in a gas-fired melt pot prior to being fed to an exchange column. The molten potassium chloride flows down through a packed column, where it is contacted by ascending sodium vapors coming from a gas-fired reboiler. The reaction yields elemental potassium and sodium chloride, which is withdrawn continuously from the base of the apparatus. The elemental potassium is withdrawn as an overhead product. No process water is used so there are no waterborne effluents.

Plant

Only one plant produces potassium metal in the U.S. It uses no process water and there are no waterborne effluents.

BPT, BAT and NSPS Limitations

BPT, BAT and NSPS limitations were promulgated March 12, 1974 (40 CFR 415.112), 415.113 and 415.115). All subparts require zero discharge of process wastewater pollutants to navigable waters.

It has been determined that the potassium metal subcategory will be excluded from the development of revised BAT and NSPS limitations under Paragraph 8 of the Settlement Agreement. Maintaining the existing regulations will eliminate the discharge of toxic pollutants.

Potassium Permanganate

Summary of Determinations

It has been determined that no further effort be given to developing BPT, BAT, NSPS, and Pretreatment regulations for the Potassium Permanganate Subcategory. The basis for this determinations is that there is only one plant manufacturing Potassium Permanganate. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Manganese ore is slurried with potassium hydroxide solution and treated with oxygen to produce potassium manganate. This intermediate product and the ore wastes are recovered by centrifugation and the solids are then leached to dissolve the manganate. The resulting slurry is filtered to remove the ore wastes and the manganate converted in electrolytic cells. The permanganate is crystallized from the solution to form the product.

TABLE 26.27-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY

POTASSIUM IODIDE

Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	9
308 Data on file for	4
With total capacity of	1,985 kkg/year
With total production of	1,300 kkg/year
Representing capacity	NA
Representing production	50 percent
Plant production range:	
Minimum	79 kkg/year
Maximum	634 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	27 years
Maximum	42 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

Potassium Sulfate

Summary of Determinations

It has been determined that no further effort be given to developing or revising BPT, BAT and NSPS for the Potassium Sulfate Subcategory. The bases for this determination are there is an existing regulation for BAT and NSPS that requires zero discharge of process wastewater pollutants (40 CFR 415.133 and 415.135). The subcategory is excluded under Paragraph 8 of the Settlement Agreement. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Potassium sulfate is produced by the reaction in solution of potassium chloride with langbeinite ore. Langbeinite ore is a natural sulfate of potassium and magnesium ($K_2SO_4 \cdot MgSO_4$), usually intermixed with sodium chloride. When the reacted solution is partially evaporated, potassium sulfate precipitates out, and is recovered by centrifugation or filtration from the brine liquor, dried, and sold. The remaining brine liquor containing magnesium chloride is the source of raw waste. Depending on the sodium content of the ore used, the brine is either sold (low sodium content) or is ponded. In the latter case, the brine liquor is recycled or evaporated and the mud is landfilled. Therefore, no discharge results from the production of potassium sulfate.

Plants

There are approximately eight producers of commercial grade potassium sulfate in the United States.

Sodium Bicarbonate

Summary of Determinations

It has been determined that no further effort will be given to developing revised BAT and NSPS regulations for the Sodium Bicarbonate Subcategory. The basis for this determination is the existing BPT, BAT and NSPS regulations specify zero discharge of process wastewater pollutants to navigable waters. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Sodium bicarbonate is produced by reaction of sodium carbonate with water and carbon dioxide under pressure. The bicarbonate precipitates from the solution and is filtered, washed, dried, and packaged. Wastewater from the filtration is used in product scrubbers and then returned to the process.

Plants

Four plants produce sodium bicarbonate in the United States.

BPT, BAT and NSPS Limitations

BPT, BAT and NSPS limitations were promulgated March 12, 1974 (40 CFR 415.142, 415.143 and 415.145). All subparts require zero discharge of process wastewater pollutants to navigable waters.

It has been determined that the sodium bicarbonate subcategory will be excluded under Paragraph 8 of the Settlement Agreement. The basis for the determination is that maintaining the existing regulations will eliminate the discharge of toxic pollutants.

Sodium Carbonate

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT, NSPS, or Pretreatment regulations for the Sodium Carbonate Subcategory. The bases for this determination are: 1) no wastewater is discharged to navigable waters from the plants using natural deposits to produce sodium carbonate, and 2) only one plant exists that uses the Solvay Process to produce sodium carbonate. This subcategory is excluded under Paragraph 8 of the Settlement Agreement. The Solvay Process does have a discharge but because there is only one plant, it is inappropriate to write a regulation for the subcategory.

Production Processes and Effluents

Two methods are used for the production of sodium carbonate. One method is the recovery from natural sodium carbonate deposits and the other method is the Solvay process. The wastewater resulting from the use of natural deposits is sent to evaporation ponds and no water is discharged to navigable streams. In the Solvay process, sodium chloride (brine) is purified and saturated with ammonia and then chlorinated. The reacted solution is filtered and sodium bicarbonate is removed as a filter cake. The filter cake is calcined to produce sodium carbonate, driving off moisture and carbon dioxide. The production of sodium carbonate by the Solvay process requires the use of large volumes of water for non-contact cooling and process contact purposes and generates large loads of suspended solids, alkalinity, and ammonia.

Plants

Only one plant uses the Solvay process to produce sodium carbonate. The Solvay process is energy intensive and generates large pollution loads. The process is being replaced by production from natural deposits. It is unlikely that new Solvay process plants will be built in the future. The industry profile is presented in Table 26.32-1.

The other plants using natural deposits have zero discharge.

Status of Regulations

The regulation originally established has been remanded by the court. The Solvay process does have a discharge but because there is only one plant it is inappropriate to write regulations for this subcategory.

Sodium Chloride

Summary of Determinations

It has been determined that no further effort be given to developing or revising BAT and NSPS regulations for the Sodium Chloride Subcategory. The basis for this determination is that there are existing BAT and NSPS regulations that prohibit discharge of process wastewater (40 CFR 415.163 and 415.165). The subcategory is excluded under Paragraph 8 of the Settlement Agreement. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Sodium chloride is produced by three methods: 1) solar evaporation of sea water, 2) solution mining of natural brines, and 3) mining of rock salt.

In the solar evaporation process, salt water is concentrated by evaporation in open ponds to yield a saturated brine solution. After saturation is reached, the brine is fed to a crystallizer, wherein sodium chloride precipitates, leaving behind a concentrated brine solution (bittern) consisting of sodium, potassium, and magnesium salts. The precipitated sodium chloride is recovered for sale and the brine is recycled from the operation.

The brine in the second process is first aerated to remove hydrogen sulfide. The brine is then pumped to settling tanks where it is treated with caustic soda and soda ash to remove most of the calcium, magnesium, and iron present as insoluble salts. After clarification to remove these insolubles, the brine is then sent to multiple effect evaporators. As water is removed, salt crystals form and are removed as a slurry. The slurry is washed with fresh brine to remove calcium sulfate. The washed slurry is filtered, the mother liquor is returned to evaporators, and the crystals from the filter are dried and screened. Wastes are generated from the multiple effect evaporators and driers, basic brine purification, and from water treatment. Zero aqueous discharge can be accomplished by replacing barometric condensers with non-contact exchangers, eliminating packing station wastes by more efficient design, and recycling all process water.

Mining of rock salt produces no process wastewater.

related wastewater during the screening of one plant. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Process and Effluents

Sodium hydrosulfide is produced by reaction of hydrogen sulfide with sodium hydroxide. Sodium hydrosulfide is used in the manufacture of sodium sulfide, other chemicals, and paper (Kraft). It is also used in dehairing of hides and industrial wastewater treatment. Process wastewater may be derived from filter backwash water.

The subcategory profile data are given in Table 26.35-1.

Toxic Pollutants

Toxic pollutants found in the waste during screening of one plant were phenol (76 $\mu\text{g/l}$) and naphthalene (90 $\mu\text{g/l}$) which are below treatability levels. Due to the very small flows and waste loads generated by this industry, this subcategory is excluded under Paragraph 8 of the Settlement Agreement

Status of Regulations

Subpart BD has been reserved for this subcategory.

Sodium Metal

Summary of Determinations

It has been determined that no further effort be given to developing or revising BPT, BAT, NSPS, or Pretreatment regulations for the Sodium Metal Subcategory. The basis for this determination is that the small quantities of toxic pollutants found during screening are far below accepted treatability levels. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Sodium metal is manufactured with chlorine by electrolysis of fused sodium chloride. It is used in the production of tetraethyl lead, sodium cyanide, sodium peroxide, and titanium and zirconium metals. In liquid form, it is used as a nuclear reactor coolant; it is also used as a light, thermally conductive solid in various applications.

The industry profile for this subcategory is given in Table 26.36-1.

