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**Supplement For  
PRETREATMENT**

**to the**

**Development Document  
for the**

**INORGANIC CHEMICALS  
MANUFACTURING**

**POINT SOURCE CATEGORY**



**U.S. ENVIRONMENTAL PROTECTION AGENCY**

**JULY 1977**

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SUPPLEMENT FOR PRETREATMENT  
TO THE DEVELOPMENT DOCUMENT

FOR THE  
INORGANIC CHEMICALS MANUFACTURING  
POINT SOURCE CATEGORY

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## ABSTRACT

This document presents the findings of a study by the Environmental Protection Agency of the inorganic chemical industry for the purpose of developing pretreatment standards for existing sources to implement section 307(b) of the Federal Water Pollution Control Act, as amended.

The development of data and identified technology presented in this document relate to waste waters generated in the following specific segments of the inorganic chemical industry: aluminum chloride, aluminum sulfate, calcium carbide, calcium chloride, copper sulfate, ferric chloride, lead oxide, nickel sulfate, nitrogen, oxygen, potassium dichromate, potassium iodide, silver nitrate, sodium bicarbonate, and sodium fluoride. The pretreatment levels corresponding to these technologies also are presented.

Supporting data and rationale for development of pretreatment levels based on best practicable pretreatment technology are contained in this report.

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## SECTION I

### CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance, the Inorganic Chemicals Manufacturing Point Source Category was divided into Major and Significant Inorganic Products. This report deals with fifteen segments of the Major and Significant Inorganic Products Categories which may discharge process wastewater to Publicly Owned Treatment Works (POTWs) and for which effluent limitations guidelines and standards have been promulgated.

The fifteen product segments covered in this document are: aluminum chloride ( $\text{AlCl}_3$ ), aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), calcium carbide ( $\text{CaC}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), copper sulfate ( $\text{CuSO}_4$ ), ferric chloride ( $\text{FeCl}_3$ ), lead monoxide ( $\text{PbO}$ ), nickel sulfate ( $\text{NiSO}_4$ ), nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), potassium iodide ( $\text{KI}$ ), silver nitrate ( $\text{AgNO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), and sodium fluoride ( $\text{NaF}$ ).

For the purpose of establishing pretreatment standards, that portion of the industry included in this report is subcategorized by chemical product, with the exception of nitrogen and oxygen which are combined into one subcategory. The consideration of factors such as geographic location, land availability, plant size, process(es), waste water treatment and control techniques employed, and the types of POTW receiving the discharges support these conclusions. Distinctions between wastes produced by each product segment and the control and treatment techniques available to reduce the discharge of pollutants to POTW further support the subcategorization chosen.

Available data from chemical industry directories and contacts with industry on the discharge type and number of plants within each chemical subcategory are presented in Table 1. On the basis of information available at this time, it is apparent that only a small percentage of the industry discharges process waste water to POTWs.

Historical data from the literature, information supplied by industry, and data collected during on-site visits were compiled and evaluated pursuant to development of pretreatment standards for each of the chemical subcategories. Based on the information collected, the major types and characteristics of process waste water generated have been identified, existing and potential pretreatment technologies have been described, and costs

**TABLE 1. NUMBER OF PLANTS AND DISCHARGE TYPE BY CHEMICAL SUBCATEGORY**

CHEMICAL SUBCATEGORY	TOTAL NO. OF PLANTS	NO. OF DIRECT DISCHARGERS	NO. OF ZERO DISCHARGERS	NO. OF POTW* DISCHARGERS	NO. OF UNKNOWN DISCHARGERS
Aluminum chloride	13	3	5	0	5
Aluminum sulfate	84	8	13	0	63
Calcium carbide	4	1	2	0	1
Calcium chloride	12	3	2	1	6
Copper (cupric) sulfate	16	8	4	0	4
Ferric (iron) chloride	21	3	2	2	14
Lead monoxide	17	1	3	0	13
Nickel sulfate	11	1	0	3	7
Nitrogen and Oxygen	193	71	1	33	88
Potassium dichromate	1	1	0	0	0
Potassium iodide	4	1	1	2	0
Silver nitrate	3	1	1	0	1
Sodium bicarbonate	3	2	1	0	0
Sodium fluoride	4	2	2	0	0

\*Publicly owned treatment works

accrued by implementation of these technologies have been assessed. Where data for actual POTW dischargers was lacking, data on direct dischargers were used to characterize the industry.

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## SECTION II

### RECOMMENDATIONS

These regulations establish two sets of pretreatment requirements for the subcategories mentioned. The first set, the "prohibited discharge" standards, are designed to prevent inhibition of, or interference with, the municipal treatment works, by prohibiting the discharge of pollutants of a nature or in a quantity that would endanger the mechanical or hydraulic integrity of the works. Except for minor changes, these prohibited discharge standards are identical to the prohibitions contained in the general pretreatment regulation now found in (40 CFR 128.131). The "prohibited discharge" standards are as follows: No pollutant (or pollutant property) introduced into a publicly owned treatment works shall interfere with the operation or performance of the works. Specifically, the following wastes shall not be introduced into the publicly owned treatment works:

1. Pollutants which create a fire or explosion hazard in the publicly owned treatment works.
2. Pollutants which will cause corrosive structural damage to treatment works, but in no case pollutants with a pH lower than 5.0, unless the works is designed to accommodate such pollutants.
3. Solid or viscous pollutants in amounts which would cause obstruction to the flow in sewers, or other interference with the proper operation of the publicly owned treatment works.
4. Pollutants at either a hydraulic flow rate or pollutant flow rate which is excessive over relatively short time periods so that there is a treatment process upset and subsequent loss of treatment efficiency.

The second set of standards, known as categorical pretreatment standards, contain specific numerical limitations based on an evaluation of available technologies in a particular industrial subcategory. The specific numerical limitations are arrived at separately for each subcategory, and are imposed on pollutants or pollutant properties which may interfere with, pass through, or otherwise be incompatible with publicly owned treatment works. These pretreatment standards are presented in Table 2.

**TABLE 2. SUMMARY OF PRETREATMENT STANDARDS FOR SEVERAL  
SUBCATEGORIES OF THE INORGANIC CHEMICALS INDUSTRY**

SUBCATEGORY	PARAMETER	PRETREATMENT STANDARD (mg/l)	
		Maximum for any one day	Average of daily values for 30 consecutive days not to exceed
ALUMINUM CHLORIDE	pH (range)*	5.0 - 10.0	5.0 - 10.0
ALUMINUM SULFATE	Zn	5.0	2.5
COPPER SULFATE	Cu	1.0	0.5
	Ni	2.0	1.0
FERRIC CHLORIDE	Cr (hex)	0.18	0.09
	Cr (total)	1.8	0.9
	Cu	1.0	0.5
	Ni	2.0	1.0
	Zn	5.0	2.5
LEAD MONOXIDE	Pb	2.0	1.0
NICKEL SULFATE	Ni	2.0	1.0
	Cu	1.0	0.5
POTASSIUM DICHROMATE	Cr (hex)	0.18	0.09
	Cr (total)	1.8	0.9
SILVER NITRATE	Ag	1.0	0.5
SODIUM FLUORIDE	Fluoride	50.0	25.0

\*pH units

In addition, as guidance for local POTW authorities, zinc limits of 2.5 mg/l (30 day average) and 5.0 mg/l (daily maximum) are recommended for discharges from aluminum chloride manufacturing plants.

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## SECTION III

### INTRODUCTION

#### PURPOSE AND AUTHORITY

##### General

The Environmental Protection Agency (EPA or Agency) is developing regulations concerning pretreatment standards for existing sources and pretreatment standards for new sources pursuant to Sections 307(b) and (c) of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1317(b) and (c) 86 Stat. 816 et seq., P.L. 92-500) (the Act). These regulations would replace the existing regulations on pretreatment standards by establishing specific pretreatment standards for the several segments of the Inorganic Chemical Industry. The specific chemical segments included in this document are: aluminum chloride ( $AlCl_3$ ), aluminum sulfate ( $Al_2(SO_4)_3$ ), calcium carbide ( $CaC_2$ ), calcium chloride ( $CaCl_2$ ), copper sulfate ( $CuSO_4$ ), ferric chloride ( $FeCl_3$ ), lead oxide ( $PbO$ ), nickel sulfate ( $NiSO_4$ ), nitrogen ( $N_2$ ), oxygen ( $O_2$ ), potassium dichromate ( $K_2Cr_2O_7$ ), potassium iodide ( $KI$ ), silver nitrate ( $AgNO_3$ ), sodium bicarbonate ( $NaHCO_3$ ), and sodium fluoride ( $NaF$ ).

##### Legal Authority

Section 307(b) of the Act requires the Administrator to promulgate regulations establishing pretreatment standards for the introduction of pollutants into treatment works which are publicly owned for those pollutants which are determined not to be susceptible to treatment by such treatment works, or which would interfere with the operation of such treatment works. Pretreatment standards established under this section shall be established to prevent the discharge of any pollutant into treatment works which are publicly owned, which pollutant interferes with, passes through, or otherwise is incompatible with such works.

Section 307(c) provides that the Administrator shall promulgate pretreatment standards for any source which would be a new source subject to Section 306 if it were to discharge pollutants to navigable waters, simultaneously with the promulgation of standards of performance under Section 306 for the equivalent category of new sources. Such pretreatment standards shall prevent the discharge of any pollutant into such treatment works, which pollutant may interfere with, pass through, or otherwise be incompatible with such works.

### Purpose of Proposed Regulations

Subsequent to the promulgation of pretreatment standards (40 CFR 128) on November 8, 1973, the Agency has proposed and promulgated numerous pretreatment standards relative to specific industry category waste water discharges for both existing sources and new sources.

Additionally, the Agency plans to clarify and simplify the existing pretreatment standards. General provisions regulations (40 CFR 403) have been proposed which cover both existing sources and new sources. The general provisions regulations set forth the basis for pretreatment standards and certain general prohibitions. Specific numerical pretreatment limitations for particular pollutants will be set forth in the same subpart as the effluent limitations and new source performance standards for the industry subcategory to be regulated.

The new regulations establish two sets of pretreatment standards under the authority of Section 307 (b) of the Act. The first set, known as prohibited discharge standards, are designed to prevent inhibition or interference with the municipal treatment works by prohibiting the discharge of pollutants of such nature or quantity that the mechanical or hydraulic integrity of the publicly owned treatment works is endangered. These prohibited discharge standards, with minor changes, are identical to the prohibitions contained in the general pretreatment regulation now found at 40 CFR 128.131. The second set, known as categorical pretreatment standards, apply to existing sources in this specific industrial subcategory. These standards contain numerical limitations based upon available technologies to prevent the discharge of any pollutant into a POTW, which pollutant may interfere with, pass-through or otherwise be incompatible with such works.

With respect to the subcategories governed by these regulations, the general pretreatment requirements set forth in 40 CFR Part 128 are superseded. Those requirements were proposed on July 19, 1973 (38 FR 19236) and published in final form on November 8, 1973 (38 FR 30982). They limit the discharge of pollutants which pass through or interfere with the operation of publicly owned treatment works, but do not set numerical limitations or explicitly list particular pollutants to be regulated. The provisions of the present regulation overlap to a considerable degree with the language of the general pretreatment requirements, while at the same time setting specific numerical limitations on certain pollutants. For the purpose of clarity, sources affected by the present regulation are exempted from 40 CFR

Part 128. This decision is particularly warranted, because the provisions of 40 CFR Part 128 have sometimes been a source of confusion in the past, and because new general pretreatment regulations have been proposed (42 FR 6476, February 2, 1977) which will revoke and replace 40 CFR Part 128 upon promulgation.

### Statutory Considerations

The Federal Water Pollution Control Act Amendments of 1972, 33 U.S.C. Section 1251 et seq., were designed by Congress to achieve an important objective--to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters." Primary emphasis for attainment of this goal is placed upon technology based regulations. Industrial point sources which discharge into navigable waters must achieve limitations based on Best Practicable Control Technology Currently Available (BPCTCA) by July 1, 1977 and Best Available Technology Economically Achievable (BATEA) by July 1, 1983 in accordance with Sections 301(b) and 304(b). New sources must comply with New Source Performance Standards (NSPS) based on Best Available Demonstrated Control Technology (BADCT) under Section 306. Publicly owned treatment works (POTW) must meet "secondary treatment" by 1977 and best practicable waste treatment technology by 1983 in accordance with Section 301(b) and 201(g) (2) (A).

Users of a POTW also fall within the statutory scheme as set out in Section 301(b). Such sources must comply with pretreatment standards promulgated pursuant to Section 307.

Sections 307(b) and (c) are the key sections of the Act in terms of pretreatment. Both provide that the basic purpose of pretreatment is "to prevent the discharge of any pollutant through treatment works...which are publicly owned, which pollutant interferes with, passes through, or otherwise is incompatible with such works." The intent is to require treatment at the point of discharge complementary to the treatment performed by the POTW. Duplication of treatment is not the goal; as stated in the Conference Report (H.R. Rept. No. 92-1465, page 130), "In no event is it intended that pretreatment facilities be required for compatible wastes as a substitute for inadequate municipal waste treatment works." On the other hand, pretreatment by the industrial user of a POTW of pollutants which are not susceptible to treatment in a POTW is absolutely critical to attainment of the overall objective of the Act, both by protecting the POTW from process upset or other interference, and by preventing discharge of pollutants which would pass through or otherwise be incompatible with

such works. Thus, the mere fact that an industrial source utilizes a publicly owned treatment works does not relieve it of substantial obligations under the Act. The purpose of this regulation is to establish appropriate standards for several segments of the Inorganic Chemical Industry.

In determining numerical pretreatment standards, the initial step was to classify the pollutants discharged by a source to a POTW in terms of the statutory criteria of interference, pass through, or other incompatible effect. These pollutants fall, generally, into three classes. The first class is composed of those pollutants which are similar, in all material respects, to the pollutants which are found in municipal sewage and which the typical POTW is designed to treat. For such pollutants, no national pretreatment standards will be established. The second class of pollutants has those which, in large quantities, would interfere with the operation of a POTW but which would be adequately treated by the POTW when received in limited quantities. Such pollutants will be subject to pretreatment standards designed to allow their release into the POTW in treatable amounts.

Finally, the third class of pollutants includes those which are of a nature that would require the maximum feasible pretreatment to prevent interference with the POTW or pass through of the pollutant or other incompatibility. Such pollutants will be subject to pretreatment standards based upon the practical limits of technology.

In assessing the capabilities of POTWs and the effect upon them of various pollutants, the Agency, because it is developing uniform national standards, has focused upon the typical biological treatment system. Provision will be made for variances to standards, where appropriate, for users of a POTW where the POTW is of a fundamentally different nature from those on which the standards were based.

For the purpose of establishing technology-based pretreatment standards for industrial users of a POTW, the Agency has utilized, together with other pertinent data, the information developed in the course of establishment of effluent limitations and new source performance standards for the corresponding industrial point-source categories. While differences, particularly in terms of economic or technical parameters, between direct dischargers and users of a POTW will be considered, technology based pretreatment standards for existing sources will often tend to reflect BPCTCA. Although the Act does not elaborate upon the criteria to be applied in establishing numerical pretreatment standards, the purposes of the Act, and maximum



equity between direct and indirect dischargers, will be best attained through use of this BPCTCA analogy. Where, in particular, a pollutant passes through a POTW untreated or inadequately treated, the source discharging such a pollutant causes essentially the same environmental insult as a direct discharger of the same pollutant and should, therefore, meet essentially the same requirements. A variance provision will be included in the general regulations allowing industrial sources who are users of a POTW to apply for a variance from the numerical standard when factors relating to the industrial user which are fundamentally different from those considered in establishing the standards justify significant differences in discharge requirements.

Section 301 of the Act anticipates that pretreatment standards for existing sources would be established and compliance would be required before July 1, 1977, while Section 307(b) specifies "a time for compliance not to exceed three years from the date of promulgation" of the standard. In view of this conflict of statutory language and the fact that the pretreatment standards are only now being promulgated, the Agency believes that the compliance deadline as set forth in Section 307(b) should apply. The time for compliance with the categorical pretreatment standards will be within the shortest reasonable time, but not later than three years from the effective date. However, this does not preclude a Regional Administrator or local or state authority from establishing a more expeditious compliance date, on an individual basis, where it is appropriate. Compliance with the prohibited discharge standards is required immediately upon the effective date of these regulations, since these standards are essentially the same as 40 CFR 128.131 and since the deadline for compliance with 40 CFR 128.131 has passed.

#### Technical Basis for Pretreatment Standards

The Act requires that pretreatment standards for both new sources and existing sources be promulgated to prevent the introduction of any pollutant into a POTW which would interfere with the operation of such works or pass through or otherwise be incompatible with such works. Such standards would allow the maximum utilization of a POTW for the treatment of industrial pollutants while preventing the misuse of such works as a pass-through device. The standards also would protect the aquatic environment from discharges of inadequately treated or otherwise undesirable materials.

The primary technical strategy for establishing pretreatment standards consists of the following provisions: (1) pretreatment standards should allow materials to be discharged into a POTW when such materials are wastes which a normal POTW is designed to treat; (2) pretreatment standards should prevent the discharge of materials of such nature and quantity, including slug discharges, that would mechanically or hydraulically impede the proper functioning of a POTW; (3) pretreatment standards should limit the discharge of materials which, when released in substantial concentrations or amounts, reduce the biological effectiveness of the POTW or achievement of the POTW design performance, but which are treated when released in small or manageable amounts; and (4) the pretreatment standards should require the removal, to the limits dictated by technology, of other materials which would pass through--untreated or inadequately treated-- or otherwise be incompatible with a normal type POTW.

#### GENERAL DESCRIPTION OF INDUSTRY BY CHEMICAL SUBCATEGORY

The chemical subcategories included in this study vary in terms of production, process, raw-material sources, reagents used, and applicable pretreatment necessary for the resultant waste streams. Therefore, they are discussed separately throughout this document.

##### Aluminum Chloride

Industry Description. According to the Directory of Chemical Producers (Reference 1), there were 13 plants producing aluminum chloride ( $\text{AlCl}_3$ ) in 1974. Two of these plants (operated by the same corporation) manufacture both the hydrous and the anhydrous salts. The same source states that 11 of the 13 plants represent a combined annual capacity of 83,000 metric tons (92,000 short tons) of aluminum chloride. This sum includes 49,000 metric tons (54,000 short tons) of anhydrous product and 34,000 metric tons (38,000 short tons) of hydrous product. The major use for anhydrous aluminum chloride is as a catalyst in the synthetic polymer and petrochemical industries. The hydrous product is used as a flocculant and as a pigment fixative.

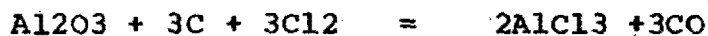
Manufacturing Processes. Anhydrous aluminum chloride is produced by injecting dry chlorine through a molten aluminum charge at  $660^\circ\text{C}$  ( $1220^\circ$ ) (Reference 2). The basic equation is:



The chlorine (usually gaseous) is introduced below the surface of the molten metal, and the product sublimes so that it is easily condensed and collected. (See Figure 1). Aluminum chloride condenses below 183°C (297°F). Theoretically, the production of 1 metric ton (0.9 short ton) of anhydrous  $\text{AlCl}_3$  requires 182 kg (400 lb) of aluminum and 726 kg (1,600 lb) of chlorine (Reference 2); however, stoichiometric chlorination rates are difficult to obtain. Scrap aluminum is frequently used as a raw material in aluminum chloride manufacturing.

Condenser off gases are usually scrubbed with wet systems to collect particulates and chlorine vapors. Caustic is sometimes added to the scrubbing media to improve chlorine collection and to relax high concentrations of hydrochloric acid in the scrubber water.

An alternative process for producing anhydrous aluminum chloride consists of reacting bauxite, coke, and chlorine at a temperature of about 870°C (1600°F). The bauxite and coke mixture is heated, and chlorine is blown into the furnace, converting alumina, (aluminum oxide) to aluminum chloride. The vapors are condensed to form a relatively pure product. The reaction equation is:



The final anhydrous product may vary in color from yellow to white to gray, depending upon the ratio of chlorine to aluminum. An excess of chloride in the product produces a yellow color, while an excess of aluminum results in a gray color due to the presence of unreacted metal.

Hydrous aluminum chloride comprises a significant portion of the total U.S. aluminum chloride production, and this compound frequently serves as a precursor in the synthesis of other chemicals. The hydrous product can be created by reacting hydrated alumina or bauxite with hydrochloric acid. The resultant solution is filtered to remove unreacted residues or muds, and the product is containerized. Further purification is sometimes required after filtration.

Emissions-control devices may be employed for control of vapors generated during the reaction, and one plant reports that the scrubber water is reintroduced to the reaction chamber.

Figure 2 is a generalized process flow diagram of hydrous aluminum chloride.

Figure 1. FLOW DIAGRAM FOR TYPICAL PRODUCTION OF ANHYDROUS ALUMINUM CHLORIDE

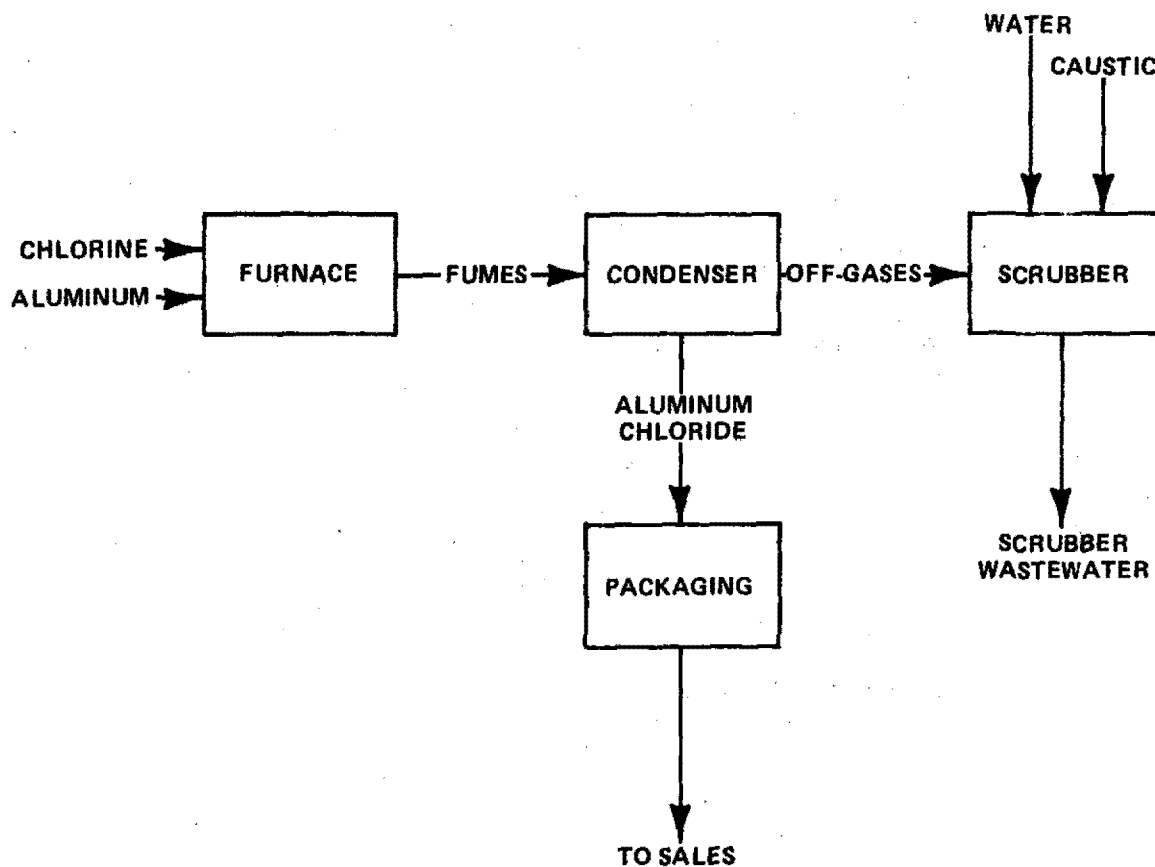
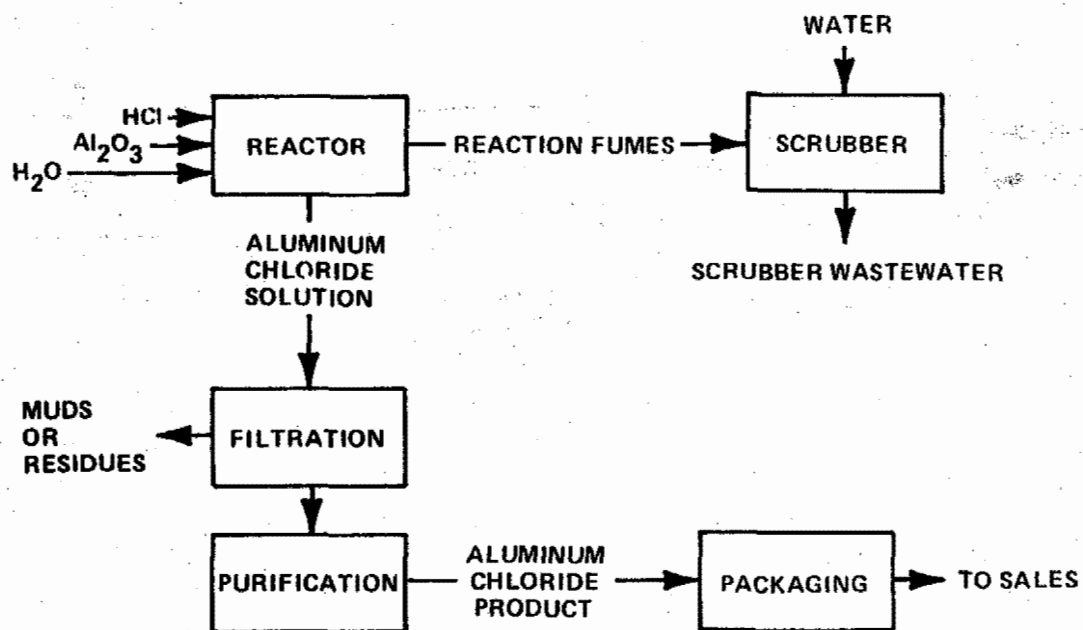


Figure 2. FLOW DIAGRAM FOR TYPICAL PRODUCTION OF HYDROUS ALUMINUM CHLORIDE



There were no POTW dischargers found in the aluminum chloride subcategory. Of the seven plants where process-water discharge status has been determined, three are direct dischargers, while one plant has achieved zero discharge status. The remaining three plants do not employ process water.

### Aluminum Sulfate

Industry Description. The term "alum" has been loosely applied, and a true alum is a double sulfate of aluminum or chromium and a monovalent metal (or radical) (Reference 3). However, in keeping with present terminology, "alum" in this document refers only to aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ). The most important commercial application for alum is as a flocculant (coagulant) in water treatment; thus, three large U.S. cities are listed in the ranks of alum producers. The second most prominent use is in the papermaking industry, where iron-free alum is required for the sizing of paper.

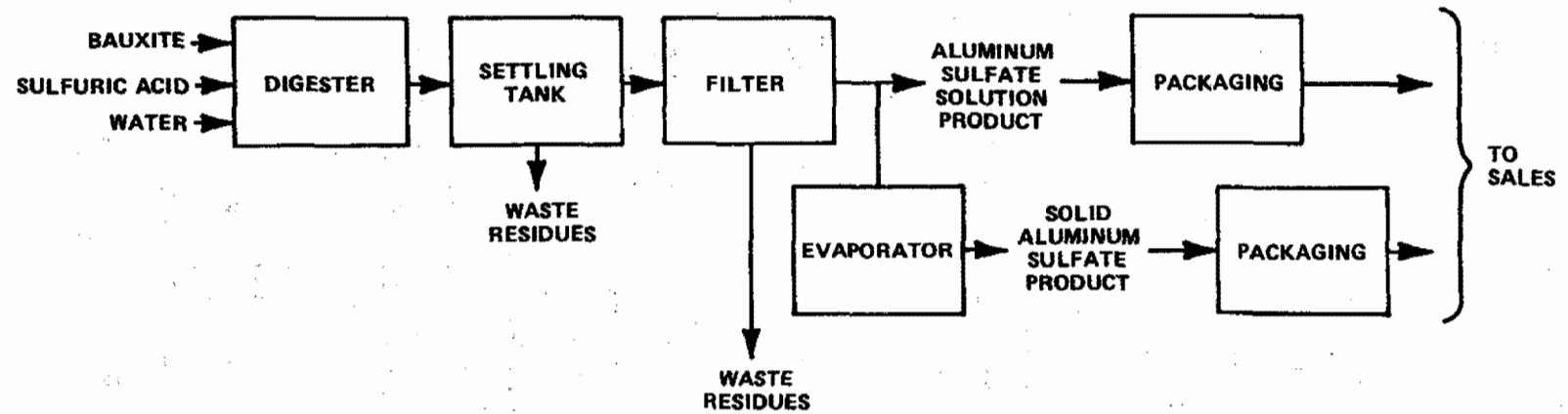
The Directory of Chemical Producers (Reference 1) lists 82 plants as producing alum in 1974. Of these, fifteen are known to make iron-free grade alum. The total annual production of alum exceeds 1.1 million metric tons (1.2 million short tons).

Manufacturing Processes. Aluminum sulfate is produced by the reaction of concentrated sulfuric acid with bauxite, clay, and other compounds containing aluminum oxide. Iron-free alum is often produced by utilizing relatively pure hydrated alumina (aluminum oxide) as a source of aluminum. The general equation of the reaction is (Reference 4):



In this typically batch operation, the aluminum-bearing material and acid are reacted in a digester, where heat is usually added to promote reactivity. The whole mixture (water and solids) is fed to a settling tank, where the insolubles (muds) are removed. Some muds are washed to recover entrained aluminum sulfate solution. The overflow from the settling tank is further purified by clarification or filtration. Other steps taken to remove impurities include addition of materials such as aluminum powder (for iron reduction), activated carbon (for color control), and polyelectrolyte (to improve settling). The resultant solution can be sold or routed to an evaporation stage for alum-crystal production. A generalized flow diagram for alum production is displayed in Figure 3.

**Figure 3. FLOW DIAGRAM FOR TYPICAL PRODUCTION OF ALUMINUM SULFATE**



There are many modifications to the generalized flow diagram in practice today. One municipal alum producer digests bauxite with sulfuric acid and employs the resultant slurry as a flocculant to improve turbidity characteristics of city drinking water. (Clearly, there are no settling or purification steps which follow digestion.) Many plants impound the waste residues (muds) and associated transport water for recycle after settling. The acidic water is fed back to the digester. Other plants discharge residue transport water, residue wash water, and filtrate generated by purification steps. One plant uses a wet scrubber to collect dusts from various pickup points (presumably, bauxite crushing and grinding) throughout the plant and shunts a portion of the scrubber recycle stream to the alum digesters. The same plant diverts a portion of its mud wash water to settling ponds and, eventually, to discharge.

There are no known POTW dischargers in this subcategory, and the discharge status of most plants is unknown. At the plants evaluated, total recycle is common practice at alum manufacturing plants, and dischargers are presumably a minority in the industry.

#### Calcium Carbide

Industry Description. Production of calcium carbide ( $\text{CaC}_2$ ) falls under two categories: the Inorganic Chemicals Manufacturing category and the Ferroalloy Manufacturing category. Calcium carbide production is categorized and regulated according to the type of furnace used. All production of calcium carbide from covered furnaces is in the Ferroalloy Manufacturing category (40C.F.R. 424, Subparts D&E). Open (uncovered) furnaces is included in the Inorganic Chemicals Manufacturing category.

Three plants using uncovered furnaces were studied for this report. The three plants produce an approximate total of 87,000 metric tons (96,000 short tons) annually, which accounts for nearly 25% of the total annual (all furnace types) calcium carbide production.

Manufacturing Process. Calcium carbide is produced by reacting calcium oxide (lime or limestone) with carbon (in the form of coke, petroleum coke, or anthracite) at 2000 to 2200°C (3630 to 3990°F) in either an electric or an arc furnace. The general equation for the reaction is:

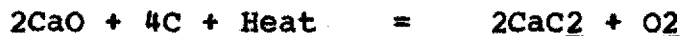




Figure 4 is a basic flow diagram of calcium carbide production.

The raw materials are crushed and dried before addition to the furnace. The furnace is cooled with a noncontact system. The product is air-cooled, crushed, screened, and packaged or stored. Since the production process is dry, the only discharges are dusts and furnace off-gases.

No calcium carbide plant contacted discharges to a POTW.

### Calcium Chloride

Industry Description. Calcium chloride ( $\text{CaCl}_2$ ) is produced by twelve plants in the United States at present, and seven of these plants are located in Michigan, California, and Washington. The remaining plants are well dispersed throughout the nation. The Directory of Chemical Producers (Reference 1) states that nine of the plants represent a combined annual capacity of 1.029 million metric tons (1.135 million short tons), with a significant portion of the total attributable to production from natural sources in Michigan. The major uses for calcium chloride are for road deicing, dust control, and concrete treatment (Reference 2).

Manufacturing Processes. Classically, calcium chloride has been extracted as a joint product from natural salt brines, and as a byproduct of soda ash (sodium carbonate) manufacture via the Solvay process. Both methods are similar after the raw brines have been purified: the solutions containing calcium chloride are concentrated and crystallized. However, other, less complex processes, such as reaction of limestone and hydrochloric acid are practiced to produce smaller quantities of the salt. It is these smaller operations which are likely to be located in an urban environment where POTW discharge is feasible.

The brine recovery process is practiced in Michigan by two large operations, and the process flow diagram for one plant appears in Figure 5. Briefly, the salts are solution-mined, and the resulting brines are separated, iodine, bromine, and magnesium compounds being routed to other recovery circuits. The remaining solution is then partly evaporated to remove sodium chloride by precipitation. The sodium chloride removal involves a large degree of brine recycling. The brine is further purified by addition of other reagents to remove sodium, potassium, and magnesium salts by precipitation and further evaporation. The purified concentrate is then evaporated to dryness to recover calcium chloride. The product may be sold as a hydrated solid or diverted to a flaker to form hydrated flakes. Anhydrous

Figure 4. FLOW DIAGRAM OF STANDARD PROCESS FOR PRODUCTION OF CALCIUM CARBIDE

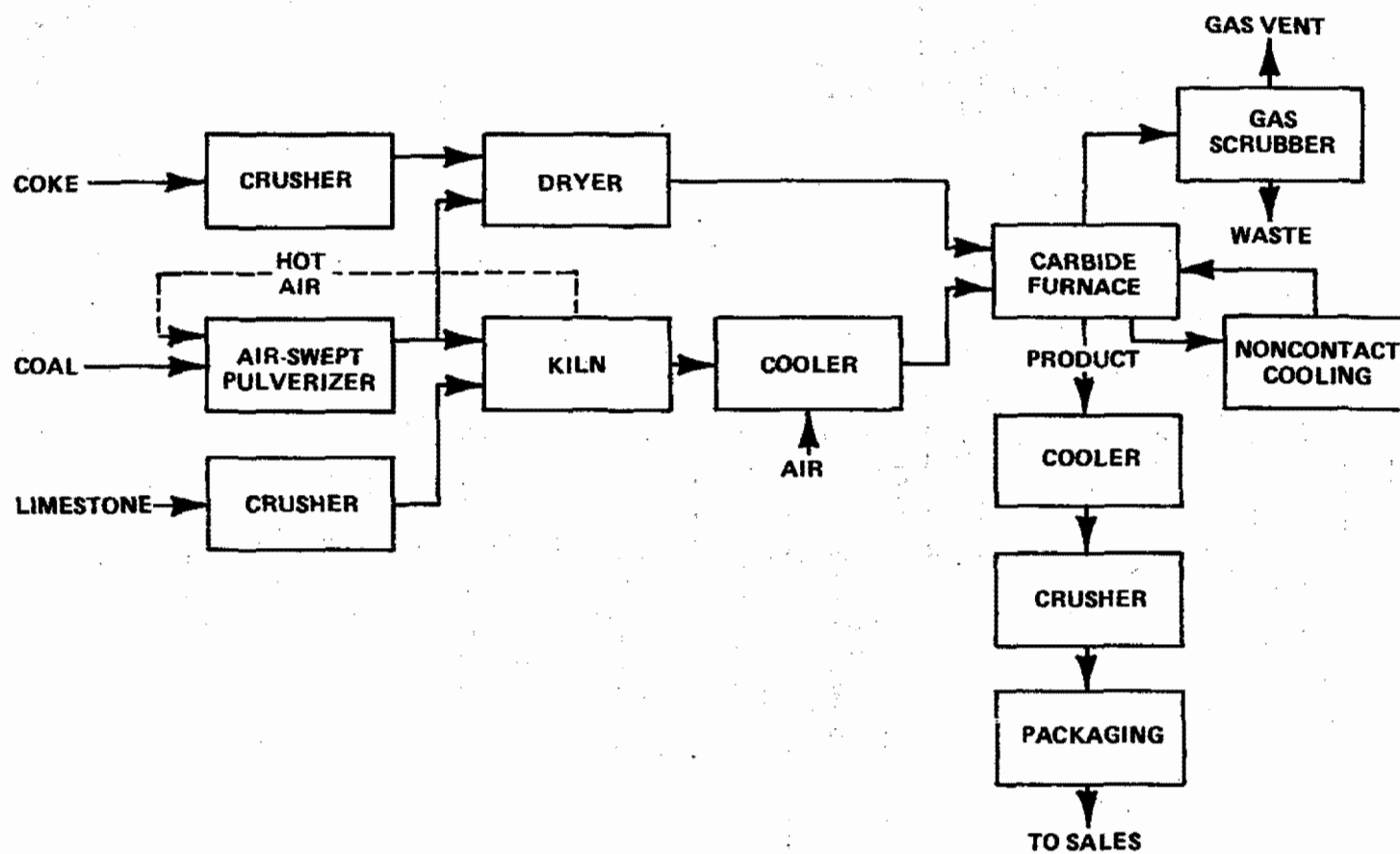
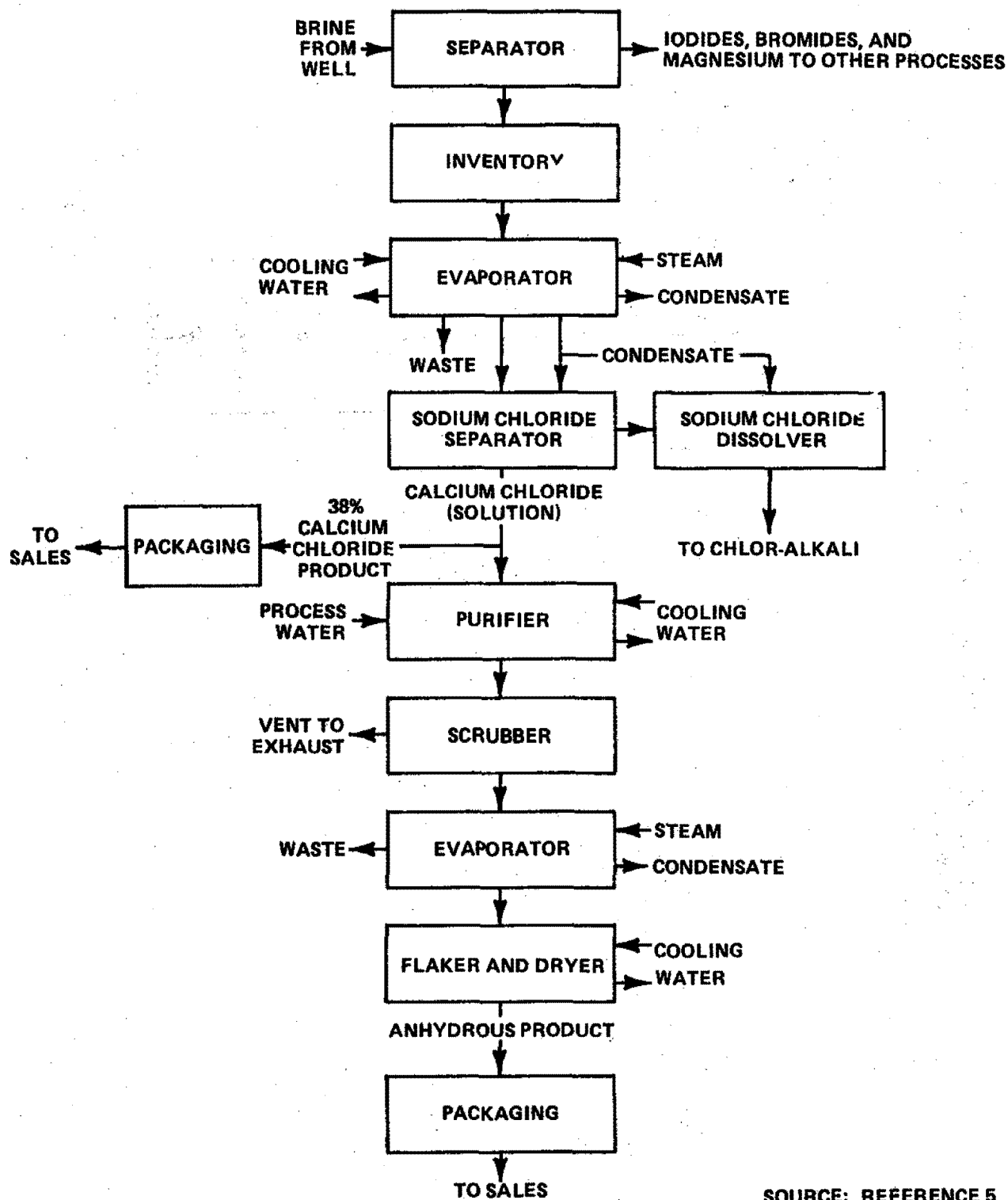


Figure 5. FLOW DIAGRAM FOR PRODUCTION OF CALCIUM CHLORIDE FROM NATURAL BRINE (PLANT 19404)



SOURCE: REFERENCE 5

product may be formed by heating the hydrated product to form fused calcium chloride, which is about 95% pure. The coded material is crushed and screened for sale.

The Solvay (byproduct) calcium chloride process begins with a clarified liquor from the clarifiers. The relatively pure liquor contains calcium and sodium chlorides and a small amount of calcium sulfate. The liquor is introduced into triple-effect evaporators, where most of the sodium chloride (plus some calcium sulfate) crystallizes during the first effect. Subsequent evaporation effects occur until the specific gravity reaches a point where nearly all the sodium chloride has been crystallized and settled. The purified liquor is then thermally concentrated until it becomes a molten mass. The product can be cooled directly to form a hydrated solid calcium chloride or converted to anhydrous product.

A third process for calcium chloride manufacture consists of reacting limestone (calcium carbonate) with hydrochloric acid to form a solution containing about 36% calcium chloride. Solid waste from the process consists of insolubles left as residues from limestone digestion. A similar process involves reaction of calcium carbonate (in the presence of hydrogen peroxide and calcium oxide) with hydrochloric acid to form a pure solution, which is subsequently concentrated and dried to form a solid product. A generalized flow diagram for this type of process is shown in Figure 6.

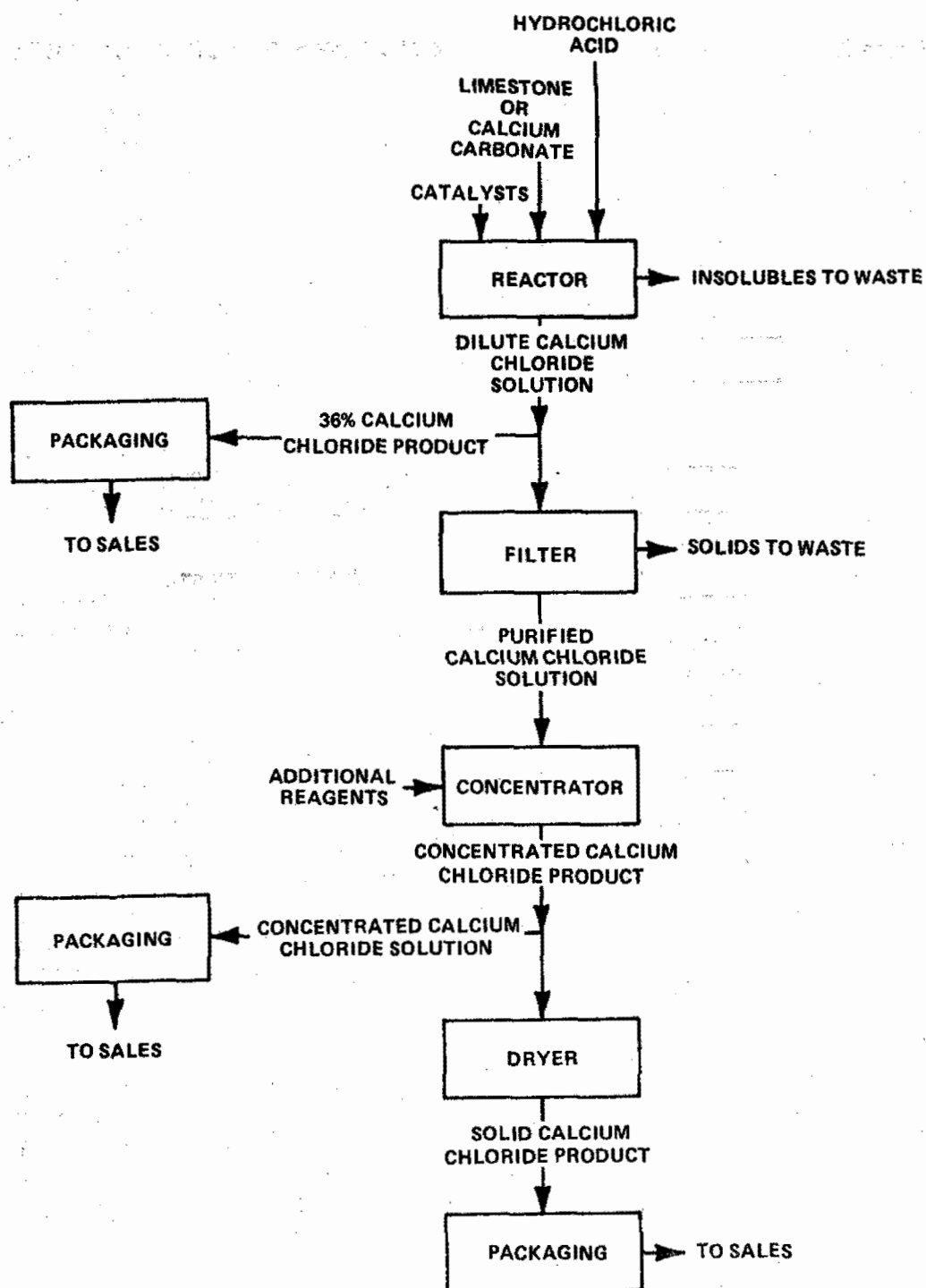
An additional process for synthesizing high-purity solid calcium chloride is practiced at the only known POTW discharger in the industry. Two salt solutions are first filtered with bone coal and then reacted. The resultant solution is then boiled to yield a precipitate which is dehydrated in a horizontal dryer. A scrubber which collects emissions generated during the boildown step generates a waste water which contains hydrochloric acid. A flow diagram for this process is shown in Figure 7.