Toxic Metals

Data has been received on about 60 percent of the industry as a result of Section 308 letters. In addition, sampling surveys were made at two plants representing 38 percent of the industry. Toxic pollutants found during sampling were as follows:

<u>Pollutant</u>	<u>Maximum Concentration Observed $\mu\text{g/l}$</u>
Copper	31
Zinc	13
Dichlorobromomethane	33
Chloroform	10

These pollutants are at very low concentrations which are far below accepted treatability levels.

Status of Regulations

BPT regulations (40 CFR 415.182) were promulgated on March 12, 1974. These regulations have since been remanded by the court.

BAT and NSPS regulations requiring zero discharge (40 CFR 415.183) were promulgated on March 12, 1974. These regulations have been since remanded by the court. However, it has been determined that the sodium metal subcategory be excluded from BAT and NSPS regulations because data from Section 308 letters and sampling surveys indicate that toxic pollutant concentrations are far below accepted treatable levels.

Because no significant quantities of toxic pollutants are present, no further effort will be given to development of pretreatment regulations for this subcategory.

Sodium Silicate

Summary of Determinations

It has been determined that no further effort be given to developing BPT, BAT, NSPS, and Pretreatment regulations for the Sodium Silicate Subcategory. The basis for this determination is that the small quantities of toxic pollutants found during screening are below accepted levels of treatability. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Sodium silicate is manufactured both in liquid and anhydrous powdered form. It has many industrial uses, such as additives in adhesives, flocculants, and cleaning agents. It is also used in the production of soap and household detergents. Sources of process wastewater include contact cooling water, filter backwash, gas scrubbers and tank cleaning.

The industry profile for this subcategory is given in Table 26.37-1.

Toxic Pollutants

Data has been received on about 63 percent of the industry as a result of Section 308 letters. In addition, a sampling survey was made at one plant which represents about 6 percent of the industry. The following pollutants were detected: nickel, copper, and zinc. These levels are below accepted treatability levels. In addition, the sampling data was taken from wastewaters receiving insufficient treatment. The wastes were ponded to remove suspended solids consisting essentially of sand and other silicates. Normally the pH of the wastes would be lowered to 9 and receive additional settling. However the dissolved silicate and high pH are considered beneficial by sewerage authorities in the removal of solids in primary and secondary settling systems.

Maximum concentrations of toxic pollutants found during sampling are:

<u>Pollutant</u>	<u>(μg/l)</u>
Copper	347
Nickel	121
Zinc	181

Status of Regulations

BPT, BAT, and NSPS regulations (40 CFR 415.192) requiring zero discharge of pollutants were promulgated on March 12, 1974. These regulations have since been remanded by the court and are not in effect.

Because no significant quantities of toxic pollutants are present, no further effort will be given to development of pretreatment regulations for this subcategory.

Sodium Silicofluoride

Summary of Determinations

This subcategory has been excluded from the present study but will be included in the Phase II, Inorganic Chemicals, review.

Production Processes and Effluents

Sodium silicofluoride is used in the manufacture of sodium fluoride and in the light metal industry as a protective agent. It is also used as an insecticide, as a fluxing and opacity agent for ceramics and in detergent products.

The industry profile for this subcategory is given in Table 26.38-1.

TABLE 26.35-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	SODIUM HYDROSULFIDE
Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	12
308 Data on file for	3
With total capacity of	56,900 kkg/year
With total production of	44,700 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	3,800 kkg/year
Maximum	36,500 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	5 years
Maximum	14 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

Sodium Sulfite

Summary of Determinations

It has been determined that no further efforts be given to developing or revising regulations for the Sodium Sulfite Subcategory. The basis for this determination is that there are existing regulations for BAT and NSPS that require zero discharge of process wastewater pollutants (40' CFR 415.203 and 415.205). The subcategory is excluded under Paragraph 8 of the Settlement Agreement. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Sodium sulfite is produced by two processes. One is the direct reaction of soda ash with sulfur dioxide. There are four plants manufacturing sodium sulfite using this process. In the other process, sodium sulfite is produced as a by-product in the manufacture of phenol. Since this process is used primarily to produce phenol and its derivatives, it is not considered for this subcategory.

Sodium Thiosulfate

Summary of Determinations

It has been determined that no further effort be given to developing BPT, BAT, NSPS, or Pretreatment regulations for the Sodium Thiosulfate Subcategory. The basis for this determination is that no toxic pollutants were found at significant levels in the raw waste during screening of one plant. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Most of the sodium thiosulfate is produced by the sulfur-sodium sulfite process. It is used extensively in the development of negatives and prints in the photographic industry. It is also used in medicine, in the paper and dyeing industries, and as a bleaching agent for natural products. Process wastewater sources include filter backwash and the discharge from barometric condensers.

The subcategory profile data are given in Table 26.40-1.

Toxic Pollutants

Data has been received on about 33 percent of the industry as a result of Section 308 letters. A sampling survey at one plant indicated that toxic pollutants in the effluent are below treatment levels.

Toxic pollutants identified in the effluent were:

TABLE 26.36-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY SODIUM METAL

Total subcategory capacity rate	381,000 kkg/year
Total subcategory production rate	NA
Number of plants in this subcategory	5
308 Data on file for	3
With total capacity of	96,340 kkg/year
With total production of	78,541 kkg/year
Representing capacity	25 percent
Representing production	NA
Plant production range:	
Minimum	NA
Maximum	NA
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	NA
Maximum	NA
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1979, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA= Not Available

<u>Pollutant</u>	<u>Concentration (μg/l)</u>
Copper	91
Zinc	94

Status of Regulations

Subpart BG has been reserved for this subcategory.

Stannic Oxide

Summary of Determinations

It has been determined that no additional effort be given to developing revised BAT or NSPS regulations for this subcategory. The basis for this recommendation is that existing regulation for BPT is zero discharge. Pretreatment standards will be developed in Phase II.

Production Process and Effluents

Tin is reacted with air and oxygen in a furnace to form stannic oxide. The product is recovered with dry bag collectors and packaged for sale. There is no process wastewater from this process.

Plants

There are three plants producing stannic oxide.

BPT Limitations

Regulations for BPT were promulgated on May 22, 1975 (CFR 415.602) and require zero discharge of process wastewater pollutants. The regulations have not been challenged.

BAT and NSPS Limitations

Zero discharge regulations were proposed for BAT and NSPS on May 22, 1975. Since BPT already requires zero discharge, BAT and NSPS are being excluded under Paragraph 8 of the Settlement Agreement.

Strong Nitric Acid

Summary of Determinations

It has been determined that no further effort be given to developing regulations for the Nitric Acid (Strong) Subcategory. The basis for this determination is that no process related toxic pollutants were found at significant levels in the process wastewater during screening of two plants and verification of one plant. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

TABLE 26.37-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	SODIUM SILICATE
Total subcategory capacity rate (27 Plants)	927,300 kkg/year
Total subcategory production rate	NA
Number of plants in this subcategory	39
308 Data on file for	21
With total capacity of	NA
With total production of	431,000 kkg/year
Representing capacity	47 percent
Representing production	NA
Plant production range:	
Minimum	12,400 kkg/year
Maximum	57,300 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	7 years
Maximum	43 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1979, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

Production Processes and Effluents

Most of the strong nitric acid is produced by dehydration of dilute nitric acid. Strong nitric acid is used in the manufacture of organic compounds where nitric acid acts as an oxidizing agent instead of an acid. It is also used in the manufacture of dye intermediates and explosives. The principal wastewater source is derived from equipment washing. The industry profile data are given in Table 26.42-.

Toxic Pollutants

Toxic pollutants found in the waste streams during sampling of strong nitric acid plants were:

<u>Pollutant</u>	Maximum Concentration Observed ($\mu\text{g/l}$)	
	<u>Screening (2 Plants)</u>	<u>Verification (1 Plant)</u>
Chromium	40,000	< 50
Zinc	900	120
Lead	70	< 10
Mercury	8.6	1.2
Silver	0.69	< 15
Nickel	< 5.0	< 50
Cadmium	< 2.0	< 2.0
Cyanide	0.020	< 0.020

In a follow-up, it was found that the chromium and zinc are used as corrosion inhibitors in the cooling tower, and are not process related. Control of these pollutants should involve best management practices instead of end-of-pipe treatment.

Status of Regulations

Subpart AV has been reserved for this subcategory.

Sulfur Dioxide

Summary of Determinations

It has been determined that no further effort be given to developing BPT, BAT, NSPS, and Pretreatment regulations for the Sulfur Dioxide Subcategory. The basis for this determination is that no toxic pollutants were found at significant levels in the raw waste during screening of one plant. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Most of the sulfur dioxide is produced by air oxidation of sulfur. The major portion of sulfur dioxide production is in the gaseous form, although a small percentage is also produced in liquid form. In the

TABLE 26.38-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY

SODIUM SILICOFLUORIDE

Total subcategory capacity rate	NA
Total subcategory production rate	51,800 kkg/year
Number of plants in this subcategory	6
308 Data on file for	1
With total capacity of	7,460 kkg/year
With total production of	3,970 kkg/year
Representing capacity	NA
Representing production	7.5 percent
Plant production range:	
Minimum	NA
Maximum	NA
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	NA
Maximum	NA
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

gaseous form, it is predominantly used in on-site manufacture of sulfuric acid. It is also used in the paper and petroleum industries, as well as for fermentation control in the wine industry, for bleaching in the textile and food industries, and in the production of other chemicals. The wastewater source at one plant was a process effluent from an extraction operation.

The subcategory profile data are given in Table 26.43-1.

Toxic Pollutants

Data has been received on about 33 percent of the industry as a result of Section 308 letters. No toxic pollutants were found at significant levels in wastewaters during the screening of one sulfur dioxide plant.

Status of Regulations

Subpart BI (40 CFR 415.610, 5/22/75) has been reserved for this subcategory.

Sulfuric Acid Industry

Summary of Determinations

It has been determined that no further effort be given to developing BPT, BAT, NSPS, and Pretreatment regulations for the Sulfuric Acid Subcategory. The basis for this determination is that the small quantities of toxic pollutants found during screening are far below accepted treatability levels. This determination applies to the production of sulfuric acid by the contact process from elemental sulfur only. This subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Sulfuric acid is one of the most extensively used of all manufactured chemicals. The major industrial use is in the fertilizer industry, with on-site captive use of the product as a dominant practice. It is also used in the manufacturing of plastics, explosives, detergents, hydrofluoric acid, nuclear fuel and several other organic and inorganic products. This industry has no process wastewater, but does have cooling tower blowdown.

The industry profile data for this subcategory are given in Table 26.44-1.

Toxic Pollutants

Data has been received on about 21 percent of the industry as a result of Section 308 letters. In addition a sampling survey was made at one plant which represents less than 1 percent of the industry. Only nickel and copper were detected but were at levels far below accepted

TABLE 26.40-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	SODIUM THIOSULFATE
Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	6
308 Data on file for	5
With total capacity of	88,000 kkg/year
With total production of	70,300 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	4,400 kkg/year
Maximum	27,000 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	3 years
Maximum	51 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

treatability concentrations. They probably result from corrosion and are concentrated by recycling the cooling water. Apart from waterside corrosion some corrosion products results from acid leaks. However, NPDES permits generally require pH control and this will limit this problem.

Status of Regulations

BPT regulations (40 CFR 415.212) were promulgated on March 12, 1974. These regulations have been remanded by the court.

NSPS and BAT regulations requiring zero discharge (40 CFR 415.212) were promulgated on March 12, 1974. These regulations have been remanded by the court. Because no significant quantities of toxic pollutants are present no further effort will be given to development of pretreatment regulations for this subcategory.

Zinc Oxide

Summary of Determinations

It has been determined that no further effort be given to developing BAT, NSPS, or pretreatment regulations for Zinc Oxide Subcategory. The bases for this determination are 1) only one plant exists the generates process liquid effluents from the manufacture of zinc oxide using the wet chemical process, and 2) processes using oxidation of zinc produce no waterborne wastes. The subcategory is excluded under Paragraph 8 of the Settlement Agreement.

Production Processes and Effluents

Two major processes are used for the manufacture of zinc oxide: 1) those involving oxidation of zinc, and 2) those involving precipitation from solution followed by calcination. Two methods are used to prepare zinc oxide using the oxidation process-- the American Process and the French Process.

In the American Process, zinc ore is dried and converted to crude oxide by roasting at approximately 1000 degrees C. Zinc sinter is introduced into a reaction kiln with equal amounts of coke. The zinc vapor and carbon monoxide formed are oxidized to zinc oxide and carbon dioxide and drawn off through ducts to cyclone and baghouse collection equipment. No waterborne wastes are generated.

In the French Process, crude zinc oxide sinter and dried coke are mixed with binder and fed through briquetting rolls. The raw briquettes are fed into cokers operating at temperatures between 500 and 1000 degrees C. Zinc sinter is converted to zinc metal in vapor using electrical ore vaporizers or rotary burners. The zinc vapors are purified to remove lead and cadmium impurities. The purified zinc is then vaporized and reacted with oxygen to produce zinc oxide, which is recovered by dry collection methods, cooled, and packaged. No waterborne wastes are generated.

TABLE 26.42-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY

STRONG NITRIC ACID

Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	NA
308 Data on file for	5
With total capacity of	155,200 kkg/year
With total production of	121,000 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	5,300 kkg/year
Maximum	60,200 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	11 years
Maximum	49 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

In the wet chemical process, crude zinc oxide recovered from lead smelters is used as the raw material. The zinc oxide is leached with caustic soda solution to remove sulfate and dissolve lead salts. The undissolved zinc oxide is then recovered from the leaching mixture, washed, neutralized to remove alkali, dried, calcined, and packaged. Waterborne wastes are generated from the deleading step, desulfating step, etc.

Plants

There are about 20 zinc oxide producers in the United States. The producers include both primary and secondary. The final product of the primary producers is zinc oxide, while the secondary producers manufacture zinc oxide and use it to make zinc chloride and zinc nitrate. About 80-90 percent of the total zinc oxide produced is made by the American and French Processes, and 10 percent is made by one plant using the wet chemical process.

Zinc Sulfate

Summary of Determinations

It has been determined that no further effort be given to developing revised BAT or NSPS regulations for the Zinc Sulfate Subcategory. The basis for this determination is that existing BPT regulations specify zero discharge of process wastewaters to navigable waters. Pretreatment standards will be developed in Phase II.

Production Processes and Effluents

Zinc sulfate is produced by reaction of sulfuric acid with various crude zinc starting materials, such as zinc oxide from brass mill fumes, zinc metal residues from various sources, and zinc carbonate by-product from sodium hydrosulfite manufacture. The following basic steps are followed: reaction of the zinc containing raw material with refiltration of solids, and either evaporation to dryness or sale as solution grade. Liquors from the preceding processes are, in some cases, refined to recover by-products and other wastewaters are recycled. The only wastes are filter cake residues.

Plants

There are eighteen plants producing zinc sulfate and none are known to discharge wastes from the process system.

BPT Limitations

Regulations were promulgated on May 22, 1975 (40 CFR 415.632) requiring no discharge of process wastewater pollutants to navigable waters. The discharge of contaminated non-process wastewater is permitted. This includes rainfall runoffs, accidental spills, accidental leaks, and discharges related to personal safety equipment. All reasonable measures must be taken to prevent, reduce and control

such contact to the maximum degree feasible, and to mitigate the effects of such contact once it has occurred.

BAT and NSPS Limitations

BAT and NSPS guidelines were proposed on May 22, 1975, requiring zero discharge of process wastes to navigable waters. Since BPT already requires zero discharge, BAT and NSPS are excluded under Paragraph 8 of the Settlement Agreement.

TABLE 26.43-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY	SULFUR DIOXIDE
Total subcategory capacity rate	NA
Total subcategory production rate	NA
Number of plants in this subcategory	15
308 Data on file for	5
With total capacity of	453,000 kkg/year
With total production of	364,000 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	
Minimum	27,800 kkg/year
Maximum	170,000 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	3 years
Maximum	51 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

TABLE 26.44-1 - SUBCATEGORY PROFILE DATA SUMMARY

SUBCATEGORY SULFURIC ACID

Total subcategory capacity rate	33,619,000 kkg/year
Total subcategory production rate	NA
Number of plants in this subcategory	109
308 Data on file for	52
With total capacity of	7,758,000 kkg/year
With total production of	6,308,000 kkg/year
Representing capacity	23 percent
Representing production	NA
Plant production range:	
Minimum	5,300 kkg/year
Maximum	47,700 kkg/year
Average production	NA
Median production	NA
Average capacity utilization	NA
Plant age range:	
Minimum	3 years
Maximum	78 years
Waste water flow range:	
Minimum	NA
Maximum	NA
Volume per unit product:	
Minimum	NA
Maximum	NA

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1979 , U.S. Department of Commerce, Current Industrial Reports, December 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980