The only POTW discharger in the calcium chloride subcategory uses a municipal treatment system practicing primary settling and resultant sludge incineration. The average daily flow to the POTW is 0.45 million cubic meters (120 million gallons), and 40% of the total influent is industrial in origin.

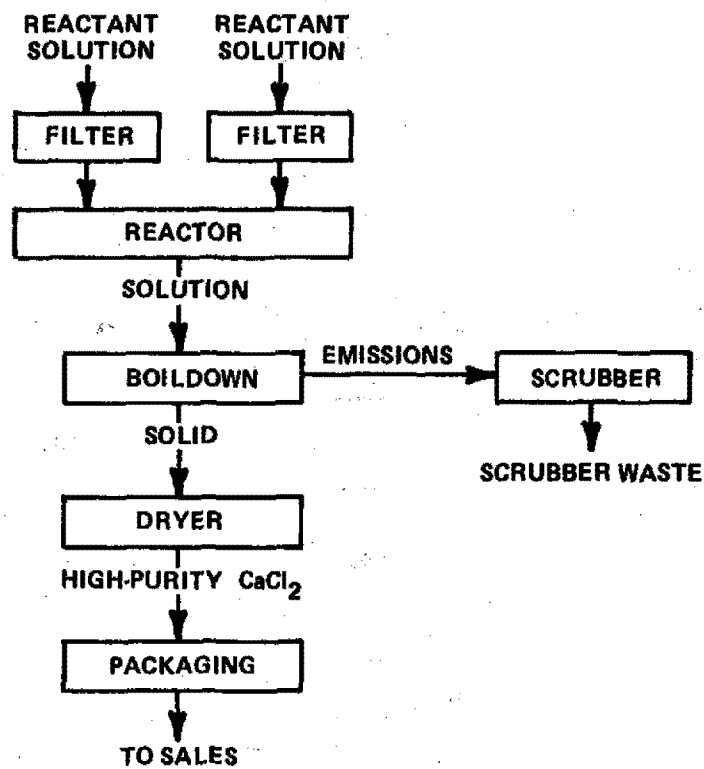
#### Copper (Cupric) Sulfate

Industry Description. The six copper sulfate plants studied account for approximately 70% of the total U.S. production

**Figure 6. GENERALIZED FLOW DIAGRAM FOR PRODUCTION OF CALCIUM CHLORIDE FROM CALCIUM CARBONATE**



**Figure 7. FLOW DIAGRAM FOR PRODUCTION OF HIGH-PURITY CALCIUM CHLORIDE (PLANT 19406)**

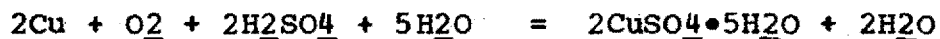


of copper sulfate. The average yearly production of the six plants combined is 23,400 metric tons (25,800 short tons).

The markets for copper (cupric) sulfate are in wood preservation (when mixed with sodium chromate), as trace components for copper-deficient soils, and for water treatment (use as an algicide).

Manufacturing Process. Copper (cupric) sulfate is produced by the action of sulfuric acid on copper. Normally, production of copper sulfate is a sideline with copper refiners. Copper shot, copper scrap, or electrolyte solutions containing copper are the raw materials used in manufacture. Either concentrated or dilute sulfuric acid may be used.

All of the plants studied produce copper sulfate pentahydrate. The process reaction is:



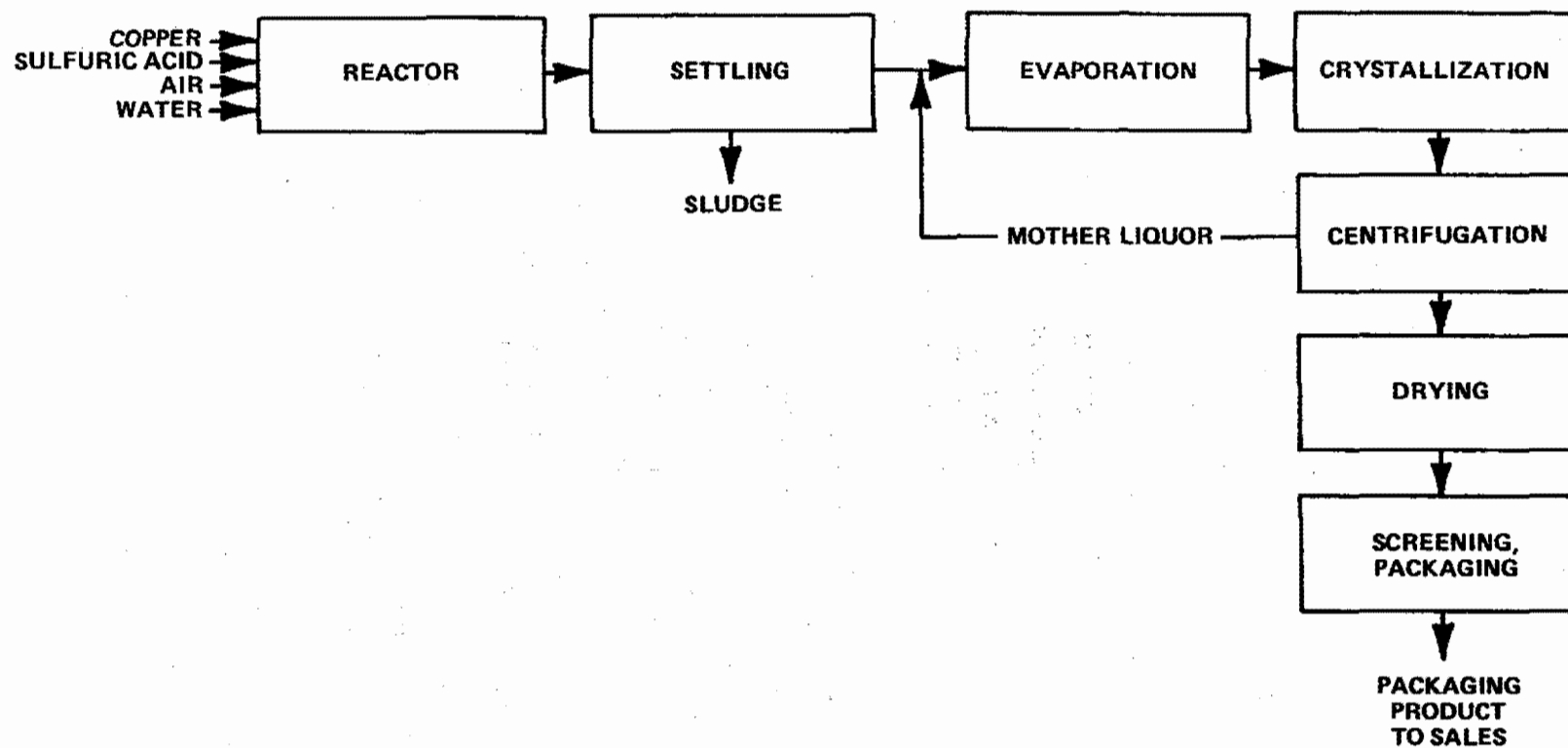
The resulting solution is sold in its entirety by four of the six plants studied. The production of the four plants is approximately 2,200 metric tons (2,420 short tons) per year. The other two plants evaporate, crystallize, and centrifuge the solution to obtain copper sulfate pentahydrate crystals. The crystals are dried, screened, and packaged. Figure 8 is a basic process diagram for copper sulfate crystal production.

All of the plants studied have minimal waste flow. The high value of copper is an incentive to recycle or recover most process wastes and to minimize the metal content in the water effluent. Not one of the copper sulfate plants studied discharges to a POTW.

Plants 19501, 19502, 19503, and 19504 produce copper sulfate solution containing approximately thirty percent copper sulfate pentahydrate. Figure 9 is a diagram of the process used at each plant to produce copper sulfate solution. Water use in the process is slight as tabulated below. The resulting solution is sold in its entirety; consequently, there is no waste water effluent.

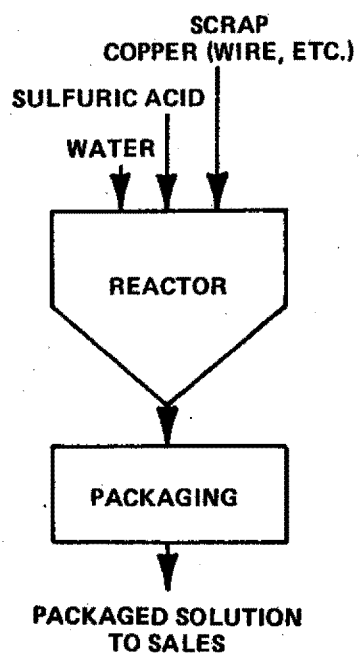
Plant Code	Production		Water Use	
	kg/day	(lb/day)	l/day	(gpd)
19501	181	(400)	64	(17)
19502	635	(1400)	227	(60)
19503	680	(1500)	246	(65)
19504	4,536	(10,000)	15,142	(4,000)

Figure 8. FLOW DIAGRAM OF STANDARD PROCESS FOR PRODUCTION OF CUPRIC SULFATE





**Figure 9. FLOW DIAGRAM OF PROCESS FOR MANUFACTURE OF CUPRIC SULFATE SOLUTION**



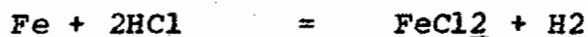
Plant 19505 produces copper sulfate crystal using crude copper shot and electrolyte solution from its refinery as the sources of copper and sulfuric acid. The only waste water flow from this plant results from noncontact cooling water, noncontact steam condensate, and treated washdown water. Treatment for the washdown water includes neutralization, settling, and filtration.

Plant 19506 uses copper shot as the raw material in crystal production. Since all of the mother liquors and wash waters are recycled at plant 19506, only the water from the barometric condenser on the vacuum crystallizer is discharged.

### Iron (Ferric) Chloride

Industry Description. There are 18 plants in the United States producing various grades of ferric chloride ( $\text{FeCl}_3$ ) (including specialty and photo grades). Total U.S. production in 1974 was 138,000 metric tons (152,000 short tons) (Reference 1). Of the 18 ferric chloride producers, two discharge process waste water to a POTW. These two indirect dischargers account for only 7% of the total U.S. production of ferric chloride. Average production of the two POTW dischargers is 4,500 metric tons/year (5,000 short tons/year). This is in contrast to several of the direct dischargers, whose annual production of ferric chloride range from 18,000 to 27,000 metric tons (20,000 to 30,000 short tons). However, it is well within the range of all ferric chloride producers (Reference 1).

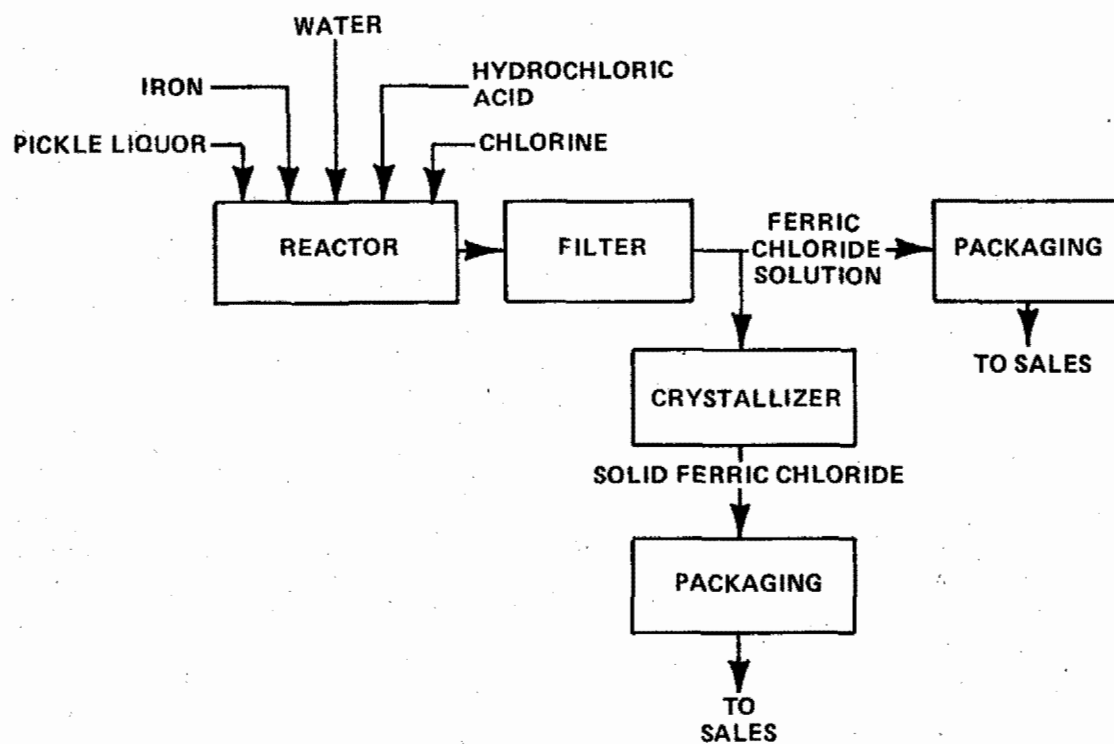
Manufacturing Process. Commercial solutions of ferric chloride are produced from iron and steel pickling liquors, which contain ferrous chloride ( $\text{FeCl}_2$ ) and hydrochloric acid. The steel pickling liquors are preheated with steam and then reacted with iron, chlorine, additional hydrochloric acid, and water to produce the desired solution. (A process flow diagram is presented in Figure 10). The overall reactions involved are:



Crystallization produces a hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), which is hygroscopic and very soluble in water.

Solutions of ferric chloride are used as a copper etchant in photoengraving, in textile dyes, for the chlorination of copper and silver ores, for pharmaceuticals production, as

Figure 10. FLOW DIAGRAM FOR TYPICAL PRODUCTION OF FERRIC CHLORIDE



an oxidizing agent in chemical synthesis, and for water purification.

Production of ferric chloride by passing chlorine gas over iron at red heat or by oxidizing anhydrous ferrous chloride with chlorine is not included in this study because this process accounts for only a small part of the total production.

### Lead Monoxide

Industry Description. The lead monoxide ( $PbO$ , or litharge) subcategory contains about 16 plants, none of which is known to discharge to publicly owned treatment works. Of the 16 plants, 11 discharge directly to surface waters or have no process waste discharge. The discharge status of the remaining five plants is unknown. There is no significant locational pattern, with plants located in 10 states from California to New York.

Manufacturing Processes. Although there are four commercially important processes for manufacturing litharge, all involve primarily the air oxidation of metallic lead; rapid cooling of the product; and, in three of the four cases, milling of the resultant coarse particles. Process diagrams are shown in Figure 11. Descriptions of the processes follow.

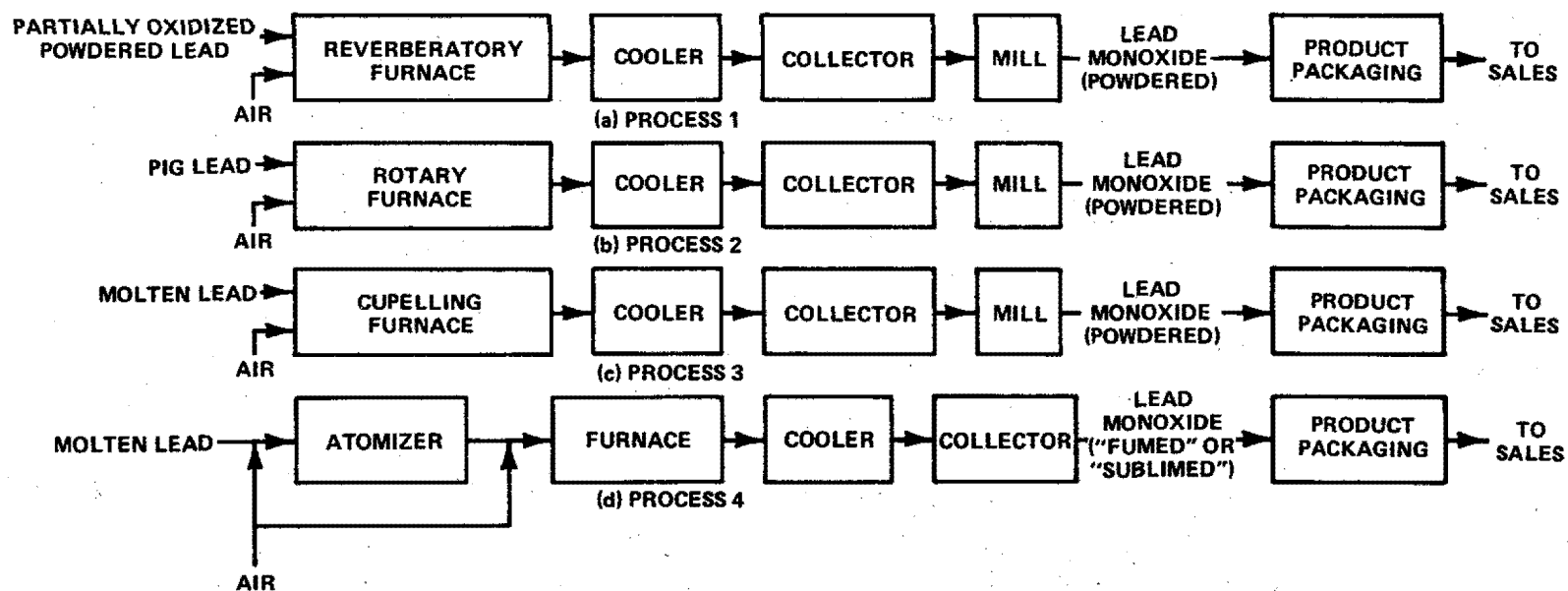
In Process 1, lead is melted in the presence of air (usually, on a flat hearth). During this low heating (never over a full red heat), a scum of lead suboxide forms. This is raked or blown aside so that more may be exposed for oxidation. The partially oxidized lead is milled to a powder and charged to a reverberatory furnace, where it is heated to about  $600^{\circ}C$  ( $1112^{\circ}F$ ) to complete the oxidation. Most litharge for storage-battery plates is made by this process.

In Process 2, pig lead is melted and stirred in the presence of air, in either a reverberatory furnace or rotary kiln, to form litharge directly.

In Process 3, lead or a lead/silver alloy is melted in a cupellation furnace at  $1,000^{\circ}C$  ( $1832^{\circ}F$ ). As air is passed through the furnace molten litharge is formed and is allowed to overflow into a receiver where it cools and solidifies. The solidified oxide is broken up and milled to desired size.

In Process 4, molten lead at  $500^{\circ}C$  ( $932^{\circ}F$ ) is atomized into an oxidizing flame in a specially built furnace where it

Figure 11. FLOW DIAGRAMS OF FOUR ALTERNATIVE PROCESSES FOR PRODUCTION OF LEAD MONOXIDE USING AIR OXIDATION OF LEAD



SOURCE: REFERENCE 2

burns to form very finely divided particles (0.25 to 0.5 micrometer) of "sublimed" litharge. The fine powder is cooled rapidly and collected. No other processing is necessary.

In all cases, the product must be cooled quickly to less than 300°C (572°F) to avoid the formation of red lead (Pb<sub>3</sub>O<sub>4</sub>). The products from the first three mentioned processes must be milled to suitable size (1.5 to 8 micrometers).

Most of the plants in this subcategory do not use water in the chemical manufacturing process. The major water-using operations are noncontact cooling and washdown of dusts from plant surfaces. For this reason, only plants practicing washdown of dusts will have any significant process waste water discharge. All lead oxide plants which utilize compressed air in the manufacturing process will have a process waste water discharge from compressor "blowdown," although the quantity of this waste water will be minor. Plants which do not employ water cooled compressors and utilize good housekeeping procedures in conjunction with the dry vacuuming of dusts will have no process waste water to discharge.

Raw materials used in the process consist of powdered pig lead (partially oxidized lead) and air. No other chemical reagents are necessary. On a basis of 1 metric ton (1.1025 short tons) of litharge product, 948 kg (2090 lb) of pig lead is consumed. The amount of air required is variable. Theoretically, 50.3 cubic meters (1,775 cubic feet) of air is required per metric ton of litharge at standard temperature and pressure (Reference 2).

None of the 11 lead monoxide producing plants contacted in this subcategory were identified as discharging process waste waters to a POTW.

### Nickel Sulfate

Industry Description. There are 12 known plants in the United States producing solutions of nickel sulfate (NiSO<sub>4</sub>) and nickel sulfate hexahydrate crystals. Total U.S. production in 1972 was 13,400 metric tons (14,800 short tons). Production at individual plants ranges from 90 metric tons (100 short tons) per year to 6,800 metric tons (7,600 short tons) per year (Reference 6).

Of the 12 nickel sulfate producers, only three discharge process waste water to a POTW. These three indirect

dischargers account for approximately 30% of the total U.S. production of nickel sulfate.

Manufacturing Processes. The raw materials for the production of nickel sulfate include metallic nickel, nickel oxide, spent nickel-plating solutions, and spent nickel catalysts. The processes employed vary, depending in the raw materials. However, the basic process involves reacting the raw material with sulfuric acid to produce a nickel sulfate solution. The reaction with nickel oxide as feed is:



The resultant solution is filtered to remove particulates and may be treated with sulfides, lime, sulfuric acid, etc., when necessary to remove metallic impurities. The purified nickel sulfate solution is then either sold, used in-plant, or crystallized to a hexahydrate for sale. A basic process flow diagram is presented in Figure 12.

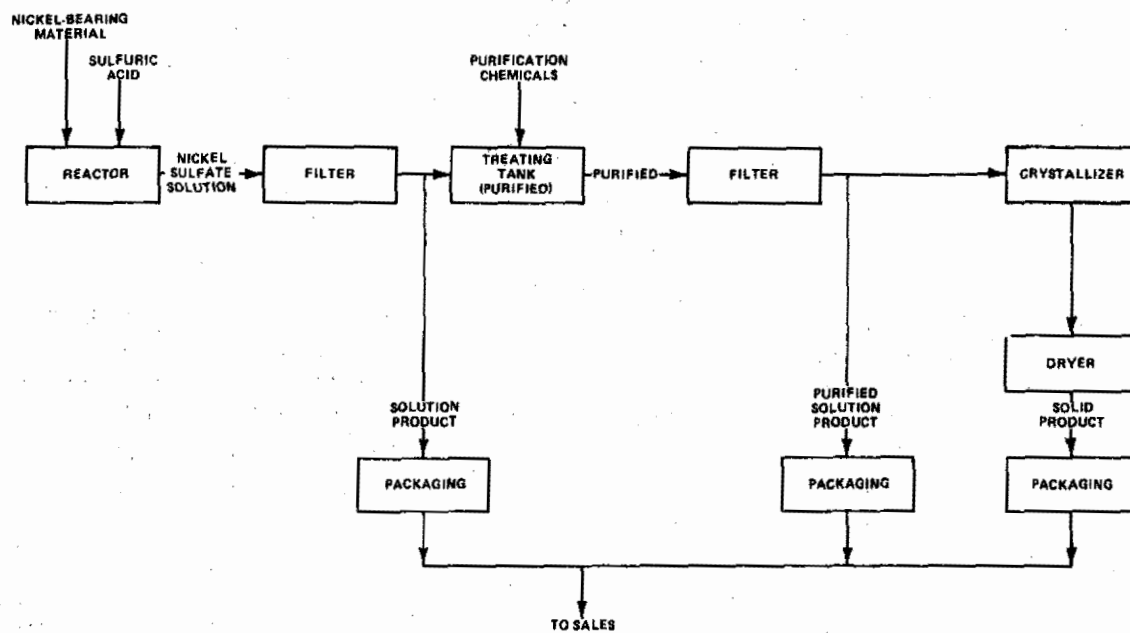
Nickel sulphate is used in electroplating baths, for the production of other nickel compounds, as a mordant in dyeing and printing fabrics, and in blackening zinc and brass.

#### Nitrogen and Oxygen

Industry Description. The nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) production subcategory of the inorganic chemicals industry encompasses a vast number of processing plants which manufacture gaseous and liquid products via air separation. Current survey figures indicate that the industry consists of approximately 193 plants, representing some 25 companies (Reference 1), and is capable of producing nitrogen and oxygen in annual quantities exceeding 22 million metric tons (24 million short tons). A breakdown of this production data reveals that approximately 7.3 million metric tons (8.1 million short tons) of nitrogen and 15.3 million metric tons (16.9 million short tons) of oxygen are produced annually in the United States (Reference 7).

Production capacities of air-separation plants range from 11 to 9,100 metric tons (12 to 10,000 short tons) of chemical per day, with the average plant producing approximately 535 metric tons (590 short tons) of combined product daily (Reference 1). Note that production figures quoted for air-separation plants frequently reflect total nitrogen and oxygen produced, rather than individual product data. In discussing this subcategory, combined product figures are used unless some significant process distinction exists in a

Figure 12. FLOW PROGRAM FOR TYPICAL PRODUCTION OF NICKEL SULFATE





particular plant which precludes this method of utilizing production data.

Location of air-separation plants throughout the country is frequently dependent on the desired application of the chemical being produced. A number of these air-separation plants are known to be on-site locations providing high-purity product for use in specific industrial processes. Common examples are the plants which manufacture high-grade oxygen for use in the steel industry and those which produce pure nitrogen for textile mills. These on-site air-separation plants are responsible for producing a significant portion of the total nitrogen and oxygen manufactured by the industry. Smaller plants may be located adjacent to an industrial complex and, although not on-site, may opt to supply a direct line for gas transportation to the industry. In addition to directly servicing the industries, many of these plants also manufacture gaseous products for commercial distribution.

Manufacturing Processes. The standard industrial process utilized in manufacturing nitrogen and oxygen is air separation. The fundamental technology for this process was developed in the early part of this century and is one of the oldest chemical processes in existence.

The basic process is as follows: Filtered atmospheric air is compressed, purified by removing its carbon dioxide and water-vapor components, cooled by a series of heat exchangers, and fractionally distilled into the desired products in a double-column rectifier. Various technological modifications of the fundamental process have resulted in minor distinctions, as can be seen in the process flow diagrams which follow. Figure 13 represents a typical high-pressure system with reciprocating-type air compressors, caustic scrubber, and activated-alumina air dryer. This system is somewhat older chronologically than the one shown in Figure 14. The latter is a low-pressure cycle employing centrifugal compressors and a series of reversing exchangers which serve to both cool and purify the air. The function of the exchangers is analogous to that of the caustic scrubber and activated alumina of the older system--i.e., they accomplish both carbon dioxide removal and evaporation of excess water vapor. The argon-recovery step in Figure 13 is optional in the air-separation process and is employed in accordance with the needs of the individual plant.

For those plants which are producing nitrogen only, the distinguishing design modification is in the rectifier column. A single low-pressure column is substituted for the

Figure 13. FLOW DIAGRAM OF TYPICAL HIGH-PRESSURE AIR-SEPARATION PROCESS (MODIFIED CLAUDE CYCLE) FOR PRODUCTION OF NITROGEN AND OXYGEN

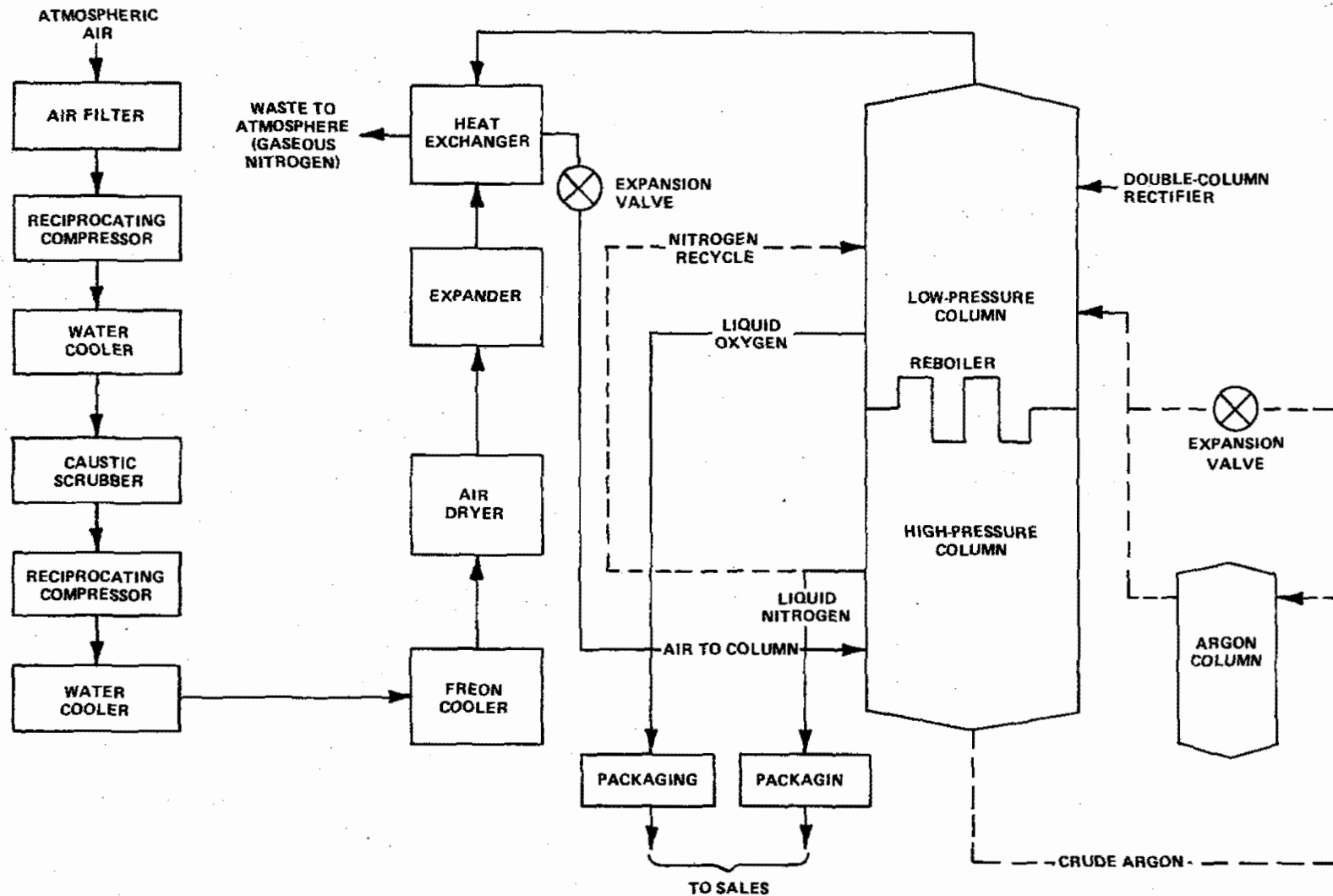
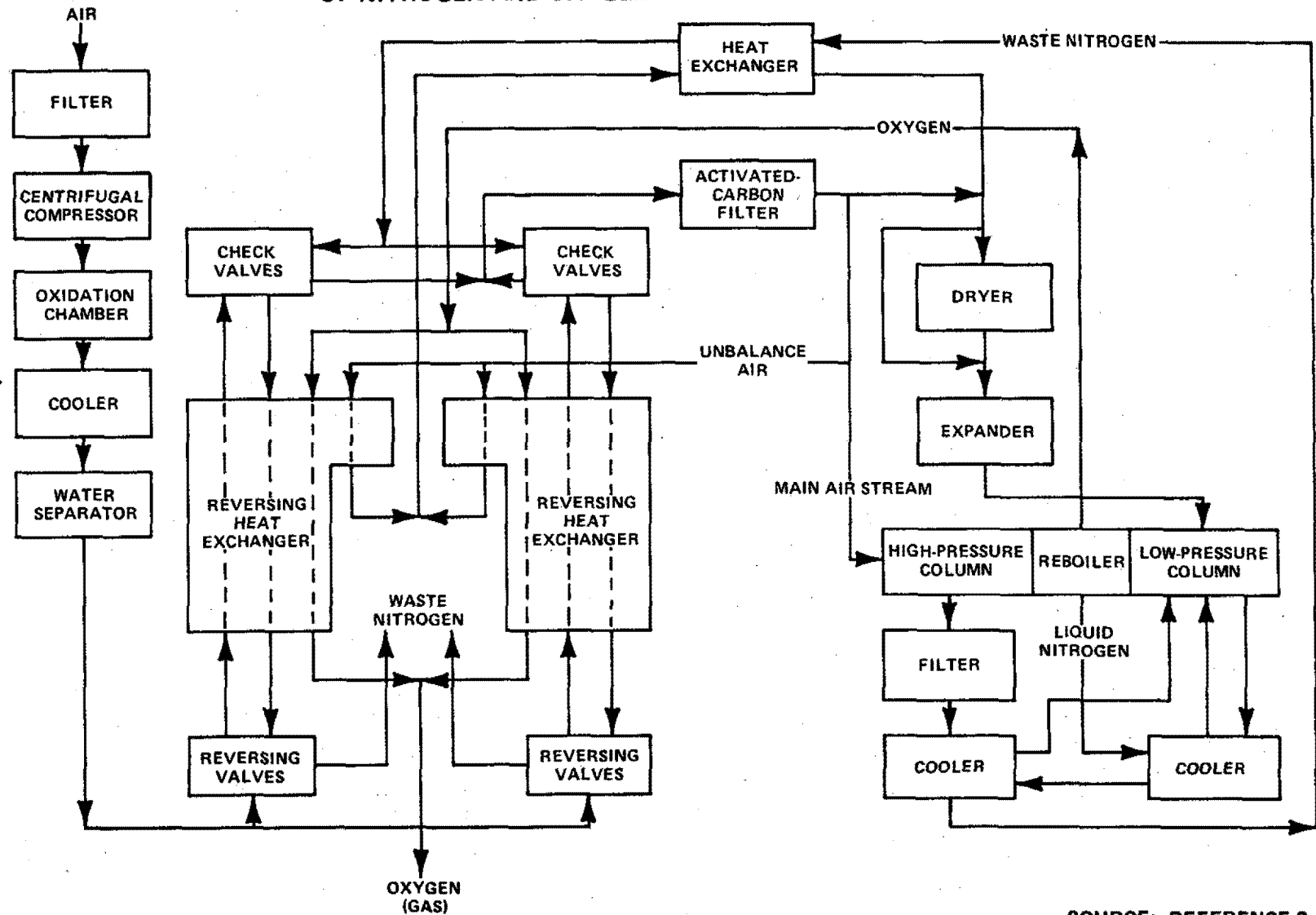


Figure 14. FLOW DIAGRAM OF LOW-PRESSURE AIR-SEPARATION PROCESS  
(MODIFIED LINDE-FRANKL CYCLE) USED IN TYPICAL PRODUCTION  
OF NITROGEN AND OXYGEN

39



SOURCE: REFERENCE 2

double-column rectifier, and the oxygen rich mixture formed in the column is wasted rather than recovered.

Commercial oxygen utilization, particularly in industrial applications has undergone considerable growth in recent years. Demand for the chemical (notably, in the steel industry) has increased significantly due to the development of new processes which are highly oxygen consumptive.

In the chemical industry, manufacture of acetylene and ammonia accounts for a significant portion of the total oxygen utilized by this industry. Planned new processes in the cement and copper refining industries, as well as continued use in missile and rocket development, should sustain the rate of growth in oxygen manufacturing.

High-purity nitrogen gas has several industrial applications, the most notable being in the textile industry, where it is used in the production of nylon and other synthetics. Secondary uses include the manufacture of plate glass and the preservation of certain processed foods.

Of the 193 air-separation plants identified in the industry, the majority discharge their process waste waters directly to surface streams. However, according to information provided by the industry, at least 33 are known to be discharging to POTWs.

Data compiled on these POTWs indicate that 26 percent of those receiving industrial process waters are primary treatment facilities, with flows ranging from 1,500 to 41,600 cubic meters/day (0.4 to 11.0 mgd). The remaining POTWs are secondary treatment facilities, with flows ranging from 4,900 to 3,400,000 cubic meters/day (1.3 to 900 mgd). The average amount of industrial flow handled by a primary plant is 13 percent of the total daily flow, with secondary plants handling an average industrial flow of 20 percent.

There appears to be no particular distinction between the characteristics of process waste waters discharged directly to the surface as compared to those discharged to POTWs.

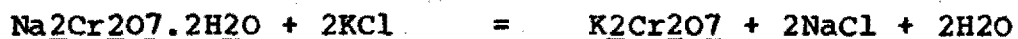
#### Potassium Dichromate

Industry Description. The single plant known to manufacture potassium dichromate ( $K_2Cr_2O_7$ ) does not presently discharge process-associated waste water to a POTW.

Annual domestic production for potassium dichromate is estimated to be 4,000 metric tons (4,400 short tons) (Reference 4). This chemical finds use as an oxidizing

agent (chemicals, dyes, intermediates, and as an analytical reagent). It is also used in brass pickling compositions; electroplating; pyrotechnics; explosives; safety matches; textiles; dyeing and printing; glass; chrome glues and adhesives; chrome tanning leather; wood stains; poison fly paper; process engraving and lithography; photography; pharmaceutical preparations; synthetic perfumes; chrome alum manufacture; pigments; alloys; and ceramic products.

Manufacturing Process. Only one U.S. plant is known to manufacture potassium dichromate. The production process employed at this plant involves the reaction of a sodium dichromate dihydrate solution with potassium chloride according to:



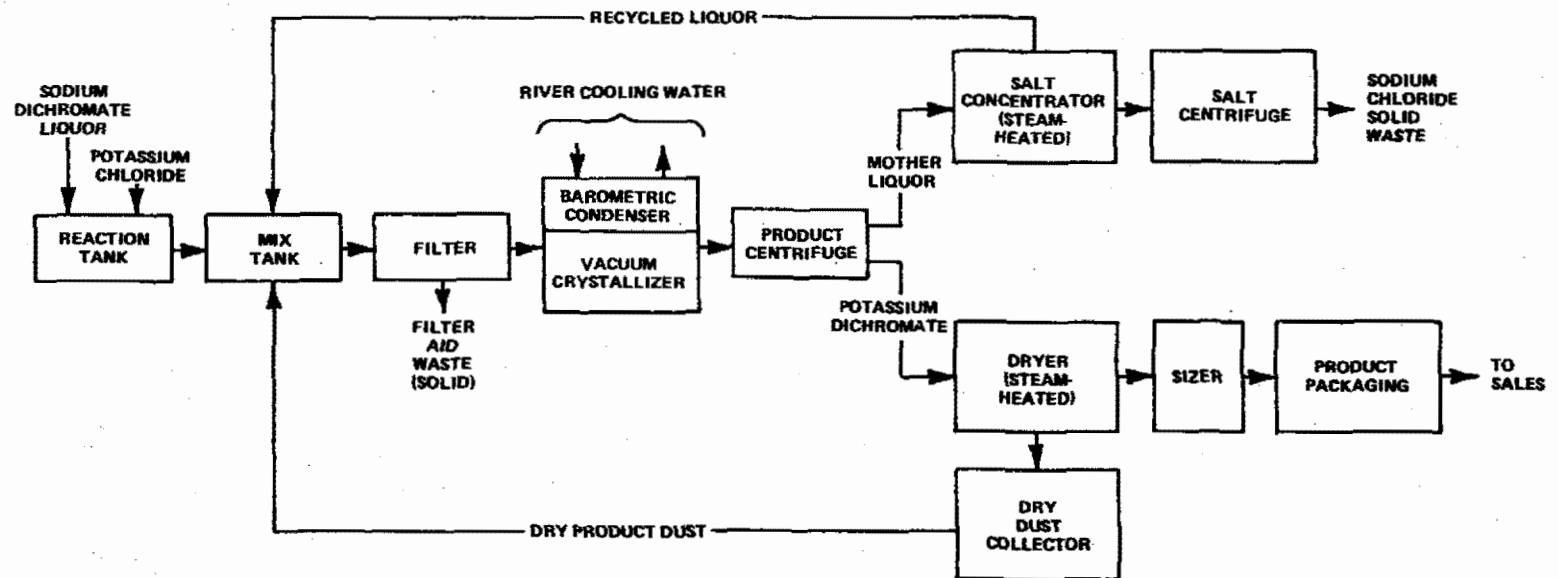
From a hot solution of these salts, potassium dichromate is crystallized by vacuum cooling. (Sodium chloride is crystallized by subsequent evaporation.) The potassium dichromate crystals are separated from the mother liquor by centrifugation, then dried and sized prior to packaging. (The sodium chloride solids collected by evaporation of the mother liquor are discarded as solid waste.) Residual mother liquor is recycled to the initial reaction tank. This process is presented schematically in Figure 15.

### Potassium Iodide

Industry Description. The total U.S. production of potassium iodide (KI) is accounted for by four plants. Geographically these plants are widely distributed, two being located on the East Coast, one on the West Coast, and the fourth in the Mississippi Valley Region. Annual domestic production for 1972 amounted to 998 metric tons (1,100 short tons) (Reference 6).

Manufacturing Processes. At each of the four plants which presently comprise this industry subcategory, the manufacturing process employed yields potassium iodide in batch quantities. The number of batches produced per year at any one plant varies with demand and over a period of years can change greatly. Plants engaged in the manufacture of potassium iodide are typically also engaged in the manufacture of a multitude of other chemical products, both inorganic and organic. At one of these plants, as many as 600 different chemicals are produced in the period of a year.

Figure 15. FLOW DIAGRAM FOR TYPICAL PRODUCTION OF POTASSIUM DICHROMATE



SOURCE: REFERENCE 4

The production processes employed at two of the domestic plants are similar, essentially involving the reaction of iodine with potassium hydroxide in solution according to:



About 80% of the iodate crystallizes from the reaction mixture and is further processed as a byproduct. Of the remainder, 90% is decomposed to iodide during evaporation, fusion, and heating of the iodide solution in a gas-fired furnace:



The fused potassium iodide is redissolved in distilled water and treated with carbon dioxide for pH adjustment and small amounts of barium carbonate, potassium carbonate, hydrogen sulfide, and iron iodide to precipitate sulfate and heavy-metal impurities. Following this purification step, the potassium iodide is recrystallized from solution in a series of steam-heated crystallizers, collected by centrifugation, dried, screened, and packaged for sale. A schematic representation of this process is presented in Figure 16.

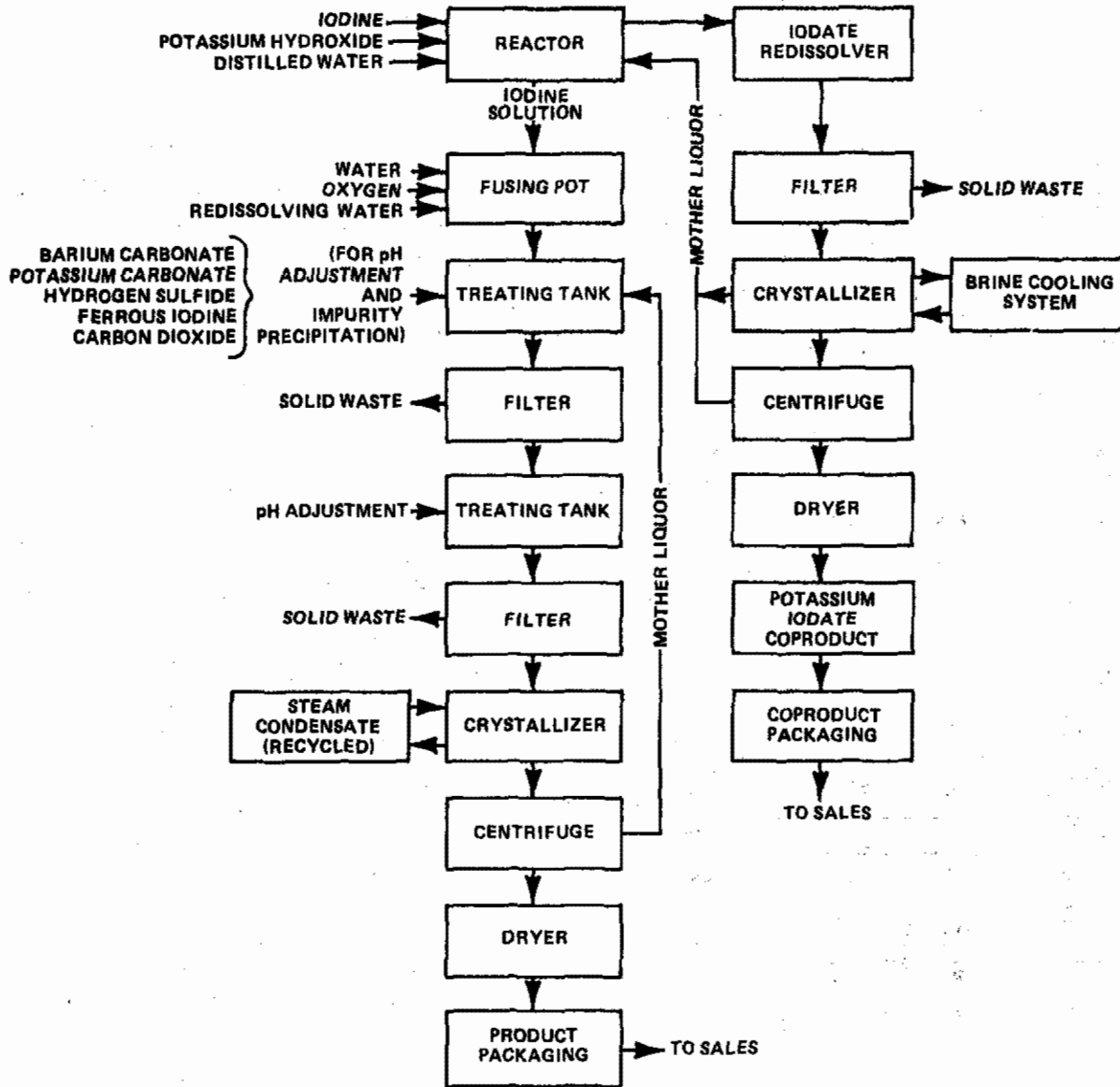
An alternate method of production, which avoids the formation of the iodate, is referred to as the iron and carbonate process. This process, as practiced by one U.S. plant, is presented schematically in Figure 17. Basically, this process involves the reaction of iron powder with iodine in solution. The compound formed, ferrousferriiodide ( $\text{Fe}_3\text{I}_8 \cdot 16\text{H}_2\text{O}$ ), is then reacted with a slight excess of potassium carbonate solution:



A small amount of barium hydroxide and potassium sulfide is also added during this step to precipitate trace sulfate and heavy-metal impurities. Waste solids are removed by filtration. The potassium iodide solution is concentrated by evaporation and subsequently cooled to effect crystallization. The slurry leaving the crystallizers is centrifuged to separate the residual mother liquor and potassium iodide crystals. The crystals are subsequently dried, sifted, and packaged for sale, while the mother liquor is recycled to the evaporator.

The manufacturing process employed at the fourth domestic plant (Figure 18) is similar to the iodine/potassium hydroxide process. At this plant, iodine and potassium hydroxide are also the major reactants. However, in this process, iron powder is added as a reaction catalyst. The

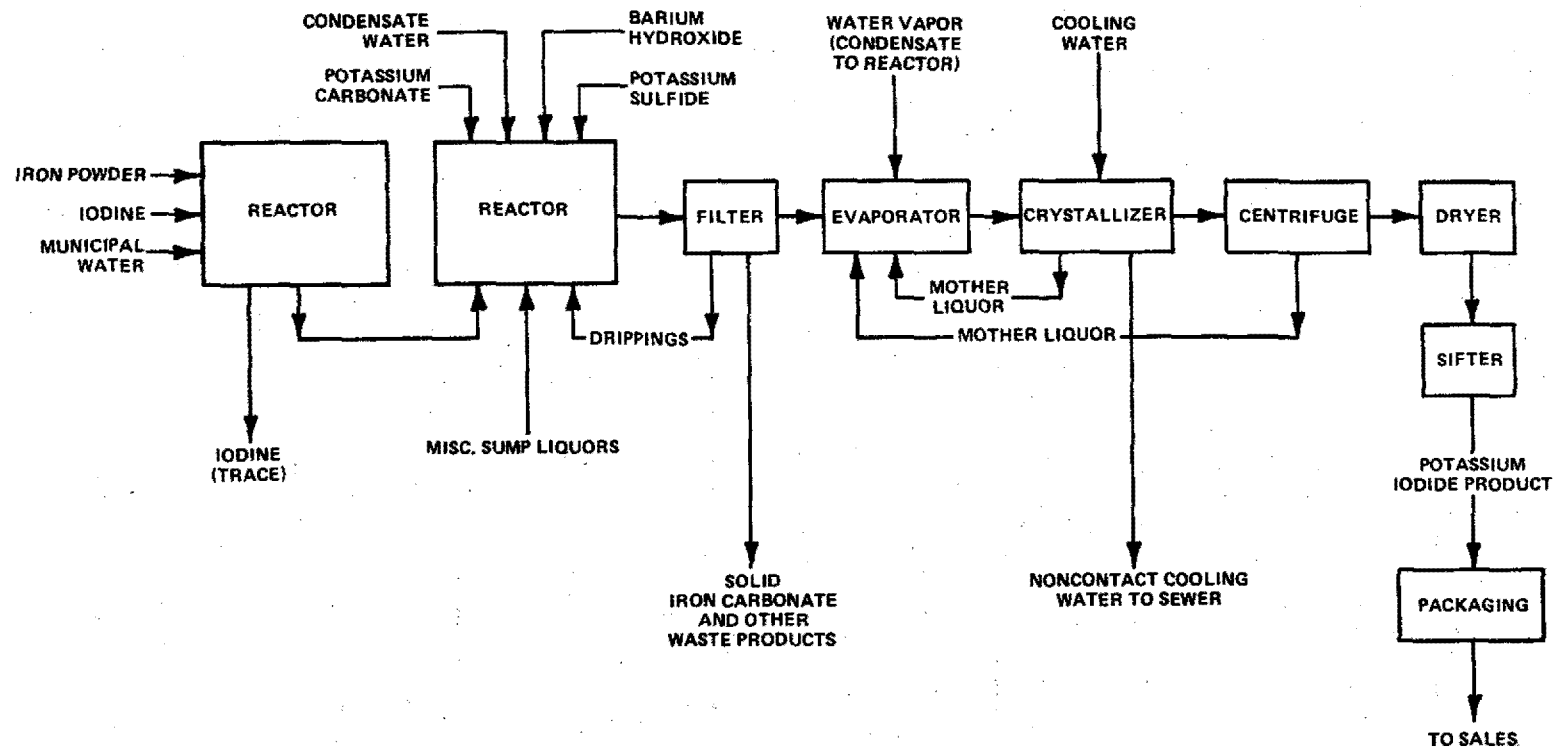
**Figure 16. FLOW DIAGRAM OF IODINE/POTASSIUM HYDROXIDE PROCESS FOR PRODUCTION OF POTASSIUM IODINE AND BYPRODUCT POTASSIUM IODATE**



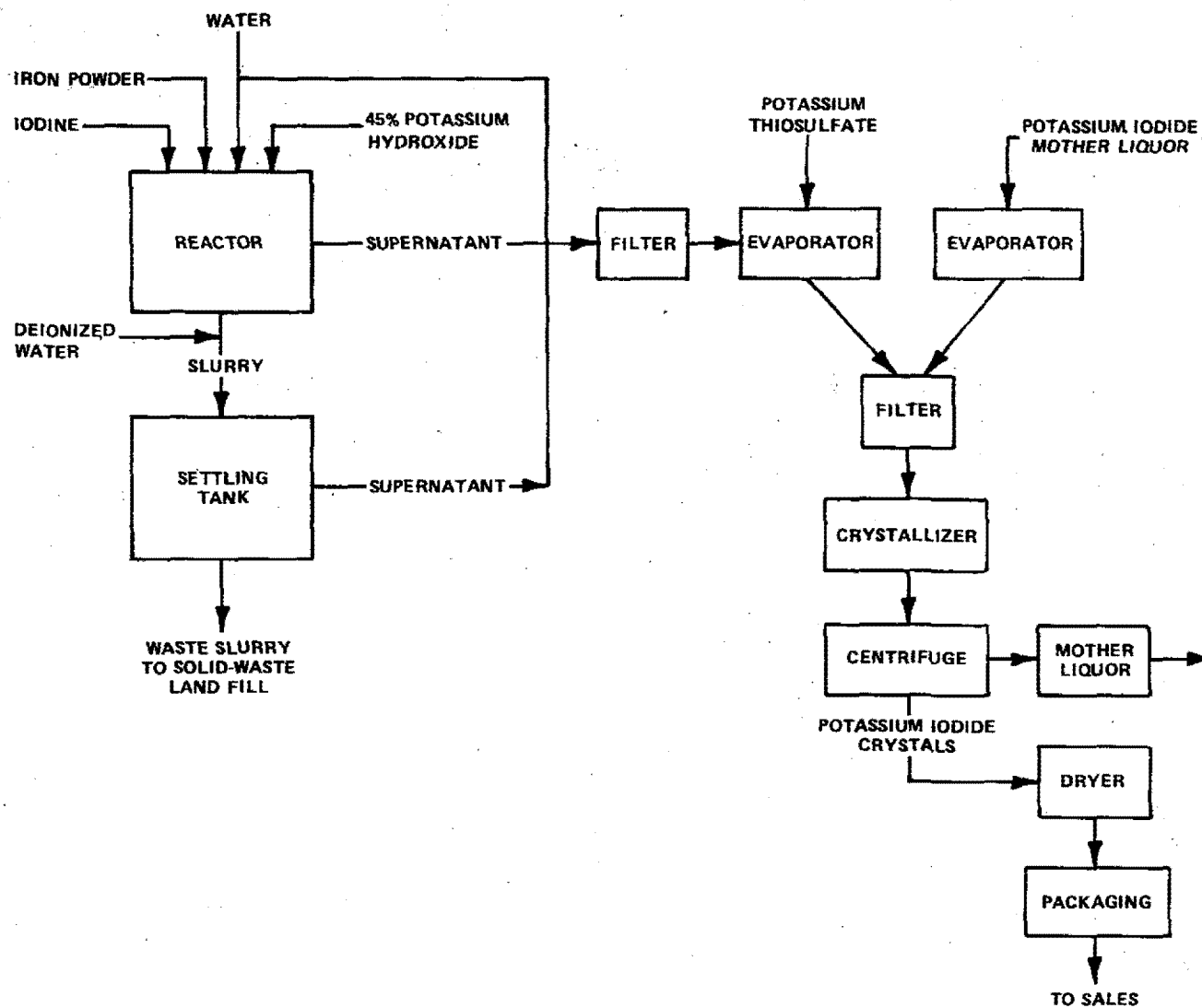
SOURCE: REFERENCE 5



Figure 17. FLOW DIAGRAM OF IRON CARBONATE PROCESS FOR PRODUCTION OF POTASSIUM IODIDE



**Figure 18. FLOW DIAGRAM OF IRON-CATALYST PROCESS FOR PRODUCTION OF POTASSIUM IODIDE**



ferric hydroxide and iodate formed during the reaction are discarded as waste solids. Any residual iodate in the supernatant is subsequently reduced to iodide by the addition of a small amount of potassium thiosulfate. This process is also unique to the extent that no water is used for cooling during crystallization. At this plant, crystallization is effected simply by pouring the slurry produced by evaporation into nickel pans and allowing sufficient time for the crystals to grow.

Two of the four plants engaged in the manufacture of potassium iodide presently discharge their production-related waste waters to POTWs. Both POTWs provide only primary treatment; however, at one, secondary treatment is in the design stage. One of these POTWs presently treats 435,300 cubic meters/day (115 mgd), 40 percent of which is industrial waste water. The other POTW treats 984,000 cubic meters per day (260 mgd).

Potassium iodide is used in photographic emulsions, in animal and poultry feeds (to the extent of 10 to 30 mg/kg (ppm)), in table salt, and in analytical chemistry. It also has a number of medical uses.

### Silver Nitrate

Industry Description. There are three significant plants in the United States producing silver nitrate ( $\text{AgNO}_3$ ). Total U.S. production of silver nitrate in 1971 was 3,100 metric tons (3,400 short tons).

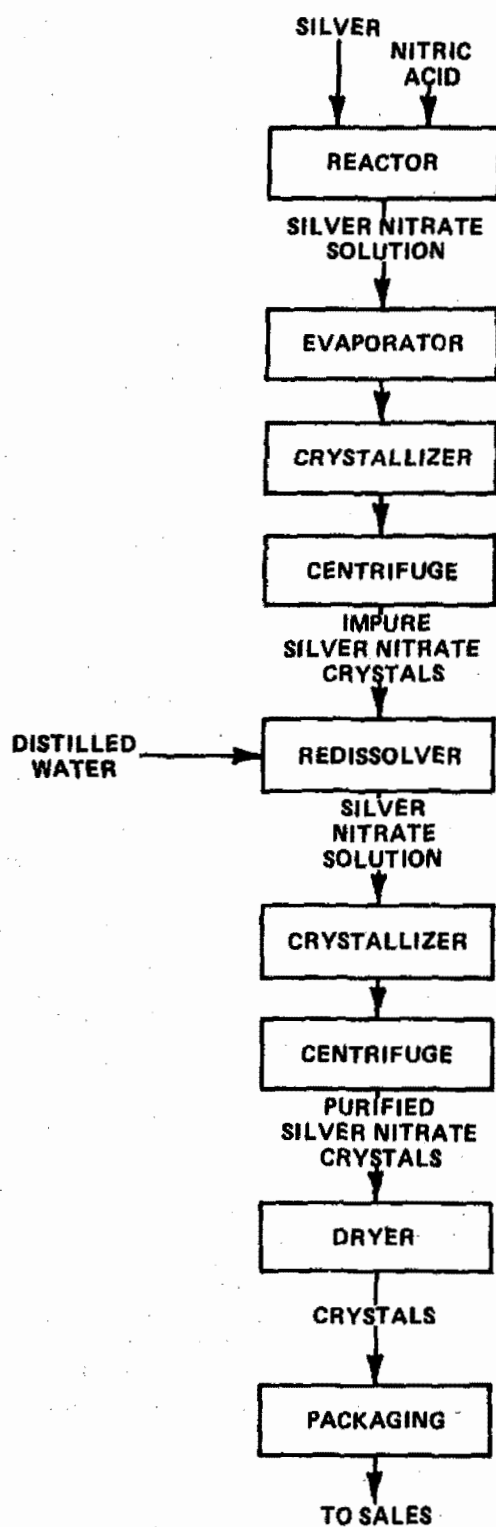
Manufacturing Process. Silver nitrate is produced by dissolving purified silver (up to 99.97% pure) in medium-strength nitric acid. The resultant silver nitrate solution is evaporated to a concentration of 85% and is then crystallized by cooling; the crystals are separated by centrifugation. The silver nitrate crystals are then purified by redissolution in hot distilled water, recrystallization, and recentrifugation (Reference 5). A simplified process flow diagram is presented in Figure 19. The basic reaction is:



Silver nitrate is the starting material for the preparation of many other silver compounds. Most silver nitrate is used in the photographic industry. Other uses include the manufacture of other silver salts, mirror production, silver plating, as a component of inks, and as a disinfectant.

### Sodium Bicarbonate

Figure 19. FLOW DIAGRAM FOR TYPICAL PRODUCTION OF SILVER NITRATE



Industry Description. The sodium bicarbonate ( $\text{NaHCO}_3$ ) manufacturing industry presently contains three known plants, none of which discharges to a POTW. Two of the plants discharge directly to surface waters, and one plant is achieving zero discharge of process waste water. These three plants accounted for 88% of the total U.S. production in 1973 of 250,000 metric tons (275,000 short tons). Since 1973, a fourth plant, accounting for the remaining 12% of the 1973 U.S. production, has closed down its operation (Reference 6).

Manufacturing Process. Sodium bicarbonate, also known as bicarbonate of soda and baking soda, is produced by the reaction of sodium carbonate (soda ash) with water and carbon dioxide under pressure:



The commercial material is prepared by dissolving soda ash with stirring. Then, insoluble impurities are settled out, and the solution is cooled to about  $40^\circ\text{C}$  ( $104^\circ\text{F}$ ). Carbonation of this solution with purified kiln gas is carried out in a tower similar to that used in the Solvay process. As the carbon dioxide is adsorbed, a suspension of sodium bicarbonate forms. The slurry is filtered and the cake washed on rotary drum filters. The cake is then dried and packaged for sale. This standard production process is illustrated in Figure 20.

Sodium bicarbonate is also a minor byproduct of soda-ash manufacture.

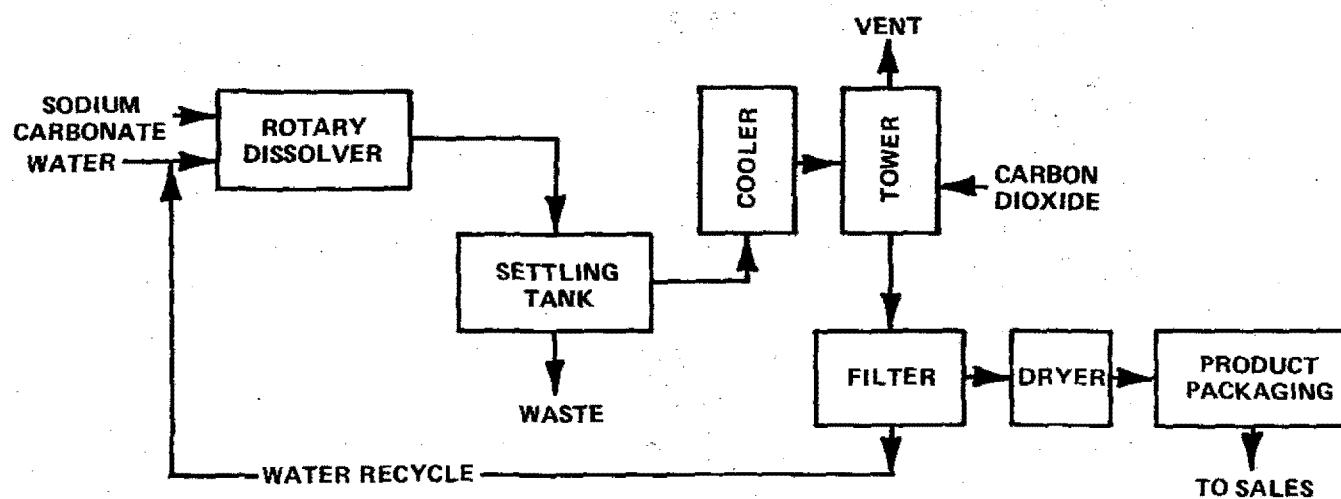
Sodium bicarbonate is usually sold at least 99.0% pure to meet the requirements of the U.S. Pharmacopoeia (Reference 8). The material is used in foods; chemicals; pharmaceuticals; fire extinguishers; and a variety of other industries, such as rubber, plastics, and paper and textile processing.

### Sodium Fluoride

Industry Description. There are four known plants presently manufacturing sodium fluoride ( $\text{NaF}$ ) in the United States. The three plants for which sufficient data are available are discussed in this document. These three plants account for the majority of the U.S. production in 1974 of 6,455 metric tons (7,100 short tons).

Of the four sodium fluoride producers, none discharge process waste water to a POTW. All of the plants achieve

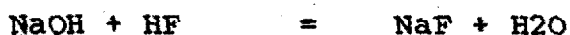
Figure 20. SIMPLIFIED FLOW DIAGRAM OF SOLVAY PROCESS FOR PRODUCTION OF SODIUM BICARBONATE



SOURCE: REFERENCE 2

zero discharge or discharge directly to surface waters after treatment.

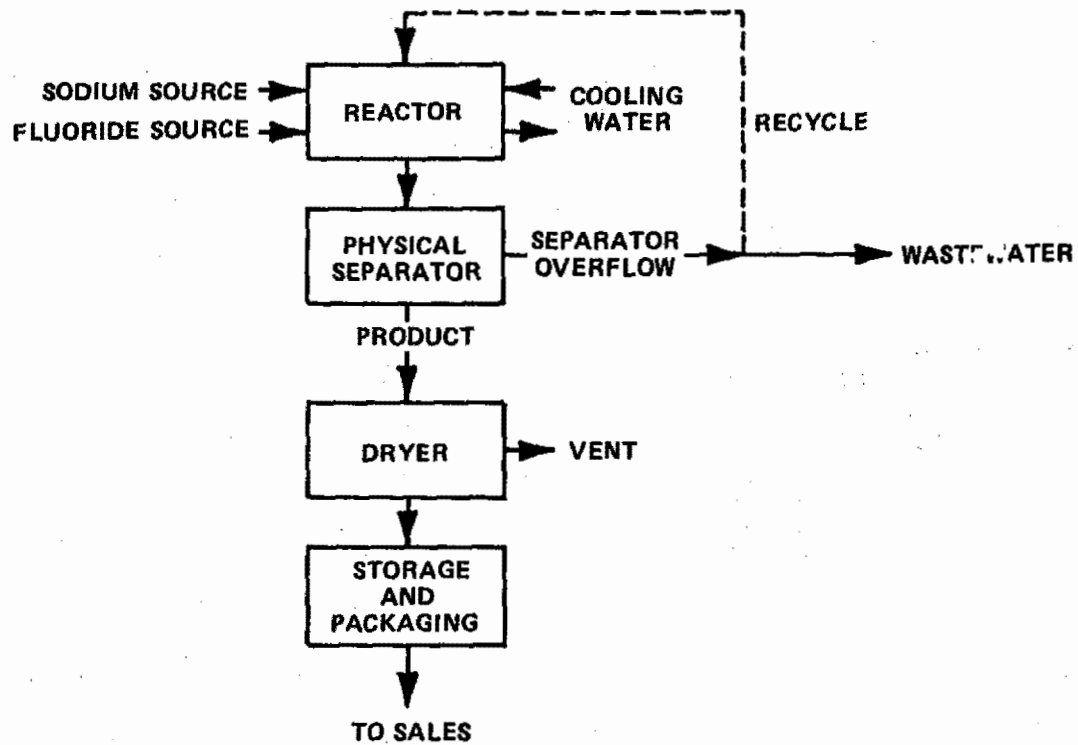
Manufacturing Processes. Sodium fluoride is produced in this country by three different chemical reactions:



As can be seen by the above equations, the first and third processes produce no byproducts. Consequently, simple settling, filtration, and drying result in a sodium fluoride product of about 99% purity. The second process produces a sodium silicate byproduct which must be segregated from the sodium fluoride product by use of a multistage separator. A generalized process flow diagram for sodium fluoride production is presented in Figure 21.

The principal uses of sodium fluoride are in the manufacture of rimmed steel, for the fluoridation of water, in heat-treating salts, for pickling stainless steel, in soldering and metallurgical fluxes, as a preservative for wood, in adhesives, as an insecticide, in the manufacture of coated papers, as a fluxing agent in vitreous enamels, and as an antiseptic in breweries and distilleries.

**Figure 21. GENERALIZED FLOW DIAGRAM FOR PRODUCTION OF SODIUM FLUORIDE**





## SECTION IV

### INDUSTRY SUBCATEGORIZATION

#### INTRODUCTION

##### General

For the purpose of establishing pretreatment standards for dischargers to POTWs, the Inorganic Chemicals Manufacturing Industry category has been segmented into subcategories based on the specific inorganic products manufactured. Although similar waste water constituents may be generated from various product groupings and may be treated to similar concentrations, water requirements are specific for each chemical manufacturing process. Guidelines based on production volume must reflect this difference.

Additional consideration has been given to the need for further subcategorization within the industry. To this end, this section describes the characteristics of those segments of the Inorganic Chemical Industry covered in this document which discharge to POTWs, or are most likely to discharge to POTWs, and presents the rationale employed to decide whether further subcategorization is warranted.

##### Objectives of Subcategorization

The objective of subcategorization of the Inorganic Chemical Industry segment discharging to POTWs is to establish recommended pretreatment standards for existing and new sources which are specific and uniformly applicable to a given subcategory.

##### FACTORS CONSIDERED

Factors taken into consideration for further subcategorization of the segments of the Inorganic Chemical Industry discharging to POTWs included geographic location, land availability, plant size, process employed, types and volumes of waste water generated, and types of POTWs receiving discharges.

##### FACTORS INFLUENCING SUBCATEGORIZATION IN ALL CHEMICAL SUBCATEGORIES

##### Approach to Subcategorization

The first subcategorization step was to examine the chemical subcategories and evaluate the factors influencing subcategorization for the industry as a whole. The factors

considered important in subcategorization of the industry are listed above under "Factors Considered." Following is a discussion of each of the general factors considered for all chemical subcategories. (For some chemical subcategories, additional factors were also considered.)

#### Geographic Location

The chemical industry, as a whole, is widely dispersed throughout the country. The raw-material source, additional chemicals produced, and product markets greatly influence plant location. Those plants discharging to POTWs are usually located in or near large urban areas which have municipal sewer systems. However, the location of the facilities does not influence the characteristics of waste water treatability.

#### Land Availability

Plants discharging to POTWs are generally located in or near large urban areas which, typically, have sewer systems. The use of impoundment and settling ponds for pretreatment and control of waste water may often be difficult, due to a lack of available land. However, these problems are common to most POTW dischargers within the inorganic chemical industry.

#### Plant Size

Plant size and production were not found to affect the characteristics of the wastes produced. Differences in plant size may influence the economic impact of recommended technologies, but not the nature of the effluents and their treatment. Thus, subcategorization by plant size was considered unwarranted.

#### Process Employed

Within the inorganic chemical industry, the basic unit operations employed are often the same. They include digestion, evaporation, crystallization, filtration, etc. However, within each chemical subcategory, the raw material, process sequence, controls, recycle potential, handling, and quality control vary greatly. Therefore, subcategorization by process is not warranted.

#### Types and Volumes of Wastewater

Water use and waste water generation are dependent upon choice of process employed or process requirements, the use of noncontact cooling, the potential for reuse or recycle of

water, and housekeeping practices. This factor was determined not to be the most direct or most suitable means of subcategorization.

### Types of POTWs

Most municipal treatment plants have primary settling or secondary biological treatment systems. Treatment is directed at the reduction of suspended solids and BOD. The biological treatment systems are much more susceptible to upsets caused by the presence of potentially toxic material in the influent than are primary treatment systems. However, both offer very little reduction of metals and other pollutants commonly found in industrial wastes. Physical/chemical-treatment systems which do offer treatment of industrial wastes are rare. Because POTW dischargers within the industry discharge only to primary or secondary treatment systems, neither of which offers significant treatment of industrial pollutants, subcategorization on this basis is considered unwarranted.

### FACTORS INFLUENCING SUBCATEGORIZATION BY CHEMICAL SUBCATEGORY

#### Aluminum Chloride

Geographic Location. From a geographical standpoint, only one aluminum chloride plant is located West of the Mississippi, and seven of the remaining Eastern plants reside in New York, New Jersey, and Ohio. Though the producers of this salt are situated largely within municipalities, there were no POTW dischargers reported for this subcategory.

None of the factors related to geographic location, such as rainfall/ evaporation rates or topography, was found to constitute a basis for subcategorization.

Land Availability. This criterion is frequently a limiting factor, particularly in urban areas, where waste water treatment (pretreatment) may require large areas for evaporation, impoundments, or settling basins. However, the relatively low volumes of waste water generated at these plants precluded the need for large settling basins and negate the need for subcategorization of aluminum chloride plants on the basis of land availability.

Plant Size. Plant size may or may not be related to waste water volume, but it is generally not a factor in terms of waste water quality. From information collected during this

study, there appears to be no connection between aluminum chloride plant size and waste water character or treatment.

Process Employed. In the aluminum chloride manufacturing industry, the processes for synthesizing hydrous and anhydrous products are different. In addition, emissions generated by both processes are dissimilar. Both processes, however, frequently employ wet scrubbers, which generate similar wastes. Therefore, the processes employed for producing aluminum chloride do not justify subcategorization.

Types and Volumes of Waste Water. Emissions-control scrubber water is the major source of process waste water reported for the aluminum chloride industry. Though discharge volumes may vary, depending upon the degree of recycle, all wastes are amenable to pretreatment by convention pH adjustment and settling to reduce pollutant concentrations.

Emissions-Control Practices. Emissions-control practices vary between plant locations and product type. Usually where chloride-rich product is manufactured, emissions control is a necessity. However, a given plant may produce white or gray aluminum chloride in the same furnace that recently produced the yellow salt. These emissions may or may not require scrubbing, depending on air ordinances. Therefore, subcategorization on the basis of emissions-control practices becomes very unmanageable, and this factor has been rejected as a criterion for subcategorization of aluminum chloride plants.

Types of POTW. Since there are no known POTW dischargers in this subcategory, there is no need for subcategorization on this basis.

### Aluminum Sulfate

Geographic Location. Alum (aluminum sulfate) plants are well dispersed throughout the nation. Since there are no locational differences, none of the factors related to geography (such as rainfall/evaporation rates and topography) was found to constitute a basis for subcategorization.

Land Availability. Land availability can be a limiting factor in cases where settling ponds are required for treatment and recycle purposes. However, since at this time no POTW dischargers have been identified, subcategorization based on land availability is unwarranted.

Plant Size. Plant size may or may not be related to waste water volume, but it is generally not a factor in terms of waste water quality. From information collected during this study, there appears to be no connection between plant size and waste water characteristics or treatment.

Process Employed. The basic process for alum production is constant throughout the industry, though many minor process modifications exist. However, these modifications do not result in waste water characteristics or volumes which would remain untreatable by currently practiced technologies. Therefore, process employed cannot be considered a factor for subcategorization.

Types and Volumes of Waste Water. Process modifications, raw material, and waste recycle produce qualitative and quantitative differences in waste water among alum producers. However, the technologies available to reduce pollutants are applicable to all wastes generated by the industry. Therefore, there is insufficient basis for subcategorization.

Types of POTW. Since there are no known POTW dischargers in the subcategory, there is no need for subcategorization due to this factor.

#### Calcium Carbide

The factors of subcategorization (geographic location, land availability, plant size or age, production methods, waste volume and content, etc.) do not vary widely in the portion of the calcium carbide industry which is regulated by the Inorganic Chemical Industry category. Therefore, subcategorization of the manufacture of calcium carbide is not considered necessary.

#### Calcium Chloride

Geographic Location. As mentioned in Section III, calcium chloride producers are located throughout the U.S., with no obvious regional trends. As would be expected, plants utilizing natural brines are located near the resource. Several smaller plants operating on a batch basis are located near or in cities, and these plants are prime candidates for POTW-discharge status. However, only one such discharger has been identified, and this factor does not constitute a basis for subcategorization.

In addition, none of the factors related to geographic location (such as rainfall/evaporation rates and topography) was found to be an adequate basis for subcategorization.

Land Availability. Generally, smaller plants which might be located in municipalities produce limited quantities of product from relatively small volumes of raw materials. This situation almost precludes any attendant problems which might result from land availability. At larger plants studied, plant operators report that land availability is no major problem, because these plants were designed with large holding and settling ponds in mind, and additional space for expansion and development was set aside for this purpose.

Plant Size. There is a large variation in plant production size in the calcium chloride manufacturing industry. Annual plant capacities vary from less than 270 metric tons (300 short tons) to about 450,000 metric tons (500,000 short tons). The larger plants are usually associated with natural salt deposits in Michigan or with the Solvay process, but this does not negate the existence of small natural brine and small byproduct producers. A relatively large calcium chloride producer is unlikely to utilize a POTW because of the surcharge structure. The three largest producers are direct dischargers. Therefore, plant size almost certainly influences the quantity and quality of waste; for the purpose of establishing pretreatment standards, however, there is no justification for subcategorization.

Process Employed. In this industry, the process employed is a direct consequence of the raw material. The processes have been described in Section III, and it is evident that much variation exists from plant to plant. The raw material and the process bear directly upon waste water quality. Though waste water quality varies with process, it is evident that pH control is the common factor for all waste water. Based upon this logic, there is no basis for subcategorization due to process employed.

Types and Volumes of Waste Water. As discussed above, the waste water quality, as well as quantity, varies from plant to plant. In fact, some processes generate no waste water. However, a common pretreatment (i.e., pH control) is sufficient to render all waste waters amenable to treatment by POTWs. Therefore, the types and volumes of waste water are not sufficiently different to warrant subcategorization.

Types of POTW. There is only one known POTW discharger in the calcium chloride manufacturing industry. The characteristics of this POTW have been described in Section III, and it is evident that pretreated calcium chloride waste water can be accommodated at any type of biological or physical/chemical POTW. Therefore, POTW characteristics do not form sufficient basis for subcategorization.

### Copper (Cupric) Sulfate

Copper (cupric) sulfate plants are not concentrated in specific areas of the country. The plants are usually located in conjunction with copper refineries.

The plants studied for this report have different amounts of discharges, ranging from none to treated wash water. The copper sulfate manufacturing industry uses the same type of raw materials in the different plants: copper shot, scrap copper, sulfuric acid, and water. The scrap used at some of the plants (copper wire, for instance) is of high quality and does not present any significant waste problems of its own. The processes used in the plants are similar; therefore, process waste waters from the processes are similar.

Due to the potential similarity of waste waters from copper sulfate producing plants, subcategorization is not considered necessary.

### Iron (Ferric) Chloride

Geographic Location. The two iron (ferric) chloride manufacturing operations discharging to POTWs are located within large metropolitan areas. As such, there is no need to subcategorize based on geographic location.

Land Availability. Typically, POTW dischargers are located in urban areas, where the amount of space available for the installation of pretreatment equipment may be limited. Facilities which require a great deal of land--most notably, settling ponds--may be difficult to install. These problems are common to all known indirect dischargers in the ferric chloride industry. Therefore, there is no need to subcategorize based on land availability.

Plant Size. The two ferric chloride manufacturing operations discharging to POTWs are of approximately the same size. Therefore, there is no need to subcategorize the ferric chloride manufacturing industry on the basis of plant size.

Process Employed. Basic ferric chloride manufacture involves the reaction of pickle liquors, iron, chlorine, hydrochloric acid, and water to produce a 40% ferric chloride solution. The solution may or may not be filtered to remove impurities. Any variations in raw-material mix, the reaction process itself, and filtration techniques have little effect on the nature of wastes produced, nor do they

affect waste treatability. Therefore, subcategorization is unwarranted.

Types and Volumes of Waste Waters. Because some variability is found in the types and quantities of waste waters generated during the production of ferric chloride, the design of a pretreatment system must be tailored to each operation. However, the general types of treatment employed and the treatability of the wastes remain the same. Therefore, there is no need to subcategorize the industry based on the types and volumes of waste waters generated.

Types of POTW. One of the ferric chloride plants discharges to a primary municipal treatment plant. The other discharges to a secondary, activated-sludge plant. However, plans are underway at the primary plant to upgrade the system to a secondary, biological-treatment system. Therefore, subcategorization based on types of POTWs is not necessary.

#### Lead Monoxide

Factors taken into consideration as possible justification for further subcategorization of the lead monoxide manufacturing industry included:

- (1) Geographic location
- (2) Land availability
- (3) Plant production and size
- (4) Type of processing employed
- (5) Types and volumes of waste generated
- (6) Topography
- (7) Climate and rainfall
- (8) Facility age
- (9) End product(s)

No POTW dischargers were identified within the lead monoxide industry. The basic factors which determine whether an industry discharges directly or discharges to a POTW are economics and availability of a POTW.

In the lead monoxide manufacturing industry, most criteria for subcategorization bear directly upon one basic factor: the source of process waste water. General factors, such as end products, climate, rainfall, topography, and facility age, proved to be of minor importance as criteria for additional subcategorization. All segments of the lead monoxide subcategory--whether discharging to POTWs, discharging directly, or with no discharge or process waste water--use some form of lead metal as the raw material. The various manufacturing processes are very similar in that



they all heat the lead and, by subjecting the molten lead to air at controlled temperatures, oxidize it to form lead monoxide. With lead monoxide manufacturing plants located from coast-to-coast, there are large variations in land availability, water use, facility age, and treatment technologies employed. However, when the relatively small process waste water flows generated from plant washdown and compressor blowdown are taken into consideration, these differences within the industry do not justify any further division of this subcategory. Thus, all lead monoxide plants discharging process waste waters are considered within the same subcategory.

### Nickel Sulfate

Geographic Location. The three known nickel sulfate producers discharging to POTWs are located in or near large metropolitan areas. Consequently, there is no need to subcategorize the industry based on geographic location.

Land Availability. Typically, POTW dischargers are located in urban areas, where there is often very little space available for the installation of pretreatment equipment. Facilities such as settling ponds, which require a great deal of land, may be difficult to install. This problem is universal to all nickel sulfate producers discharging to POTWs. Therefore, there is no need to subcategorize based on land availability.

Plant Size. The establishment of a criterion for subcategorization based on plant size is unwarranted. Plant size has no effect on the nature of waste water generated, nor on its treatability.

Process Employed. Basic nickel sulfate manufacture involves the reaction of nickel metal, nickel oxide, or waste nickel materials with sulfuric acid. Various techniques are employed to purify the nickel sulfate solution. In addition, both nickel sulfate solutions and crystalline nickel sulfate hexahydrate are produced. Variabilities in raw material, process, and purification techniques have little effect on the nature of wastes produced, nor on their treatability. Therefore, subcategorization is unwarranted.

Types and Volumes of Waste Waters. Because some variation is found in the types of waste water generated during the production of nickel sulfate, pretreatment systems must be tailored to individual plant requirements. However, the general pretreatment technique employed and the waste water treatability remain the same. Therefore, there is no need

to subcategorize the nickel sulfate industry based on the types and volumes of waste waters discharged.

Types of POTW. All three known POTW dischargers direct their process waste waters to secondary, biological-treatment plants. Therefore, subcategorization based on the receiving POTW is unnecessary.

#### Nitrogen and Oxygen

Geographic Location and Land Availability. Neither of these factors is considered valid ground for subcategorization, since the air-separation process for production of nitrogen and oxygen requires no geographically confined raw material, nor does it require a vast land area for efficient manufacture of product or handling of process waste water.

Plant Size. Plant size is not considered to be a significant factor for rationalizing subcategorization, since the types and quality of wastewater being produced are not dependent on facility size or production capacity.

Process Employed. Although minor differences in process exist with respect to type of air compression, process cooling, and air purification, no one modification is so distinct that it would necessitate special subcategorization on the basis of process employed. The Linde process of air separation via molecular sieves is not covered in this document, because it is generally used primarily by small on-site producers and represents an insignificant percentage of total production. Therefore, process is not considered a factor for subcategorization in this supplemental document.

Types and Volumes of Waste Water. Contact process wastes throughout the industry are generally produced in such limited quantities that handling and treatment require no distinctive or elaborate technology.

Types of POTW. Due to the fact that limited volumes of contact process waste water (principally, oily compressor condensate) are produced and are frequently mixed with noncontact cooling water after treatment, the dilution factor is such that the type and size of POTW handling the wastes need not be specifically adaptable to accommodate these discharges.

#### Potassium Dichromate

Further subcategorization of the potassium dichromate subcategory is unnecessary since, at present, it consists of only one known manufacturer.

### Potassium Iodide

Based on information acquired from telephone contacts with members of the potassium iodide manufacturing industry, review of the available literature, and compilation of data provided by industry, it was determined that none of the factors given earlier in this section warrants further subcategorization of the potassium iodide subcategory.

The manufacturing processes employed by the four producers of potassium iodide do not differ significantly with respect to the reagents used or the character and treatability of the waste water associated with production. In all instances, this waste water does not originate directly from within the production process, but rather is the result of water used for noncontact cooling, equipment washdown, or cleanup of spills.

Factors such as plant size, age, and geographic location have little effect on the technology of treatment in general. Likewise, due to the nature of the waste water discharged, the type of POTW receiving these discharges was not found to warrant further subcategorization.

### Silver Nitrate

No silver nitrate manufacturing operations have been identified as discharging process waste water to a POTW. No rationale was found for subcategorization of those silver nitrate producers discharging directly to surface waters; therefore, subcategorization of any future POTW dischargers is not indicated.

### Sodium Bicarbonate

Geographic Location. For discharge to a POTW to be a cost-effective method for the treatment of sodium bicarbonate manufacturing process waste water, the manufacturing facility must be located in or near a sewered area serviced by a POTW. As such, there is no need to subcategorize the industry based on geographic location.

Land Availability. Typically, POTW dischargers are located in urban areas, where there may be very little space available for the installation of treatment equipment. Facilities such as settling ponds or waste water-impoundment-areas, which may require large areas of land, may be difficult to install. Since this problem is common to most POTW dischargers, there is no need to subcategorize based on land availability.

Plant Size. The establishment of a criterion for subcategorization based on plant size is unwarranted. Plant size or production has no effect on the nature of the waste water generated, nor on its treatability.

Types and Volumes of Waste Water. Any significant differences in the quantity and quality of process waste water can be attributed to the use of water recycling and to good housekeeping practices, since the manufacturing process is standard throughout the industry. Therefore, there is no need to subcategorize based on the types and volumes of waste waters produced.

Types of POTW. There are presently no known plants discharging sodium bicarbonate process waste waters to POTWs. However, one plant has plans under development to discharge process waste water from sodium bicarbonate production to a POTW beginning in 1979.

### Sodium Fluoride

Geographic Location. For discharge to a POTW to be a cost-effective method for the treatment of sodium fluoride manufacturing process wastewater, the manufacturing facility must be located in or near a sewered area serviced by a POTW. This is the case only in metropolitan areas; as such, there is no need to subcategorize the industry based on geographic location.

Land Availability. Typically, POTW dischargers are located in urban areas, where there may be limited space available for the installation of treatment equipment. Facilities, such as settling ponds, which require a great deal of land would be difficult to install. Since this problem is common to most POTW dischargers, there is no need to subcategorize based on land availability.

Plant Size. The establishment of a criterion for subcategorization based on plant size is unwarranted. Plant size has no effect on the nature of waste water generated, nor on its treatability.

Types and Volumes of Waste Water. Both sodium fluoride manufacturing processes which produce a process waste discharge typically involve a batch reaction of caustic soda (sodium hydroxide) with a fluoride source (hydrofluoric acid or sodium silicofluoride). While some variation is expected in the character and type of waste water generated during the production of sodium fluoride, the waste water can typically be characterized by high concentrations of suspended solids, dissolved solids, and fluoride. The

general pretreatment techniques employed and the wastewater treatability remain the same. Therefore, there is no need to subcategorize the sodium fluoride industry based on the types and volumes of waste waters discharged.

Types of POTW. There are presently no sodium fluoride manufacturing plants which discharge process waste waters to POTWs. However, given the availability of a POTW, changes in the economics of waste treatment caused by alterations in discharge limitations, production, etc., may make it more desirable for a plant with no discharge or a direct discharger to become a POTW discharger. For this reason, existing sodium fluoride plants were considered as potential POTW dischargers.

#### SUMMARY OF RECOMMENDED SUBCATEGORIZATION

Based upon the preceding discussion and choice of final subcategories, a summary of subcategories recommended for those segments of the Inorganic Chemical Industry discharging to POTWs and covered by this document is presented in Table 3. The discussions in the sections which follow address the subcategories presented in that table.

**TABLE 3. SUMMARY OF SUBCATEGORIES RECOMMENDED FOR INORGANIC  
CHEMICAL INDUSTRY**

SUBCATEGORY	SIC CODE
ALUMINUM CHLORIDE	1819
ALUMINUM SULFATE	1819
CALCIUM CARBIDE	1819
CALCIUM CHLORIDE	1819
COPPER (CUPRIC) SULFATE	1819
IRON (FERRIC) CHLORIDE	1819
LEAD OXIDE	1819
NICKEL SULFATE	1819
NITROGEN AND OXYGEN	1813
POTASSIUM DICHROMATE	1819
POTASSIUM IODIDE	1819
SILVER NITRATE	1819
SODIUM BICARBONATE	1812
SODIUM FLUORIDE	1819

## SECTION V

### WASTE CATEGORIZATION

#### INTRODUCTION

This section discusses the sources of waste water within that portion of the Inorganic Chemical Industry covered by this document which discharges to POTWs. In addition, this section identifies raw waste water constituents and quantifies the constituents on the basis of concentrations and loadings for each of the specified chemicals. Where data were unavailable to adequately define pollutant loadings, concentration data alone were used to characterize the waste water.

Data used for waste water characterization were accumulated from the widest possible base. Effluent data presented for each subcategory were derived from historical effluent data supplied by the industry and various regulatory and research bodies and, in some cases, from current data for effluent samples collected and analyzed during this study. Where data from POTW dischargers were sparse or unavailable, applicable data from direct dischargers were incorporated into the characterization.

In this section, the principal specific water uses common to all covered subcategories in the industry are briefly summarized first. Then, for each subcategory, processes employed and associated water use are described, sources of waste water are discussed, and waste water characteristics are given.

#### SPECIFIC WATER USES IN ALL SUBCATEGORIES

##### General

The principal water uses in inorganic chemical processing plants are process water and noncontact cooling water.

The term "process waste water" means any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, by product, or waste product.

Process water often comes from several different sources in a chemical plant. Contact cooling or heating water usage includes quenching, slurrying, barometric condensers, contact steam drying, etc. Transport water is often used for transporting reactants or products to various unit operations in either solution, suspension, or slurry form.

Contact wash water usage includes ore washing to remove fines, filter cake washing to remove impurities, cleaning of insoluble product vapors, and absorption processes in which water is reacted with a gaseous material to produce an aqueous solution. Other miscellaneous water uses include floor washing and cleanup, storage and shipping tank washing, pump and vacuum seals, ion exchange regeneration, etc. Product water generally is that which stays with the product as an integral part.