NA = Not Available

REFERENCES

1. U.S. Environmental Protection Agency. Major Inorganic Products, Development Document. EPA-440/1-74-007a, 1974.
2. U.S. Environmental Protection Agency. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Significant Inorganic Products. EPA-440/1-75-037, 1975. 358 Pp.
3. Calspan Corp. Addendum to Development Document for Effluent Limitations Guidelines and New Source Performance Standards. Major Inorganic Products Segment of Inorganic Chemicals Manufacturing Point Source Category. Contract No. 68-01-3281, 1978.
4. Sampling Screening Procedure for the Measurement of Priority Pollutants. U.S. Environmental Protection Agency, 1976. 6 Pp.
5. Coleman, R.T., J.D. Colley, R.F. Klausmeier, D.A. Malish, N.P. Meserole, W.C. Micheletti, and K. Schwitzgebel. Treatment Methods for Acidic Wastewater Containing Potentially Toxic Metal Compounds. EPA Contract No. 68-02-2608, U.S. Environmental Protection Agency, 1978. 220 Pp.
6. Kraus, K.A., and H.O. Phillips. Processes for Removal and/or Separation of Metals from Solutions. U.S. Patent 3,317,312, U.S. Patent Office, May 2, 1967. 9 Pp.
7. Scott, M.C. Heavy Metals Removal at Phillips Plating. WWEMA Industrial Pollution Conference, St. Louis, Missouri, 1978. 16 Pp.
8. Scott, M.C. Sulfex[®] - A New Process Technology for Removal of Heavy Metals from Waste Streams. The 32nd Annual Purdue Industrial Waste Conference, Lafayette, Indiana, 1977. 17 Pp.
9. Patterson, J.W., and R.A. Minear. Wastewater Treatment Technology. Illinois Institute of Technology, 1973.
10. Patterson, J.W. Wastewater Treatment Technology. Ann Arbor Science Publishers, Inc. Ann Arbor, Michigan, 1975.
11. Schlauch, R.M., and A.C. Epstein. Treatment of Metal Finishing Wastes by Sulfide Precipitation. EPA-600/2-75-049, U.S. Environmental Protection Agency, 1977. 89 Pp.
12. Campbell, H.J., Jr., N.C. Scrivner, K. Batzar, and R.F. White. Evaluation of Chromium Removal from a Highly Variable Wastewater Stream. «The 32nd Annual Purdue Industrial Waste Conference, Lafayette, Indiana, 1977. 38 Pp.

13. Wing, R.E., C.L. Swanson, W.M. Doane, and C.R. Russell. Heavy Metal Removal with Starch Xanthate-Cationic Polymer Complex. J. Water Pollution Control Federation, 46 (8): 2043-2047, 1974.
14. Wing, R.E. Heavy Metal Removal from Wastewater with Starch Xanthate, In: Proceedings of the 29th Annual Purdue Industrial Waste Conference, Lafayette, Indiana, 1974. Pp. 348-356.
15. Wing, R.E. Removal of Heavy Metals from Wastewater with Starch Xanthate-Cationic Polymer Complex. The 46th Annual Conference of the Water Pollution Control Federation, Cleveland, Ohio, 1973. 38 Pp.
16. Wing, R.E. Removal of Heavy Metals from Wastewater with Starch Xanthate. Presented at the Traces of Heavy Metals in Water: Removal and Monitoring Conference, Princeton, New Jersey, 1973. Pp. 258-273.
17. Swanson, C.L., R.E. Wing, W.M. Doane, and C.R. Russell. Mercury Removal from Wastewater with Starch Xanthate Cationic Polymer Complex. Environmental Science & Technology 7(7): 614-619, 1973.
18. Hanway, J.E., Jr., R.G. Mumford, and D.G. Barth. A Promising New Process for Removing Heavy Metals from Wastewater. Civil Engineering-ASCE 47(10): 78-79, 1976.
19. Hanway, J.E., Jr., R.G. Mumford, and P.N. Mishra. Treatment of Industrial Effluents for Heavy Metals Removal Using the Cellulose Xanthate Process. The 71st Annual Meeting of the American Institute of Chemical Engineers, Miami, Florida, 1978. 21 Pp.
20. Wing, R.E., L.L. Navickis, B.K. Jasberg, and W.E. Rayford. Removal of Heavy Metals from Industrial Wastewaters Using Insoluble Starch Xanthate. EPA-600/2-78-085, U.S. Environmental Protection Agency, 1978. 116 Pp.
21. DeJong, G.J., and Ir. C.J.N. Rekers. The Akzo Process for the Removal of Mercury from Wastewater. Journal of Chromatography 102: 443-451, 1974.
22. Van der Heem, P. The Removal of Traces of Heavy Metals from Drinking Water and Industrial Effluent with Ion Exchangers. The Regional American Chemical Society Meeting, 1977. 16 Pp.
23. Chemical Marketing Recorder, July 24, 1978.
24. Slen, T.T., M. Chem, and J. Lauber. Incineration of Toxic Chemical Wastes. Pollution Engineering 10(10):42, 1978.
25. TRW Systems Group. Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste. NTIS PB-224589, 1973.

26. Ellerbusch, F., and H.S. Skrovronek. Oxidative Treatment of Industrial Wastewater. Industrial Water Engineering 14(5):20-29, 1977.
27. Knopp, P.V., and T.L. Randall. Detoxification of Specific Organic Substances by Wet Oxidation. The 51st Annual Conference of Water Pollution Control Federation, 1978.
28. Arthur D. Little, Inc. Treatment Technology Handbook.
29. Schell, W.J. Membrane Ultrafiltration for Water Treatment. Envirogenics Systems Co.
30. Vanderborght, B.M., and R.E. Van Grieken. Enrichment of Trace Metals in Water Adsorption of Activated Carbon. Analytical Chemistry 49 (2):311-316, 1977.
31. Cheremisinoff, P.N., and F. Ellerbusch. Carbon Adsorption Handbook. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1978.
32. Jacobs Engineering Group Inc. Study of the Application of BAC to Industrial Wastewater. Office of Water Research and Technology, U.S. Environmental Protection Agency, 1978.
33. Otsubo, K., S. Yamazaki, and Y. Sakuraba. Advanced Water Treatment for Fluoride-Containing Wastewater. Hitachi Hyoron 58(3):219-, 1976. Trans. For Rockwell Intl.
34. Zabban, W., and H.W. Jewett. The Treatment of Fluoride Wastes. In: Proceedings of the 22nd Annual Purdue Industrial Waste Conference, Lafayette, Indiana, 1967. Pp. 706-716.
35. Rubel, F., Jr., and R.D. Woosley. Removal of Excess Fluoride from Drinking Water. EPA-570/9-78-001. U.S. Environmental Protection Agency, 1978. 16 Pp.
36. Wu, Y.C. Activated Alumina Removes Fluoride Ions From Water. Water Sewage Works 125(6):76-82, 1978.
37. Maier, F.J. Partial Defluoridation of Water. Public Works 91 (11), 1960.
38. Maier, F.J. New Fluoride Removal Method Cuts Costs. Engineering News-Record 148 (24):40, 1952,
39. Kennedy, D.C., M.A. Kimler, and C.A. Hammer. Functional Design of a Zero-Discharge Wastewater Treatment System for the National Center for Toxicological Research. In: Proceedings of the 31st Annual Purdue Industrial Waste Conference, Lafayette, Indiana, 1976. Pp. 823-830.

40. Hannah, S.A., M. Jelus, and J.M. Cohen. Removal of Uncommon Trace Metals by Physical and Chemical Treatment Processes. Journal Water Pollution Control Federation 49(11):2297-2309, 1977.
41. Maruyama, T., S.A. Hannah, and J.M. Cohen. Removal of Uncommon Trace Metals by Physical and Chemical Treatment Processes. Journal Water Pollution Control Federation 49(11):2297-2309, 1977.
42. Gulledege, H.H., and J.T. O'Connor. Removal of Arsenic (V) from Water by Adsorption on Aluminum and Ferric Hydroxides. Journal American Water Works Association 65 (8):548-552, 1973.
43. Gupta, S., and K.Y. Chen. Arsenic Removal by Adsorption. Journal Water Pollution Control Federation 50 (3):493, 1978.
44. Larsen, H.P., J.K. Shou, and L.W. Ross. Chemical Treatment of Metal-Bearing Mine Drainage. Journal Water Pollution Control Federation 45 (8):1682-1695, 1973
45. Nilsson, R. Removal of Metals by Chemical Treatment of Municipal Wastewater. Water Research 5:51-60, 1971
46. Sorg, T.J., O.T. Love, and G.S. Logsdon. Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations. EPA-600/8-77-005. U.S. Environmental Protection Agency, 1977. 73 Pp.
47. Colley, J.D., C.A. Muela, M.L. Owen, N.P. Meserole, J.B. Riggs, and J.C. Terry. Assessment of Technology for Control of Toxic Effluents from the Electric Utility Industry. EPA-600/7-78-090. U.S. Environmental Protection Agency, 1978.
48. Smithson, G.R., Jr. An Investigation of Techniques for Removal of Chromium from Electroplating Wastes. EPA 12010 EIE. U.S. Environmental Protection Agency, 1971, 91 Pp.
49. Patterson, J.W., H.E. Allen, and J.J. Scala. Carbonate Precipitation for Heavy Metals Pollutants. Journal Water Pollution Control Federation 49(12):2397-2410, 1977.
50. Sabadell, J.E. Traces of Heavy Metals in Water Removal Processes and Monitoring. EPA-902/9-74-001. U.S. Environmental Protection Agency, 1973.
51. U.S. Environmental Protection Agency. Environmental Multi-Media Assessment of Selected Industrial Inorganic Chemicals. EPA Contract No. 68-03-2403, 1977.
52. JRB Associates, Inc. An Assessment of pH Control of Process Waters in Selected Plants. Draft Report to the Office of Water Programs, U.S. Environmental Protection Agency, 1979.
53. Energy and Environmental Analysts, Inc. Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic

Chemicals Industry. Prepared for Office of Water Planning and Standards, U.S. Environmental Protection Agency, 1980.