The term "noncontact cooling water" means any water used for cooling which does not come into direct contact with any raw material, intermediate product, waste product, or finished produce. If the water is used without contacting the reactants, such as in a tube in shell heat exchanger or trombone cooler, the water will not be contaminated with process-waste water pollutants. Noncontact cooling water is generally either recycled cooling water which is cooled by cooling towers or spray ponds, or once-through cooling water whose source is generally a river, lake, or tidal estuary.

#### PROCESS-WASTE CHARACTERIZATION FOR ALUMINUM CHLORIDE SUBCATEGORY

##### Process Description and Water Use

Anhydrous aluminum chloride is synthesized largely by reacting chlorine with molten aluminum and condensing the resultant aluminum chloride vapors. The salt is formed by digesting aluminum oxide in hydrochloric acid and then purifying the solution which results. Water usage associated with both product types falls into three major groupings:

##### Process Water--which includes uses such as

- Dilution for process solutions
- Emissions control
- Water-treatment reagent preparation
- Equipment and plant washdown
- Leaks and spills (associated cleanup)

##### Noncontact Cooling Water--which includes water involved in

- Boiler and steam generation
- Compressor cooling and condensate
- Furnace-jacket cooling

##### Potable Water--which includes sanitary water

##### Sources of Wastewater



Figure 22 is an overall schematic of water use at Plant 19101, which produces both hydrous and anhydrous aluminum chloride. The 74.6 cubic meters/day (19,700 gpd) volume of process water is consumed by emissions control, washdown, and hydrous product. The two sources of process waste water are emissions scrubbing and plant washdown, which result in a daily waste water volume of 50.7 cubic meters (13,400 gal). All wastewater sources, including runoff, are combined for treatment and discharge.

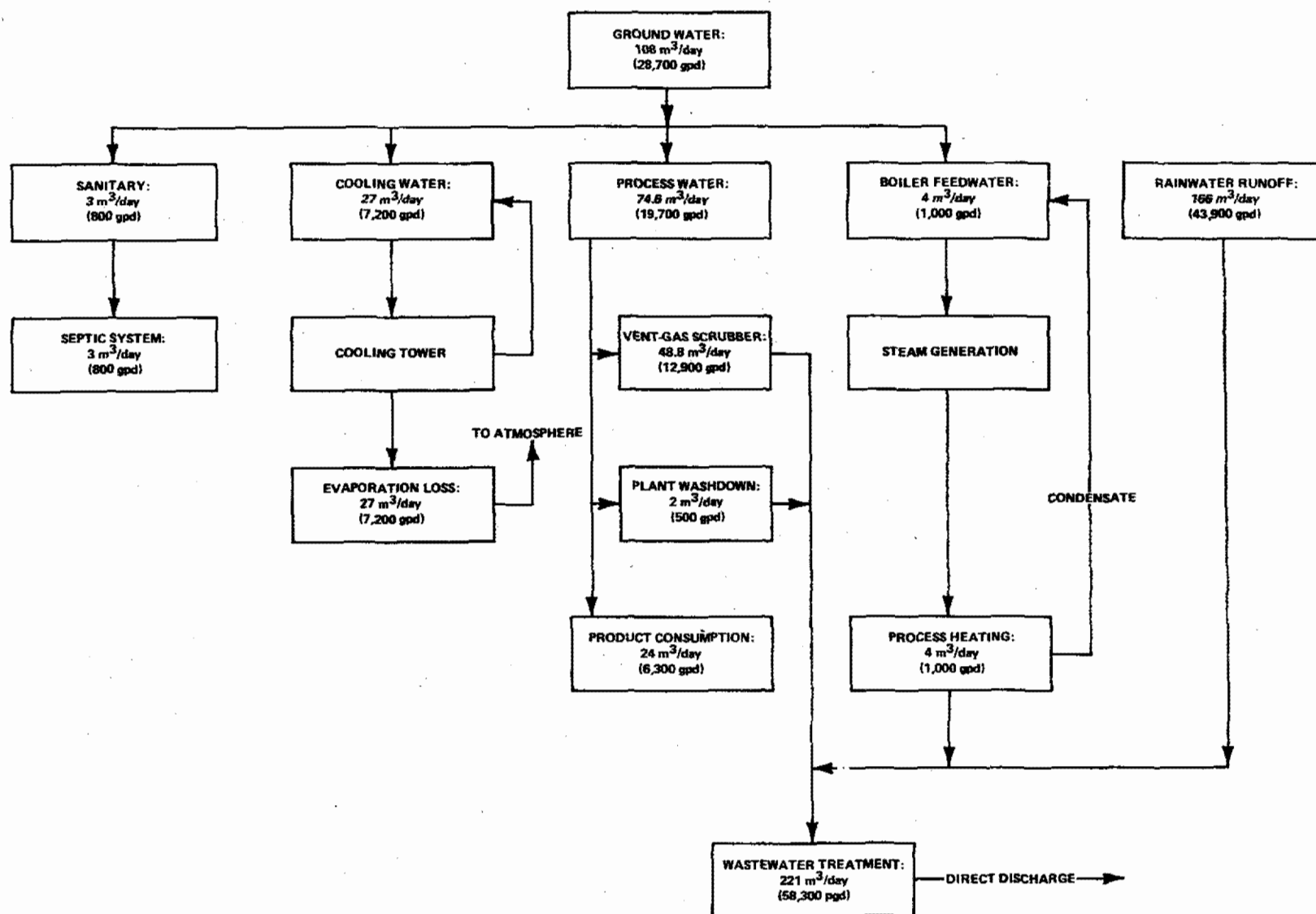
#### Wastewater Characteristics

During anhydrous aluminum chloride production, the furnace fumes are vented to a condenser to recover the product, while the condenser tail gases proceed to emissions-control devices. The emissions generated during aluminum oxide digestion for production of the hydrous salt are also vented to emissions-control devices. The emissions generated during production of both product types, but during anhydrous production in particular, may or may not require scrubbing, depending upon product grade and local air regulations. The two types of scrubber waste waters (if wet emissions devices are used) can be expected to have similar waste characteristics, typified by low pH and elevated TDS (total dissolved solids) concentrations. The low pH results from hydrolysis of aluminum chloride and absorption of hydrochloric acid and chlorine.

Scrap aluminum is frequently used during production of the anhydrous salt, and the scrubber water can be expected to resemble that generated by the secondary aluminum industry. At secondary aluminum plants, molten aluminum is lanced with chlorine to remove impurities (particularly, magnesium) in a process called demagging. The emissions generated during demagging are collected in scrubbers and sent to waste. Demagging-scrubber waste water contains many of the impurities found in aluminum scrap; similarly, the scrubbers from anhydrous aluminum chloride production collect impurities from the raw materials. Since chemical analyses of aluminum chloride scrubber waste water are not available, Table 4 shows characteristics of raw demagging-scrubber water from three plants in the secondary aluminum industry which are POTW dischargers.

At plants where refined aluminum is used for production of the anhydrous salt and where purified aluminum oxide is employed for production of the hydrous salt, the scrubber waste water is expected to exhibit much lower concentrations of pollutants such as heavy metals. The low pH and high TDS characteristics can be expected to remain, however.

Figure 22. FLOW DIAGRAM SHOWING TYPICAL WATER USE IN PRODUCTION OF ALUMINUM CHLORIDE (PLANT 19101)



**TABLE 4. RAW WASTE CHARACTERISTICS OF CHLORINE DEMAGGING  
SCRUBBER WASTEWATER FROM SECONDARY ALUMINUM INDUSTRY**

PARAMETER	CONCENTRATION (mg/l)		
	PLANT A*	PLANT B†	PLANT C**
pH	1.65**	3.65**	3.70**
TSS	934	138	44
Oil and Grease	< 1	1	<1
COD	—	169	—
Al	474	16,600	1.8
Cd	0.18	1.82	0.076
Cr	0.23	0.03	0.44
Cu	4.82	0.06	0.05
Pb	0.89	0.20	0.02
Ni	0.06	<0.02	0.03
Na	17.6	26	13.8
Zn	12.0	38.7	2.38
Chloride	3,583	22,500	442
Fluoride	<0.11	<1	0.33

\*Average of seven samples.

†Average of eight samples.

\*\*Average of four samples.

Total dissolved solids loadings will generally be higher in aluminum chloride waste water, as opposed to secondary aluminum waste water, because chlorination in the aluminum chloride industry occurs over extended periods, and techniques for reducing chlorine emissions are not highly developed.

Routine plant washdowns may contain minor spills and leaks, but these can usually be differentiated from major spills. These wastes generally contribute appreciably to the total process water flow. Raw waste characteristics are not available for plant washdowns, but these wastes can be integrated with other process waste water and treated (pretreated) for discharge. Abbreviated raw waste characteristics for a mixed scrubber, plant-washdown, and boiler-condensate stream of 204 cubic meters/day (54,000 gpd) at aluminum chloride Plant 19102 are shown in Table 5.

PROCESS-WASTE CHARACTERIZATION FOR ALUMINUM SULFATE  
SUBCATEGORY

Process Description and Water Use

Alum (aluminum sulfate) is produced by reacting aluminum-containing materials (usually, bauxite) with sulfuric acid. The resultant solution is purified to yield a product which can be sold or dehydrated to form crystals. Water usage associated with alum production falls into three major categories:

Process Water--which includes uses such as  
Dilution for process solutions  
Emissions control  
Water-treatment reagent preparation  
Equipment and plant washdown  
Leaks and spills (associated cleanup)

Noncontact Cooling Water--which includes  
water involved in  
Boiler and steam generation  
Compressor cooling and condensate  
Reactor-vessel heating  
Noncontact cooling

Potable Water--which includes sanitary water

Sources of Wastewater

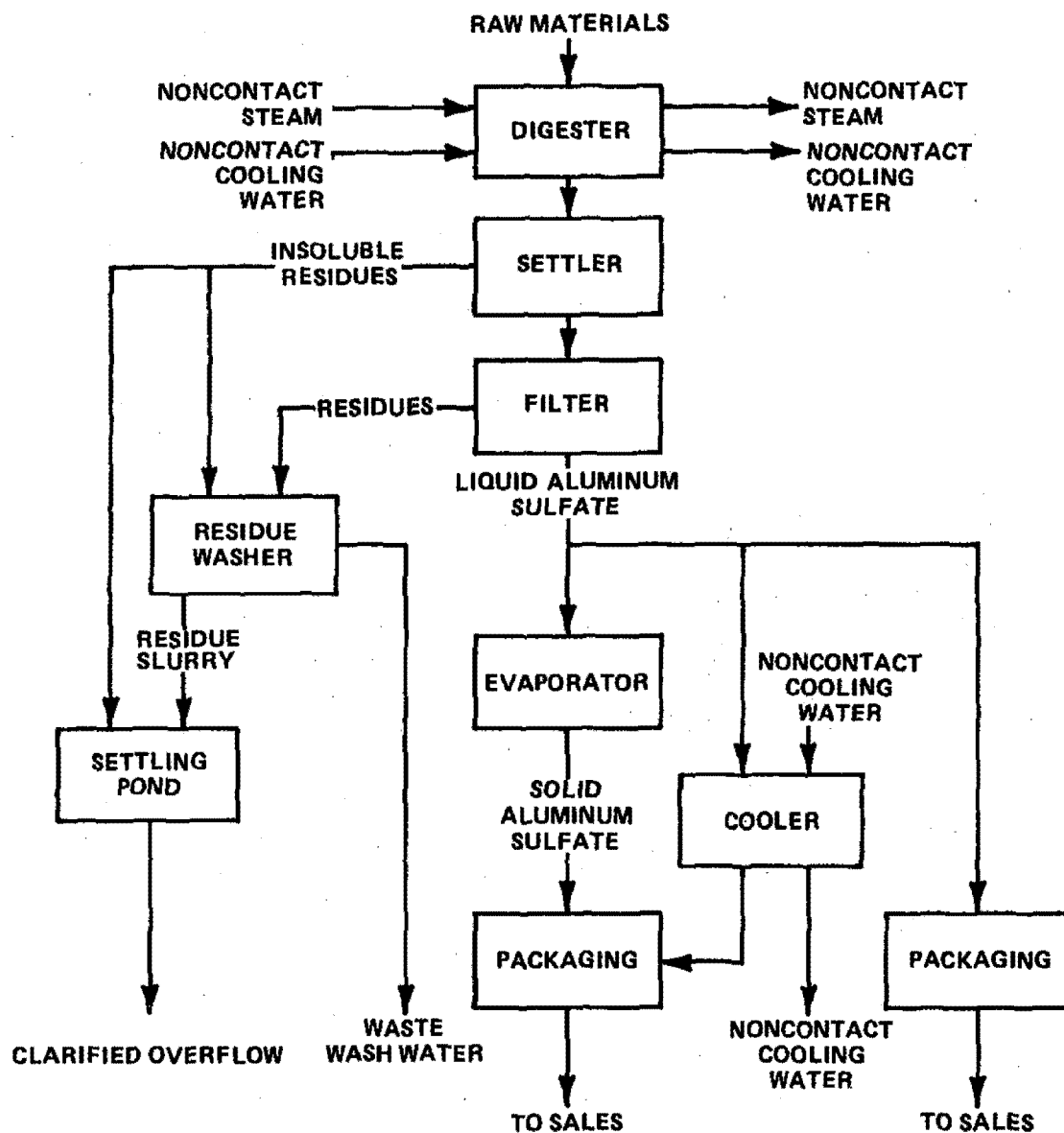
Figure 23 is a composite schematic showing many of the water uses and waste water sources (excluding sanitary and potable) originating from alum plants. The temperature and

**TABLE 5. CHEMICAL COMPOSITION OF COMBINED RAW WASTEWATERS FROM PRODUCTION OF ALUMINUM CHLORIDE (PLANT 19102)**

PARAMETER	AVERAGE DAILY CONCENTRATION (mg/l)
pH	1.5 to 9.0*
TSS	32
COD	89
Al	44

\*Value in pH units.

Figure 23. FLOW DIAGRAM SHOWING GENERALIZED SOURCES AND USES OF WATER IN PRODUCTION OF ALUMINUM SULFATE



reaction rate in the digester can be grossly controlled by use of steam and/or noncontact cooling water, but many plants employ steam to hasten reaction time. Noncontact cooling water is also used at a few plants where coolers are employed to crystallize alum from solution.

The settling-tank underflow, which consists of compounds such as silicon dioxide, titanium dioxide, aluminum oxide, and aluminum sulfate (when bauxite is digested), is diverted to a wash system at some plants for alum reclamation. The residue-wash water is discarded after use at some plants. At other plants where residue washing is not practiced, the muds may be fed to a settling pond or series of ponds, where the transport water may be settled and discharged or recycled. Vessel-cleanout water (not shown in Figure 23) is either discharged or returned to the cycle, depending upon plant practice.

Generally, the sources of process waste water are spent liquor from settling ponds, wash water from residue washing, and water from equipment and plant washdown. Each of these streams contains residual sulfuric acid, but the two latter streams are much-diluted versions of the former. These streams are typically mixed before discharge.

#### Wastewater Characteristics

Table 6 is a compilation of chemical data representing waste water discharges from various alum producers. The data have been collected largely from Army Corps of Engineers Discharge Application forms and represent total alum-plant discharges in most cases. The data serve to provide a general description of waste water quality. As expected, the waste water contains traces of many of the raw-material constituents. These trace materials (such as metals) are solubilized during digestion, mud washing, and settling in ponds. Waste loads may vary due to impurities in different ores used.

#### PROCESS-WASTE      CHARACTERIZATION      FOR      CALCIUM      CARBIDE SUBCATEGORY

##### Process Description and Water Use

There is no process water involved in the production of calcium carbide. Any contact of water with calcium carbide results in the production of acetylene. The airborne wastes from the calcium carbide process are all dusts (coke and coal fines, limestone powder, and calcium carbide from the packing station). Coke, coal, and limestone fines, which

**TABLE 6. CHEMICAL COMPOSITIONS OF RAW WASTEWATERS FROM PRODUCTION OF ALUMINUM SULFATE**

PARAMETER	CONCENTRATION (mg/l)*			
	19201*	19202*	19203*	19206†
pH	3.5**	3.8**	—	—
TDS	43,000	4,000	—	—
TSS	46,000	68	—	—
Al	7,700	1,750	> 500	—
Cd	0.070	0.001	< 0.005	< 0.01
Cr	—	1.3	0.5	3
Cu	—	0.4	3.0	1
Fe	13	30.8	> 500	—
Pb	1.8	0.5	0.37	< 0.1
Hg	0.0054	0.0001	0.0002	< 0.001
Ni	—	0.6	—	2
Zn	1.0	1.0	15	0.4
Fluoride	—	0.66	—	—
Sulfate	5,000	2,750	—	21,500

\*Based on data from Army Corps of Engineers Applications

†Industry data — liquid fraction of waste slurry.

\*\*Value in pH units.



constitute a significant fraction of the feed materials, may be profitably returned to the system.

Dry bag collection of airborne fines eliminates waterborne wastes and makes it possible to reuse these fines. It also significantly reduces energy requirements by avoiding high energy drying costs needed for recovery of water wastes.

Two of the three plants studied utilize dry dust collection and recycle. The third plant employs a venturi scrubber on furnace offgases. Table 7 characterizes the water use at the three plants studied.

All cooling in calcium carbide production is accomplished by noncontact systems. Noncontact cooling water is recycled or lost by evaporation, except for small amounts of cooling-tower blowdown. Figure 24 illustrates the process and water use at Plant 19301. A small amount of water is used intermittently at Plant 19301, at the furnace exit, to decrease the temperature of the offgases to the collector. This is a noncontact process, and all of the water is lost by evaporation.

Water for noncontact cooling systems is generally softened by ion exchange (zeolite process) before use. Softening prevents excessive scaling in the cooling equipment. Discharge of industrial noncontact cooling water to a POTW does not have any deleterious effect on the operations of a typical POTW.

#### Sources of Wastewater

The only source of process waste water in calcium carbide production discharge is wet-scrubber waste water.

Only one of the plants studied (19303) uses a wet scrubber to control the carbide-furnace emissions. At this site, the scrubber waste water is pumped to a settling pond. Over 90% of the water is eventually recycled to the scrubber system. Only a slight discharge can be expected from the settling pond.

#### Wastewater Characteristics

The available data defining the scrubber effluent after settling at Plant 19303 are given below.

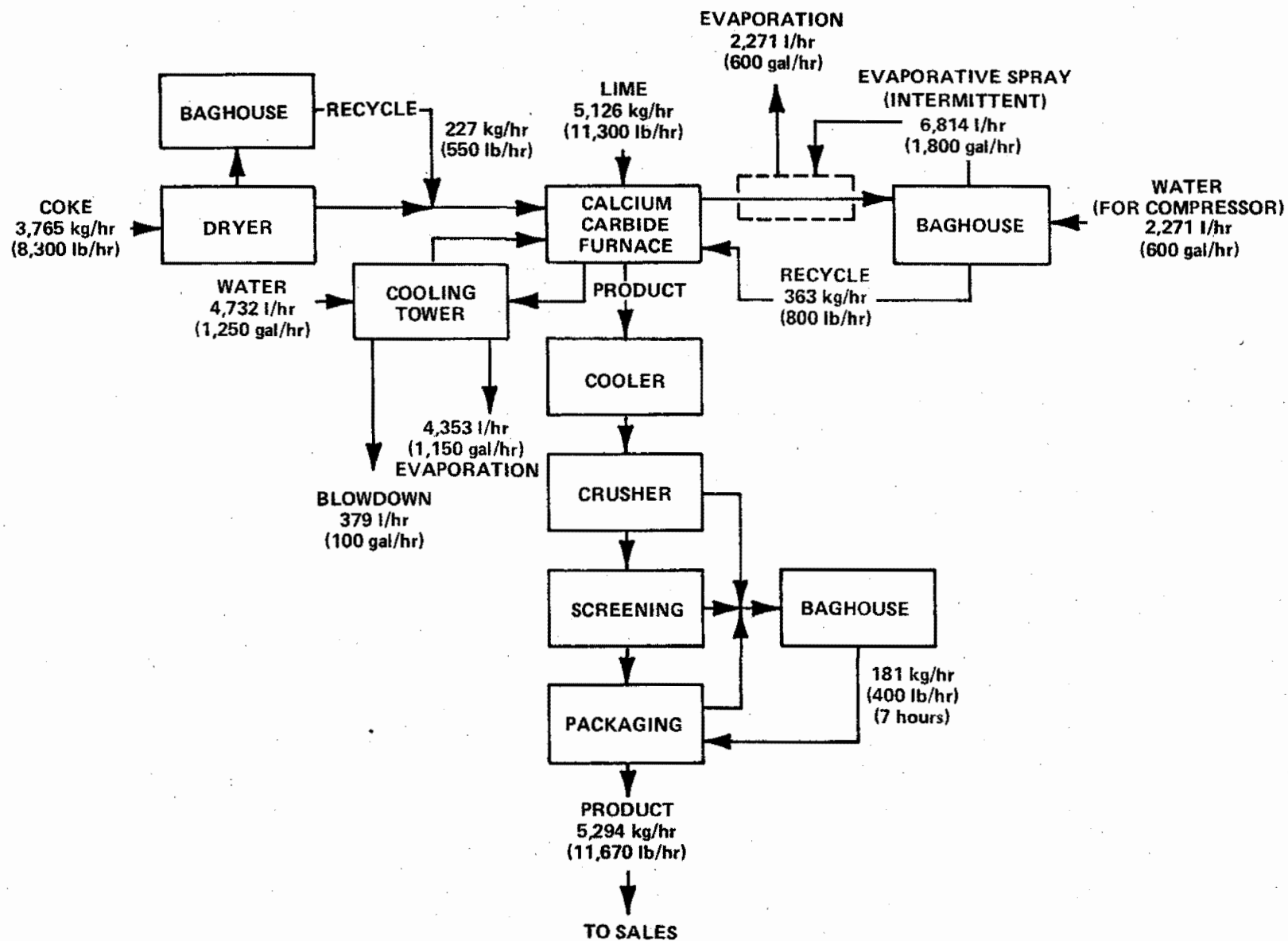
<u>Intake Water</u>		<u>Scrubber Water After Settling</u>
pH (units)	average 6.5	range: 7.1 to 9.2    average: 7.8

TABLE 7. CHARACTERISTICS OF PLANTS PRODUCING CALCIUM CARBIDE

PLANT	AVERAGE DAILY PRODUCTION		WATER USE				EFFLUENT TREATMENT	DISCHARGE		
	metric tons	short tons	Noncontact Cooling		Emission Control			POTW* or Direct	Flow	
			m <sup>3</sup> /hr	gal/hr	m <sup>3</sup> /hr	gal/hr			m <sup>3</sup> /hr	gal/hr
19301	104	115	4.73	1,250	0	0	None	Direct	0.38	100
19302	79	87	7.87	2,080	0	0	None	—	0	0
19303	54	60	94.6	25,000	118	31,250	Settling of scrubber discharge (+90% recycle)	Direct	11.8 (+94.6)	3,125 (+25,000)

\*POTW = Publicly Owned Treatment Works.

Figure 24. FLOW DIAGRAM FOR PRODUCTION OF CALCIUM CARBIDE SHOWING WATER USE (PLANT 19301)



TSS (mg/l) (data unavailable) range: 1 to 150 average: 40

The increase in pH is due to the presence of lime powder in the furnace offgases which is solubilized in the venturi scrubber. Eighty-percent removal of suspended solids by settling can be expected. The scrubber water at Plant 19303 contains a relatively small amount of suspended solids after settling. The suspended-solids concentration after settling is well within the limits set by many POTW that handle inorganic chemical process discharges.

PROCESS-WASTE CHARACTERIZATION FOR CALCIUM CHLORIDE  
SUBCATEGORY

Process Description and Water Use

Calcium chloride is manufactured from soda ash (sodium carbonate) wastes, obtained from natural salt deposits, and produced by reacting calcium carbonate with hydrochloric acid. Water uses associated with these various processes falls into three major groupings:

Process Water--which includes uses such as  
Dilution for process solutions  
Transport media  
Emissions control  
Water-treatment reagent preparation  
Equipment and plant washdown  
Leaks and spills (including associated cleanup)

Noncontact Cooling Water--which includes  
water involved in  
Boiler and steam generation  
Compressor cooling and condensate  
Noncontact cooling

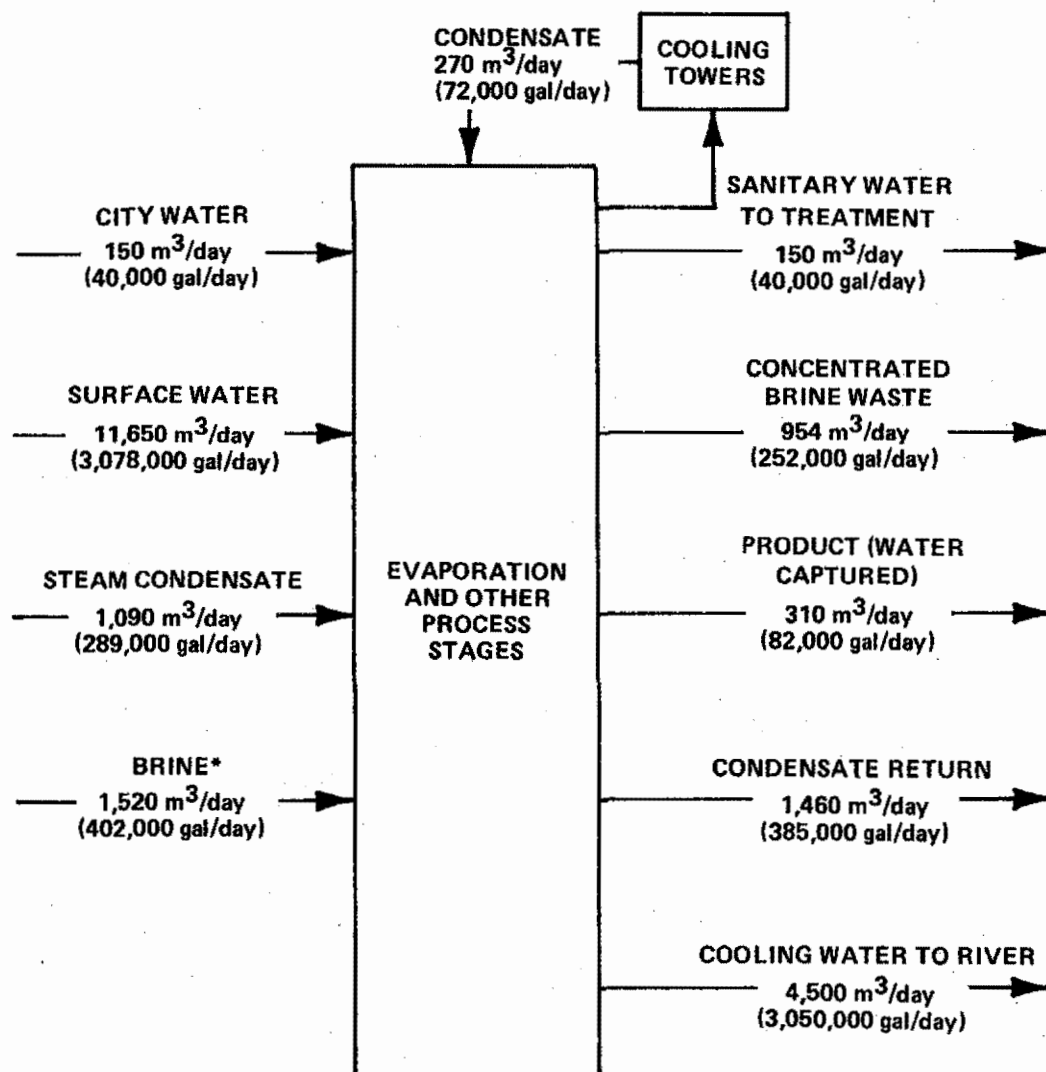
Potable Water--which includes sanitary water

Sources of Wastewater

The discussion which follows is largely concerned with the use and sources of process waste water, although other major types of water are mentioned.

Since the scheme for production of calcium chloride from natural brine at Plant 19404 is so complex, only a simple water-balance diagram is presented here. (See Figure 25). City water is introduced to the plant at an average daily flow of 150 cubic meters (40,000 gal) for use as sanitary and potable water and is discharged to the central water-treatment system at the same relative volume. Surface water

Figure 25. FLOW DIAGRAM SHOWING WATER BALANCE FOR PRODUCTION OF CALCIUM CHLORIDE FROM NATURAL BRINE (PLANT 19404)



\*NOT RAW MATERIAL

is used at a daily volume of about 11,650 cubic meters (3,078,000 gallons) for cooling purposes, and most of this water returns to a river. The difference is attributable to evaporation.

The steam condensate, which enters the process at a daily volume of about 1,090 cubic meters (289,000 gallons), is recycled with a diversion to the cooling towers. The condensate recycle apparently picks up water from the raw brine solution. The water contained in the raw brine solution (labelled "brine" in Figure 25) is partially incorporated into the condensate recycle system, into the product, and into the waste brine as a transport medium for disposal.

The only source of process waste water is the concentrated brine waste, which is disposed of via a well (which penetrates the originating geologic formation) at a daily discharge volume of 954 cubic meters (252,000 gallons). The concentrated brine is created by redissolving the salt removed from the calcium chloride liquor. There are no wastewater chemical characteristics available for this stream.

Four other major water-use changes at the plant have helped to reduce the discharge volume considerably, and two process-waste water sources have been eliminated as a result.

The Solvay process (production of soda ash) produces large amounts of calcium chloride as a byproduct. Sodium chloride, in addition to a small amount of calcium sulfate, is present in the Solvay waste liquor. After calcium chloride has been extracted from the liquor, dissolved constituents are either returned to the soda-ash waste stream or discharged.

At Plant 19401, overflows which occur during operational upsets, and waste solutions which are not diverted to the soda-ash waste stream, are discharged to surface waters. Information on waste water quantity and waste water quality is unavailable for these wastes because this normally internal stream is not monitored; however, it is expected that high TDS loadings will be present.

Calcium chloride production from calcium carbonate is a rather simple process which generates no process waste water other than washdowns. At Plant 19410, the insoluble residues from limestone digestion are periodically removed from reaction and settling vessels as a sludge, which is routed to a water-treatment system for convenient solid-

waste disposal. The treatment system handles waste water from production of a number of organic and inorganic chemicals, and it discharges to a POTW. However, there is not a significant volume of calcium chloride waste water entrained in the sludge to consider this plant a POTW discharger.

Plant 19412, which produces calcium chloride from a pure calcium carbonate raw material, generates no process waste water other than a daily reported volume of 1 cubic meter (300 gal) for washdown which is treated before discharge to surface waters. This treatment system also accommodates waste from a number of co-located chemical production processes.

#### Wastewater Characteristics

At Plant 19406, which produces high-purity calcium chloride, the only source of process waste water (excluding washdown) is a scrubber which collects emissions generated during a boil-down step. The waste water, which contains hydrochloric acid, is mixed with other waste streams from reagent-grade chemical production before being neutralized and discharged to a POTW. The waste water has a low pH and may contain high chloride concentrations, depending upon the volume of gas scrubbed.

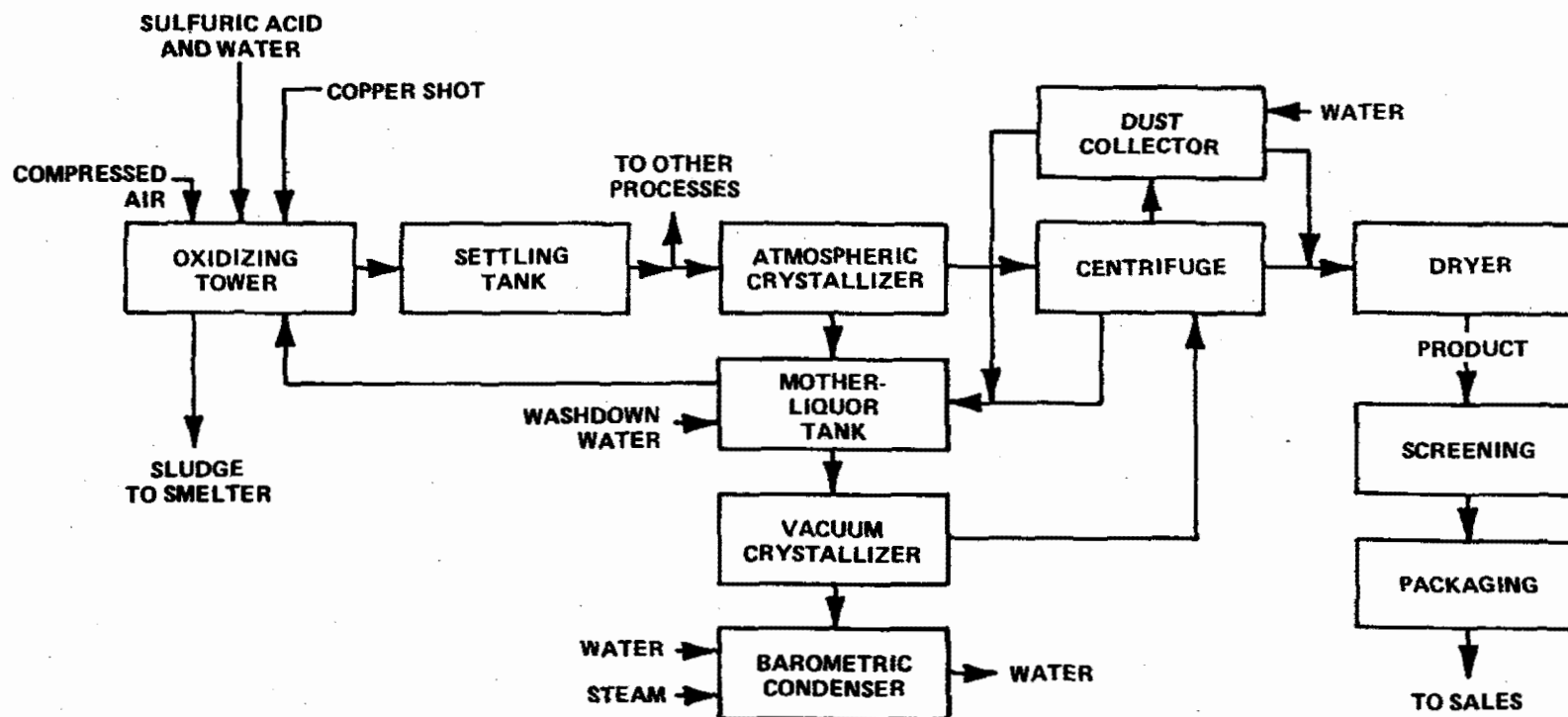
#### PROCESS-WASTE CHARACTERIZATION FOR COPPER (CUPRIC) SULFATE SUBCATEGORY

##### Process Description and Water Use

Plant 19506 mixes shot copper, 93% sulfuric acid, water, and air in a steam-heated oxidizing tower. The sludge produced is returned to the on-site copper smelter for treatment. The resulting copper (cupric) sulfate solution is sent to a settling tank and then to an atmospheric crystallizing tank. A process diagram is given in Figure 26. The mother liquor from the crystallizing tank is eventually recycled to the oxidizing tower. The crystals from the tank are centrifuged, after which the product is dried, screened, and bagged. The liquor from the centrifuge is also recycled to the oxidizing tower.

Mother-liquor solution at Plant 19506 is also sent to a vacuum crystallizer as needed. The slurry resulting from this stage is centrifuged and processed further. The water from the barometric condenser connected to the vacuum crystallizer is discharged without treatment.

Figure 26. FLOW DIAGRAM FOR PRODUCTION OF CUPRIC SULFATE (PLANT 19506)





Plant 19505 uses copper shot, air, and electrolyte from an adjacent copper refinery to produce copper sulfate. Upon exiting the oxidizer reactor, the resulting mixture is filtered and settled. The filter cake is returned to the plant's smelter for recovery of precious metals. The copper sulfate filtrate is processed through an evaporator, which utilizes noncontact steam. The concentrated solution is then sent to a crystallizer, which is cooled by noncontact water. There is some recycling of the noncontact cooling water. The copper sulfate crystals are separated from the mother liquor by centrifugation. The mother liquor is recycled to the evaporator, and the crystals are dried, screened, and packaged.

### Sources of Wastewater

The potential sources of waste water from copper sulfate manufacture are: mother liquor from centrifugation, weak liquor from the crystallizers, washdown water, cooling water, steam condensate, water from the barometric condensers, and water from the dust-collection apparatus.

None of the plants studied has all of the above waste water sources. Table 8 gives the characteristics and discharge sources for the six copper sulfate producers covered by this document.

The only process waste water discharged from Plant 19506 is barometric condensate. It is discharged at an hourly rate of 34.7 cubic meters (9,166 gallons). There is no apparent loss from the vacuum crystallizer to the barometric condenser during normal operation. Once a year, the condenser system is shut down for approximately 15 minutes. At this time, an overflow of 19 liters (5 gallons) occurs. Contamination of the barometric condensate from crystallizer overflow in this quantity is negligible.

### Wastewater Characteristics

All waste waters are economically recycled at Plant 19505 except for the evaporator noncontact steam condensate and the crystallizer noncontact cooling water. The condensate and cooling water are discharged without treatment.

A third waste water is discharged separately at Plant 19505. This discharge is highly variable, amounting to 18,900 to 22,700 liters (5,000 to 6,000 gallons) per day, and results from spills and washdowns. This waste stream is treated before discharge. Treatment consists of lime neutralization, settling, and filtration. The sludge produced in treatment is taken to an approved landfill site.

TABLE 8. CHARACTERISTICS OF PLANTS PRODUCING CUPRIC SULFATE

PLANT	CuSO <sub>4</sub> PRODUCT	AVERAGE DAILY PRODUCTION		COPPER SOURCE	WATER USE						DISCHARGE	
		metric tons	short tons		process	noncontact cooling	noncontact steam	barometric condenser	dust control	washdown	presence	source
19501	Solution	0.18	0.20	Scrap	Yes	No	No	No	No	No	No	—
19502	Solution	0.63	0.70	Scrap	Yes	No	No	No	No	No	No	—
19503	Solution	0.68	0.75	Scrap	Yes	No	No	No	No	No	No	—
19504	Solution	4.53	5.00	Scrap	Yes	No	No	No	No	No	No	—
19505	Crystals	36.2	40.0	Scrap, Shot	Yes	Yes	Yes	No	No	Yes	Yes	-Noncontact cooling -Noncontact steam -Treated wash
19506	Crystals	21.9	24.1	Shot	Yes	No	No	Yes	Yes	Yes	Yes	-Barometric condenser

The available data for the washdown effluent at Plant 19505 are given below.

	<u>Concentration (mg/l)</u>	
	<u>before treatment</u>	<u>after treatment</u>
copper	average: 433	average: 0.48 range: 0.14 to 1.25
nickel	average: 159	average: less than 0.5
pH	(not available)	7.3 to 11.1 (pH units)

Figure 27 shows the production and treatment process used at Plant 19505.

PROCESS-WASTE CHARACTERIZATION FOR IRON (FERRIC) CHLORIDE SUBCATEGORY

Process Description and Water Use

Waste pickle liquors are preheated and reacted with iron, chlorine, and hydrochloric acid to produce ferric chloride solution. The solution is either filtered and packaged for sale or filtered and evaporated to recover solid product. A process diagram is given in Figure 28 for Plant 19601. At some plants, no additional hydrochloric acid is used over that in the pickle liquor.

At Plant 19602, byproduct chlorine offgases from other on-site operations are used as a chlorine source. The offgases are cleaned with water in a contactor, to remove particulates, before being directed to the ferric chloride production process. Plant 19602 also employs a scrubber to remove small quantities of chlorine gas not absorbed in the ferric chloride solution. A process flow diagram for Plant 19602 is presented in Figure 29.

Water use during ferric chloride production includes:

- (1) Process water used in the reaction to achieve the desired solution specifications.
- (2) Scrubber water to remove particulates from incoming chlorine gas.
- (3) Caustic scrubber water to absorb residual chlorine in process tail gases.
- (4) Wash water to remove solid material from filters.

Figure 27. FLOW DIAGRAM FOR PRODUCTION OF CUPRIC SULFATE (PLANT 19505)

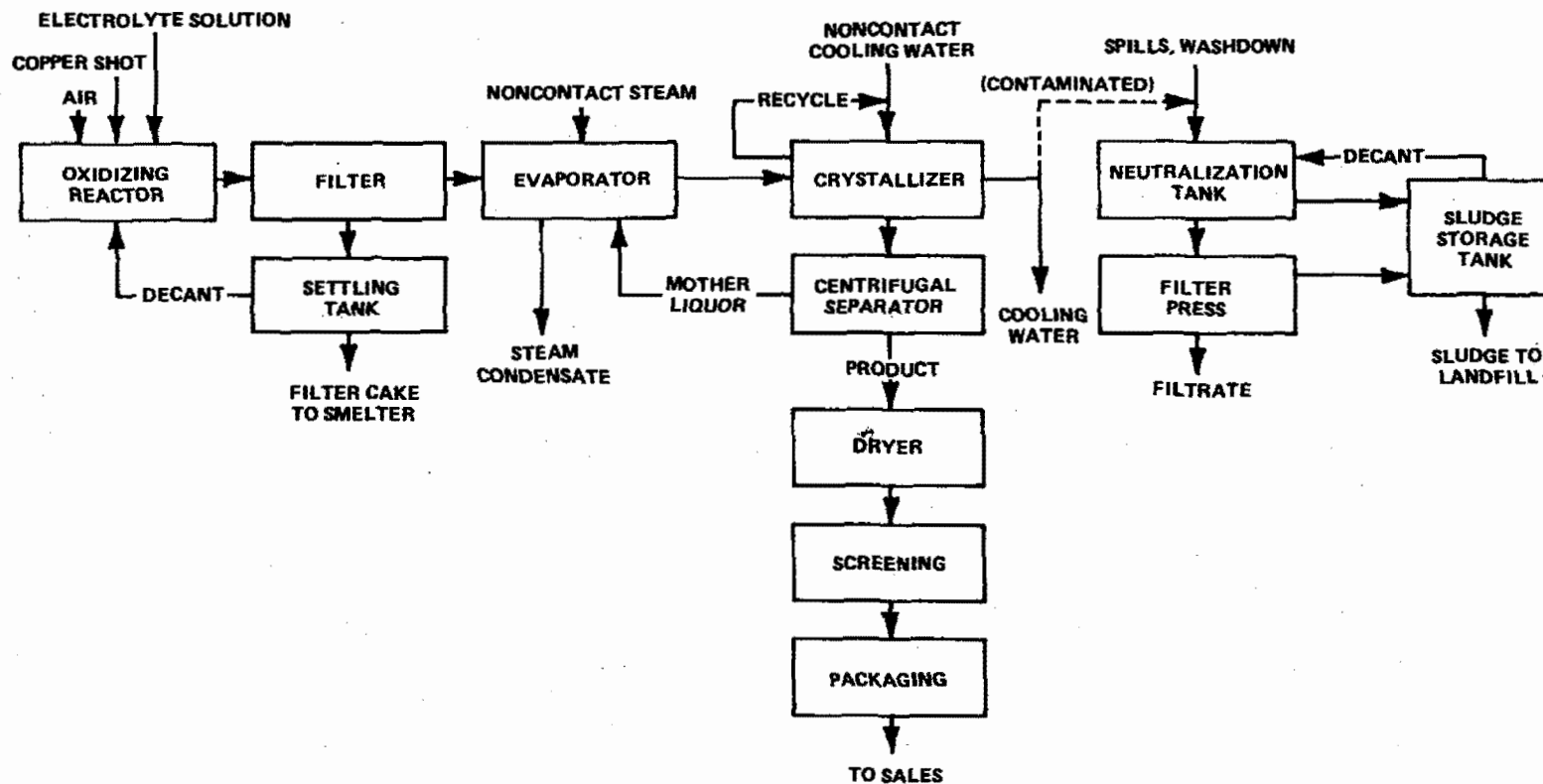


Figure 28. FLOW DIAGRAM FOR PRODUCTION OF FERRIC CHLORIDE (PLANT 19601)

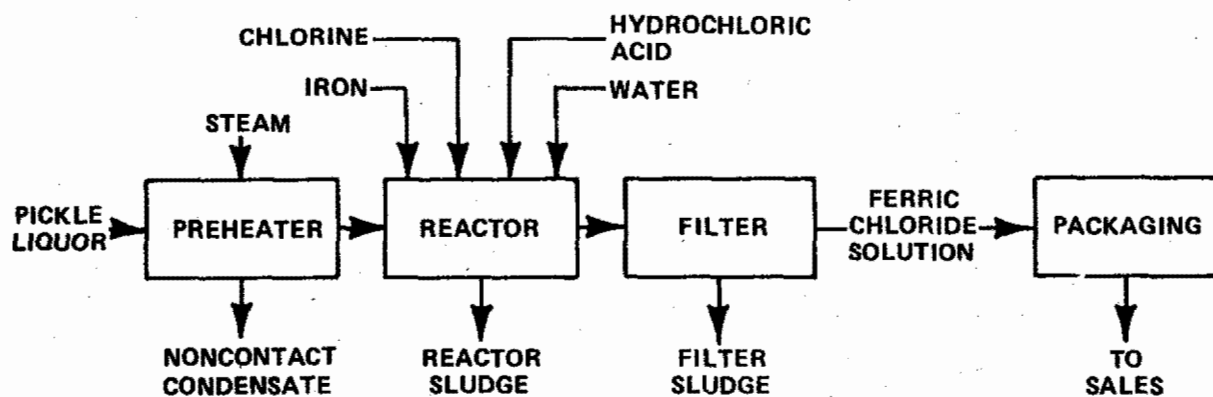
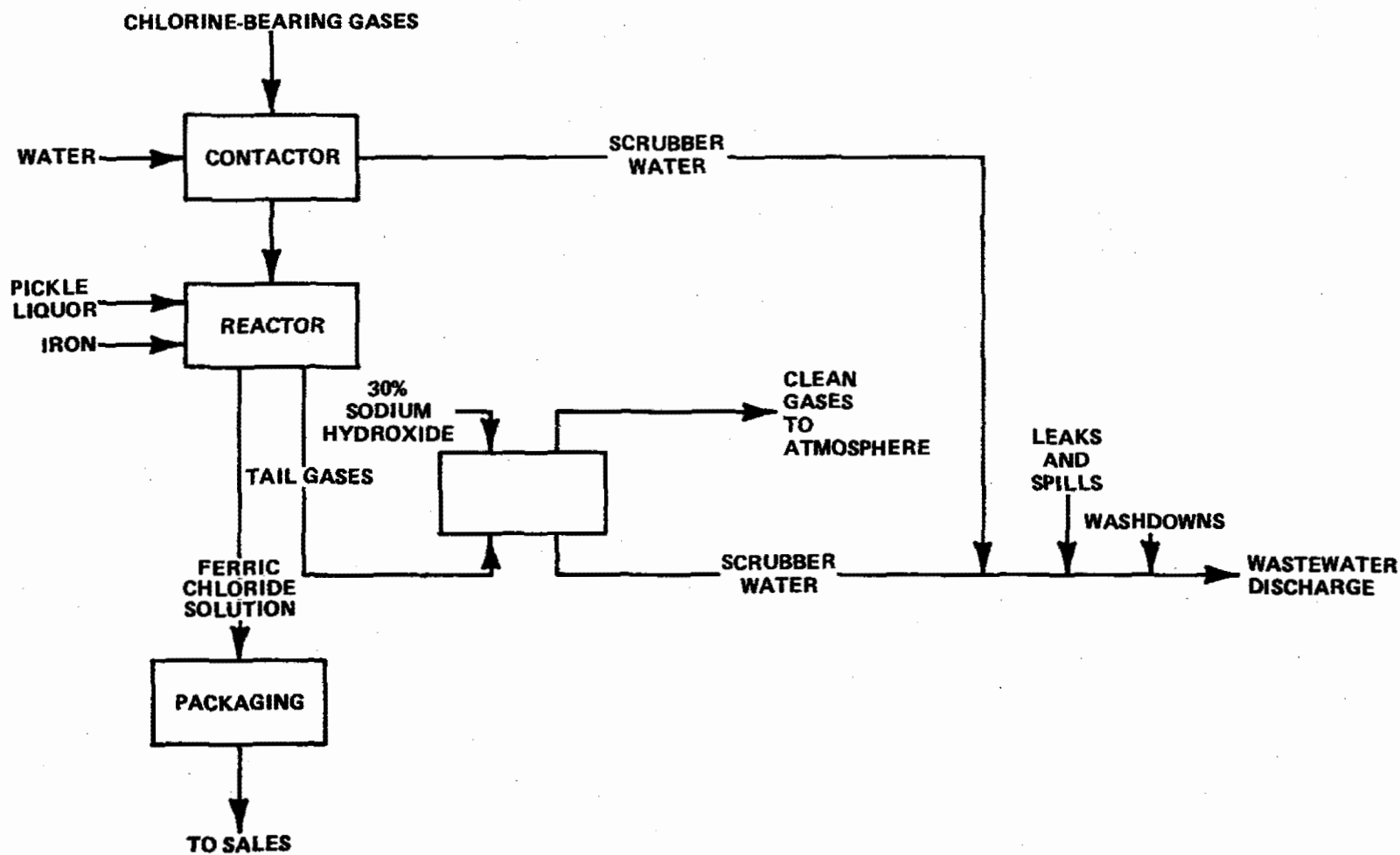


Figure 29. FLOW DIAGRAM FOR PRODUCTION OF FERRIC CHLORIDE  
(PLANT 19602)



(5) Miscellaneous washdown water.

Sources of Wastewater

Incoming Chlorine-Gas Scrubber Water. Approximately 45 cubic meters (12,000 gallons) of waste water are generated daily at Plant 19602 by cleaning particulates from incoming byproduct chlorine gases. This operation is unique. In general, industrial-grade chlorine is used as a raw material for ferric chloride production, and no precleaning is necessary.

Tail-Gas Scrubber Water. Residual chlorine present in tail gases from the reaction process are scrubbed with 30% sodium hydroxide in an absorption tower. The scrubber solution is recycled except for a small purge stream.

Filter Wash Water. Solids removed from the raw ferric chloride solution collect on the filter media and must be removed. The filters are washed with water, resulting in a slurry containing 15% solids. Plant 19601 daily generates 2 cubic meters (500 gallons) of this slurry.

Floor and Equipment Washings. Periodically, during production, equipment and floor areas are washed to remove spilled raw material and product. At Plant 19601, 4 cubic meters (1000 gallons) of water are used each day for equipment and floor washdowns. Plant 19602 daily uses 30 cubic meters (7,000 gallons) of water for routine maintenance--even though its production is one tenth that of Plant 19601. This variability is undoubtedly due to differences in both general housekeeping practices and to cleanup techniques.

Leaks and Spills. Leaks and spills can be a major source of process waste water. At Plant 19601, 270 cubic meters (72,000 gallons) of wastewater are generated each day from leaks. Plant 19602, on the other hand, reports no leaks from their ferric chloride manufacturing process. The corrosiveness of process materials, equipment age, maintenance, and plant-safety programs significantly affect the frequency and degree of leaks and spills.

Wastewater Characteristics

General. Data on the chemical characteristics of waste water generated solely from ferric chloride production are unavailable. Therefore, a theoretical waste water was developed, based on raw material characteristics, waste water type, mode of generation, and limited historical in-

formation. The rationale employed in characterizing the waste water is presented below.

The major source of pollutants in waste water generated from ferric chloride production is the pickle liquor feed. Besides iron, the pickle liquor contains a variety of trace elements, including hexavalent chromium (Cr HEX), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn). The chemical characteristics of a typical pickle liquor are given in Table 9.

Analysis of each individual waste water generated during ferric chloride production produced the conclusions which follow.

Tail-Gas Scrubber Water. The tail-gas scrubber is used to remove residual chlorine from process off-gases. Metals are not expected in the tail gas except in very small quantities--particularly, in light of the low reaction temperatures encountered. Because sodium hydroxide is used as the scrubbing medium, the pH of the scrubber waste water is of concern. However, its effect will be minimized after it is combined with other acidic process waste water.

Filter Wash Water. It is known from historical data that the filter wash water from ferric chloride production contains 15% solids. These solids include 50,000 mg/l iron and 4,000 mg/l miscellaneous materials (Reference 5). The total concentration of trace metals in pickle liquor is approximately 300 mg/l. If it is assumed that significant percentages of the miscellaneous materials present in filter wash water are the trace metals in pickle liquor, the concentrations of these trace metals in the filter wash water should be ten times their concentration in pickle liquor.

Floor and Equipment Washings. Wastewater generated from floor and equipment washings at other inorganic chemical manufacturing operations has approximately 20,000 mg/l total suspended solids (TSS) and 36 mg/l total trace metals. Pickle liquor has 300 mg/l total trace metals. If these data are extrapolated to washings from ferric chloride production, the waste water will contain 20,000 mg/l TSS and about one tenth the concentration of trace metals in pickle liquor. It may also be inferred that the iron concentration of floor and equipment washings will have one tenth the iron concentration of pickle liquor.

Leaks and Spills. Leaks and spills consist of essentially pure pickle liquor and ferric chloride which have been diluted with water. A spill, which may pose a health



**TABLE 9. CHEMICAL COMPOSITION OF TYPICAL IRON PICKLE LIQUOR  
FROM PRODUCTION OF FERRIC CHLORIDE**

PARAMETER	CONCENTRATION (mg/l)
Cr (total)	13
Cu	10
Fe	9,000*
Pb	2.2
Mn	230
Ni	14
Zn	12

\*Assuming 20%  $\text{FeCl}_2$  in pickle liquor

problem as well as harm equipment, will be diluted up to one hundred times. Their occurrence, however, is rare. Leaks, on the other hand, are quite common and can be significant. A pump seal may leak 4 l/minute (1 gpm) of water, 10% of that being process material. The resultant waste water will thus contain one tenth the concentration of pollutants found in pickle liquor.

The chemical characteristics of waste water generated from ferric chloride production, based on the above rationale, are presented in Tables 10 and 11. Table 10 presents the waste water characteristics for a plant which has a large volume of leaks and spills, such as Plant 19601. Table 11 details the waste water characteristics of a plant, such as Plant 19602, which has virtually no waste water associated with leaks and spills.

#### PROCESS-WASTE CHARACTERIZATION FOR LEAD MONOXIDE SUBCATEGORY

##### Process Description and Water Use

At Plant 19701, lead monoxide is prepared by the Barton Oxide Process, which is the same as Process 4 described in Section III of this document. Dusts are controlled throughout the process by the use of cyclones and dry bag collectors. Floor dust is vacuumed. No process water is used. Indirect cooling water is used for cooling the oxide in the furnace-discharge conveyor. A process diagram is given in Figure 30.

At Plant 19702, the lead monoxide manufacturing process is the same as Process 2 described in Section III. Washdown of dusts from plant surfaces is practiced at this plant. A process diagram of Plant 19702 is given in Figure 31.

##### Sources of Wastewater

There are two sources of process waste water in the lead monoxide manufacturing industry: plant washdown and compressor blowdown, the major source being plant washdown. Compressor blowdown is highly variable in composition and quantity, although the quantity produced is small by nature. Noncontact cooling is the only other water-using operation in the lead monoxide manufacturing industry.

##### Wastewater Characteristics

Equipment and Plant Washdown. Equipment and plant washdowns, dust control, and chemical spill cleanups are generally considered to be housekeeping procedures. In the lead monoxide manufacturing industry, these procedures are

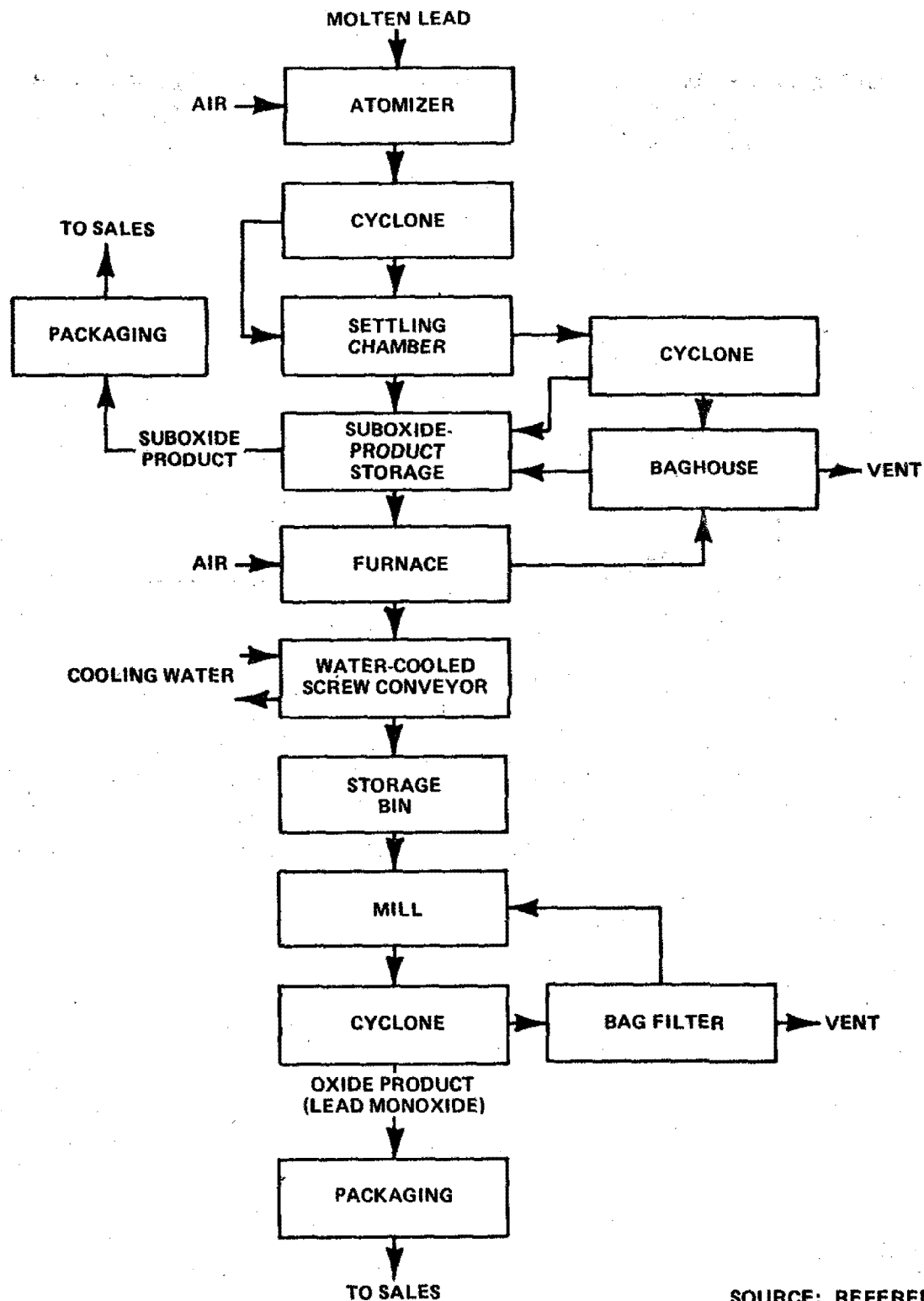
**TABLE 10. CHEMICAL COMPOSITION OF AVERAGE WASTEWATER FROM PRODUCTION OF FERRIC CHLORIDE (PLANTS WITH LARGE LEAKS AND SPILLS)**

PARAMETER	CONCENTRATION (mg/l)
TSS	11,000
Cr (total)	2.1
Cu	1.6
Fe	9,200
Pb	0.35
Mn	37
Ni	2.2
Zn	1.9

**TABLE 11. CHEMICAL COMPOSITION OF AVERAGE WASTEWATER FROM PRODUCTION OF FERRIC CHLORIDE (PLANTS WITH MINIMAL LEAKS AND SPILLS)**

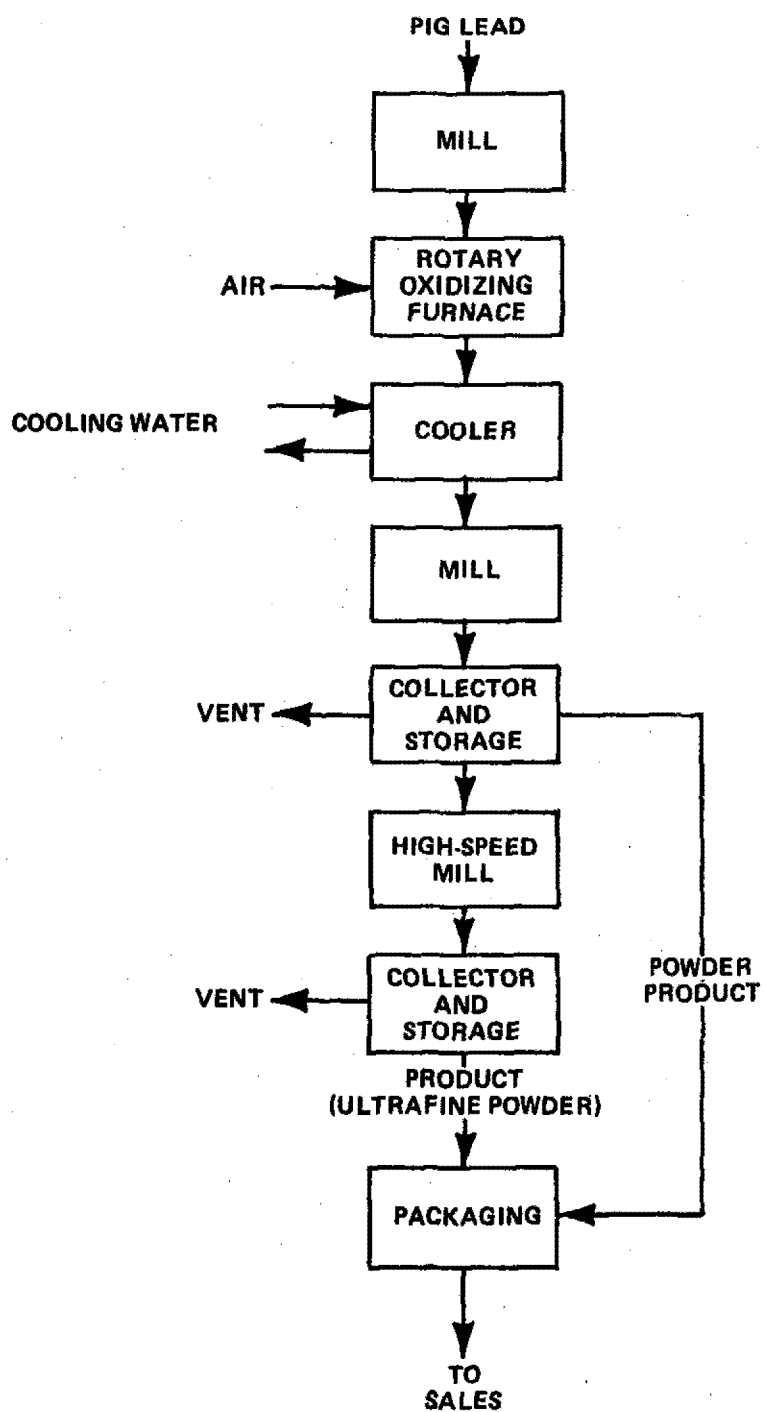
PARAMETER	CONCENTRATION (mg/l)
TSS	33,000
Cr (total)	14
Cu	11
Fe	13,000
Pb	2.4
Mn	250
Ni	15
Zn	13

Figure 30. FLOW DIAGRAM FOR PRODUCTION OF LEAD MONOXIDE (PLANT 19701)



SOURCE: REFERENCE 5

**Figure 31. FLOW DIAGRAM FOR PRODUCTION OF LEAD MONOXIDE  
(PLANT 19702)**



**SOURCE: REFERENCE 5**

necessary to control the fine lead oxide dusts formed in the firing, milling, and handling operations. A significant portion of the dusts and spills occurring in lead oxide plants contains lead monoxide.

Dust control and cleanup may be practiced with or without water. Ten lead monoxide plants use dry bag collectors and dry vacuuming for dust control and cleanup. These 10 plants are all zero dischargers. One plant employs wet dust control and cleanup ("washdown") and discharges the waste water generated to surface waters.

Due to the nature of washdown waste water, its composition and quantity may vary significantly from day to day, as well as from one plant to the next. The composition of washdown waste water is primarily dependant upon two factors:

- (1) The types and amounts of equipment, products, reagents, or other materials which the wash water directly contacts.
- (2) The volume and chemical characteristics of the clean or unused wash water.

Actual chemical characteristics of a typical washdown waste water from a lead monoxide plant are unavailable at this time. However, sufficient data were available to allow formulation of reasonable estimates of the chemical characteristics of untreated washdown water at Plant 19702.

At Plant 19702, 85 to 90% reductions in total lead and suspended solids are claimed due to the reaction of soluble lead with sulfate ions. Approximately 373 kg (820 lb) of lead compounds are recovered daily from this treatment. Since the daily process-waste water flow rate is known to be 348 cubic meters (92,000 gallons), the concentration of total lead can be calculated as follows:

$$\text{Concentration of total lead in wash water} = \frac{1}{E} \cdot \frac{\text{MPB}}{\text{MPBO}} \cdot \frac{R}{F} (1000)$$

$$= \frac{1}{0.85} \cdot \frac{207}{(207+16)} \cdot \frac{373}{348} (1000)$$

$$= 1170 \text{ mg/l}$$

where E = Removal efficiency

MPb = Molecular weight of lead

MPbO= Molecular weight of lead monoxide

R = Recovery rate of lead compounds from  
treatment (kilograms per day)

F = Flow rate of waste water  
(cubic meters per day)

This estimate is based on the assumptions that most of the lead compounds recovered are in the form of lead monoxide, and that the lead removal efficiency is 85%.

Since lead monoxide dust is the major constituent found in washwater and is fairly insoluble in the near-neutral pH range, most of the lead present will be in the form of suspended solids. For this reason, total lead concentrations and total suspended-solids concentrations will be the same for all practical purposes. This assumption is supported by laboratory testing, which showed total lead removals of 92% for settlingpond effluent using filtration. Furthermore, untreated washdown wastewater can be expected to be nearly the same as that of the water source (pH 6.9).

The estimated chemical characteristics of untreated lead monoxide plant washdown waste water discussed above are summarized in Table 12.

Compressor Blowdown. The only source of process waste water from lead monoxide production, other than plant washdown water, is air-compressor blowdown. In most cases, compressor blowdown is not considered a process waste water. However, since the blowdown comes into direct contact with a raw material, oxygen, it is a process waste.

Compressor blowdown is actually water condensate from the humidity in air, oil and grease, other particulate matter, etc., purged from the compressor. The amount of condensate generated from compressors is highly variable, being a function of compressor-air flow rate, humidity, temperature, and elevation, but can be closely estimated as follows:

Basis: 0.907 metric ton (1.0 short tons) of lead  
oxide product V, volume of air required = 45.6  
cubic meters (1,610 cubic feet) at standard  
temperature and pressure (STD)



**TABLE 12. ESTIMATED CHEMICAL COMPOSITION OF UNTREATED  
WASHDOWN WASTEWATER FROM PRODUCTION OF  
LEAD MONOXIDE (PLANT 19702)**

PARAMETER	CONCENTRATION (mg/l)
pH	6.9*
TSS	1,200
Pb	1,200

\*Value in pH units.

$$H = \frac{M_w}{M_a} \cdot \frac{p}{p-p} = \frac{18}{29} \cdot \frac{p}{p-p}$$

where H = absolute humidity, kg water vapor/kg dry air

M<sub>w</sub> = molecular weight of water, grams

M<sub>a</sub> = molecular weight of air, grams

p = partial pressure of water vapor in air,  
atmospheres

p = total pressure of the air water-vapor  
mixture, atmospheres

At standard temperature and pressure:

H = 0.016 kg water vapor/kg dry air

V, specific volume of air = 0.82 cubic meter per  
kilogram dry air

Volume of compressor condensate = 0.016 (1/0.82) (45.6)  
(per ton of lead monoxide product) = 0.89 liters  
(0.23 gal)

It can be seen from this calculation that waste water flows from compressor blowdown will be relatively small, even when one considers larger lead monoxide producers and the fact that, in actual practice, the volume of air required will be significantly higher than theoretically predicted. As an illustrative example, the daily volume of compressor blowdown at Plant 19702 is estimated to be 0.13 cubic meter (34.5 gallons) based on standard temperature and pressure, three times the theoretical oxygen requirements. The contribution of oil and grease from the above-estimated flow of compressor blowdown would produce an oil and grease concentration of less than 1 ppm in the effluent from Plant 19702.

The chemical composition of compressor blowdown is as variable as the quantities produced. However, oil and grease is usually the only pollution constituent present to any appreciable degree, as indicated in Table 13.

Oil and grease concentrations encountered in compressor blowdown are a function of the compressor design and age. There are basically two types of compressors: wet-type compressors (which use oil to lubricate cylinder walls) and dry-type compressors (which avoid contact of the gas with oil). All wet-type compressors are of the reciprocating-

**TABLE 13. CHEMICAL COMPOSITION OF BLOWDOWN FROM TYPICAL RECIPROCATING-PISTON COMPRESSOR (PLANTS PRODUCING LEAD MONOXIDE)**

PARAMETER	CONCENTRATION (mg/l)*
pH	6.4 <sup>†</sup>
TDS	560
TSS	780
Oil and Grease	1,960**
Cr (total)	0.85
Cd	<0.01
Cu	0.48
Pb	<0.02
Hg	<0.0002
Zn	0.34

\*Contractor sample collection and analysis (one 24-hour composite collected 13 December 1976).

†Value in pH units.

\*\*Contractor sample collection and analysis (four grab samples collected 13 December 1976).

piston design, although there are oil-free or dry-type reciprocating-piston compressors which utilize graphite or teflon piston rings for lubrication in low-pressure service. Centrifugal compressors and mercury-piston compressors are other examples of dry-type compressors. These oil-free compressors also produce condensate, but the condensate does not contact any oil-lubricated surfaces and, therefore, does not contain appreciable concentrations of oil and grease. Compressor blowdown from oil-free compressors is essentially clean water.

Noncontact Cooling Water. Eleven lead monoxide manufacturers employ noncontact cooling water to rapidly cool lead monoxide as it exits the furnace, thereby preventing the formation of red lead. Contamination does not occur, because the pressure gradient is from the water to the product, and the material solidifies on cooling. The result is that the noncontact cooling water is compatible with POTW operation.

PROCESS-WASTE CHARACTERIZATION FOR NICKEL SULFATE  
SUBCATEGORY

Process Description and Water Use

Nickel sulfate is produced from two types of raw materials:

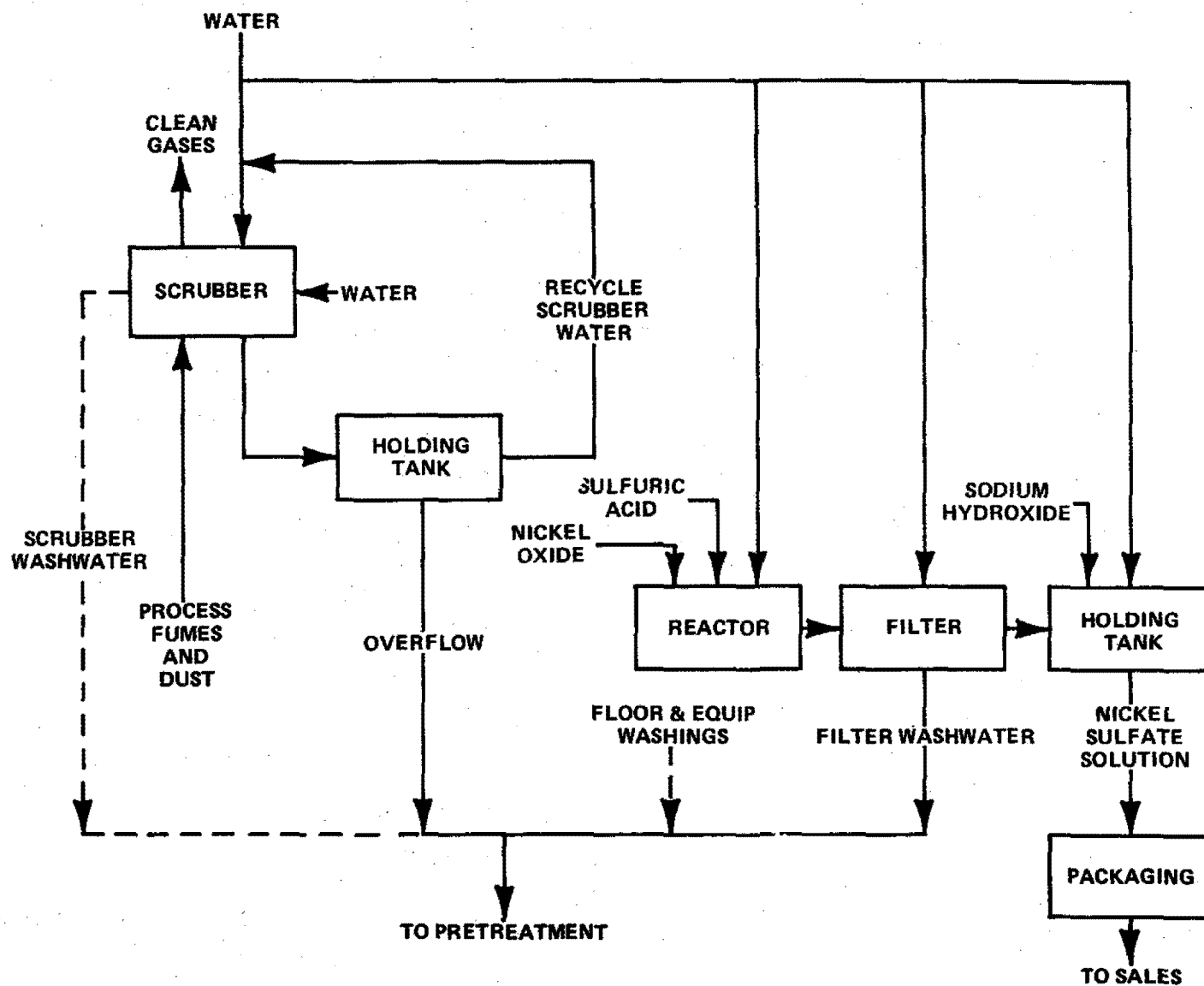
- (1) pure nickel or nickel oxide
- (2) impure nickel-containing materials--e.g., spent nickel catalysts or nickel carbonate made by addition of soda ash (sodium carbonate) to spent nickel-plating solutions.

In the first case, the metal or oxide is digested in sulfuric acid to produce a nickel sulfate solution. The solution is filtered and either packaged for sale or further processed to recover a solid material, nickel sulfate hexahydrate. Water and/or sodium hydroxide may be added to the solution prior to packaging to achieve the desired specifications.

Plant 19801, which discharges waste water to a POTW, employs this process to produce a 60% nickel sulfate solution. A process flow diagram, detailing water use at Plant 19801, is presented in Figure 32.

Water is consumed in the process to achieve the desired nickel sulfate solution. A wet scrubber is employed to clean fumes and dust from the work area. Scrubber water is recycled, with only a small bleed (10%) actually being

Figure 32. FLOW DIAGRAM FOR PRODUCTION OF NICKEL SULFATE (PLANT 19801)



discharged. Additional water is used intermittently for scrubber washdown, filter-press washing, and floor washing. Noncontact cooling water is used to cool the reactor.

The second process uses impure nickel-containing compounds as raw material, instead of pure nickel metal or oxide. The raw materials are digested with sulfuric acid to produce a nickel sulfate solution. The resulting solution must be treated in series with oxidizers, lime, and sulfides to precipitate impurities. The solution is filtered and marketed or further processed to recover the solid hexahydrate.

To recover solid product, the nickel sulfate solutions are first concentrated, filtered, and fed to a crystallizer. The resulting suspensions are fed to a classifier, where solid product is recovered. This material is then dried, cooled, screened, and packaged for sale. The recovered solids from the filtration step and the mother liquor from the classifiers are recycled back to the beginning of the process.

A process flow sheet, detailing nickel sulfate production (at Plant 19803) from impure nickel-containing compounds, is presented as Figure 33.

Water use includes:

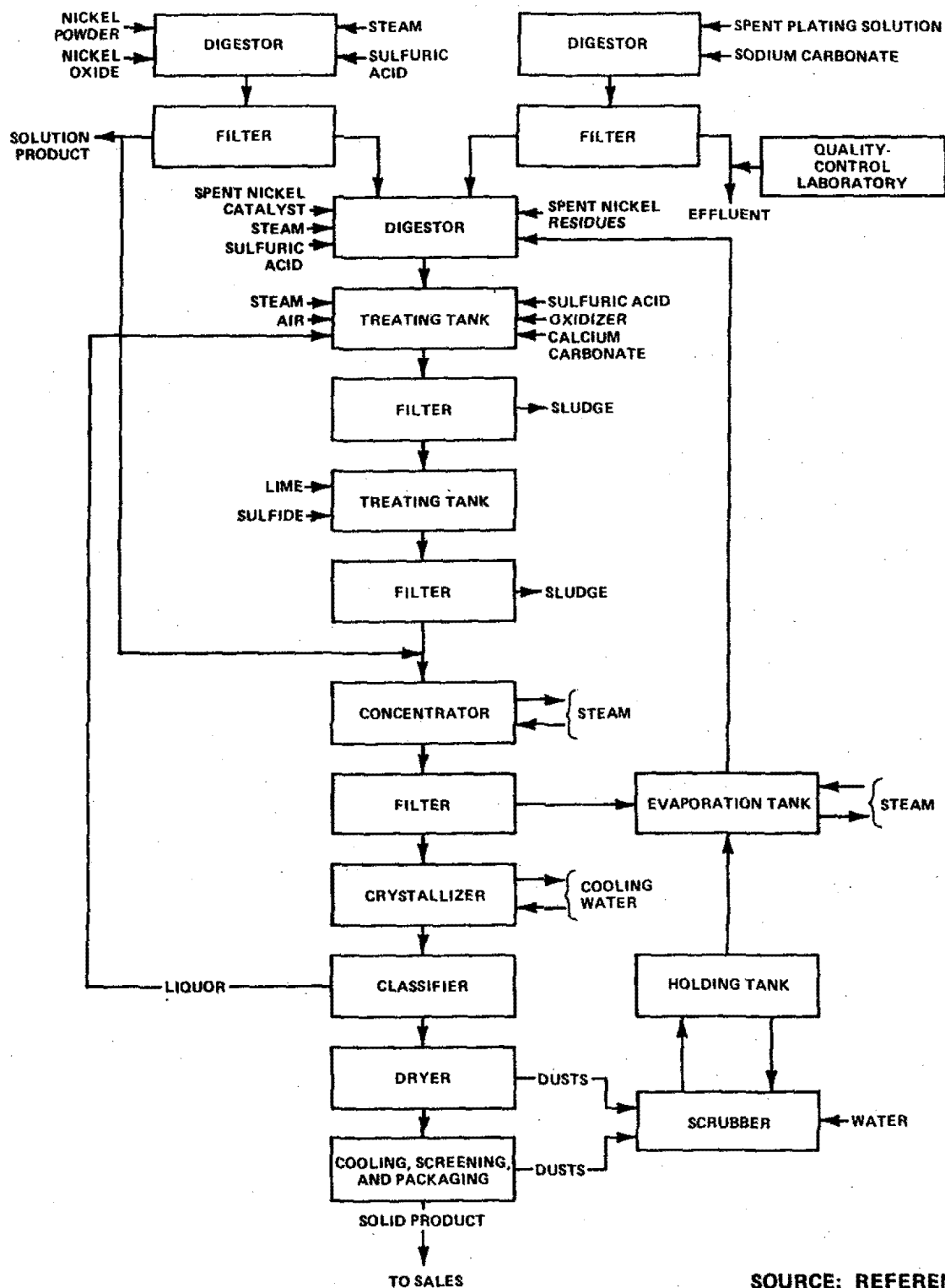
- (1) process water used in making the nickel sulfate solution
- (2) barometric-condenser water
- (3) filter-backwash water
- (4) noncontact reactor-cooling water and cooling-tower blowdown.

#### Sources of Wastewater

Wastewater generated during nickel sulfate production at Plant 19801 includes:

Scrubber Bleed Water. Fumes and dust in the work area are collected by a fan and directed to a wet scrubber. Approximately 6.8 cubic meters (1,800 gallons) of city water are used daily to clean the fumes. The scrubber water is collected in a baffled tank to facilitate settling of suspended solids and then recycled. About 0.68 cubic meter (180 gallons) overflows the tank daily and is discharged after pretreatment. The scrubber is in operation at all times during a production run (4 to 8 hours).

Figure 33. FLOW DIAGRAM FOR PRODUCTION OF NICKEL SULFATE  
(PLANT 19803)



Scrubber Washdown Water. After each production run, the scrubber is washed down with 0.08 cubic meter (20 gallons) of water to remove scale.

Filter Wash Water. After the nickel sulfate solution has been filtered, the filter press is disassembled and the filter sheets hosed off to remove caked material. The amount of water used ranges from 0.09 to 0.28 cubic meter (25 to 75 gallons) per washing.

Floor Washings. Periodically, during production, the equipment and floor area are washed to remove spilled raw materials and product. Flow from this operation can vary from 0.02 to 0.09 cubic meter (5 to 25 gallons) per operating day.

Daily total waste water generation at Plant 19801 is 1 cubic meter (300 gallons).

Wastewater generation at Plant 19803 includes:

Filtrates. Spent plating solutions are digested and treated with soda ash. The resulting solution is filtered and the solids sent for further processing. Approximately 20 cubic meters (5,000 gallons) of waste filtrate are generated daily from this operation.

Filter Sludges. During production of both aqueous and crystalline nickel sulfate, the nickel sulfate is directed to several filtration steps. (See Figure 33.) The filters must be cleaned periodically to remove caked material. Depending on the techniques employed to clean the filters and the amount of washwater used, the resultant sludges pose either a waste water or a solid-waste problem. At Plant 19803, the latter is true. However, the potential for waste water generation similar to that encountered at Plant 19801 should be considered.

#### Wastewater Characteristics

The chemical characteristics of the combined waste water from three nickel sulfate plants are presented in Table 14. Plants 19801 and 19802 both use nickel oxide as a raw material, and both are POTW dischargers. Plant 19803 uses impure nickel-bearing materials to produce nickel sulfate. Although it is a direct discharger, Plant 19803 can be considered representative of a POTW discharger employing a similar process.

Table 15 presents the chemical characteristics of each separate wastewater stream emanating from Plant 19801. The



**TABLE 14. CHEMICAL COMPOSITIONS OF RAW WASTEWATERS FROM PRODUCTION OF NICKEL SULFATE (THREE PLANTS)**

PARAMETER	CONCENTRATION (mg/l)		
	PLANT 19801	PLANT 19802	PLANT 19803
pH	9.1*	8.5*	8.2*
TDS	24,100	2,100	—
TSS	525	240	—
Cr (total)	0.16	0.007	—
Cu	5.0	68	—
Ni	360	140	12
Sulfate	228	153	—

\*Value in pH units.

**TABLE 15. CHEMICAL COMPOSITIONS OF INDIVIDUAL PROCESS WASTE STREAMS  
FROM PRODUCTION OF NICKEL SULFATE (PLANT 19801)**

PARAMETER	CONCENTRATION (mg/l)			
	SCRUBBER BLEED	SCRUBBER WASHDOWN	FILTER WASHINGS	FLOOR WASHINGS
pH	9.6*	4.8*	6.6*	7.0*
TDS	32,000	16,000	7,200	4,600
TSS	98	210	1,700	1,900
Cr (total)	0.10	0.22	0.34	0.29
Cu	1.0	16	2.4	35
Ni	32	2,200	920	440
Sulfate	260	160	153	185

\*Value in pH units.

most significant pollutant present is nickel. Other parameters, such as pH, TSS, TDS, zinc, and copper, occasionally appear in high concentrations.

Most of the heavy metals in the scrubber water are settled out in the holding tank prior to recycle. The dissolved salts, however, are not removed to any great extent; instead, they are concentrated. As a result, the scrubber water exhibits relatively low metal levels, while dissolved-solids levels are high. In the case of the washdown waters, small volumes of water are brought into contact with almost pure raw materials, products, and miscellaneous plant dusts, resulting in high suspended-solids and metal concentrations.

#### PROCESS-WASTE CHARACTERIZATION FOR NITROGEN AND OXYGEN SUBCATEGORY

##### Process Description and Water Use

In the process of air separation, the major use of water is for noncontact cooling. This water is usually on a single-pass basis, although some plants may recycle a limited volume. Frequently, the stream is characterized by varying concentrations of chromium and/or zinc, which are added as corrosion inhibitors. Noncontact cooling water, after passing through the plant cooling towers, is discharged without further treatment.

The moisture which is trapped in the compressors forms as a result of the condensation of the water-vapor portion of the incoming atmospheric air. The volume of this compressor condensate is characteristically small, although, when it contacts the lubricating oil of the compressor cylinders, an oily waste water is formed which periodically requires some pretreatment before discharge.

Another process waste stream which is generated in some air-separation plants is caustic-scrubber solution. This is found in those plants which use caustic to remove carbon dioxide impurities from the filtered air prior to separation. Again, resulting waste water volumes are limited, and the usual practice is to totally impound this waste stream and have it removed from the plant.

##### Sources of Wastewater

The sources of process waste water in the production of nitrogen and oxygen via air separation are:

- compressor condensate
- caustic-scrubber solution

noncontact cooling water (cooling-tower blowdown)  
See Figure 34.

The contact process waters of particular interest in the production of nitrogen and oxygen are compressor condensate and caustic-scrubber solution. Condensate results from the compression of the water-vapor portion of atmospheric air as it undergoes the effect of high pressure. In the older-type reciprocating compressors, lubricating oil is required in the cylinder chambers to minimize frictional effects. This oil becomes mixed with water-vapor condensate in the compressor and results in the generation of a process waste water. The compressors are blown down periodically, and the oily condensate is collected and added to a common sump area with plant-floor washings and any leaks and spills which have been collected from throughout the plant. Data available on the amount of actual compressor condensate generated in any particular plant are extremely limited. The known production volumes, which usually represent a total of combined oily wastes, are characteristically small, ranging from as little as the 0.011 l/metric ton (0.022 gal/short ton) produced at Plant 13103 to a maximum of 42.8 l/metric ton (85.6 gal/short ton) at Plant 13101, with an average of approximately 1.4 l/metric ton (2.8 gal/short ton).

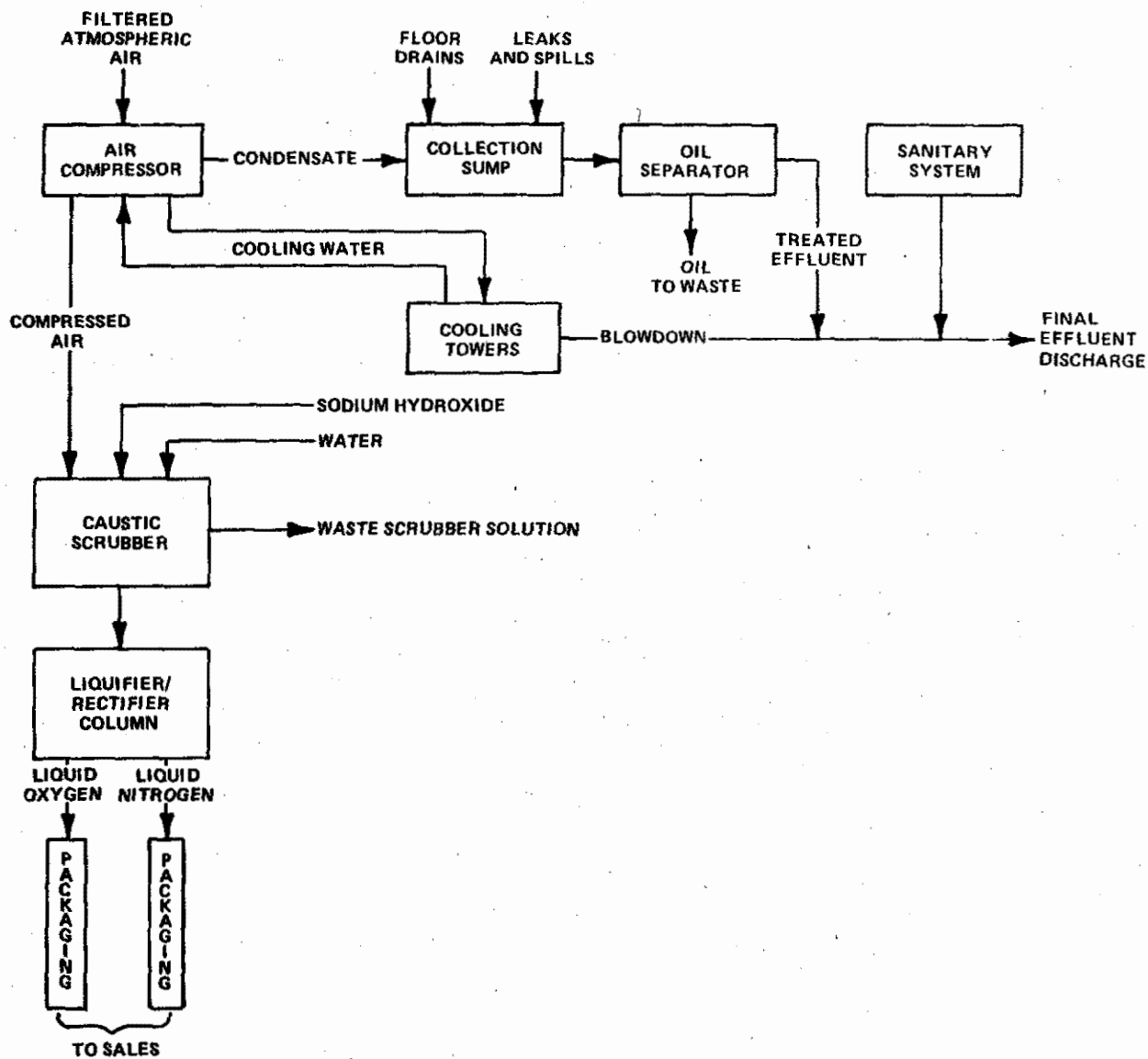
The other process waste stream mentioned (i.e., caustic-scrubber solution) is not common to many air-separation plants. The waste water is generated in the process of carbon dioxide removal, which is necessary to purify the air prior to separation. In those plants where this process is employed, it is common practice to totally impound the waste water produced so that it in no way adds to the total waste stream. No data on the waste characterization or flow of this stream are currently available.