54. Kirsch, E.J., J.E. Etzel J. Water Pollution Control Federation, Vol. 45, 359, 1973.

55. E.I. Dupont de Nemours & Company, Development Document for Effluent Limitations Guidelines and New Source Performance Standards for Simultaneous Beneficiation-Chlorination Process of TiO₂ Manufacture, Pigments Department, Edge Moor, Delaware, 1977.

56. U.S. Environmental Protection Agency, Prodeedings: Seminar on Analytical Methods for Priority Pollutants, Denver. 1977.

57. SRI International, Report No. 61B, Chlorine, Supplement B, by Yen-Chen Yen, (a private report by the Process Economics Program), Menlo Park, California, 1978.

58. U.S. Environmental Protection Agency, Development Document for Proposed Effluent Limitations Guidelines, New Source Performance Standards and Pretreatment Standards for the Steam Electric Point Source Category, (Effluent Guidelines Division, Office of Water and Waste Management, Washington, D.C.), 1979.

59. U.S. Environmental Protection Agency, Quality Criteria for Water, (EPA-44/9-76-023), Washington, D.C., 1976.

60. U.S. Environmental Protection Agency, Development Document for Proposed Effluent Limitations Guidelines and Standards for the Inorganci Chemicals Manufacturing Point Source Category, (Effluent Guidelines Division, Office of Water and Waste Management, Washington, D.C.), 1980.

61. U.S. Environmental Protection Agency, Treatability Studies for the Inorganic Chemicals Manufacturing Point Source Category, (Effluent Guidelines Division, Office of Water and Waste Management, Washington, D.C.), 1980.

62. E. I. duPont de Nemours & Company, Comments on Proposed Development Document for Effluent Limitations Guidelines and Standards for the Titanium Dioxide - Chloride Ilmenite Process Subcategory of the Inorganic Chemicals Point Source Category, Wilmington, Delaware, 1980.

63. U.S. Environmental Protection Agency, Economic Impact Analysis of Pollution Control Technologies for Segments of the Inorganic Chemicals Manufacturing Industry. EPA 440/2-81-023, 1982.

BIBLIOGRAPHY

- Andco Environmental Processes, Inc. Andco Chromate and Heavy Metal Removal System. 1977
- Anderson, J.R., and C.O. Weiss. Method for Precipitation of Heavy Metal Sulfides. U.S. Patent 3,740,331. U.S. Patent Office. June 19, 1973.
- Birkett, J.D. Electrodialysis - An Overview. Industrial Water Engineering 14 (5):6-9, 1977.
- Bowen, L.B., J.H. Mallison, and J.H. Cosgrove. Waste Recovery: Zinc Recovery from Rayon Plant Sludge. Chemical Engineering Progress 73(5):50-54, 1977.
- Case, O.P. Metallic Recovery from Wastewaters Utilizing Cementation. EPA 670/2-74-008. U.S. Environmental Protection Agency, 1974. 36 Pp.
- Cheng, M.H., J.W. Patterson, and R.A. Minear. Heavy Metals Uptake by Activated Sludge. Journal Water Pollution Control Federation 47(2):362-376, 1975.
- Cheremisinoff, P.N., and Y.H. Habib. Cadmium, Chromium, Lead, Mercury: A plenary Account for Water Pollution. Part 2 Removal Techniques. Water and Sewage Works 119(8):46-51, 1972.
- Cohen, J.M. Trace Metal Removal by Wastewater Treatment. EPA Technology Transfer, 1977.
- Current Industrial Reports Inorganic Chemicals. U.S. Department of Commerce Bureau of the Census, 1977.
- Davis, H.J., F.S. Model, and J.R. Leal. PBI Reverse Osmosis Membrane for Chromium Plating Rinse Water. EPA-600/2-78-040. U.S. Environmental Protection Agency, 1978. 35 Pp.
- Dean, J.G., F.L. Bosqui, and K.H. Lanouette. Removing Heavy Metals from Wastewater. Environmental Science and Technology 6(6):518-522, 1972.
- Dow Chemical Company. Selecting Ion Exchange Resins for Water Treatment Applications. Industrial Water Engineering 14(5):11-13, 1977.
- Energy and Environmental Analysis, Inc. Draft Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemicals Industry. 1978.
- FMC Corp. Industrial Wastewater Treatment. A guidebook to Hydrogen Peroxide for Industrial Wastes. Philadelphia, Pennsylvania.

FMC Corp. Hydrogen Peroxide. Chemical and Technical Data. Philadelphia, Pennsylvania.

Ford, D.L. Putting Activated Carbon in Perspective to 1983 Guidelines. Industrial Water Engineering 14(3):20-27, 1977.

General Technology Corporation. Draft Contractor Document for Major Inorganic Chemicals. 1973.

General Technology Corporation. Final Contractor Document for Major Inorganic Chemicals. 1973.

Greek, B.F., and W.F. Fallwell. Chlorine, Major Alkalies Still in Doldrums. Chemical and Engineering News 56(6):8-11, 1978.

Grover, P. A Waste Stream Management System. Chemical Engineering Progress 73(12):71-73, 1977.

Haggenmacher, J.H. Chromate Removal Decreases Blowdown to Below 0.05 ppm Hexavalent Chrome. Chemical Processing, 1977.

Hoyle, D.L. Designing for pH Control. Chemical Engineering 83(24):121-126, 1976.

Jacobs Engineering Group Inc. Estimating Standards.

Jenkins, S.H., D.G. Keight, and R.E. Humphreys. The Solubility of Heavy Metal Hydroxides in Water, Sewage and Sewage Sludge - I. The Solubility of Some Metal Hydroxides. Int. J. Air Wat. Poll. 8:537-556, 1964.

Jenkins, S.H., D.G. Keight, and A. Ewins. The Solubility of Heavy Metal Hydroxides in Water, Sewage, and Sewage Sludge - II The Precipitation of Metals by Sewage. Int. J. Air Wat. Poll. 8:679-693, 1964.

Keating, E.J., R.A. Brown, and E.S. Greenberg. Phenolic Problems Solved with Hydrogen Peroxide Oxidation. The 33rd Annual Industrial Waste Conference, West Lafayette, Indiana, 1978. 20 Pp.

Kibble, W.H. Hydrogen Peroxide Helps Solve Industrial Wastewater Problems. Industrial Wastes 26-29, 1978.

Knocke, W.R., T. Clevenger, M.M. Ghosh, and J.T. Novak, Recovery of Metals from Electroplating Wastes. The 33rd Annual Industrial Waste Conference, West Lafayette, Indiana. 1978. 37 Pp.

Lanuouette, K.H. Heavy Metals Removal. Chemical Engineering Deskbook Issue 84(22):73-80, 1977.

Linstedt, K.D., C.P. Houck, and J.T. O'Connor. Trace Element Removals in Advanced Wastewater Treatment Processes. Journal Water Pollution Control Federation 43(7):1507-1513, 1971.

Mir, L., W. Eykamp, and R.L. Goldsmith. Current and Developing Applications for Ultrafiltration. Industrial Water Engineering 14(3):14-19, 1977.

Morton, S.D., and E.W. Sawyer. Clay Minerals Remove Organics, Viruses and Heavy Metals from Water. Water and Sewage Works 123 (Reference No. 1976):R117-R120, 1976.

Porter, J.W., Brothers, G.W., and W.B. Whitton. Cost Estimating Guidelines for Wastewater Treatment Systems. EPA 17090 DRU. U.S. Environmental Protection Agency, 1970. 96 Pp.

Resources Conservation Co. The RCC Brine Concentrator. Renton, Washington

Richardsons Estimating Standards. Means Cost Data. 1978.

Rizzo, J.L., and A.R. Shepard. Treating Industrial Wastewater with Activated Carbon. Chemical Engineering 84(1):95-100, 1977.

Rosenzweig, M.D. Mercury Cleanup Routes - I Chemical Engineering 82(2):60-61, 1975.

Sabadell, J.E., ed. Traces of Heavy Metals in Water Removal Processes and Monitoring. EPA-902/9-74-001. U.S. Environmental Protection Agency, 1973. 342 Pp.

Shen, Y.S. Study of Arsenic Removal from Drinking Water. Journal American Water Works Association 65(8): 543-548, 1973.

Sigworth, E.A., and S.B. Smith. Adsorption of Inorganic Compounds by Activated Carbon. Journal American Water Works Association 64(6):386-390, 1972.

Smith, R. Cost of Conventional and Advanced Treatment of Wastewater. Journal Water Pollution Control Federation 40(9):1546-1574, 1968.

Sonksen, M.K., F.M. Sittig, E.F. Maziarz. Treatment of Oily Wastes by Ultrafiltration/Reverse Osmosis. A Case History. The 33rd Annual Industrial Waste Conference, West Lafayette, Indiana, 1978. 28 Pp.

Stanford Research Institute. Directory of Chemical Producers U.S.A. 1977.

Stinson, G.F. Electrochemical Wastewater Treatment Process. Personal Communication. 1978.

Theim, L.D. Badorek, and J.T. O'Connor. Removal of Mercury From Drinking Water Using Activated Carbon. Journal American Water Works Association 68 (8):447-451, 1976.

Thompson, G.S., Jr. First Annual Conference on Advanced Pollution Control for the Metal Finishing Industry. EPA-600/8-78-010. U.S. Environmental Protection Agency, 1978. 143 Pp.

S.K. Williams Company. Wastewater Treatment and Reuse in a Metal Finishing Job Shop. EPA-670/2-74-042. U.S. Environmental Protection Agency, 1978. 143 Pp.

Wiseman, S., and B.T. Bawden. Removing Refractory Compounds From Wastewater. Chemical Engineering Progress 73(5):60-64, 1977.

Zabban, W., and R. Helwick. Defluoridation of Wastewater. The 30th Annual Industrial Waste Conference, West Lafayette, Indiana, 1975. 38 Pp.

Zievers, J.F., R.E. Wing, S. Crain, and D. Gordon. Practical Use of Starch Insoluble Xanthates. Industrial Filter and Pump Mfg. Co. 1977. 20 Pp.

APPENDIX A

ANALYSIS OF LONG-TERM EFFLUENT
MONITORING DATA FOR
THE INORGANIC CHEMICALS INDUSTRY

Introduction

This appendix contains tabulated summaries of the statistical parameters derived from the analysis of long-term effluent monitoring data collected by industry and reported to the EPA or State regulatory agencies during the last two or three years. The particular sets of data selected for analysis are taken from plants which apply a well defined treatment technology to process wastewaters from single product or product group manufacturing operations associated with a specific subcategory. Data have been excluded which represent wastewaters diluted with noncontact cooling water or commingled with waste sources from unrelated products. Each table in the appendix indicates the actual number of observations on which the calculated statistical parameters are based. The derivation of the parameters was discussed in Section 8.2 of the development document.

The statistical performance information presented here was taken into consideration in the development of limitations for each subcategory studied in detail in the main report. These were expressed as the Concentration Bases (mg/l) and Effluent Unit Mass Loadings (kg/kg) for each pollutant assuming the model plant flow conditions and applying the specified pollutant removal technologies at each level of treatment. The tables on the following pages summarize the available historical effluent monitoring results and give the individual plant performance characteristics in concentration and loading units for both daily and monthly measurements. Variability factors shown on each table were used to calculate the plant "Performance Standards" shown in the right hand column of each table. Similarly, the Variability Factor Ratio (VFR) used in this report is the variability factor for daily measurements divided by variability factor for 30-day average data.

In general, the effluent data base acquired included NPDES monitoring data collected during the period from January 1, 1975 through June 30, 1976. Firms who monitored over this time period provided up to 18 months of 30-day average data and as many as 547 measurements of daily or 24-hour data. In cases where monitoring was done less frequently than daily, perhaps omitted on weekends, or only weekly measurements, the actual number of observations used in the calculation is recorded for each parameter.

Included in Appendix A are statistical measures appropriate to the analysis of long-term monitoring data and the historical performance of inorganic chemical pollutant discharge levels. The statistics presented include measures of the amount or level of pollutant

discharge, such as long-term average, minimum level, and maximum level for both daily, or 24-hour measurements, as well as 30-day average measurements.

Also given in the table is the coefficient of variation, CV, which reflects the dispersion of measurements above and below the long-term average level. Other measures of variability that may be of interest, such as range or standard deviation are also calculated for any parameter from any information given herein. In addition to statistics of pollutant level and variation of pollutant level, variability factors are given for each parameter. A variability factor is the ratio of an upper percentile of the distribution of pollutant measurements to the long-term average pollutant level. The basis of the particular upper percentile chosen for variability factors is explained as a footnote to the table.

The historical performance of each firm, using the variability factor, is given for each parameter and is expressed in the same units as the long-term average.

For reference, the tables in Appendix A are organized by inorganic chemical subcategory and the manufacturing process in that subcategory. For each plant, as many as six tables are included. These tables appear in the following order.

1. Daily measurements of pollutant concentrations in effluent stream given in parts per million (ppm).
2. Daily measurements of total effluent discharge load measured in kilograms per day.
3. 30-day averages of pollutant concentration (ppm).
4. 30-day averages of total effluent pollutant load (kg/day).
5. Daily measurements of pollutant unit loadings in the effluent streams given in kilograms of pollutant per thousand kilograms of product (kg/kg).
6. 30-day averages of pollutant unit loadings in the effluent stream given in kilograms of pollutant per thousand kilograms of product (kg/kg).

Table A-1a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #A

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	530	.006	.014	.021	.286	1.88	.026
TSS	530	1.00	7.4	62.	.581	3.04	22.5
Chlorine	428	0.08	.638	1.50	.463	2.28	1.46
(Total Residual)							

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-1b
Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #A

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	530	.015	.031	.047	.129	1.66	.051
Chlorine	420	.156	1.44	3.40	.463	2.54	3.65
(Total Residual)							

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-1c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #A

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	18	.008	.014	.020	.293	1.47	.021
TSS	18	5.1	7.4	12.9	.355	1.58	11.7
Chlorine (Total Residual)	18	.380	.638	.847	.194	1.38	0.88

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-1d

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #A

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	18	.020	.031	.037	.197	1.33	.041
Chlorine	18	.91	1.44	2.23		1.50	2.16

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-1e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #A

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	530	.027	.055	.084			.090
Chlorine (Total Residual)	420	.00028	.0026	.006			.006

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-1f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #A

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	18	.035	.055	.065			.072
Chlorine	18	1.6	2.52	3.91			3.8

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-2a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #B

Parameter (ug/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	516	.041	.634	2.87	.910	4.52	2.87

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-2b

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #B

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	516	.0005	.011	.088	.818	4.35	.046

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-2c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Chlorine Subcategory
Mercury Cell Process
Plant #B

Parameter (ug/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	17	.325	.634	1.15	.293	1.45	0.919

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-2d

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #B

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	17	.005	.011	.019		1.45	.015

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-2e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #B

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	516	.0037	.082	.658			.344

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-2f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #B

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	17	.037	.082	.14			.11

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-3a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #C

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	349	.0005	.014	.136	2.29	9.45	0.132

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-3b

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #C

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	349	.0001	.003	.088	2.33	10.22	.028

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-3c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #C

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	17	.0009	.014	.062	1.21	2.99	.042

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-3d

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #C

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	17	.0002	.003	.014	1.33	3.22	.0088

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-3e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #C

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	349	.0006	.017	.485			.154

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-3f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #C

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	17	.0011	.016	.077			.0485

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-4a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #D

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	82	.002	.004	.011	.500	2.24	0.009
Chlorine (Total Residual)	49	2.0	19.1	62	1.01	4.96	94.7

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-4b

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #D

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	82	.021	.047	.118	.383	2.20	.104
Chlorine (Total Residual)	49	20.5	203	663	1.03	5.04	1026

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-4c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #D

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	22	.003	.004	.008	.250	1.60	0.006
Chlorine (Total Residual)	14	4.0	19.1	57.8	.969	2.91	55.6

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-4d

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #D

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	22	.032	.047	.098	.340	1.66	.079
Chlorine (Total Residual)	14	39.1	203	616	.945	2.89	588

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-4e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Mercury Cell Process
Plant #D

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	82	.386	.864	2.17			1.91
Chlorine (Total Residual)							

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-4f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Mercury Cell Process
Plant #D

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Mercury	22	.588	.864	1.8			1.45
Chlorine (Total Residual)							

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-5a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Diaphragm Cell Process
Plant #E

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	153	.045	1.42	5.40		4.12	5.85

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-5b

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Diaphragm Cell Process
Plant #E

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	12	.460	1.42	5.40	.824	1.58	2.25

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-5e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Chlorine
Diaphragm Cell Process
Plant #E

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	153	.205	6.46	24.6			26.6

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-5f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Chlorine
Diaphragm Cell Process
Plant #E

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	12	2.09	6.46	24.6			10.24

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-7a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Hydrofluoric Acid/
Plant #G

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Fluoride	15	4.54	16.7	27.2	.449	1.74	29.0
TSS	16	7.26	28.6	52.2	.441	1.72	49.2

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-7e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Hydrofluoric Acid/
Plant #G

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Fluoride	15	99.1	365	594			633
TSS	16	158.5	624	1140			1074

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-8b

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Chloride Process
 Plant #H

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Aver	Max	CV	*	P
Chromium	394	.000	.013	.210	1.69	7.78	.097
Copper	394	.000	.027	.190	1.04	5.20	.139
Zinc	394	.000	.028	.108	.679	3.42	.097
TSS	394	0.40	8.34	176.	1.92	8.35	69.7

* - 99% Of the daily maximum measurements expected to be less than the performance standard, P.