Equipment and plant washdowns are accomplished with minimal waste water production. In air-separation plants, washdown streams are commonly characterized by the presence of some oil and grease from compressor crankcases, but no data are available on the actual concentration of this additive. Leaks and spills are infrequent occurrences and are of no real significance to the total waste production. Plant 13102 indicates that only one minor leak of approximate 38 l/day (10 gal/day) of crankcase oil occurred within one full year of operation.

#### Wastewater Characteristics

Table 16 gives a summary of the raw waste characteristics of a compressor-condensate stream. Since adequate raw data

Figure 34. FLOW DIAGRAM SHOWING GENERALIZED WASTEWATER FLOWS IN PRODUCTION OF NITROGEN AND OXYGEN



**TABLE 16. CHEMICAL COMPOSITION OF WASTE LOADING FOR UNTREATED COMPRESSOR-CONDENSATE STREAM FROM PRODUCTION OF NITROGEN AND OXYGEN (PLANT 13101)**

PARAMETER	CONCENTRATION (ppm)*	WASTE LOAD	
		kg/1000 metric tons	lb/1000 short tons
pH	6.4 <sup>†</sup>	—	—
TDS	560	24	48
TSS	780	33	66
Oil and Grease	1,960	84	170
Cd	< 0.01	< 0.00043	< 0.00086
Cr (total)	0.85	0.036	0.072
Cu	0.48	0.020	0.041
Pb	< 0.02	< 0.00086	< 0.0017
Hg	< 0.0002	< 0.00001	< 0.00002
Zn	0.34	0.015	0.030

\* Analysis based on composite of four individual grab samples taken over 8-hour period.

<sup>†</sup> Value in pH units.

characterizing this process waste stream have not been readily available from the industry, particular emphasis is placed on the data given in this table, which represent actual waste water samples taken during a plant visit. The data reflect the composition of a compressor-condensate stream produced in an air-separation plant employing reciprocating compressors. The samples were taken under normal plant operating conditions.

Most data available from the industry characterize only the effluent stream of compressor condensate after it has passed through some oil removal system; frequently, the stream has been highly diluted by its combination with large volumes of noncontact cooling water prior to discharge. Since the condensate stream itself is of particular interest, because it contacts the process, the combined effluent data have limited value in the waste characterization of this individual stream.

#### PROCESS-WASTE CHARACTERIZATION FOR POTASSIUM DICHROMATE SUBCATEGORY

##### General

At present, a single plant (Plant 19901) is known to manufacture potassium dichromate. Water use and waste water sources at this plant are described in this section. However, it must be noted that this plant does not presently discharge process-related waste water to a POTW.

##### Process Description and Water Use

Potassium dichromate is prepared by reaction of potassium chloride with sodium dichromate. Potassium chloride is added to the dichromate solution, which is then pH-adjusted, saturated, filtered, and vacuum-cooled to precipitate crystalline potassium dichromate. The product is recovered by centrifugation, dried, sized, and packaged. The mother liquor from the product centrifuge is then concentrated to precipitate sodium chloride, which is removed as a solid waste from a salt centrifuge. The process liquid is recycled back to the initial reaction tank.

Water is used directly in the production process as the medium in which the raw materials are mixed and reacted. Water is also used for noncontact cooling in the vacuum-crystallization step of the process. (See Figure 15.)

##### Sources of Wastewater

All water used directly in the process at Plant 19901 is either consumed by evaporation or recycled. Water used for noncontact cooling during the vacuum-crystallization step is discharged. In the past, the use of barometric condensers as the cooling apparatus allowed contamination of the cooling water by chromium from the process. As a result, cooling water discharges from Plant 19901 have contained as much as 249 mg/l of chromium. However, completion of recent pollution-control projects, including the replacement of the barometric condensers with heat exchangers to provide only noncontact cooling, have reportedly eliminated the contamination of cooling water.

Solid wastes generated by this process include the crystalline sodium chloride and filter aids. These are hauled away for landfill disposal by a contractor.

#### Wastewater Characteristics

No waste water is discharged directly from the process at Plant 19901. Approximately 245 cubic meters (65,000 gallons) of water are added daily as makeup to the process, and this is subsequently consumed by evaporation in the process. The volume of cooling water used daily is 1,325 cubic meters (350,000 gallons).

#### PROCESS-WASTE CHARACTERIZATION FOR POTASSIUM IODIDE SUBCATEGORY

##### General

The character of waste water generated in this industry subcategory is determined largely by the source of the discharge and the use made of this water prior to discharge. The characteristics of the raw wastewater and the volume of discharge are significant factors to the extent that they effectively determine both the treatment alternatives available and the cost of treatment. Water usage, the source and character of the waste waters generated, and the volumes of waste water generated-typical for this industry subcategory-are identified and discussed below.

##### Process Description and Water Use

Plant 20102, which is located on the East Coast, produces an average of 57 metric tons (63 short tons) of potassium iodide per annum. The manufacturing process employed has been schematically presented in Figure 16 and is known as the iron carbonate process. This process involves the reaction of iron powder with iodine in aqueous solution. An intermediate compound, ferrosferriiodide, is formed which



is subsequently reacted with potassium carbonate to yield potassium iodide. Small amounts of barium hydroxide and potassium sulfide are added to precipitate any trace sulfate or heavy-metal impurities present. Following this purification step, the potassium iodide solution is concentrated by evaporation and cooled to effect crystallization. The crystals are separated by centrifugation, dried, sifted, and packaged. Residual mother liquor collected during centrifugation is recycled to the evaporator.

As indicated in Figure 16, water used directly in the process provides the necessary medium in which the production reaction is effected. As discussed in Section III, the purification steps, if any, of a process are also necessarily carried out in an aqueous medium. A second process related use of water is for noncontact cooling during the crystallization step. Three of the four plants which presently manufacture potassium iodide use water in this capacity. Another use of water is as boiler feed water. Finally, at all plants in this industry, a small quantity of water is used for equipment and production area washdown and cleanup of spills.

#### Sources of Wastewater

At each of the four plants engaged in the manufacture of potassium iodide, water used directly in the process is not discharged; rather, it is lost from the process by evaporation. This loss is purposely initiated during the fusing and evaporation steps of the iodine/potassium hydroxide and iron carbonate processes, respectively. At three of the plants, solid-waste slurries and purification sludges from the process are handled as such and are either removed by a commercial solid-waste contractor or sent to a land fill. At the remaining plant, the purification sludges and process-associated waste water are discharged without treatment to a POTW.

The primary source of process waste water in this industry is that water which is used for equipment and production-area washdown and cleanup of product or reagent spills. Water used for noncontact cooling is also discharged. However, with the exception of temperature, the character of this water remains essentially unchanged while it is being used.

#### Wastewater Characteristics

Substances which can be expected to occur at elevated concentration in the waste water are the raw materials and

products associated with the production process. These materials and products are total suspended solids, total dissolved solids, barium, iron, sulfide, potassium iodide, potassium iodate and iodine.

The volumes of waste water discharged vary from plant to plant. Wastewater resulting from equipment washdowns and cleanup of spills averages 0.15 to 1.14 cubic meters (39 to 300 gallons) daily. Water used for noncontact cooling averages 5.90 to 32.6 cubic meters (1,560 to 8,600 gallons) daily. Water is not used for cooling purposes at one plant in this industry. One of the three plants which does use water for cooling recycles 100% of this water.

<u>PROCESS-WASTE</u>	<u>CHARACTERIZATION</u>	<u>FOR</u>	<u>SILVER</u>	<u>NITRATE</u>
<u>SUBCATEGORY</u>				

General

There are three significant plants known to be producing silver nitrate in the U.S. None of these plants discharge process waste water to a POTW. However, it is anticipated that a silver nitrate producer discharging to a POTW would be similar in nature to a silver nitrate producer with a direct discharge.

Processes employed in silver nitrate production are basic to the entire industry. It is unlikely that an indirect discharger would implement a radically new process. Of course, water use will vary from plant to plant. However, the economics achieved by recycling and recovering silver-bearing wastes provide a great impetus to reduce waste water generation. This impetus is present irrespective of the mode of discharge. In light of the above, information on silver nitrate producers discharging process waste water directly to surface waters is next used to describe that portion of the silver nitrate subcategory discharging to POTWs.

Process Description and Water Use

At Plant 20201, pure silver is dissolved in distilled nitric acid, and the resulting solution is fed to a steam-heated evaporator. The NO<sub>x</sub> gases from the dissolver are mixed with air and recycled evaporator condensate and converted to nitrogen dioxide, which is used to remake nitric acid for the process. The tail gases from the nitric acid recovery unit are scrubbed with a caustic solution prior to venting to the atmosphere. The concentrated mother liquor from the evaporator is sent to a crystallizer, and the crystals formed are centrifuged and washed with demineralized water.

The mother liquor and wash water from the centrifuge are recycled to the evaporator after treatment to remove heavy-metal impurities. The silver nitrate crystals from the centrifuge are redissolved in low-pressure steam, recrystallized, recentrifuged, rewashed, dried, and packaged. The mother liquor from the second crystallizer is sent to another steam-heated evaporator for concentration and recycled to both crystallizers. Simplified process chemical reactions are:



The process at Plant 20201 is shown in Figure 35.

The process used at Plant 20202 is the same as that described above with the exception that extensive use is made of stream recycling, as can be seen from the diagram in Figure 36.

Water use at Plant 20201 includes:

- (1) Centrifuge wash water
- (2) Water for redissolution of crystals
- (3) Caustic-scrubber solution of  $\text{NO}_x$  emissions control
- (4) Floor and equipment washings
- (5) Noncontact cooling water is used in the nitric acid recovery unit, the crystallizers, and the evaporators.

Water use at Plant 20202 is similar to that at Plant 20201. However, Plant 20202 uses clean water in its nitric acid recovery unit rather than recycled evaporator condensate.

#### Sources of Wastewater

Evaporator Condensate. A waste condensate is generated from the barometric condensers used in the manufacture of supersaturated solutions for the crystallizers. At Plant 20201, part of the condensate from the second evaporation step are recycled to the nitric acid recovery unit. The remaining condensate, about 1.5 cubic meters (400 gallons) each day, is combined with the emissions-control scrubber water, 0.38 cubic meter (100 gallons) daily, and directed to the silver-recovery process.

Centrifuge Wash Water. Wastewater generated during centrifugation of crystals is directed to the chemical-purification unit for metal removal.

Figure 35. FLOW DIAGRAM FOR PRODUCTION OF SILVER NITRATE  
(PLANT 20201)

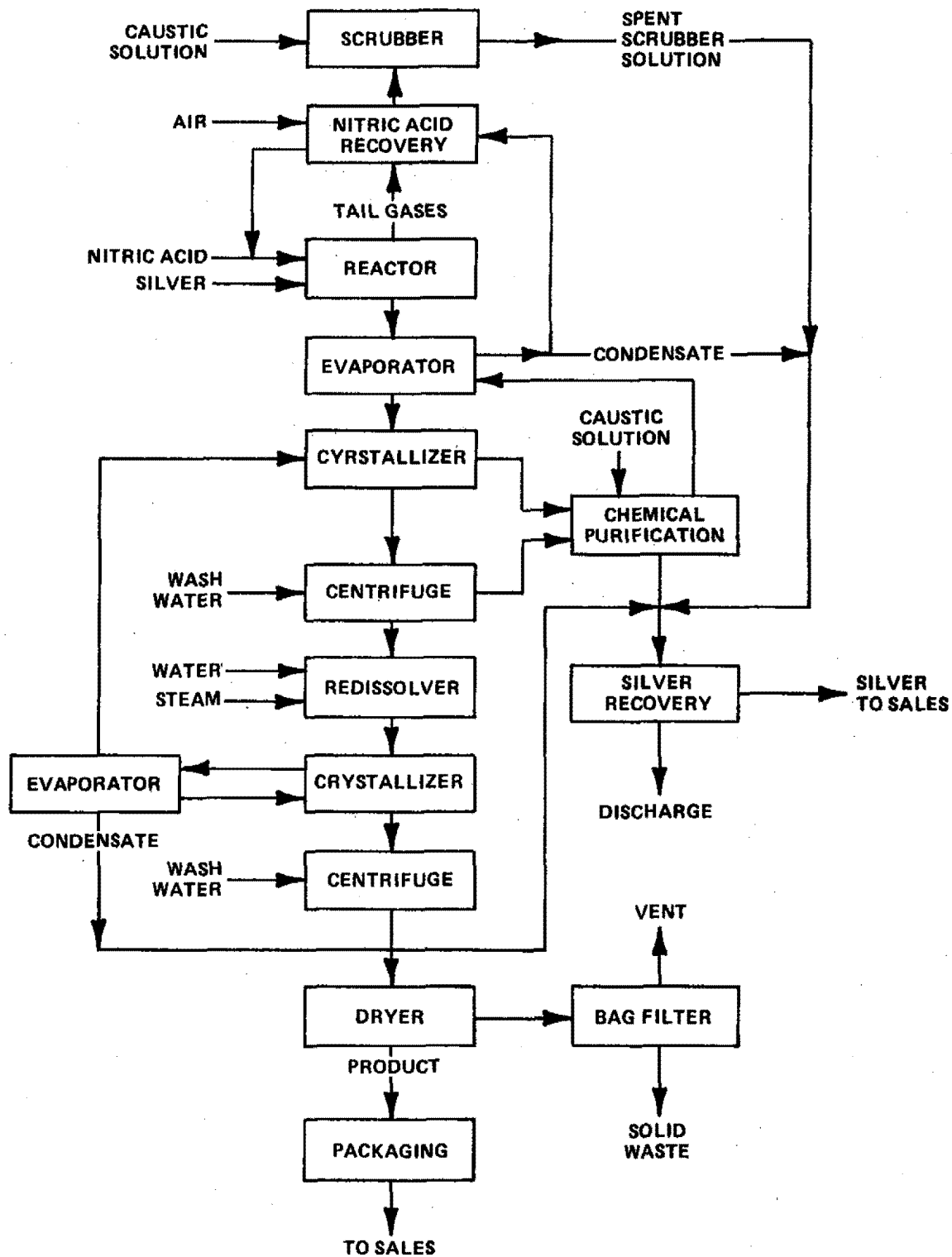
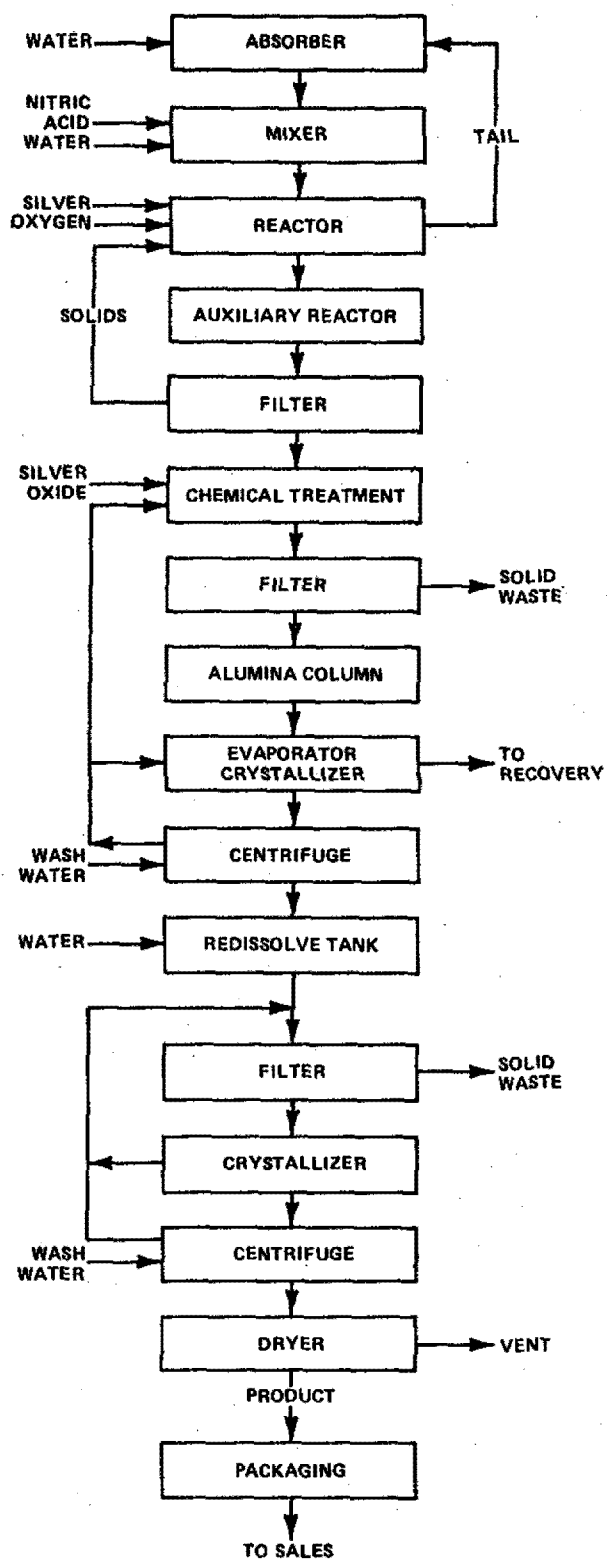


Figure 36. FLOW DIAGRAM FOR PRODUCTION OF SILVER NITRATE (PLANT 20202)



SOURCE: REFERENCE 5

Chemical-Purification Wastewater. Solution from the initial crystallization step is treated with sodium hydroxide to remove metals. The resultant waste stream is sent to the silver-recovery process at both plants.

Floor and Equipment Washings. At Plant 20201, equipment and work areas are periodically washed with 2.6 cubic meters (700 gallons) of water each day. This wash water is directed to the silver-recovery process.

Nox Emissions-Control Scrubber Water. A caustic solution is used to remove NO<sub>x</sub> emissions from the nitric acid recovery unit at Plant 20201. The scrubber waste water is directed to a separate part of the plant for silver recovery. The gaseous NO<sub>x</sub> products from the reactor in Plant 20202 are entirely reconverted to nitric acid, which is recycled. This eliminates the need for a gas scrubber and the resultant nitrate-bearing scrubber wastes.

Silver-Recovery Wastewater. The emissions-control scrubber water, evaporator condensate, chemical-purification waste water, and washdowns are sent to the silver-recovery process, where 99+% of the silver is removed. The remaining waste water is discharged to the industrial treatment system.

#### Wastewater Characteristics

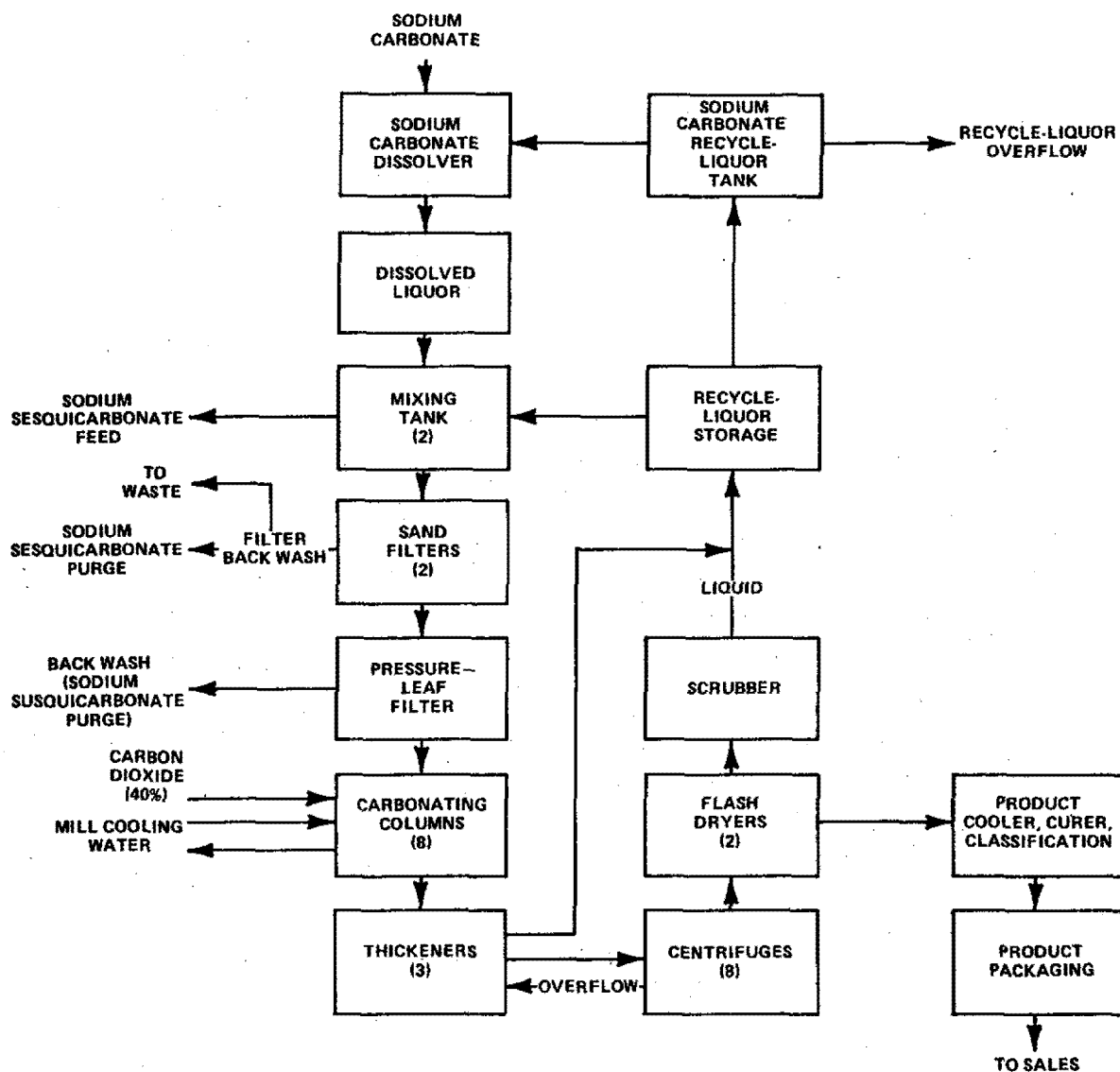
The waste water associated with silver nitrate production may contain as much as 5 mg/l silver, after processing at the silver-recovery plant. Because waste water streams from many production operations are combined, the presence and levels of trace metals in silver nitrate process waste water are unknown. However, the use of relatively pure raw material and the active removal of metallic impurities within the process prevent the introduction of significant quantities of metallic pollutants in the waste water.

#### PROCESS-WASTE CHARACTERIZATION FOR SODIUM BICARBONATE SUBCATEGORY

##### Process Description and Water Use

Sodium bicarbonate is manufactured by the carbonation of a sodium carbonate solution. Plants 12101 and 12102 are located within complexes manufacturing soda ash (sodium carbonate) by the Solvay process. Figure 37 illustrates the Solvay sodium bicarbonate process. There is one facility, Plant 12103, which uses mined soda ash as a raw material.

Figure 37. FLOW DIAGRAM OF SOLVAY PROCESS FOR PRODUCTION OF SODIUM BICARBONATE (PLANT 12101)



Water usage data for Plant 12101 are shown below. Most of the water is used for noncontact cooling purposes.

TYPE OF WATER	<u>m3/day (mgd)</u>	<u>l/metric ton (gal/short ton)</u>	RECYCLED
Cooling	1,430 (0.378)	5,430 (1,300)	None
Process	119 (0.031)	455 (109)	Variable

Process water includes dissolution water used in the reaction, scrubber water from drier emissions control, filter-backwash water, and miscellaneous washdown waters. A process flow diagram indicating water use at Plant 12101 is given as Figure 37.

#### Sources of Wastewater

The sources of waste water at Plant 12101 are:

- Recycle liquor
- Filter backwash
- Noncontact cooling water
- Spills, leaks, and washdowns
- Compressor blowdown

These operations are also expected to be the primary sources of wastewater at other sodium bicarbonate plants, since standard manufacturing processes are employed.

#### Wastewater Characteristics

Recycle-Liquor Overflow. Slurry thickener overflow and dryer emissions control scrubber water are combined and directed to a recycle-liquor storage tank. Under normal flow conditions, this recycle liquor is returned to the soda ash dissolver to be reused in the process. Excess recycle liquor is directed to other manufacturing processes within the plant complex. Occasionally, the amount of recycle liquor generated exceeds the requirements of both the soda ash dissolver operation and the other miscellaneous plant operations utilizing this byproduct. Under these conditions, a recycle-liquor overflow is generated which is discharged to the plant complex treatment system.

On a yearly basis, this waste water flow averages 75.7 cubic meters (20,000 gallons) each day.

The major wastes produced from the manufacture of sodium bicarbonate result from this operation. Recycle-liquor overflow contains about 10 kg (22 lb) of undissolved sodium



bicarbonate per metric ton (1.1 short tons) of product and an average of about 38 kg (84 lb) of dissolved sodium carbonate per metric ton (1.1 short tons) of product. The chemical character of recycle-liquor overflow is shown in Table 17.

Filter Backwash. Sand and/or pressure-leaf filters may be used in the sodium bicarbonate manufacturing process to purify the dissolved soda ash input to the carbonating columns. Plant 12101 uses both sand and pressure-leaf filters in series to remove suspended solids from the dissolved soda ash liquor prior to carbonation. It is necessary to periodically backwash these filters to prevent clogging of the filters, with resulting head loss and slow filtration rates.

The volume of filter backwash is highly variable but is typically only 2 to 5% of the plant throughput (Reference 9). The chemical characteristics of filter backwash are also highly variable. Sufficient data were not available to characterize this process waste water, but filter backwash is by nature expected to contain high levels of suspended solids. Dissolved solids may also be present in significant quantities, depending upon the extent that dissolved soda ash liquor, which is high in dissolved solids, is retained in the filter cake, and on the initial dissolved-solids concentration of the filter-backwash water.

Noncontact Cooling Water. Noncontact cooling water is employed in the manufacture of sodium bicarbonate to maintain a temperature of about 40°C (104°F) in the carbonation columns. There are no chemical data available relative to noncontact cooling water. However, it may be assumed that its composition is at least compatible with POTW operation, because the source of noncontact cooling water is a lake, and this water has no direct contact with the product.

Leaks, Spills, and Washdown Waterwater. Wastewater emanating from leaks, spills, and facility washdowns (i.e., hosing, mopping, etc.) may contain high levels of sodium bicarbonate product as suspended solids and would, therefore, merit consideration as process waste waters. However, large leaks and spills are not common to the industry, for two reasons. First, the materials used in the process are neither highly acidic or highly basic, and corrosion of pipes, fittings, and other hardware is not a problem. Secondly, a large portion of sodium bicarbonate production is food-grade product, and good housekeeping procedures for such facilities are a must.

**TABLE 17. ESTIMATED CHEMICAL CHARACTERISTICS OF UNTREATED SLURRY THICKENER OVERFLOW FROM PRODUCTION OF SODIUM BICARBONATE (PLANT 12101)**

PARAMETER	CONCENTRATION (mg/l)*
pH	7.6 to 8.2 <sup>†</sup>
TDS	136,800
TSS	36,000

\*Calculated from waste loadings and wastewater flow data.

<sup>†</sup>Value in pH units.

Compressor Blowdown. Compressors may be used in the manufacture of sodium bicarbonate to inject carbon dioxide into the bottom of the carbonating columns. Compressed carbon dioxide is a raw material in the sodium bicarbonate manufacturing process, and, since compressor condensate directly contacts this raw material, it may be considered a process waste water. Carbon dioxide may be purchased for use in this process, thus eliminating the source of this waste water.

Chemical characteristics of compressor blowdown are extremely variable, being dependant upon the water-vapor content of the carbon dioxide gas and on compressor design and age. Pollutants from this source are carbon dioxide and oil and grease.

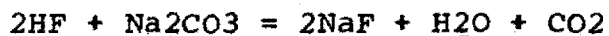
PROCESS-WASTE CHARACTERIZATION FOR SODIUM FLUORIDE  
SUBCATEGORY

Process Description and Water Use

Sodium fluoride is produced from three different processes:

- (1) Reaction of soda ash (sodium carbonate) with hydrofluoric acid.
- (2) Reaction of caustic soda (sodium hydroxide) with sodium silico-fluoride.
- (3) Reaction of caustic soda with hydrofluoric acid.

In the first process listed, anhydrous hydrofluoric acid (hydrogen fluoride) and soda ash are reacted, and hydrogen fluoride fumes and carbon dioxide are scrubbed with a soda ash solution. The product from the reactor is a slurry of sodium fluoride, which is vacuum-filtered to recover the fluoride. The product is then dried and packaged. The overall process reaction is:



Plant 20301 employs this process, with no resulting discharge of process waste water. A process diagram detailing water use at Plant 20301 is presented in Figure 38. Total water consumption at Plant 20301 averages 2,300 liters of municipal water per metric ton (550 gallons per short ton) of sodium fluoride product. This is used primarily for boiler feed, with a small amount used as makeup water in the scrubber.

The second process is used at Plant 20302 and is illustrated in Figure 39. At Plant 20302, sodium silicofluoride is reacted with a solution of caustic soda and water in a batch

Figure 38. FLOW DIAGRAM FOR PRODUCTION OF SODIUM FLUORIDE  
(PLANT 20301)

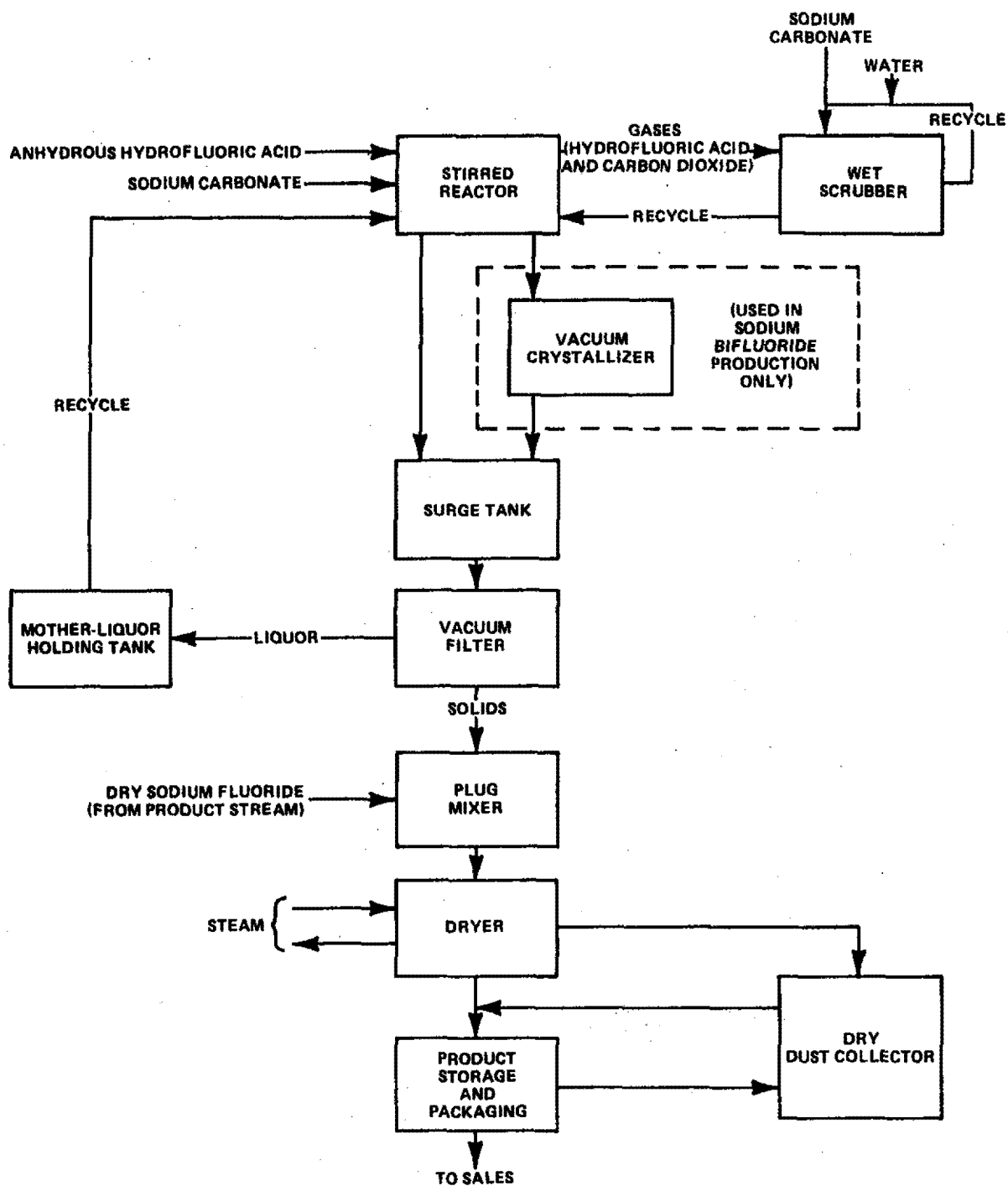
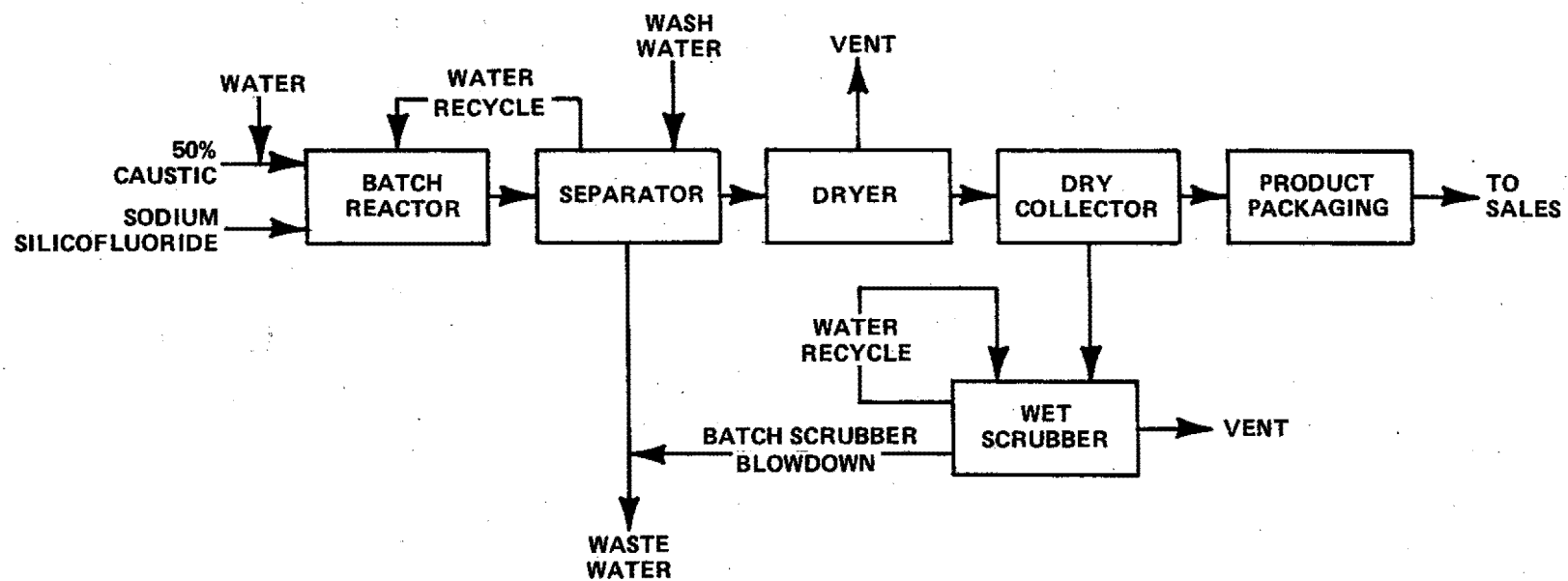


Figure 39. FLOW DIAGRAM FOR PRODUCTION OF SODIUM FLUORIDE (PLANT 20302)



SOURCE: REFERENCE 5

reactor. The product, a mixture of sodium fluoride, sodium silicate, and water, is sent to a multi-stage separator, where the sodium fluoride is separated from the soluble sodium silicate. The sodium fluoride product is washed, dried, and collected in a dry cyclone for packaging. The wash water from the separator is recycled to the reactor. Soluble sodium silicate and sodium fluoride in an alkaline solution constitutes the byproduct waste stream from this process. A recycle wet scrubber, used to remove sodium fluoride dusts from the vent on the dry collector, is blown down to the silicate waste effluent. The reaction for the process is:



Total water consumption at Plant 20302 averages 3,860 liters per metric ton (925 gallons per short ton) of sodium fluoride product. This water is used for dilution of the caustic soda, washing the product, and wet scrubbing. No cooling water or steam is used in the process. In addition, the process reaction produces 217 liters of water per metric ton (52 gallons per short ton) of product. Untreated waste water data from the plant is shown in Table 18.

The third process is very similar in principle to the second process just discussed. Both processes involve a batch reaction in aqueous solution, producing a sodium fluoride precipitate which is separated from solution, dried, and packaged for sale. The fundamental difference between the two processes is in the separation operation. The second process utilizes a multiple-stage separator to selectively remove sodium fluoride from the solution, which also contains sodium silicate. This third process employs a less-complex separation using a settling tank, since the reaction precipitate does not contain a substantial amount of impurities. The reaction for the process is:



Plant 20303 employs this process, with the resulting waste water produced discharged directly. Figure 40 illustrates the sodium fluoride manufacturing process and water uses at Plant 20303.

Total water consumption at Plant 20303 averages 23,485 liters per metric ton (5,640 gallons per short ton) of sodium fluoride product. This water is used for dilution of the caustic soda, for washdown, and for noncontact cooling of the batch reactor. The process reaction produces 434 liters of water per metric ton (104 gallons per short ton) of sodium fluoride, but this water is not recycled and,

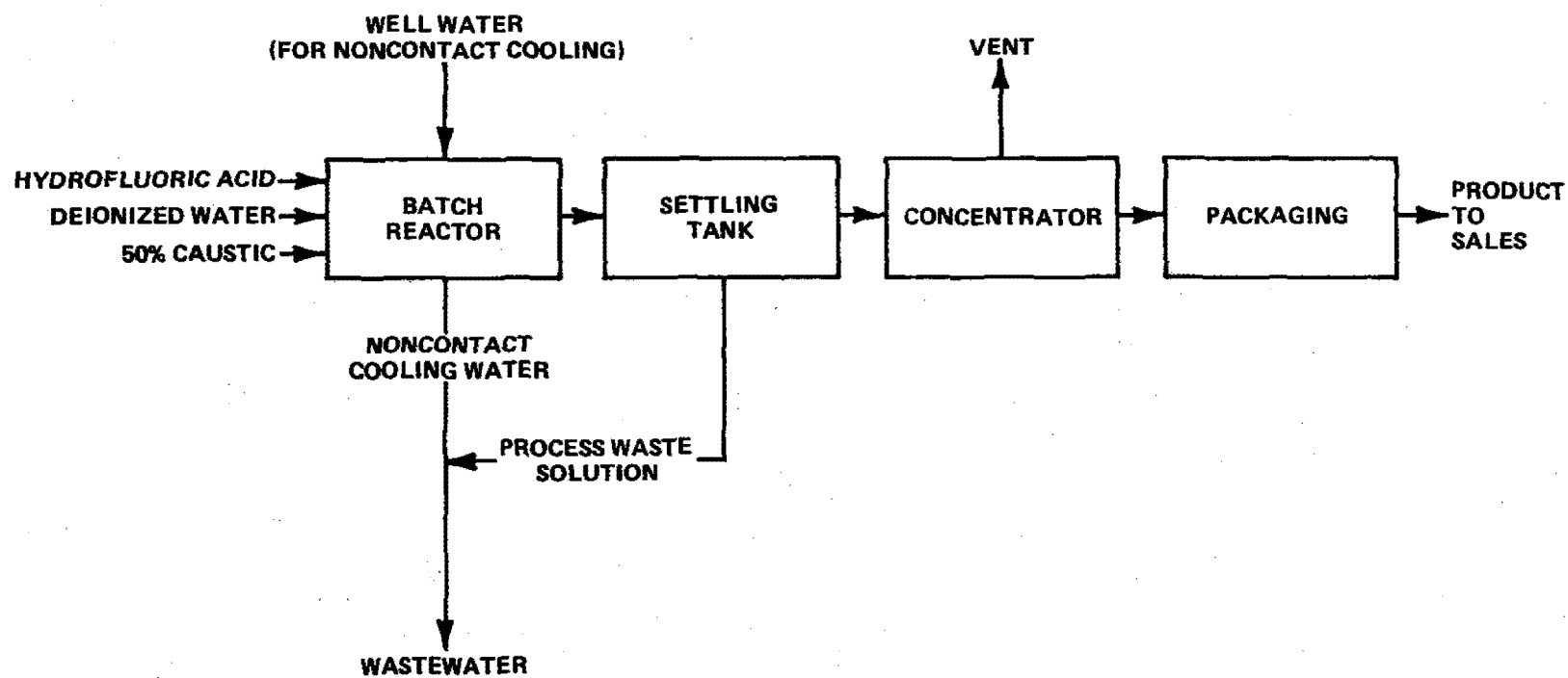
**TABLE 18. CHEMICAL COMPOSITION OF UNTREATED WASTEWATER FROM PRODUCTION OF SODIUM FLUORIDE (PLANT 20302)**

PARAMETER	CONCENTRATION (mg/l)*
pH	> 12**
TDS	165,000
TSS	2,500
Fluoride	16,000

\*Company monitoring data (Sample collected 28 November 1973).

\*\*Value in pH units.

Figure 40. FLOW DIAGRAM FOR PRODUCTION OF SODIUM FLUORIDE (PLANT 20303)





therefore, has no effect on the consumption of water at Plant 20303. Table 19 compares water use at this plant to those of plants using other sodium fluoride manufacturing processes.

#### Sources of Wastewater

Process waste water generated during sodium fluoride production at Plant 20301 consists of filtrate mother liquors, washdown waters, and wetscrubber water. All of these wastes are recycled, resulting in no discharge of process waste water from this plant.

Process wastes at Plant 20302 consist of separated silicate liquors containing soluble sodium fluoride, wet-scrubber blowdown, product wash water, and product dusts from the packaging operation. The product dusts and product wash water are recycled to the reactor. The other wastes amount to 1,995 liters per metric ton (478 gallons per short ton) of sodium fluoride product and are combined with wastes from other parts of the complex.

Sources of process waste water flows at Plant 20303 include direct process contact water and washdowns. Direct process contact water is from settling-tank overflow and amounts to 1,780 liters per metric ton (427 gallons per short ton) of sodium fluoride produced on an average daily basis. Washdown contributes ten times this amount, or 17,800 liters per metric ton (4,270 gallons per short ton), to the total process waste water effluent of 19,580 liters per metric ton (4,700 gallons per short ton) of sodium fluoride product. This waste water is combined with the waste effluents from the production of numerous other chemicals and discharged to a central treatment facility, where the wastes are processed prior to final discharge to a surface receiving stream.

#### Wastewater Characteristics

Chemical characteristics of untreated sodium fluoride process waste water at Plant 20302 are presented in Table 18. This waste water is characterized by high concentrations of pH, TSS, TDS, and fluoride. The pH can be attributed to the use of concentrated caustic soda as a raw material for the process. Suspended solids present in the waste water are most likely silicates, wasted from the separator, and sodium fluoride particles from scrubber blowdown. The excessively high dissolved-solids content of the process waste water is due to high concentrations of sodium ions and fluoride ions in the separator waste water. Fluorides in the process effluent are present in dissolved and suspended form. Both the scrubber blowdown and

**TABLE 19. WATER CONSUMPTION OF PROCESSES FOR PRODUCTION OF  
SODIUM FLUORIDE (THREE PLANTS)**

WATER-USING OPERATION	WATER CONSUMPTION					
	PLANT 20301		PLANT 20302		PLANT 20303	
	l/metric ton	gal/short ton	l/metric ton	gal/short ton	l/metric ton	gal/short ton
Boiler Feed	2,300	551.3	—	—	—	—
Noncontact Cooling	—	—	—	—	12,593	3,018.5
Evaporation	—	—	618	148.1	—	—
Wet Scrubber	—	—	476	114.1	—	—
Process Waste	—	—	2,984	715.3	681	163.2
Reaction Product*	—	—	-217	52.0	—	—
Washdown	—	—	—	—	10,211	2,447.6
<b>Total Water Consumption</b>	<b>2,300</b>	<b>551.3</b>	<b>3,861</b>	<b>925.5</b>	<b>23,485</b>	<b>5,629.4</b>

\*Water produced from chemical reaction. This is a water source and has a negative effect on water consumption if recycled to the process.

separator wastes contribute to the high fluoride content of process waste water from Plant 20302.

Chemical characteristics of untreated sodium fluoride process wastewaters at Plant 20303 are not available, due to combination of these wastes with those of numerous other chemical processes.

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## SECTION VI

### SELECTION OF POLLUTANT PARAMETERS

#### INTRODUCTION

During the course of the investigation preceding development of the pretreatment standards, a wide range of potential pollutant parameters was identified. The identification of potential pollutant parameters for each subcategory covered in this study was based on: (1) the presence of a particular pollutant in the raw source material; (2) chemicals used in processing the desired chemical; (3) the presence of the pollutant in the untreated waste water from a subcategory; and (4) the availability of pretreatment control technology to remove the pollutant. The potential pollutant parameters were then divided into (a) those parameters selected as pollutants of significance (with the rationale for their selection) and (b) those that are not deemed significant (with the rationale for their rejection).