Table A-8c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Titanium Dioxide
Chloride Process
Plant #H

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Aver	Max	CV	*	P
Chromium	13	.000	.004	.013	.750	2.46	0.010
Copper	13	.000	.010	.030	.700	2.43	0.024
Zinc	13	.001	.012	.026	.500	1.93	0.023
TSS	13	1.20	3.14	8.60	.599	1.98	6.22

* - 95% of the monthly averages are expected to be within the performance standard, p.

Table A-8d

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Chloride Process
 Plant #H

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Chromium	13	.002	.013	.043	.769	2.62	.033
Copper	13	.000	.027	.100	.852	2.74	.073
Zinc	13	.004	.028	.051	4.29	1.80	.051
TSS	13	2.60	8.34	24.0	.695	2.14	17.9

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-8e

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Chloride Process
 Plant #H

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Aver	Max	CV	*	P
Chromium	394	.000	.178	2.88			1.33
Copper	394	.000	.37	2.6			1.9
Zinc	394	.000	.384	1.48			1.33
TSS	394	5.49	114	2415			956

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-8f

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Chloride Process
 Plant #H

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Chromium	13	.027	.178	.59			.453
Copper	13	.000	.37	1.37			1.0
Zinc	13	.055	.384	.70			.70
TSS	13	35.7	114	329			246

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-9a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Titanium Dioxide
Sulfate Process
Plant #I

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	26	.001	.009	.020	.444	2.03	0.018
Chromium	26	.010	.021	.070	.857	4.23	0.088
Iron (total)	30	.40	3.25	19.1	1.42	6.74	21.9
Iron (diss)	153	.080	.279	4.98	2.01	8.64	2.41
Lead	26	.002	.017	.050	.765	3.67	0.062
Nickel	26	.010	.029	.080	.690	3.52	0.102
Zinc	26	.010	.027	.300	2.11	9.93	0.268
TSS	183		35.8		1.71	7.70	276.

* - 99% Of the daily maximum measurements expected to be less than the performance standard, P.

Table A-9a-1

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #1
 April 76 through September 78

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	109	.001	.058	.100	.762	3.85	.224
Chromium	128	.010	.072	.400	.755	3.81	.275
Iron**	854	.010	.620	59.9	5.58	13.5	8.39
Lead	128	.002	.068	.100	.609	3.15	.214
Nickel	128	.010	.080	.680	.883	4.39	.354
Zinc	128	.010	.151	1.14	1.35	6.41	.966
TSS	899	.000	21.2	975	3.11	11.0	233

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** 04-76 to 08-78

Table A-9a-2

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 78 through February 79

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	22	.1	.1	.1	0	1	.1
Chromium	22	.10	0.27	0.74	0.74	3.73	1.01
Iron	22	212	390	605	0.31	1.94	757
Lead	22	.1	.1	.1	0	1	.1
Nickel	22	.1	0.15	0.35	0.47	2.58	0.39
Zinc	22	.1	0.67	1.8	0.75	3.81	2.55
TSS **	22	35.6	257	1135	1.12	5.46	1403

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** 09-78 to 01-79

Table A-9a-3

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 79 through April 81

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	82	0.10	0.10	0.10	0	1.0	0.10
Chromium	81	0.05	0.23	0.67	0.87	4.4	1.0
Iron	84	202	330	582	0.22	1.5	495
Lead	82	0.10	0.10	0.10	0	1.0	0.10
Nickel	82	0.05	0.14	0.53	0.86	4.3	0.60
Zinc	54	0.05	0.50	1.18	1.2	5.8	2.9
TSS**	30	11	50	398	1.18	5.8	290

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** April 81

Table A-9b-1

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Titanium Dioxide
Sulfate Process
Plant #I
April 76 through September 78

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	109	.004	.432	.908	.782	3.95	1.70
Chromium	128	.045	.526	2.65	.707	3.61	1.90
Iron**	854	1.00	4.29	3,854	5.78	13.6	585
Lead	128	.008	.503	.908	.634	3.27	1.65
Nickel	128	.047	.576	3.99	.790	3.98	2.29
Zinc	128	.049	1.07	55.1	1.33	6.32	6.76
TSS	899	26	1,350	58,820	2.79	10.5	14,120

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** 04-76 to 08-78

Table A-9b-2

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 78 through February 79

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	22	6.95	6.95	6.95	0	1.0	6.95
Chromium	22	6.95	18.76	51.41	0.74	3.73	69.98
Iron	22	14,730	27,097	42,035	0.31	1.94	52,568
Lead	22	6.95	6.95	6.95	0	1.0	6.95
Nickel	22	6.95	10.42	24.32	0.47	2.56	26.88
Zinc	22	6.95	46.55	125.06	0.75	3.81	177.36
TSS**	22	2,474	17,856	78,860	1.12	5.46	97,493

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** 09-78 to 01-79

Table A-9b-3

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 79 through April 81

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	82	8.2	8.2	8.2	0	1.0	8.2
Chromium	81	4.1	18.8	54.8	0.87	4.4	81.8
Iron	84	16,521	26,990	47,599	0.22	1.5	40,484
Lead	82	8.2	8.2	8.2	0	1.0	8.2
Nickel	82	4.1	11.4	43.3	0.86	4.3	49.0
Zinc	54	4.1	40.9	96.5	1.2	5.8	237
TSS**	30	900	4,089	32,551	1.18	5.8	23,718

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** April 81

Table A-9c-1

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #1
 April 76 through September 78

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	26	.003	.058	.100	.722	2.43	.142
Chromium	30	.010	.072	.130	.524	2.04	.147
Iron**	28	.060	.620	3.74	1.51	4.00	2.47
Lead	30	.004	.068	.100	.578	2.14	.147
Nickel	30	.010	.080	.245	.594	4.39	.354
Zinc	30	.010	.151	.815	1.03	3.05	.406
TSS	30	1.58	21.2	74.8	1.03	3.04	64.3

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 04-76 to 08-78

Table A-9c-2

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 78 through February 79

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	5	.1	.1	.1	0	1	1
Chromium	5	.10	0.27	0.48	0.48	1.79	0.48
Iron	5	244.4	390	502.9	0.25	1.41	550
Lead	5	.1	.1	.1	0	1	.1
Nickel	5	.1	0.15	0.25	0.37	1.61	0.24
Zinc	5	0.30	0.67	0.83	0.64	2.05	1.37
TSS**	5	51.6	257	595	0.750	2.23	573

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 09-78 to 01-79

Table A-9c-3

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 79 through April 81

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	20	0.10	0.10	0.10	0	1.0	0.10
Chromium	20	0.05	0.23	0.47	0.52	1.9	0.44
Iron	20	261	330	418	0.13	1.2	396
Lead	20	0.10	0.10	0.10	0	1.0	0.10
Nickel	20	0.05	0.14	0.41	0.67	2.1	0.29
Zinc	13	0.12	0.50	0.78	0.45	1.7	0.85
TSS**	20	48	50	214	0.35	1.6	80

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 09-79 to 04-81

Table A-9d-1

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 April 76 through September 78

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	26	.016	.432	.780	.743	2.47	1.07
Chromium	30	.064	.526	.862	.549	2.09	1.10
Iron**	28	4.00	42.9	294	1.59	4.14	177
Lead	30	.021	.503	.852	.602	2.19	1.10
Nickel	30	.065	.576	1.49	.569	2.13	1.23
Zinc	30	.074	1.07	5.62	.996	2.97	3.18
TSS	30	116	1,350	4,797	1.01	2.99	4,041

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 04-76 to 08-78

Table A-9d-2

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 78 through February 79

=====							
Parameter	Historical Summary Statistics					Variability Factors	Performance Standards
(kg/day)	No	Min	Avg	Max	CV	*	P

Cadmium	5	6.95	6.95	6.95	0	1	6.95
Chromium	5	6.95	18.76	33.4	0.48	1.79	33.4
Iron	5	16,981	27,097	34,941	0.25	1.41	38,214
Lead	5	6.95	6.95	6.95	0	1	6.95
Nickel	5	6.95	10.42	17.4	0.37	1.61	16.68
Zinc	5	2.4	46.55	57.7	0.640	2.05	95.19
TSS**	5	3,585	17,856	41,340	0.750	2.23	39,812