#### GUIDELINE PARAMETER-SELECTION CRITERIA

The final selection of parameters for use in developing pretreatment standards was based primarily on the following criteria:

- (1) Constituents which are frequently present in inorganic chemical plant discharges in concentrations deleterious to human, animal, fish and aquatic organisms, and which pass through or are removed in only small quantities at a POTW.
- (2) Constituents which have a toxic effect on the microbial population of a POTW, thus decreasing or completely halting the treatment capabilities of the POTW.
- (3) Constituents which tend to clog, corrode, or in some way harm the POTW's equipment and facilities.
- (4) The existence of technology for the reduction or removal, at an economically practicable cost, of the pollutants in question.

## SIGNIFICANCE AND RATIONALE FOR SELECTION OF POLLUTANT PARAMETERS

### Acidity and Alkalinity--pH

Although not a specific pollutant, pH is related to the acidity or alkalinity of a waste water stream. It is not a linear or direct measure of either; however, it may properly be used as a surrogate for monitoring to control both excess acidity and excess alkalinity in water. The term pH is used to describe the hydrogen-ion/hydroxyl-ion balance in water.

Technically, pH is the hydrogen-ion concentration or activity present in a given solution. pH numbers are the negative logarithms of the hydrogen ion concentration. A pH of 7 indicates neutrality or a balance between free hydrogen and free hydroxyl ions. Solutions with a pH above 7 are alkaline, while a pH below 7 indicates that the solution is acid.

Knowledge of the pH of water or waste water is useful in determining necessary measures for corrosion control, pollution control, and disinfection. Waters with a pH below 6.0 are corrosive to waterworks structures, distribution lines, and household plumbing fixtures, and such corrosion can add such constituents to drinking water as iron, copper, zinc, cadmium, and lead. Low-pH waters tend not only to dissolve metals from structures and fixtures but also to redissolve or leach metals from sludges and bottom sediments. The hydrogen-ion concentration can affect the "taste" of the water; at a low pH, water tastes "sour."

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. For example, metallocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. Similarly, the toxicity of ammonia is a function of pH. The bactericidal effect of chlorine, in most cases, is less as the pH increases, and it is economically advantageous to keep the pH close to 7.

### Total Suspended Solids (TSS)

Suspended solids include both organic and inorganic materials. The inorganic compounds include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, and animal and vegetable waste products. These solids may settle out rapidly, and bottom deposits are

often a mixture of both organic and inorganic solids. Solids may be suspended in water for a time and then settle to the bed of the stream or lake. These solids, discharged with man's wastes, may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration, and impair the photosynthetic activity of aquatic plants.

Suspended solids in water interfere with many industrial processes and cause foaming in boilers and incrustations on equipment exposed to such water--especially, as the temperature rises. They are undesirable in process water used in the manufacture of steel, in the textile industry, in laundries, in dyeing, and in cooling systems.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often damaging to life in the water. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a food source for sludgeworms and associated organisms.

Disregarding any toxic effect attributable to substances leached out by water, suspended solids may kill fish and shellfish by causing abrasive injuries and by clogging the gills and respiratory passages of various aquatic fauna. Indirectly, suspended solids are inimical to aquatic life, because they screen out light, and they promote and maintain the development of noxious conditions through oxygen depletion. This results in the killing of fish and fish food organisms. Suspended solids also reduce the recreational value of the water.

Floor and equipment washings, filter-backwash water, emissions-control scrubber water, centrifuge washwater, and leaks and spills may have high total-suspended-solids levels.

### Oil and Grease

Because of widespread use, oil and grease occur often in waste water streams. These oily wastes may be classified as follows:

- (1) Light Hydrocarbons--These include light fuels, such as gasoline, kerosene, and jet fuel, and miscellaneous solvents used for industrial processing, degreasing, or cleaning purposes. The presence of these light hydrocarbons may make the removal of other, heavier oily wastes more difficult.
- (2) Heavy Hydrocarbons, Fuels, and Tars--These include the crude oils, diesel oils, #6 fuel oil, residual oils, slop oils, and (in some cases) asphalt and road tar.
- (3) Lubricants and Cutting Fluids--These generally fall into two classes: non-emulsifiable oils (such as lubricating oils and greases) and emulsifiable oils (such as watersoluble oils, rolling oils, cutting oils, and drawing compounds). Emulsifiable oils may contain fat, soap, or various other additives.
- (4) Vegetable and Animal Fats and Oils--These originate primarily from processing of foods and natural products.

These compounds can settle or float and may exist as solids or liquids, depending upon factors such as method of use, production process, and temperature of waste water.

Oil and grease, even in small quantities, cause troublesome taste and odor problems. Scum lines from these agents are produced on water treatment-basin walls and other containers. Fish and water fowl are adversely affected by oils in their habitat. Oil emulsions may adhere to the gills of fish, causing suffocation, and the flesh of fish is tainted when microorganisms that were exposed to waste oils are eaten. Deposition of oil in the bottom sediments of water can serve to inhibit normal benthic growth. Oil and grease exhibit an oxygen demand.

Levels of oil and grease which are toxic to aquatic organisms vary greatly, depending on the type and the species susceptibility. However, it has been reported that crude oil in concentrations as low as 0.3 mg/l is extremely toxic to freshwater fish. It has been recommended that public water-supply sources be essentially free from oil and grease.

Oil and grease in quantities of 100 l/sq km (10 gal/sq mile) show up as a sheen on the surface of a body of water. The presence of oil slicks prevents the full aesthetic enjoyment of water. The presence of oil in water can also increase



the toxicity of other substances being discharged into the receiving bodies of water. Municipalities frequently limit the quantities of oil and grease that can be discharged to their waste watertreatment system by industry.

### Aluminum (Al)

Aluminum is an abundant metal found in the earth's crust (8.1%), but it is never found free in nature. Pure aluminum, a silvery white metal, possesses many desirable characteristics. It is light; has a pleasing appearance; can easily be formed, machined, or cast; has a high thermal conductivity; is nonmagnetic and nonsparking; and stands second among metals in the scale of malleability and sixth in ductility.

Although the metal itself is insoluble, some of its salts are readily soluble. Other aluminum salts are quite insoluble, however; consequently, aluminum is not likely to occur for long in surface water, because it precipitates and settles or is absorbed as aluminum hydroxide and aluminum carbonate. Aluminum is also nontoxic, and its salts are used as coagulants in water treatment. Aluminum is commonly used in cooking utensils, and there is no known physiological effect on man from low concentrations of this metal in drinking waters.

### Chromium

Chromium is an elemental metal, usually found as a chromite ( $\text{FeCr}_2\text{O}_4$ ). The metal is normally processed by reducing the oxide with aluminum.

Chromium and its compounds are used extensively throughout industry. The metal is used to harden steel and as an ingredient in other useful alloys. Chromium is also used in the electroplating industry as an ornamental and corrosion-resistant plating on steel and can be used in pigments and as a pickling acid (chromic acid).

The two most prevalent chromium forms found in industry waste waters are hexavalent and trivalent chromium. Chromic acid, used in industry, is a hexavalent chromium compound which is partially reduced to the trivalent form during use. Chromium can exist as either trivalent or hexavalent compounds in raw waste streams. Hexavalent chromium treatment involves reduction to the trivalent form prior to removal of chromium from the waste stream as a hydroxide precipitate.

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date. The recommendation for public drinking water supplies is that such supplies contain no more than 0.05 mg/l total chromium.

The toxicity of chromium salts to fish and other aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects--especially, those of hard water. Studies have shown that trivalent chromium is more toxic to fish of some types than hexavalent chromium. Other studies have shown opposite effects. Fish food organisms and other lower forms of aquatic life are extremely sensitive to chromium, and it also inhibits the growth of algae. Therefore, both hexavalent and trivalent chromium must be considered harmful to particular fish or organisms.

#### Copper (Cu)

Copper is an elemental metal that is sometimes found free in nature and is found in many minerals, such as cuprite, malachite, azurite, chalcopyrite, and bornite. Copper is obtained from these ores by smelting, leaching, and electrolysis. Significant industrial uses are in the plating, electrical, plumbing, and heating equipment industries. Copper is also commonly used with other minerals as an insecticide and fungicide.

Traces of copper are found in all forms of plant and animal life, and it is an essential trace element for nutrition. Copper is not considered to be a cumulative systemic poison for humans, as it is readily excreted by the body, but it can cause symptoms of gastroenteritis, with nausea and intestinal irritations, at relatively low dosages. The limiting factor in domestic water supplies is taste. Threshold concentrations for taste have been generally reported in the range of 1.0 to 2.0 mg/l of copper, while concentrations of 5 to 7.5 mg/l have made water completely undrinkable. It has been recommended that the copper in public water supply sources not exceed 1 mg/l.

Copper salts cause undesirable color reactions in the food industry and cause pitting when deposited on some other metals, such as aluminum and galvanized steel. The textile industry is affected when copper salts are present in water

used for processing of fabrics. Irrigation waters containing more than minute quantities of copper can be detrimental to certain crops. The toxicity of copper to aquatic organisms varies significantly, not only with the species, but also with the physical and chemical characteristics of the water, including temperature, hardness, turbidity, and carbon dioxide content. In hard water, the toxicity of copper salts may be reduced by the precipitation of copper carbonate or other insoluble compounds. The sulfates of copper and zinc, and of copper and cadmium, are synergistic in their toxic effect on fish.

Copper concentrations less than 1 mg/l have been reported to be toxic-particularly, in soft water--to many kinds of fish, crustaceans, mollusks, insects, phytoplankton, and zooplankton. Concentrations of copper, for example, are detrimental to some oysters above 0.1 ppm. Oysters cultured in sea water containing 0.13 to 0.5 ppm of copper deposit the metal in their bodies and become unfit as a food substance.

### Iron (Fe)

Iron is an abundant metal found in the earth's crust. The most common iron ore is hematite, from which iron is obtained by reduction with carbon. Other forms of commercial ores are magnetite and taconite. Pure iron is not often found in commercial use, but it is usually alloyed with other metals and elements, the most common being carbon.

Iron is the basic element in the production of steel and steel alloys. Iron with carbon is used for casting of major parts of machines, and it can be machined, cast, formed, and welded. Ferrous iron is used in paints, while powdered iron can be sintered and used in powder metallurgy. Iron compounds are also used to precipitate other metals and undesirable minerals from industrial waste water streams.

Iron is chemically reactive and corrodes rapidly in the presence of moist air and at elevated temperatures. In water and in the presence of oxygen, the resulting products of iron corrosion may be pollutants in water. Natural pollution occurs from the leaching of soluble iron salts from soil and rocks and is increased by industrial waste water from pickling baths and other solutions containing iron salts.

Corrosion products of iron in water cause staining of porcelain fixtures, and ferric iron combines with tannin to produce a dark violet color. The presence of excessive iron

in water discourages cows from drinking and, thus, reduces milk production. High concentrations of ferric and ferrous ions in water kill most fish introduced to the solution within a few hours. The killing action is attributed to coatings of iron hydroxide, precipitated on the gills. Iron-oxidizing bacteria are dependent on iron in water for growth. These bacteria form slimes that can affect the esthetic values of bodies of water and cause stoppage of flows in pipes.

Iron is an essential nutrient and micronutrient for all forms of growth. Drinking-water standards in the U.S. have set a recommended limit of 0.3 mg/l of iron in domestic water supplies, based not on physiological considerations, but rather on the aesthetic and taste considerations of iron in water.

### Lead (Pb)

Lead is used in various solid forms, both as a pure metal and in several compounds. Lead appears in some natural waters--especially, in those areas where mountain limestone and galena are found. Lead can also be introduced into water from lead pipes by the action of the water on the lead.

Lead is a toxic material that is foreign to humans and animals. The most common form of lead poisoning is called plumbism. Lead can be introduced into the body from atmospheres containing lead, or from food and water. Lead cannot be easily excreted and is cumulative in the body over long periods of time, eventually causing lead poisoning with the ingestion of an excess of 0.6 mg per day over a period of years. It has been recommended that 0.05 mg/l lead not be exceeded in public watersupply sources.

Chronic lead poisoning has occurred among animals at levels of 0.18 mg/l of lead in soft water and by concentrations under 2.4 mg/l in hard water. Farm animals are poisoned by lead more frequently than any other poison. Sources of this occurrence include paint and water, with the lead in solution as well as in suspension. Each year, thousands of wild water fowl are poisoned from lead shot that is discharged over feeding areas and ingested by the water fowl. The bacterial decomposition of organic matter is inhibited by lead at levels of 0.1 to 0.5 mg/l.

Fish and other marine life have had adverse effects from lead and salts in their environment. Experiments have shown that small concentrations of heavy metals, especially lead, have caused a film of coagulated mucus to form, first over

the gills and then over the entire body, probably causing suffocation of the fish due to this obstructive layer. Toxicity of lead is increased with a reduction of dissolved-oxygen concentration in the water.

### Nickel (Ni)

Elemental nickel seldom occurs in nature, but nickel compounds are found in many ores and minerals. As a pure metal, it is not a problem in water pollution, because it is not affected by, or soluble in, water. Many nickel salts, however, are highly soluble in water.

Nickel is extremely toxic to citrus plants. It is found in many soils in California--generally, in insoluble form--but excessive acidification of such soil may render its nickel soluble, causing severe injury to or the death of plants. Many experiments with plants in solution cultures have shown that nickel at 0.5 to 1.0 mg/l is inhibitory to growth.

Nickel salts can kill fish at very low concentrations. Data for the fathead minnow show death occurring in the range of 5 to 43 mg/l, depending on the alkalinity of the water.

Nickel is present in coastal and open ocean concentrations in the range of 0.1 to 6.0 micrograms per liter, although the most common values are 2 to 33 micrograms per liter. Marine animals contain up to 400 micrograms per liter, and marine plants contain up to 3,000 micrograms per liter. The lethal limit of nickel to some marine fish has been reported to be as low as 0.8 ppm (mg/l) (800 micrograms per liter). Concentrations of 13.1 mg/l have been reported to cause a 50-percent reduction of photosynthetic activity in the giant kelp (Macrocystis pyrifera) in 96 hours, and a low concentration has been found to kill oyster eggs.

### Silver (Ag)

Silver is a soft, lustrous, white metal that is insoluble in water and alkali. It is readily ionized by electrolysis and has a particular affinity for sulfur and halogen elements. In nature, silver is found in the elemental state and combined in ores such as argentite ( $\text{Ag}_2\text{S}$ ), cerargyrite ( $\text{AgCl}$ ), proustite ( $\text{Ag}_3\text{As}_3$ ), and pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ).

From these ores, silver ions may be leached into ground waters and surface waters; but, since many silver salts, such as the chloride, sulfide, phosphate, and arsenate, are insoluble, silver ions do not usually occur in significant concentration in natural waters.

Silver is used extensively in electroplating, photographic processing, electrical-equipment manufacture, soldering and brazing, and battery manufacture. Of these, the two major sources of soluble silver wastes are the photographic and electroplating industries, with about 30% of U.S. industrial consumption of silver going into the photographic industry. Silver is also used in its basic metal state for such items as jewelry and electrical contacts.

While metallic silver itself is not considered to be poisonous for humans, most of its salts are poisonous due to anions present. Silver compounds can be absorbed in the circulatory system, and reduced silver can be deposited in the various tissues of the body. A condition known as argyria, a permanent greyish pigmentation of the skin and mucous membranes, can result. Concentrations in the range of 0.4 to 1 mg/liter have caused pathologic changes in the kidneys, liver, and spleen of rats.

Silver is recognized as a bactericide, and doses as low as 0.000001 to 0.5 mg/l have been reported as sufficient to sterilize water.

#### Zinc (Zn)

Occurring abundantly in rocks and ores, zinc is readily refined into a stable pure metal and is used extensively as a metal, an alloy, and a plating material. In addition, zinc salts are also used in paint pigments, dyes, and insecticides. Many of these salts (for example, zinc chloride and zinc sulfate) are highly soluble in water; hence, it is expected that zinc might occur in many industrial wastes. On the other hand, some zinc salts (zinc carbonate, zinc oxide, zinc sulfide) are insoluble in water, and consequently, it is expected that some zinc will precipitate and be removed readily in many natural waters.

In soft water, concentrations of zinc ranging from 0.1 to 1.0 mg/l have been reported to be lethal to fish. Zinc is thought to exert its toxic action by forming insoluble compounds with the mucous that covers the gills, by damage to the gill epithelium, or possible by acting as an internal poison. The sensitivity of fish to zinc varies with species, age, and condition, as well as with the physical and chemical characteristics of the water. Some acclimatization to the presence of the zinc is possible. It has also been observed that the effects of zinc poisoning may not become apparent immediately, so that fish removed from zinc-contaminated to zinc-free water may die as long as 48 hours after the removal. The presence of copper in water may increase the toxicity of zinc to aquatic organisms,

while the presence of calcium or hardness may decrease the relative toxicity.

A complex relationship exists among zinc concentrations, dissolved oxygen, pH, temperature, and calcium and magnesium concentrations. Prediction of harmful effects has been less than reliable, and controlled studies have not been extensively documented.

Concentrations of zinc in excess of 5 mg/l in public water-supply sources cause an undesirable taste which persists through conventional treatment. Zinc can have an adverse effect on man and animals at high concentrations.

Observed values for the distribution of zinc in ocean waters vary widely. The major concern with zinc compounds in marine waters is not one of acute lethal effects, but rather one of the long-term sublethal effects of the metallic compounds and complexes. From the point of view of acute lethal effects, invertebrate marine animals seem to be the most sensitive organisms tested.

A variety of freshwater plants tested manifested harmful symptoms at concentrations of 10 mg/l. Zinc sulfate has also been found to be lethal to many plants, and it could impair agricultural uses of the water.

#### Fluoride and Fluorine (F)

Fluorine is the most reactive of the nonmetals and is never found free in nature. It is a constituent of fluorite or fluorspar (calcium fluoride) and cryolite (sodium aluminum fluoride). Due to their origins, fluorides in high concentrations are not common constituents of natural surface waters; however, they may occur in hazardous concentrations in ground waters.

Fluoride can be found in plating rinses and in glass-etching rinse waters. Fluorides are also used as a flux in the manufacture of steel, for preserving wood and mucilages, as a disinfectant, and in insecticides.

Fluorides in sufficient quantities are toxic to humans, with doses of 250 to 450 mg giving severe symptoms and 4.0 grams causing death. A concentration of 0.5 g/kg of body weight has been reported as a fatal dosage.

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause

mottled enamel in children; for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay--especially, among children. The recommended maximum levels of fluoride in public water-supply sources range from 1.4 to 2.4 mg/l.

Fluorides may be harmful in certain industries--particularly, those involved in the production of food, beverages, pharmaceuticals, and medicines. Fluorides found in irrigation waters in high concentrations (up to 360 mg/l) have caused damage to certain plants exposed to these waters. Chronic fluoride poisoning of livestock has been observed in areas where water contained 10 to 15 mg/l fluoride. Concentrations of 30 to 50 mg/l of fluoride in the total ration of dairy cows is considered the upper safe limit. Fluoride from waters apparently does not accumulate in soft tissue to a significant degree; it is transferred to a very small extent into milk, and to a somewhat greater degree into eggs. Data for fresh water indicates that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

#### SIGNIFICANCE AND RATIONALE FOR REJECTION OF POLLUTANT PARAMETERS

##### General

A number of pollution parameters besides those selected and just discussed were considered in each category but were rejected for one or more of these reasons:

- (1) Simultaneous reduction is achieved with another parameter which is limited.
- (2) Treatment technologies available at this time to reduce concentrations or loads of the parameter (i.e., total artificial evaporation, ion exchange, or reverse osmosis) are uneconomical or impractical.
- (3) The parameter was not usually observed in quantities sufficient to warrant regulations.
- (4) There are insufficient data on loadings or treatment methods which might be employed.



Parameters listed in this section are parameters which have been rejected as not applicable for the control of effluent quality for the chemicals considered under this study.

#### Total Dissolved Solids (TDS)

Raw material and product salts present in process waste water create extremely high dissolved-solids levels. However, dilution of the waste water within the sewer to reduce its toxicity and, more importantly, the lack of practical and economical technology to remove dissolved solids preclude control.

#### Calcium (Ca)

Calcium as an elemental metal does not occur naturally, because it is oxidized readily in air and reacts in water. Its most common form is limestone.

Calcium is used as a reducing agent in preparing other metals and as a dextrodizer, desulfurizer, or decarburizer for various ferrous and nonferrous alloys. It is also used as an alloying agent with aluminum, beryllium, copper, lead, and magnesium.

Calcium is essential to human body development, and minimum daily requirements have been set for proper nutrition. Calcium contributes to the hardness in water. Calcium reduces the toxicity of many chemical compounds and is used extensively in water treatment in the form of lime.

#### Potassium (K)

One of the more common elements, potassium constitutes 2.4 percent of the crust of the earth and occurs in many minerals. It is one of the most active metals and reacts vigorously with oxygen and water. For this reason, it is not found free in nature, but only in the ionized or molecular form. Potassium resembles sodium in many of its properties, and potassium salts can be substituted for sodium salts in many industrial applications. The sodium salts, however, are generally less expensive and, hence, more frequently used. For fertilizers, some varieties of glass, and a few other purposes, potassium salts are indispensable. Because the common salts of potassium are extremely soluble, they are not readily separated from water by natural process other than evaporation.

In low to moderate concentrations, potassium is essential as a nutritional element for man, animals and plants. At higher levels, however, it acts as a cathartic towards

humans and can be toxic to fish in soft or distilled waters. The toxicity towards fish can be reduced by calcium and, to a lesser extent, by sodium.

#### Sodium (Na)

Sodium is present in several chemical industry effluents. However, there are insufficient data on sodium and no economical or practical technology for its removal available at this time to justify consideration of sodium as a harmful pollutant.

#### Carbonate (CO<sub>3</sub>)

There are insufficient data for dissolved carbonates to justify consideration of this ion as a harmful pollutant.

#### Chloride (Cl)

While chloride concentrations in many cases are elevated, there are no economical or practical methods for removal at this time which can be employed on a large scale.

#### Sulfate (SO<sub>4</sub>)

Although, in some cases, industry sulfate concentrations were found to be high, sulfate is relatively nontoxic and is present in the natural environment in high concentrations. No practical treatment methods exist to remove sulfate at this time on a large scale. Lime treatment, in itself, causes sulfate to precipitate out as gypsum.

## SECTION VII

### CONTROL AND PRETREATMENT TECHNOLOGY

#### INTRODUCTION

In the context of this supplement to the main effluent guidelines document for the Inorganic Chemicals Industry, the term "control technology" refers to practices employed to reduce the volumes of waste water discharged to POTWs. "Pretreatment technology" refers to practices applied to waste water streams to reduce the concentrations of pollutants in the streams before discharge to municipal systems.

The control and pretreatment technologies available to that part of the Inorganic Chemicals Industry discharging to POTWs are, in many ways, the same as those available to that segment of the industry which directly discharges or recycles process waste water. The very significant difference is that POTW dischargers may, and do, avail themselves of public facilities for treatment of process waste water. As a result, process waste water discharges from POTW users generally receive less treatment or, in many cases, no treatment before discharge. The principal pretreatment technology employed is pH adjustment, precipitation, and solids removal prior to discharge to POTWs.

The practice of water recycle as a control measure appears to be employed to at least the same degree by POTW dischargers as by direct dischargers. Water recycle by POTW dischargers may be the result of minimizing--or, in some cases, completely avoiding--sewer-district user fees which are based, in part, on volumes discharged to the POTWs. Thus, there is added impetus for the POTW discharger to recycle process water above that of reducing water consumption.

#### CONTROL AND PRETREATMENT TECHNOLOGY AVAILABLE

##### Scope

Each of the techniques currently employed in those segments of the Inorganic Chemicals Industry covered by this document, as well as technology which might be employed in present or future operations for control or pretreatment of wastes, is discussed in this subsection in general terms. Details as they apply to typical operations in each subcategory of the industry are given under "TYPICAL PRETREATMENT OPERATIONS" for that chemical subcategory (by subcategory name), later in this section. The intervening

material describes "TECHNIQUES FOR REDUCTION OF WASTEWATER VOLUME" and discusses the approach used in the detailed discussions for the chemical subcategories.

### Clarifiers and Thickeners

A method of removing large amounts of suspended solids from waste water is the use of clarifiers, which are essentially large tanks with directing and segregating systems. The design of these devices provides for concentration and removal of suspended and settleable solids in one effluent stream and a clarified liquid in the other. Through proper design, application, and operation, clarified waters may have extremely low solids content.

Clarifiers may range in design from simple units to more complex systems involving sludge-blanket pulsing or sludge recycle to improve settling and increase the density of the sludge. Settled solids from clarifiers are removed periodically or continuously for either disposal or recovery of contained metal values.

Thickeners are used when the main purpose is to produce a clarified overflow with a concentrated effluent in the underflow.

Clarifiers have a number of distinct advantages over settling ponds:

- (1) Less land space is required. Area-for-area, these devices are much more efficient in settling capacity than ponds.
- (2) Influences of rainfall are reduced compared to ponds. If desired, the clarifiers can be covered.
- (3) Since the external construction of clarifiers consists of concrete or steel (in the form of tanks), infiltration and rainwater runoff influences do not exist.
- (4) Clarifiers can generally be placed adjacent to a plant, making reclaim water available nearby with minimal pumping requirements.

The use of flocculants to enhance the performance of clarifiers is common practice.

Clarifiers also suffer some distinct disadvantages compared to ponds:

- (1) They have mechanical parts and, thus, require maintenance.
- (2) They have limited storage capacity for either clarified water or settled solids.
- (3) The internal sweeps and agitators in clarifiers require more power and energy for operation than settling ponds.

### Flocculation

This treatment process consists basically of adding reagents to the treated waste stream to promote settling of suspended solids. The solids may be deposited in settling ponds (where high suspended solids are involved) or in clarifier tanks (in cases of lower solids loads).

Flocculating agents increase the efficiency of settling facilities and are of several general types: ferric compounds, lime, aluminum sulfate, and cationic or anionic polyelectrolytes. Causticized wheat and corn starch have also been used. The ionic types, such as alum, ferrous sulfate, lime, and ferric chloride, function by destroying the repelling double-layer ionic charges around the suspended particles and thereby allowing the particles to attract each other and agglomerate. Polymeric types function by forming physical bridges from one particle to another and thereby agglomerating the particles. Recyclable magnesium carbonate has also been proposed as a flocculant in domestic water treatment.

Flocculating agents are added to the water to be treated under controlled conditions of concentration, pH, mixing time, and temperature. They act to upset the stability of the colloidal suspension by charge neutralization and flocculation of suspended solids, thus increasing the effective diameter of these solids and increasing their subsequent settling rate.

Flocculating agents are most commonly used after the larger, more readily settled particles (and loads) have been removed by a settling pond, hydrocyclone, or other treatment.

Agglomeration, or flocculation, can then be achieved with less reagent, and with less settling load on the polishing pond or clarifier.

Flocculation agents can be used with minor modifications and additions to existing treatment systems, but the costs for the flocculating chemicals may be significant. Ionic types are used in concentrations of 10 to 100 mg/l in the waste

water, while the highest-priced polymeric types are effective in concentrations of 2 to 20 mg/l.

The effectiveness and performance of individual flocculating systems may vary over a substantial range with respect to suspended-solids removal, accessory removal of soluble components by adsorptive phenomena, and operating characteristics and costs. Specific system performance must be analyzed and optimized with respect to mixing time, flocculant addition level, settling (detention) time, thermal and wind-induced mixing, and other factors.

### Centrifugation

Centrifugation, which may be considered as a form of forced or assisted settling, may be feasible in specific control applications. The presence of abrasive components or significant amounts of the solid material smaller than approximately 5 micrometers (less than 0.0002 inch) in diameter in the treated water would tend to disqualify centrifugation as a solids-removal option.

### Neutralization

Adjustment of pH is the simplest chemical treatment practiced by industry. The addition of either acidic or basic constituents to a waste water stream to achieve neutralization generally influences the behavior of both suspended and dissolved components. In most instances of interest, waste waters are treated by base addition to achieve a pH in the range of 6.0 to 9.0.

Acid waste streams may be neutralized by addition of a variety of basic reagents, including lime ( $\text{CaO}$ ), limestone ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), magnesite ( $\text{MgCO}_3$ ), sodium hydroxide, soda ash (sodium carbonate), ammonium hydroxide, and others, to raise the pH of treated waste streams to the desired level. Lime is often used because it is inexpensive and easy to apply.

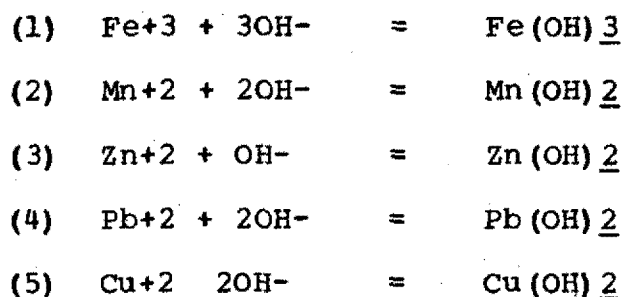
Ammonia neutralization is most frequently a processing technique, where ammonia affords a strong advantage in being volatile in the final product, allowing the recovery of nearly pure oxides. In waste treatment, its volatility is a disadvantage. Because of the COD it presents, its toxicity, and the production of undesirable nitrites and nitrates as oxidation products, its use is not widespread, and it is not desirable for waste treatment.

Since many heavy metals form insoluble hydroxides in highly basic solutions, sedimentation prior to neutralization may

prevent the resolubilization of these materials and may simplify subsequent waste-treatment requirements.

Essentially any waste water stream may be treated to a final pH within the range of 6.0 to 9.0. Generally, the stream will be sufficiently uniform to allow adequate pH control based only on the volume of flow and predetermined dosage rates, with periodic adjustments based on effluent pH. Automated systems which monitor and continuously adjust the concentration of reagents added to the waste water are also currently available and in use.

As discussed previously, pH control is often used to control solubility (also discussed below under Chemical Precipitation Processes). Examples of pH control being used for precipitating undesired pollutants are:



Reaction (1) is used for removal of iron contaminants. Reaction (2) is used for removal of manganese from manganese-containing waste water. Reactions (3), (4), and (5) are used on waste water containing copper, lead, and zinc salts. The use of lime to attain a pH of 7 will theoretically reduce heavy metals to these levels (Reference 10):

<u>Metal</u>	<u>Concentration</u> <u>(mg/l at pH 7)</u>
Cu+2	0.2 to 0.3
Zn+2	1.0 to 2.5
Cd+2	1.0

The careful control of pH, therefore, has other ancillary benefits, as illustrated above. The use of pH and solubility relationships to improve removal of waste water contaminants is further developed below.

#### Chemical Precipitation Processes

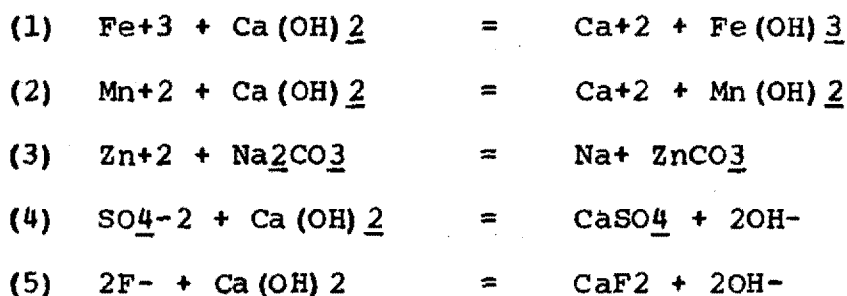
General Considerations. The removal of materials from solution by the addition of chemicals which form insoluble (or sparingly soluble) compounds with them is a common practice in both chemical-production processes and waste treatment. It is especially useful in the removal of heavy metals and fluoride from waste water effluents prior to discharge.

To be successful, direct precipitation depends primarily upon two factors:

- (1) Achievement of a sufficient excess of the added ion to drive the precipitation reaction to completion.
- (2) Removal of the resulting solids from the waste stream.

If the first requirement is not met, only a portion of the pollutant(s) will be removed from solution, and desired effluent levels may not be achieved. Failure to remove the precipitates formed prior to discharge is likely to lead to redissolution, since ionic equilibria in the receiving stream will not, in general, be those created in treatment. Effective sedimentation or filtration is, thus, a vital component of a precipitation treatment system and frequently limits the overall removal efficiency. Sedimentation may be effected in the settling pond itself, in secondary or auxiliary settling ponds, or in clarifiers.

The use of precipitation for waste water treatment varies from lime treatment (to precipitate sulfates, fluorides, hydroxides, and carbonates) to sodium sulfide precipitation of copper, lead, and other toxic heavy metals. Alum precipitation is also in use, to remove fluorides to lower levels than lime precipitation. The following equations are examples of precipitation reactions used for waste water treatment:



One drawback of the precipitation reactions is that the varying solubilities of unknown interactions of several metal compounds, and the possibility of widely divergent



formation and precipitation rates, limit the ability of this treatment to deal with all waste constituents.

Lime Precipitation. The use of lime to cause chemical precipitation has gained widespread use in the Inorganic Chemicals Industry because of its ease of handling, economy, and effectiveness in treatment of a great variety of dissolved materials. The use of other bases is, of course, possible, as previously discussed. However, the use of lime as a treatment reagent is probably the best-known and best-studied method.

The treatment conditions, dosages, and final pH must be optimized for any given waste stream, but, in general, attainment of a pH of at least 9 is necessary to ensure removal of heavy metals; it is necessary to attain a pH of 10 to 12 in many instances.

The levels of concentration attainable in an actual operating system may vary from the limits predicted on the basis of purely theoretical considerations, but extremely low levels of metals discharged have been reached by the use of this treatment method. The minimum pH value for complete precipitation of metal ions as hydroxides is shown in Figure 41.

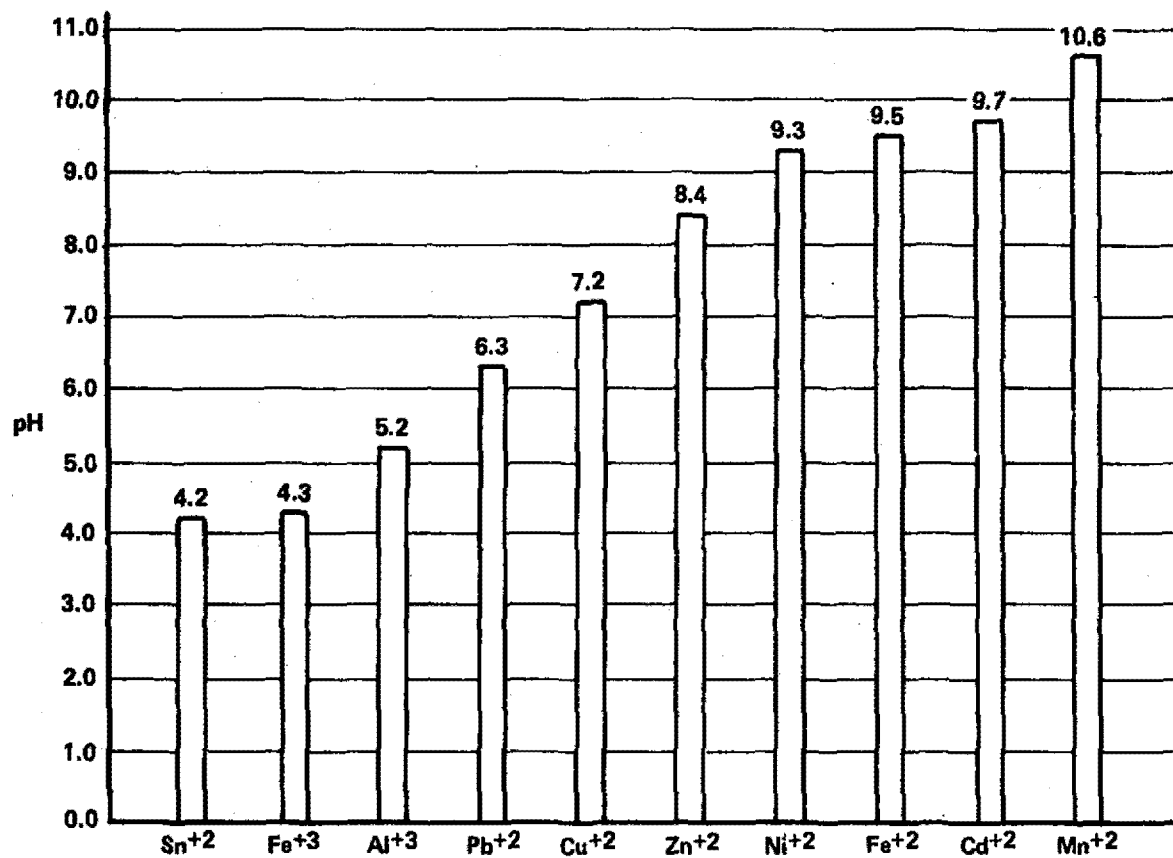
Purely theoretical considerations of metal-hydroxide solubility relationships suggest that the metal levels tabulated below are attainable (Reference 11).

Final Metal	Concentration (micrograms per liter)	pH
Cu+2	1 to 8	9.5
Zn+2	10 to 60	10
Pb	1	8
Fe (total)	1	8
(if totally ferric)		

Many factors, such as the effects of widely differing solubility products, mixed-metal hydroxide complexing, and metal chelation, render these levels of only limited value when assessing attainable concentrations in a treatment system.

Among the metals effectively removed at basic pH are: As, Cd, Cu, Cr+3, Fe, Mn, Ni, Pb, and Zn. For example, based upon published sources, industry data, and analysis of

Figure 41. MINIMUM pH VALUE FOR COMPLETE PRECIPITATION OF METAL IONS AS HYDROXIDES



LIME  
NEUTRALIZATION

LIME PRECIPITATION

samples, it appears that the concentrations given in the tabulation below are routinely and reliably attained by hydroxide precipitation (Reference 12).

Metal Concentration  
(mg/l)

As 0.05  
Cd 0.05  
Cu 0.03  
Cr+3 0.05  
Fe 1.0

Metal Concentration  
(mg/l)

Mn 1.0  
Ni 0.05  
Pb 0.10  
Zn 0.15

Lime precipitation is widely used for the control of fluoride, as well as for the removal of heavy metals. High dosages of lime contribute excess calcium ions to the solution, resulting in the precipitation of calcium fluoride. The elevated pH produced by the lime enhances the precipitation effectiveness by shifting the  $\text{HF} = \text{H}^+ + \text{F}^-$  towards the presence of free fluoride ions, which may be precipitated. Published sources (References 13, 14, 15, and 16) indicate that lime is effective in removing fluoride to concentrations of 20 mg/l or lower. Effluents from treatment with excess lime frequently approach the theoretical solubility of calcium fluoride (8 mg/l as fluoride).

Alum Precipitation. Fluoride ions may be removed, to levels appreciably lower than those obtained by lime treatment, by precipitation with alum. Effluent levels of fluoride ions on the order of 2 mg/l are reported (in References 13 and 14) as a result of alum precipitation. Because reagents costs are higher than for lime treatment, alum precipitation is particularly suited to the treatment of solutions containing relatively low initial fluoride concentrations. It seems particularly well-suited to use as a polishing step for further treatment of lime-precipitation effluents. In such applications, it is important to remove the calcium fluoride precipitate before adding the alum if maximum treatment benefits are to be realized (Reference 13).

Alum may be added as ammonium alum ( $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), or as sodium or potassium alum, and may be used with sodium hexametaphosphate, as described in Reference 13. Dosages are generally in the range of 200 mg/l to 600 mg/l of alum, depending on the initial fluoride-ion concentration and the required effluent quality. In addition to fluoride removal, the alum will, of course, serve as a flocculant and serve to remove some residual suspended solids.

TECHNIQUES FOR REDUCTION OF WASTEWATER VOLUME

Pollutant discharges from inorganic chemical manufacturing operations may be reduced by limiting the total volume of discharge, as well as by reducing pollutant concentrations in the waste stream. Techniques for reducing volumes discharged include limiting water use, excluding incidental water from the waste stream through segregation or diversion, recycle or reuse of process water, dry collection and solid wastes, and impoundment with solar evaporation.

In most cases, water use would already be reduced to the extent practical, because of the existing incentives for doing so (i.e., the high costs of pumping the high volumes of water required, limited water availability, the cost of water-treatment facilities, and POTW surcharges.)

Recycle of process water is currently practiced where it is necessary due to water shortage, where it is advantageous, or where the local permitting authority has required it. Recycle is becoming, and will continue to become, a more frequent practice. The benefits of recycle in pollution abatement are manifold and frequently are economic as well as environmental. By reducing the volume of discharge, recycle not only reduces the gross pollutant load, but also allows the employment of abatement practices which would be uneconomical on the full waste stream.

Recycle may require some treatment of water prior to its reuse. This may entail only settling of solids or pH adjustment.

Impoundment is a technique practiced at many operations in arid regions to reduce point discharges to, or nearly to, zero. Its successful employment depends on favorable climatic conditions (generally, less precipitation than evaporation, although a slight excess may be balanced by process losses and retention in product) and on availability of land consistent with process-water requirements and seasonal or storm precipitation influxes. In some instances where impoundment is not practical on the full process stream, impoundment and treatment of smaller, highly contaminated streams from specific processes may afford significant advantages.

#### APPROACH FOR REMAINDER OF SECTION

Control and pretreatment technologies employed by POTW dischargers and by direct dischargers are next discussed for each chemical subcategory. Varying degrees of pretreatment are discussed for a particular chemical when there is a series of technologies available, the application of which achieve additional pollutant reductions. In general,

pretreatment technologies which achieve pollutant reductions comparable to BPCTCA have been recommended.

#### TYPICAL PRETREATMENT OPERATIONS FOR ALUMINUM CHLORIDE SUBCATEGORY

##### Control

Because of varying air-pollution control practices, some aluminum chloride plants generate scrubber waste water, while others do not. Water-pollution control technology for the scrubber water differs between hydrous and anhydrous aluminum chloride producers because economical zero-discharge technology is not available at present for the latter. The Development Document for Effluent Guidelines for the Major Inorganic Chemicals Industry describes a system at "Plant 125" whereby the anhydrous salt scrubber water is recycled and a bleed is withdrawn for production of a 28% aluminum chloride solution. The aluminum chloride solution was reported to be sold as a flocculant. However, a recent discussion with plant personnel indicates that the bleed recovery system is not economically feasible, and the waste is being discharged untreated. A caustic neutralization and settling system is planned for the raw scrubber waste stream in the near future.

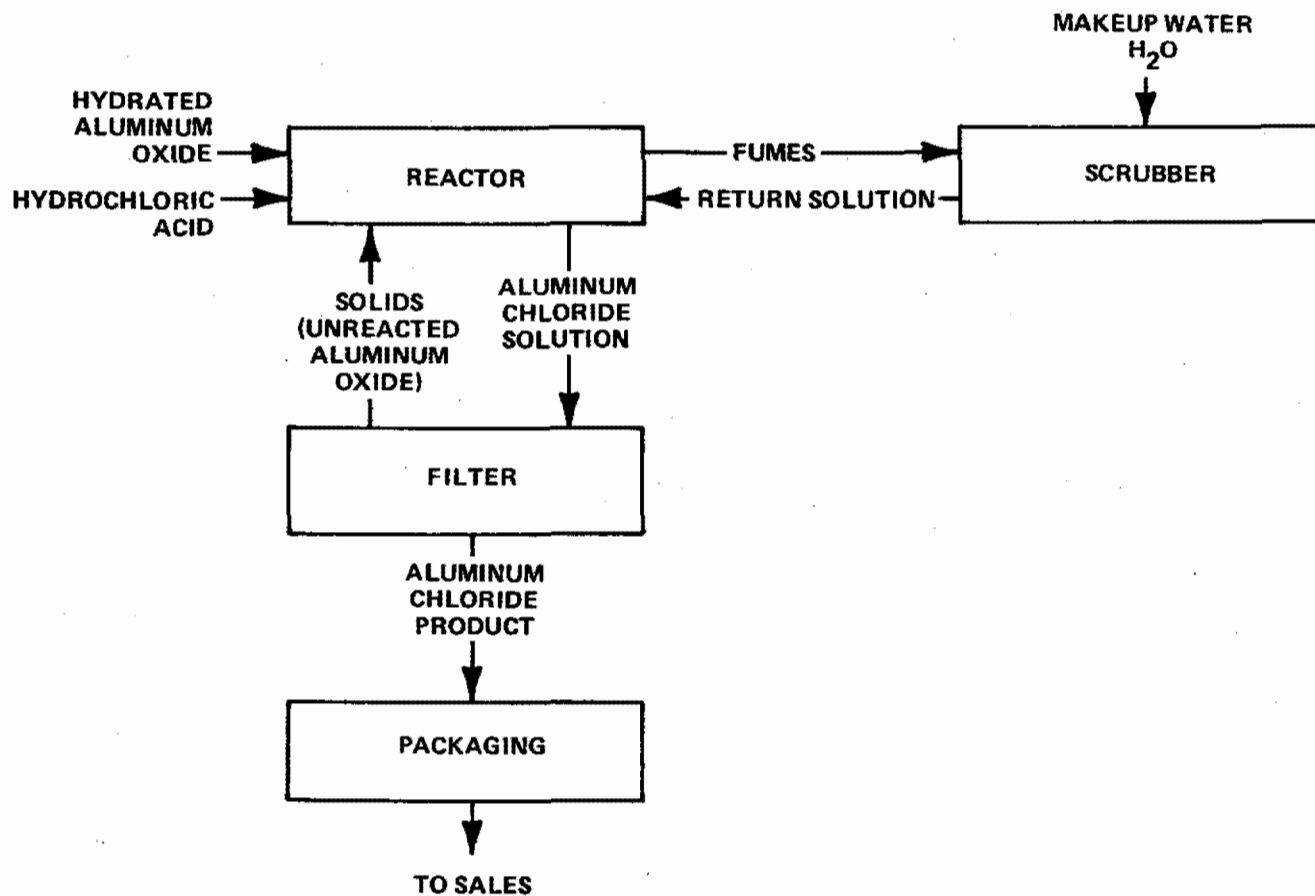
Alternately, a scrubber water reuse system is employed at Plant 19103, which produces the hydrous salt. The fumes generated during the reaction of hydrochloric acid and hydrated alumina (aluminum oxide), are captured in a wet scrubber, and the total volume of scrubber water generated is reintroduced to the reactor. Note that solids (mostly, unreacted alumina) obtained from filtration of the product are also reintroduced into the reactor, thus yielding neither solid nor liquid waste. This system is outlined in Figure 42.