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 09-78 to 01-79

Table A-9d-3

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 79 through April 81

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	20	8.2	8.2	8.2	0	1.0	8.2
Chromium	20	4.1	18.8	38.4	0.52	1.9	36.0
Iron	20	21,350	26,990	34,186	0.13	1.2	32,387
Lead	20	8.2	8.2	8.2	0	1.0	8.2
Nickel	20	4.1	11.4	33.5	0.67	2.1	23.7
Zinc	13	9.8	40.9	63.8	0.45	1.7	69.5
TSS**	20	3,926	4,089	17,502	0.35	1.6	6,543

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 09-79 to 04-81

Table A-9e-1

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 April 76 through September 78

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	109	.041	4.45	9.36			17.5
Chromium	128	.464	5.42	27.3			19.6
Iron**	854	10.3	44.2	39,711			6,028
Lead	128	.082	5.18	9.36			17.0
Nickel	128	.484	5.93	41.1			23.6
Zinc	128	.505	11.02	568			69.7
TSS	899	.268	13.91	606			145.5 (kg/kg)

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** 04-76 to 08-78

Table A-9e-2

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 78 through February 79

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	22	0.67	0.67	0.67			0.67
Chromium	22	0.67	1.82	4.99			6.79
Iron	22	152	279	433			542 (kg/kkg)
Lead	22	0.67	0.67	0.67			0.67
Nickel	22	0.67	1.01	2.36			2.6
Zinc	22	0.67	4.51	12.13			17.2
TSS**	22	25.48	183.9	812			1004 (kg/kkg)

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** 09-78 to 01-79

Table A-9e-3

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 Daily Measurements
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 79 through April 81

=====							
Parameter	Historical Summary Statistics					Variability Factors	Performance Standards
(g/kg)	No	Min	Avg	Max	CV	*	P

Cadmium	82	0.80	0.80	0.80			0.80
Chromium	81	0.40	1.82	5.32			7.93
Iron	84	170	278	490			417 (kg/kg)
Lead	82	0.80	0.80	0.80			0.80
Nickel	82	0.40	1.11	4.20			4.75
Zinc	54	0.40	3.97	9.36			23.0
TSS**	30	9.3	42.1	335			244 (kg/kg)

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

** April 81

Table A-9f-1

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 April 76 through September 78

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	26	.165	4.45	8.04			11.0
Chromium	30	.66	5.42	8.88			11.3
Iron**	28	41.2	442	3209			1,824
Lead	30	.216	5.18	8.78			11.3
Nickel	30	.67	5.94	15.4			12.7
Zinc	30	.762	11.0	57.9			32.8
TSS	30	1.2	13.9	49.4			41.6 (kg/kg)

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 04-76 to 08-78

Table A-9f-2

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 78 through February 79

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	5	0.67	0.67	0.67			0.67
Chromium	5	0.67	1.81	3.23			3.2
Iron	5	174.9	279	360			394 (kg/kg)
Lead	5	0.67	0.67	0.67			0.67
Nickel	5	0.67	1.01	1.69			0.17
Zinc	5	0.23	4.5	5.6			0.98
TSS**	5	36.9	184	426			410 (kg/kg)

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 09-78 to 01-79

Table A-9f-3

Historical Effluent Monitoring Data Summary
 with Variability Factors and Performance Standards
 30 Day Averages
 Subcategory Titanium Dioxide
 Sulfate Process
 Plant #I
 September 79 through April 81

Parameter (g/kg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cadmium	20	0.80	0.80	0.80			0.80
Chromium	20	0.40	1.82	3.72			3.49
Iron	20	220	278	352			334 (kg/kg)
Lead	20	0.80	0.80	0.80			0.80
Nickel	20	0.40	1.11	3.25			2.30
Zinc	13	0.95	3.97	6.20			6.74
TSS**	20	40.44	42.11	180.3			67.4 (kg/kg)

* - 95% of the monthly averages are expected to be within the performance standard, P.

** 09-79 to 04-81

Table A-10a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Aluminum Fluoride
Plant #J

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	152	0.11	2.28	12.8	.601	3.12	7.11

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-10b

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Aluminum Fluoride
Plant #J

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	152	0.09	2.15	15.3	.753	3.82	8.20

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-10c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Aluminum Floride
Plant #J

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	10	1.51	2.28	3.90	.601	1.55	3.54

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-10d

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Aluminum Floride
Plant #J

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	10	1.51	2.15	3.70	.326	1.54	3.30

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-10e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Aluminum Fluoride
Plant #J

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	152	.89	21.2	150			80.7

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-10f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Aluminum Floride
Plant #J

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Lead	10	14.9	21.2	36.4			32.5

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-11a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Chrome Pigments Subcategory
Plant #K

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Arsenic	23	.0096	.079	.235	.668	2.02	.156
Cadmium	23	.050	.079	.164	.339	1.56	.123
Chromium (hexavalent)	23	.028	.112	.592	1.04	2.70	.302
Chromium (Total)	23	.197	.442	.799	.404	1.66	.733
Copper	23	.038	.134	.296	.529	1.87	.250
Lead	23	.217	.412	1.635	.681	2.12	.873
Mercury	23	.0004	.001	.0018	.400	1.66	.0016
Zinc	23	.012	.04	.087	.437	1.72	.074
Cyanide (Available)	23	.0003	.019	.076	1.57	3.58	.068
Cyanide (total)	23	.025	.118	.316	.995	2.63	.310
TSS	23	0.27	11.2	33.3	.662	2.01	22.5

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-12a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Hydrogen Cyanide
Andrussow Process
Plant #L

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Ammonia	35	14.	113.	188.	.335	2.02	229

* - 99% Of the daily maximum measurements expected to be less than the performance standard, P.

Table A-12b

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Hydrogen Cyanide
Andrussow Process
Plant #L

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Ammonia	35	112	1533	2419	.365	2.14	3283

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-12c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Hydrogen Cyanide
Andrussow Process
Plant #L

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Ammonia	8	80.	113.	134.	.335	1.32	150

* - 95% Of the monthly averages are expected to be within the performance standard, P.

Table A-12d

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Hydrogen Cyanide
Andrussow Process
Plant #L

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Ammonia	8	908	1533	1941	.212	1.42	2177

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-12e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Hydrogen Cyanide
Andrussow Process
Plant #L

Parameter (kg/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Ammonia	35	.606	8.29	1309			17.8

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-12f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Hydrogen Cyanide
Andrussow Process
Plant #L

Parameter (kg/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Ammonia	8	46.9	8.29	10.5			11.8

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-13a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory
Andrussow Process
Plant #M

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cyanide (Free)	534	.01	.202	3.27	1.58	7.26	1.46
Cyanide (Total)	25	.039	.192	.460	.667	3.42	.65
Ammonia	26	.193	3.63	10.2	.636	3.51	12.7
COD	25	2.71	15.9	45.2	.552	2.90	46.1
TOC	26	.783	8.30	25.6	.845	4.22	35.0
SS	22	5	35	267	1.57	8.16	286

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-13c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Hydrogen Cyanide
Andrussow Process
Plant #M

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cyanide (Free)	19	.082	.202	.351	.391	1.78	0.359

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-13e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Hydrogen Cyanide Subcategory
Andrussow Process
Plant #M

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Cyanide	19	.457	1.12	1.95			1.99

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-15a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Nickel Sulfate
Plant #0

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Nickel	88	.080	1.83	8.33	1.21	5.84	10.7

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-15b

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Nickel Sulfate
Plant #0

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Nickel	88	1.02	8.32	44.6	1.31	6.24	51.9

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-15c

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Nickel Sulfate
Plant #0

Parameter (mg/l)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Nickel	3	1.29	1.83	2.48	1.21	1.54	2.82

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-15d

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Nickel Sulfate
Plant #0

Parameter (kg/day)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Nickel	3	5.04	8.32	11.1	.302	1.49	12.4

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-15e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
Daily Measurements
Subcategory Nickel Sulfate
Plant #0

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Nickel	88	112	912	4890			5,691

* - 99% of the daily maximum measurements expected to be less than the performance standard, P.

Table A-15f

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Nickel Sulfate
Plant #0

Parameter (g/kkg)	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
Nickel	3	553	912	1217			1,360

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-16a

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Sodium Hydrosulfite
Plant #P

Parameter	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
(kg/day)							
TSS	36	.91	3.78	41.1	1.69	3.77	14.2

* - 95% of the monthly averages are expected to be within the performance standard, P.

Table A-16e

Historical Effluent Monitoring Data Summary
with Variability Factors and Performance Standards
30 Day Averages
Subcategory Sodium Hydrosulfite
Plant #P

Parameter	Historical Summary Statistics					Variability Factors	Performance Standards
	No	Min	Avg	Max	CV	*	P
(g/kkg)							
TSS	36	16.3	67.5	734			254

* - 95% of the monthly averages are expected to be within the performance standard, P.