##### Pretreatment

Because there are no known POTW dischargers in the subcategory, there is no pretreatment technology presently in use. Of the three plants where water is known to be used for emissions control, two are direct dischargers, and the third plant has obtained zero discharge of process wastes.

As discussed in Section V, the raw waste water characteristics are similar for production of both the hydrous and anhydrous salts. Both wastes are amenable to similar treatment technology, though control technology capabilities differ, as indicated above.

Figure 42. FLOW DIAGRAM SHOWING SCRUBBER-WATER REUSE IN PRODUCTION OF HYDROUS ALUMINUM CHLORIDE (PLANT 19103)



At Plant 19101 (producing both hydrous and anhydrous salts), all plant waste water is treated by a caustic neutralization and settling system before discharge. The treatment system daily accommodates an average of 221 cubic meters (58,300 gallons) of waste water, which includes about 166 cubic meters (43,900 gallons) of rainwater runoff. This system is shown schematically in Figure 43, and effluent chemical data supplied by the industry are presented in Table 20.

At Plant 19104, a lime neutralization system is employed to treat process water from aluminum chloride production, as well as from production of a number of other inorganic and organic chemicals. This system is shown schematically in Figure 44.

#### Compatibility with POTWs

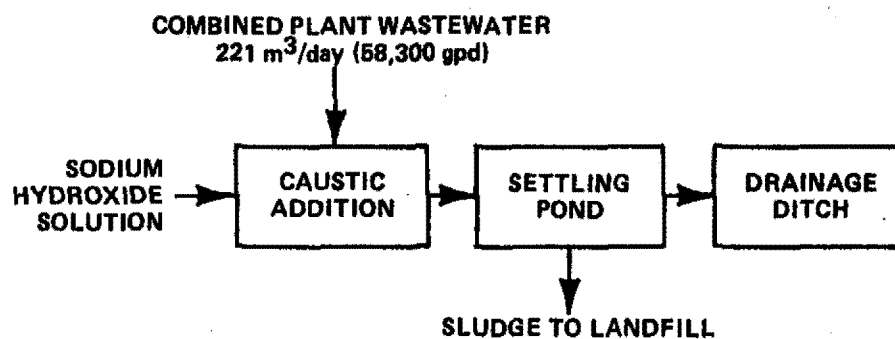
Discharges from aluminum chloride plants can contain enough aluminum to cause problems in POTW. Aluminum is acceptable in municipal treatment plants when it occurs at low concentrations, but at high concentrations it can cause excessive sludge bulking. At anhydrous aluminum plants using scrap aluminum as a raw material, zinc can be present in concentrations sufficient to inhibit POTW operation. Some incidental removals of aluminum and zinc can be expected in the POTW, but some of the aluminum and zinc, and all of the chlorides present in the wastewater can be expected to pass through the POTW. (See Table 21.). Chloride discharges should pose no threat to the POTW operation or the environment. Pretreatment may be necessary, however, for reduction of aluminum and zinc concentrations.

#### TYPICAL PRETREATMENT OPERATIONS FOR ALUMINUM SULFATE SUBCATEGORY

##### Control

As discussed in Section V, aluminum sulfate manufacturing processes differ slightly from facility to facility. All process wastes are recycled at some plants. At Plant 19204, clay has replaced bauxite as a raw material, with no effect on process operations, and a closed-cycle waste stream has been instituted to eliminate discharge. Fresh water is introduced to the system through the wash tanks, as well as through the digester. This system is shown in Figure 45. At Plant 19205, aluminum sulfate is produced by dissolving aluminum in sulfuric acid and precipitating the product from the mother liquor. All water from the centrifuge is stored and returned to the reactor. This system is shown in Figure 46. In addition, the Development Document for Effluent

**Figure 43. FLOW DIAGRAM SHOWING WASTEWATER TREATMENT USED IN PRODUCTION OF ALUMINUM CHLORIDE (PLANT 19101)**





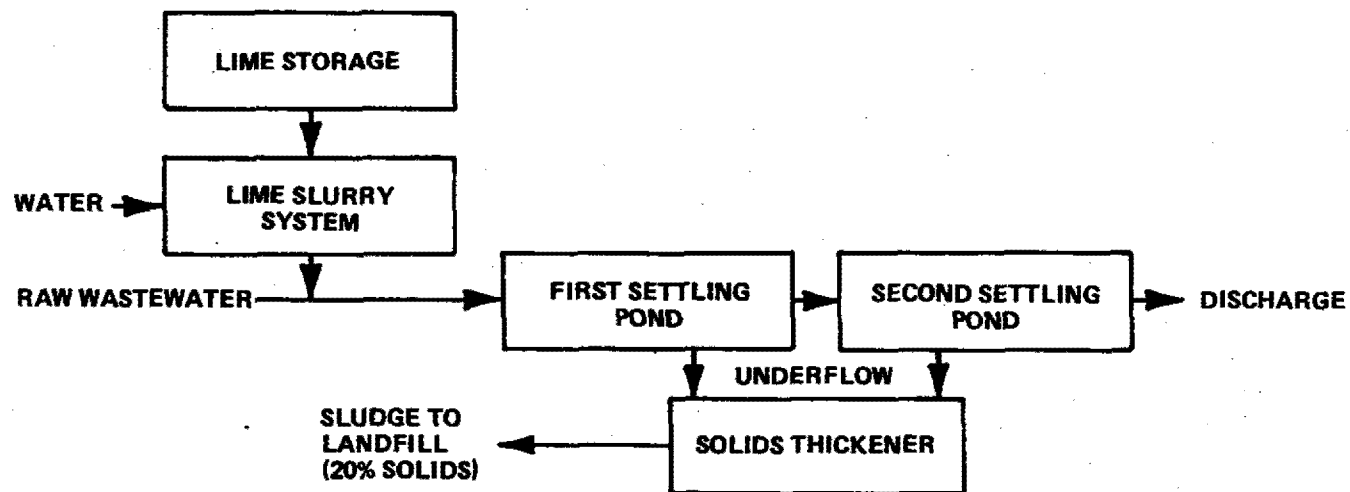
**TABLE 20. CHEMICAL COMPOSITION OF TREATED WASTEWATER FROM PRODUCTION OF ALUMINUM CHLORIDE (PLANT 19101)\***

PARAMETER	CONCENTRATION (mg/l)*	
	DAILY AVERAGE	DAILY MAXIMUM
pH	6 to 9 <sup>†</sup>	6 to 9 <sup>†</sup>
TSS	38	59
Total Solids	30,000	45,000
BOD	20	30
COD	113	175
Al	13	20
Ni	1	2

\*Industry data.

<sup>†</sup>Value in pH units.

Figure 44. FLOW DIAGRAM SHOWING WASTEWATER TREATMENT USED IN PRODUCTION OF ALUMINUM CHLORIDE (PLANT 19104)



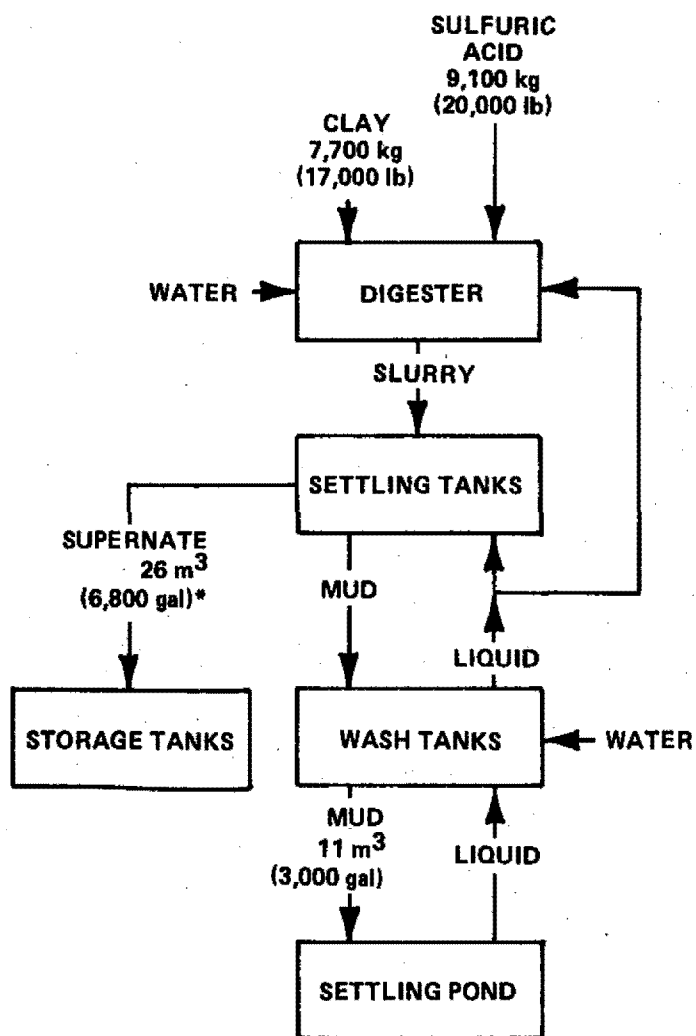
NOTE: THE SYSTEM DEPICTED TREATS WASTEWATER FROM PRODUCTION OF ALUMINUM CHLORIDE, ALUMINUM SULFATE, AMMONIUM THIOSULFATE, METHYLAMINE SOLUTION, REAGENT-GRADE ACIDS, SODIUM BISULFITE SOLUTION, SULFAMIC ACID, AND SULFUR TRIOXIDE.

**TABLE 21. INCIDENTAL REMOVAL OF POLLUTANT PARAMETERS AT POTWs**

PARAMETER	PERCENT REMOVAL EFFICIENCY - RANGE*	NUMBER OF POTWs
Al	64	1
Cd	6-86	16
Cr (total)	38-96	20
Cu	55-191	21
Fe	76-97	11
Pb	31-95	17
Ni	0-61	17
Ag	60-73	3
Zn	45-96	19
Fluoride	6-16	3

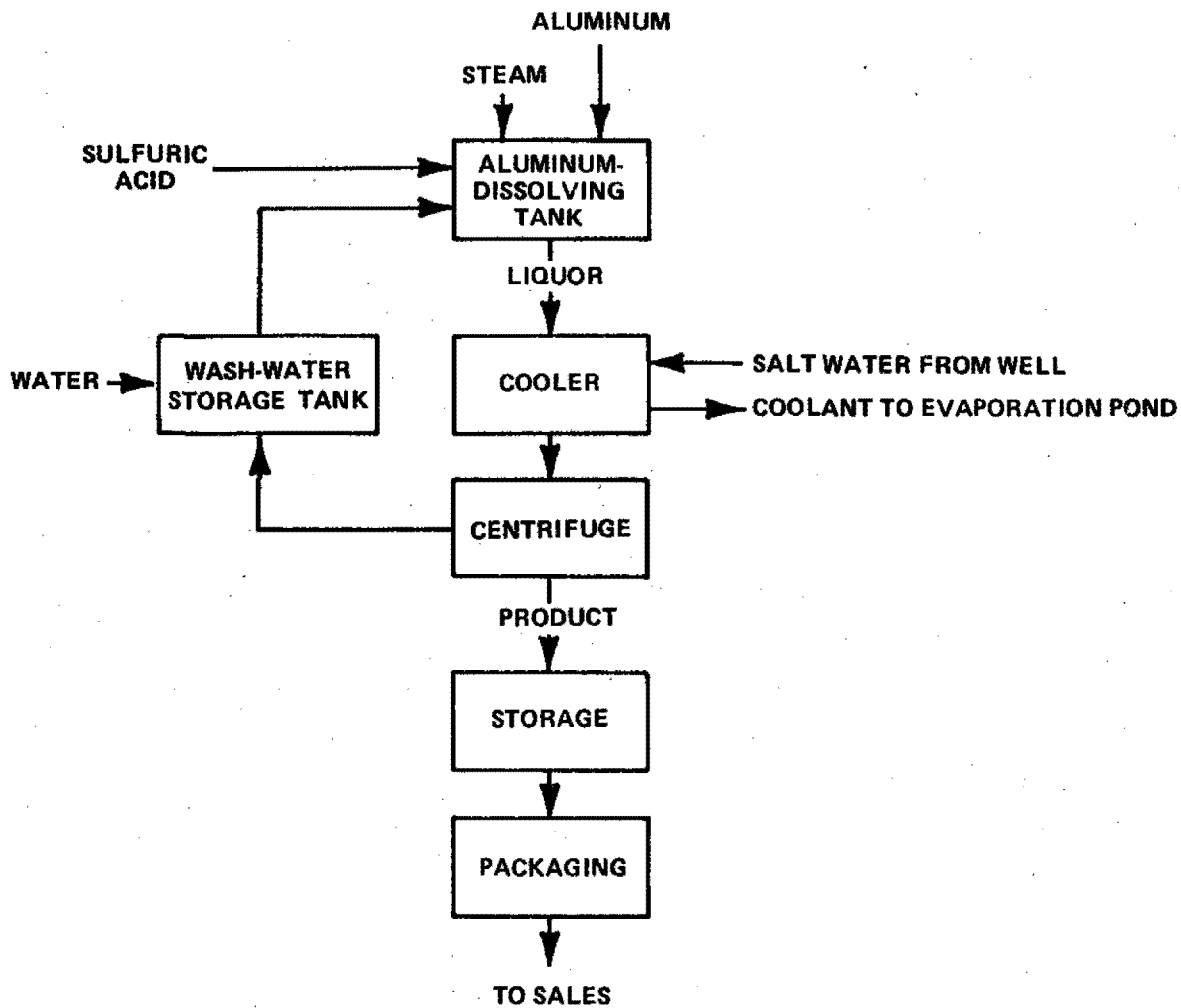
\*Based on data available from biological POTWs meeting secondary treatment performance levels.

Figure 45. FLOW DIAGRAM OF WASTEWATER-RECYCLING SYSTEM USED IN PRODUCTION OF ALUMINUM SULFATE (PLANT 19204)



\*Wastewater net flows are given on a batch basis; makeup water requirements per batch is approximately 26m<sup>3</sup> (7,000 gal).

**Figure 46. FLOW DIAGRAM OF WASTEWATER-RECYCLING SYSTEM USED IN PRODUCTION OF ALUMINUM SULFATE (PLANT 19205)**



Limitations Guideline for the Major Inorganic Chemicals Industry describes two plants (therein, coded 049 and 063) where zero discharge of process and cooling water is practiced.

#### Pretreatment

Because there are no POTW dischargers in the aluminum sulfate subcategory, there is no pretreatment technology presently existing. This condition is probably largely attributable to the fact that many aluminum sulfate plants are zero dischargers for process waste water.

Only one discharging aluminum sulfate manufacturer was found to be treating process wastes during this study. The aluminum sulfate wastewater is mixed with many other waste streams from a chemical complex and is lime-neutralized and settled before discharge. Because the treatment system is used for many products, no raw waste load or effluent data are available. The treatment system is shown in Figure 44.

The Development Document for Effluent Limitations Guidelines for the Inorganic Chemicals Industry states that current typical treatment for aluminum sulfate manufacturing discharges involves use of a settling pond to remove muds, followed by neutralization of residual sulfuric acid. However, no specific plants were enumerated as practicing this typical treatment.

#### Compatibility with POTWs

Raw wastewater from aluminum sulfate plants has been shown to contain significant quantities of aluminum, zinc and sulfate. Aluminum is acceptable in municipal treatment plants when it occurs in low concentrations, but at high concentrations it can cause sludge bulking. Zinc can be present in concentrations sufficient to inhibit POTW operation. Some incidental removals of aluminum and zinc can be expected in the POTW, but significant amounts of aluminum and zinc, and most of the sulfate present in the wastewater will pass through the POTW. (See Table 21.) Sulfate is not generally detrimental to POTW operation, and should not pose significant environmental problems. Pretreatment to reduce zinc levels is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR CALCIUM CARBIDE SUBCATEGORY

##### Control

Most calcium carbide plants use dry dust collection. Producers such as Plants 19301 and 19302 have dry systems and, therefore, have no discharge except for occasional noncontact cooling-water blowdown.

#### Pretreatment

The most reasonable pretreatment technology for calcium carbide production employing a wet scrubber system is settling. Varying retention times result in different levels of treatment. Figure 47 diagrams the process and treatment used at Plant 19303. Over 90% of the treated scrubber effluent is recycled to the scrubber system at Plant 19303.

It has been noted that settling can achieve as much as an 80% reduction in total suspended-solids concentration. Plant 19303 reports an average suspended-solids concentration of 40 mg/l in the treated venturi-scrubber effluent.

#### Compatibility with POTWs

The wastes generated from calcium carbide production contain moderate levels of suspended solids, and do not contain other parameters that would be harmful to POTW operation or to the environment. The suspended solids in this discharge will be adequately removed by a POTW. Therefore, no pretreatment of this waste is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR CALCIUM CHLORIDE SUBCATEGORY

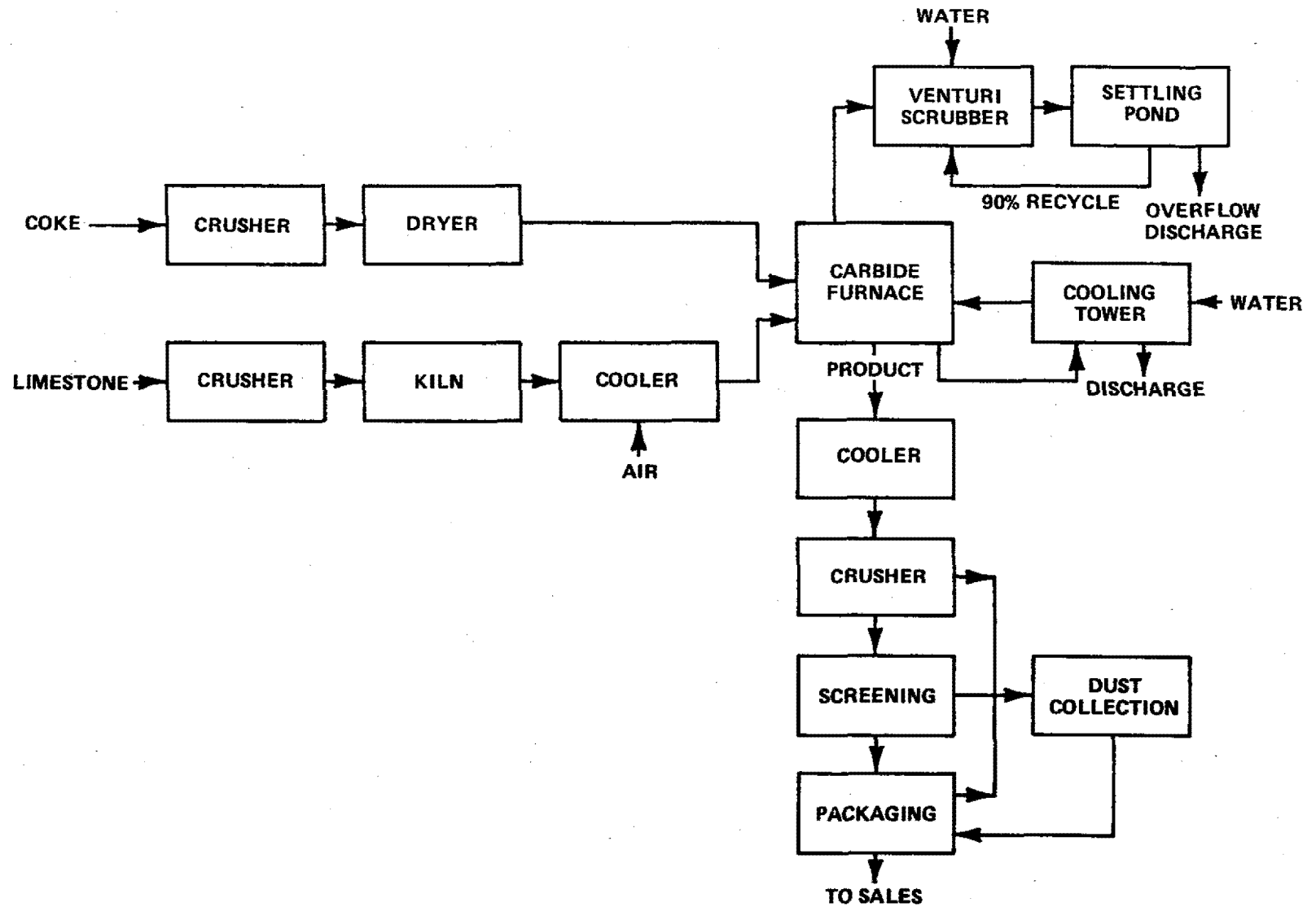
##### Control

The effects of waste water control technology upon waste volume reduction have been most pronounced at natural brine Plant 19404. A number of process and noncontact water-use changes have been instituted which reduce the single waste stream to a relatively low-volume, highly concentrated waste. Well disposal of this 954-cubic-meter/day (0.252mgd) waste brine solution to the originating geologic formation has transformed the plant to zero-discharge status in terms of process waste water being released to surface water.

##### Pretreatment

There is one POTW discharger in the calcium chloride subcategory. The pretreated waste is discharged to a POTW practicing primary settling. As described in Section V, waste water from Plant 19406 is a result of emissions

Figure 47. FLOW DIAGRAM FOR PRODUCTION OF CALCIUM CARBIDE (PLANT 19303)





control, which yields a waste containing hydrochloric acid. As shown in Figure 48, the scrubber system receives waste cooling water from other operations at the plant as makeup. The scrubber water is combined with other chemical wastes and neutralized before discharge.

As discussed in Section V, the Solvay process generates a waste liquor with a daily volume ranging from 23,000 to 26,000 cubic meters (6 to 7 million gallons). At Plant 19401, roughly 25 to 30% of this liquor is routed to the calcium chloride extraction circuit, and the resultant waste from production of the salt is combined with the waste soda ash liquor. Any calcium chloride process overflows due to operational upsets are intercepted by plant sewers and discharged to surface water. The combined soda ash and calcium chloride waste streams are treated by settling and subsequently discharged. The calcium chloride production rate (at Plant 19401) is dependent upon local market conditions, and the ratio of calcium chloride waste water to soda ash waste water varies accordingly.

Plant 19412 produces the salt from pure calcium carbonate and daily generates 1 cubic meter (300 gallons) of washdown. The washdown is treated at a central facility, which intercepts wastes from a number of reagent-grade chemical processes. The system consists of multipoint pH adjustments, multiple settling stages, flocculation, and clarification. The final treated waste is discharged to a river. The calcium chloride washdown waste contributes an insignificant volume of water to the total treatment-plant effluent.

#### Compatibility with POTWS

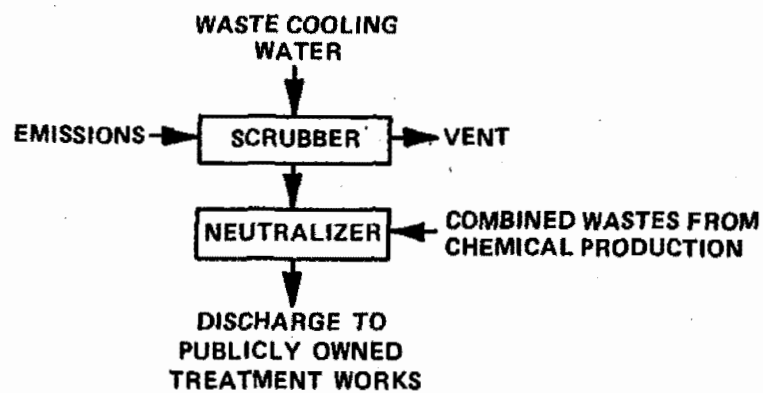
The waste streams generated from calcium chloride production contain only calcium and sodium brines that will not interfere with POTW operation. No pretreatment is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR COPPER (CUPRIC) SULFATE SUBCATEGORY

##### Control

The copper (cupric) sulfate manufacturing industry recycles almost all process waters. Mother liquors and washdowns are recycled to either the reactor tank or the crystallizer. Reactor sludges may be sent to a nearby smelter for precious-metal and copper recovery. The high value of copper justifies recovery of most wastes and minimization of the metal content of the water effluent. Noncontact cooling

**Figure 48. FLOW DIAGRAM SHOWING PRETREATMENT OF EMISSIONS - SCRUBBER WATER USED IN PRODUCTION OF CALCIUM CHLORIDE (PLANT 19406)**



waters and condensates present no difficulties to POTW operations and do not require pretreatment.

One type of waste water from copper sulfate production has potentially bad effects on POTW operations. The flow resulting from plant spills and washdowns should be treated before discharge to a POTW.

#### Pretreatment

One of the plants studied for this document has a washdown stream which is treated prior to discharge. The daily washdown flow is approximately 20 to 22 cubic meters (5,000 to 6,000 gallons) at Plant 19505. The acidic waste water is neutralized with hydrated lime at a rate of 1.10 grams/liter (10,000 pounds/millions gallons) of water treated. Figure 27 diagrams the treatment process at Plant 19505.

The waste water mixture is settled in the neutralization tank. The water is then decanted to a filter press, and the sludge from the tank is put into a storage tank. Excess water from the sludge storage tank is occasionally decanted to the neutralization tank. The filter cake from the press is taken to the sludge storage tank, and the filtrate is discharged. The thick sludges are deposited in a landfill.

Available data for the copper sulfate washdown effluent are:

	<u>Concentration (mg/l)</u>	
	<u>Before Treatment</u>	<u>After Treatment</u>
copper	average: 433	average: 0.48 range: 0.14 to 1.25
nickel	average: 159	average: less than 0.5
pH	(not available)	7.3 to 11.1 (pH units)

#### Compatibility with POTWs

The untreated wastewater from copper sulfate production can contain levels of nickel and copper which exceed the limits prescribed by most POTW. (See Table 25.) High nickel and copper levels may have a toxic effect on the biota of a POTW. In addition, only incidental removal efficiencies insufficient to achieve acceptable effluent quality can be expected at the POTW. (See Table 21.) Therefore, pretreatment to reduce metal levels is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR IRON (FERRIC) CHLORIDE SUBCATEGORY

## General

Wastewater generated during ferric chloride production includes: scrubber water, filter wash water, floor and equipment washings, and leaks and spills. Recycle is extensively used within the industry. Treatment is directed toward metal removal and pH adjustment. The pretreatment and control technologies used in the ferric chloride industry are detailed below.

## Control

The ferric chloride industry makes extensive use of recycle to control process waste water. All of the waste water generated contains ferrous or ferric chloride and, as such, is a potential raw material. Impurities present in the waste water do not affect its usefulness, since relatively impure raw material, pickle liquor, is used to begin with. To remove gross solids and to prevent the concentration of impurities, Plants 19601 and 19602 settle the ferric chloride process waste water prior to recycle.

In addition to recycling combined waste water back to the process, several control technologies are employed for individual waste streams:

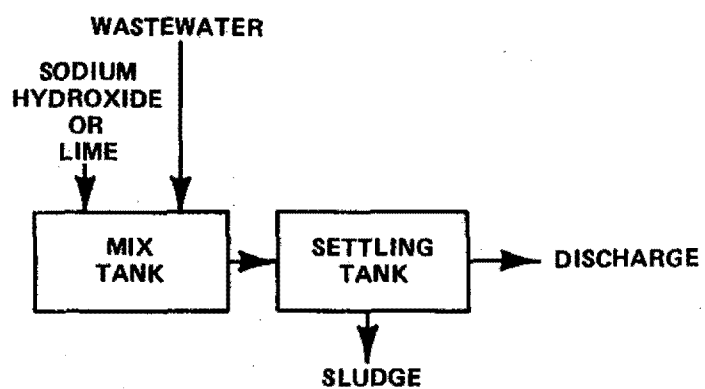
Emissions-control scrubber water--Plant 19602 recycles caustic scrubber water generated from the control of process tail gases. There is a small bleed stream, however, to remove dissolved salts concentrated in the recycle stream.

Floor and equipment washings--The quantity of water used to wash floors and process equipment varies significantly from plant to plant. Plant 19601 daily uses 4 cubic meters (1000 gallons) of water for floor and equipment washings. Plant 19602, whose production is only one tenth of plant 19601, daily generates 30 cubic meters (7,000 gallons) of waste water. To a large extent, equipment type and process layout govern the amount of washdown water required. However, good housekeeping practices and conservative washdown techniques can reduce water use.

## Pretreatment

Chemical precipitation, by pH adjustment and settling, is the most common treatment technology employed within the industry. It is illustrated in Figure 49. Either lime or sodium hydroxide is used to form insoluble metal hydroxides; the resultant floc is settled, and the supernatant is either discharged or recycled. The qualities of ferric chloride

**Figure 49. FLOW DIAGRAM SHOWING TYPICAL WASTEWATER PRETREATMENT USED IN PRODUCTION OF FERRIC CHLORIDE**



which make it ideal as a precipitation agent in waste water treatment also contribute to treatment of ferric chloride process wastewater. The iron hydroxide forms a dense floc which aids in the removal of other metals. Plant 19603 reports significant reductions in both total and hexavalent chromium as a result of floc entrapment.

Removal efficiencies of iron approach 99%. The treated-waste water characteristics from plants with and without leaks and spills are presented in Table 22. High removal efficiencies for other metals are also expected, due to the presence in the waste water of large quantities of iron floc, which will trap other metal hydroxides as it settles.

#### Compatibility with POTWs

The wastewater generated from ferric chloride production contains high concentrations of iron and the impurities (chromium, copper, nickel, and zinc) contained in the pickle liquor feed. Although iron is used for sludge conditioning at some POTW, very high concentrations (1000 mg/l and above) may inhibit biological treatment operations. Much lower concentrations of chromium, copper, nickel and zinc can interfere with POTW operation. In addition, only incidental removal efficiencies insufficient to achieve acceptable effluent quality can be expected at the POTW. (See Table 21.) Therefore, pretreatment to reduce metal levels is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR LEAD MONOXIDE SUBCATEGORY

##### General

There are two significant sources of waste water in the lead monoxide manufacturing industry: (a) washdown of equipment and floors and (b) compressor blowdown, or water condensate from air compressors. These two waste water sources are discussed separately below.

##### Control

Plant Washdown. Ten out of eleven lead monoxide manufacturing plants do not generate any washdown waste water. These ten plants utilize dry vacuuming techniques for dust control. Only one of the eleven plants produces a washdown waste water.

Compressor Blowdown. Compressor blowdown is an inherent product of the air-compression process and cannot be reduced through compressor modifications, or by recycling. However,

**TABLE 22. CHEMICAL COMPOSITIONS OF AVERAGE TREATED  
WASTEWATERS FROM PRODUCTION OF FERRIC CHLORIDE**

PARAMETER	CONCENTRATION (mg/l)	
	PLANTS WITH LEAKS AND SPILLS	PLANTS WITHOUT LEAKS AND SPILLS
TSS	110	300
Cr (total)	0.02	0.14
Cu	0.02	0.11
Fe	92	100
Pb	0.07	0.48
Mn	0.37	2.5
Ni	0.44	3.0
Zn	0.04	1.0

through the use of natural-draft furnaces, fans, or other air-inducing equipment in the oxidation of lead to lead monoxide, compressor condensate can be eliminated.

#### Pretreatment

Plant Washdown. Plant 19702 is the only lead monoxide plant known to discharge process washdown. At Plant 19702, the lead monoxide manufacturing process waste water is sumped to a small sedimentation pit, where the waste water is combined with waste water from the manufacturing of other lead chemicals. From the sedimentation pit, the combined wastewater flows through an open ditch to a 0.3-hectare (0.75-acre), unlined stabilization pond. The waste water from manufacture of the other lead chemicals contains sulfate in sufficient quantity to precipitate soluble lead as lead sulfate.

The effluent from the stabilization lagoon flows to surface water. Recently, a sand filter is believed to have been added to the end of this treatment sequence for further lead and suspended-solids removal. This treatment scheme is illustrated in Figure 50.

Treatment accomplished in the stabilization lagoon is reported to be 85 to 90% effective in reducing the lead waste content. Further lead and suspended-solids removals would be achieved by filtration. Laboratory tests using filtration of settling-pond effluent indicate that total lead concentrations are reduced by an additional 92%, producing an effluent which contains a total lead concentration of 0.058 mg/l. The effective overall lead removal attained by this treatment approach is 98 to 99%.

At plants where a waste stream containing precipitation agent such as a sulfate is not available, lime is generally used to precipitate lead as lead hydroxide.

Compressor Blowdown. No lead monoxide plants are known to employ pretreatment of compressor-blowdown waste water. As indicated under "Compatibility with POTWs" below, there appears to be little need for pretreatment of this waste water.

#### Compatibility with POTW

The waste generated from lead monoxide production contains lead and oil and grease. Oil and grease will be present in small quantities and will be adequately treated and removed by a POTW. Lead levels in the raw wastes, however, will exceed the limits prescribed by most POTW. (See Table 25.)



Figure 50. FLOW DIAGRAM OF WASTEWATER-TREATMENT SYSTEM USED IN PRODUCTION OF LEAD MONOXIDE (PLANT 19702)

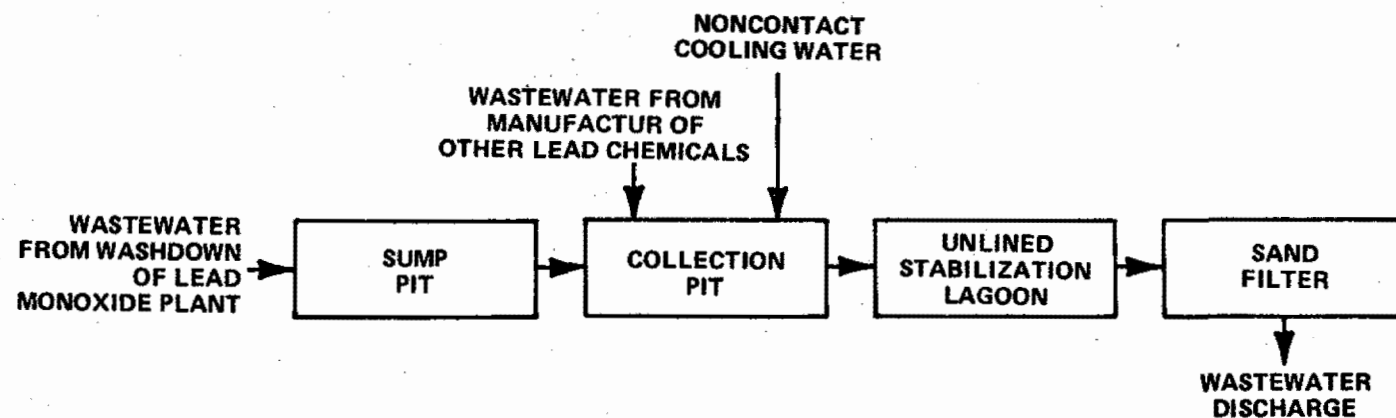


TABLE 23. CHEMICAL COMPOSITIONS OF RAW AND TREATED WASTEWATERS FROM PRODUCTION OF LEAD MONOXIDE (PLANT 19702)

PARAMETER	CONCENTRATION (mg/l)		
	PRETREATMENT INFLUENT*	SETTLING-POND EFFLUENT†	PRETREATMENT EFFLUENT AFTER FILTRATION **
pH	9.8 <sup>††</sup>	9.8 <sup>††</sup>	9.8 <sup>††</sup>
TSS	—	3.0 <sup>NPDES</sup>	0.24 <sup>est/l</sup>
Oil and Grease	—	0.49 est/c	—
Pb (total)	653 <sup>est/u</sup>	0.9	0.058
Chloride NS	345	345	345
Sulfate NS	—	31	—

\*Combined waste stream from production of lead monoxide and other lead chemicals.

† Average values based on company monitoring data for period 15 April 1973 through 1 July 1974 (30 grab samples).

\*\* Average values based on laboratory filtration tests conducted July 1973 through September 1973 (five grab samples).

†† Value in pH units.

NPDES NPDES discharge permit data.

est/c Estimated value based on untreated compressor-blowdown concentration given in Table V-10 and on a dilution factor of 4000.

est/l Estimated value based on same removal efficiency (92%) attained for lead in laboratory filtration test.

est/u Estimated values based on untreated washdown pollutant concentration given in Table V-9 and on a dilution factor of 1.52.

NS Not considered significant components of lead monoxide process wastewater.

Lead is recognized as being toxic to fish and wildlife and to humans. In addition, only incidental removal efficiencies insufficient to achieve acceptable effluent quality can be expected at the POTW. (See Table 21.) Therefore, pretreatment to reduce lead levels is indicated.

TYPICAL PRETREATMENT OPERATIONS FOR NICKEL SULFATE SUBCATEGORY

General

Wastewater generated during nickel sulfate production includes: plating solution treatment filtrates; emissions-control scrubber water; filter sludges and washwater; miscellaneous equipment and floor washings; and leaks and spills.

Control

Plating-Solution Treatment Filtrate. Plating-solution treatment filtrate offers very little potential for reuse or recycle. The gross impurities present make it unamenable for recycle to other operations within the process. Thus, Plant 19803, which makes extensive use of recycle within its process, discharges the waste filtrate from the spent plating solution treatment operation.

Emissions-Control Scrubber Water. Scrubber water at Plant 19801 is collected in a baffled tank, to facilitate settling of suspended solids, and then recycled. However, about 10% of the scrubber water must be bled off to remove dissolved salts, concentrated in the recycle stream. Other nickel sulfate manufacturers, apparently, have no need for process emissions control and, therefore, do not employ wet scrubbers.

Filter Sludges and Wash Water. Depending on the removal techniques employed, the volume and characteristics of waste water generated from washing caked material from filters can be quite variable. Large volumes of waste water, high in suspended solids, are generated if the filters are merely washed of caked material. Suspended solids levels can approach 15%. However, the use of mechanical scrapers to remove caked material can eliminate this waste water altogether; producing a solid waste instead.

The efficiency of the mechanical scraping device greatly influences waste water reduction. Plant 19803 reports only sludge production, with no waste water generated from filter cleaning. Plant 19801, on the other hand, daily generates

189 liters (50 gallons) of wastewater, due to the need for a final rinse to remove filter residues left after scraping.

Equipment and Floor Washings. Equipment and floor washings contain large quantities of raw materials and product. However, they also contain dust, grease, and other impurities that are found in the plant environment. At plants where relatively impure raw materials are handled routinely, these washings can be recycled back to the process for additional product recovery. Those plants, such as Plant 19801, which use pure nickel oxide as a starting material and, therefore, do not have purification processes, may not be able to recycle equipment and floor washings without installing purification equipment or practicing stringent product-loss control. If not recycled, these wastes would require treatment.

Because these wastes are high in suspended solids, there is little potential for their use elsewhere in the plant for cooling, gas scrubbing, etc.

#### Pretreatment

In general, waste streams from nickel sulfate production are combined prior to pretreatment and discharge to POTWs. Because these wastes are chemically similar, combined pretreatment offers many practical and economic advantages.

Plant 19801 employs metal precipitation by pH adjustment (with sodium hydroxide) and settling before discharging the treated waste water to the sewer. Figure 51 illustrates this pretreatment scheme. Plant 19803 also uses sodium hydroxide to precipitate metals. However, in this case, the waste water is directed to a sand filter for suspended-solids removal. This treatment technology is illustrated in Figure 52.

Nickel removal efficiencies of only 50% are experienced at Plant 19801. At Plant 19803, 79% nickel removal efficiency is achieved. The inability of simple gravity settling to remove nickel is probably due to the low density of the nickel hydroxide floc formed. Sand filtration offers a more effective technique for removal of low-density suspended materials. The chemical characteristics of treated waste water discharged from Plants 19801 and 19803 are presented in Table 24.

The most practical and cost-effective techniques for pretreatment of nickel sulfate waste water may be chemical precipitation, gravity settling of gross suspended solids, and effluent polishing by sand filtration. This approach

**Figure 51. FLOW DIAGRAM SHOWING WASTEWATER PRETREATMENT USED IN PRODUCTION OF NICKEL SULFATE (PLANT 19801)**

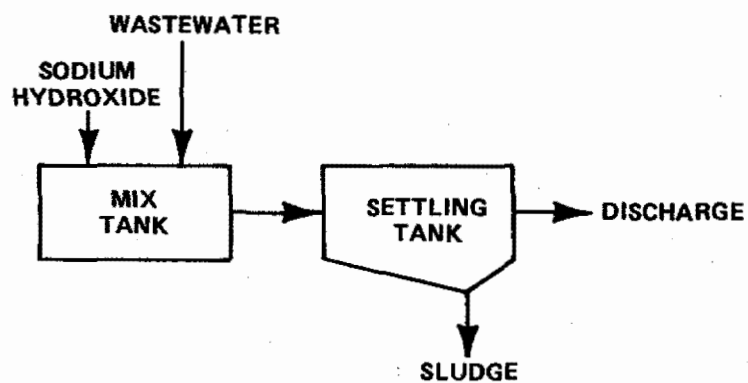
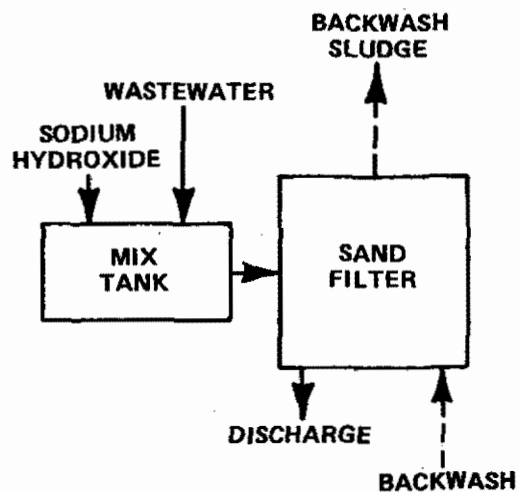


Figure 52. FLOW DIAGRAM SHOWING WASTEWATER PRETREATMENT USED IN PRODUCTION OF NICKEL SULFATE (PLANT 19803)



**TABLE 24. CHEMICAL COMPOSITIONS OF TREATED WASTEWATERS  
FROM PRODUCTION OF NICKEL SULFATE (TWO PLANTS)**

PARAMETER	CONCENTRATION (mg/l)	
	PLANT 19801	PLANT 19803
pH	8.9*	10.2*
TSS	30	—
Ni	180	3.0

\*Value in pH units.

takes advantage of the relatively low cost of gravity settling and of the enhanced settling due to synergistic effects of other materials present in the waste water. At the same time, it makes use of the sand filter's ability to remove unsettlable suspended solids without the need for frequent backwashings to remove large quantities of solids. This treatment system is illustrated in Figure 52.

#### Compatibility with POTW

The various waste streams generated from nickel sulfate production contain levels of nickel--and, in some cases, copper--which exceed the limits prescribed by most POTWs. (See Table 25.) Nickel concentrations in the combined waste water discharged from nickel sulfate manufacturing plants, in general, range from 12 to 360 mg/l Ni. Copper levels in waste water discharged to POTWs range from 5 to 70 mg/l. These levels of nickel and copper may have a toxic effect on the biota of a POTW. In addition, only incidental removal efficiencies insufficient to achieve acceptable effluent quality can be expected at the POTW (Reference 17). Therefore, pretreatment to reduce metal levels is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR NITROGEN AND OXYGEN SUBCATEGORY

##### Control

Although the basic single process of air separation for the production of nitrogen and oxygen remains the same, various technological modifications have already enhanced the associated control practices with regard to certain process waste waters. Modern air-separation plants--particularly, those built within the last 15 years--have specified the installation of minimal-oil or oil-free type compressors. This modification has eliminated the gross production of oily compressor condensate common to the older, reciprocating-type compressors.

In addition, the use of caustic-scrubber solutions has been diminished as a result of the development of a system of reversing exchangers for the removal of carbon dioxide impurities. In this system, carbon dioxide and water vapor, which enter under high pressure, are condensed, then evaporated and purged from the system by low-pressure nitrogen. This technology has served to eliminate the production of a caustic wastestream.

With regard to possible water reuse in the process, recycle of any condensate water is precluded by the presence of oil



**TABLE 25. EFFLUENT LIMITATIONS IMPOSED BY PUBLICLY OWNED TREATMENT WORKS (POTWs)**

<b>PARAMETER</b>	<b>CONCENTRATION RANGE (mg/l)</b>
pH	4.5 - 11.0
TSS	250 - 1,500
Oil and Grease	100 - 600
Al	40 - 800
As	0.1 - 3.0
Ba	1.0 - 15
Cd	0.2 - 15
Cr (total)	0.75 - 25
Cr (hexavalent)	0.1 - 10
Cu	0.2 - 17
Fe	4.0 - 100
Pb	0.1 - 5.0
Hg	0.0005 - 0.3
Ni	0.2 - 10
Ag	0.2 - 5.0
Zn	1.0 - 16.5
Fluoride	2.5 - 60

\*Value in pH units.

and grease, which, if returned to the system, would tend to foul the heat exchangers.

Finally, note that many air-separation plants have opted to utilize biodegradable corrosion inhibitors for cooling water when possible.

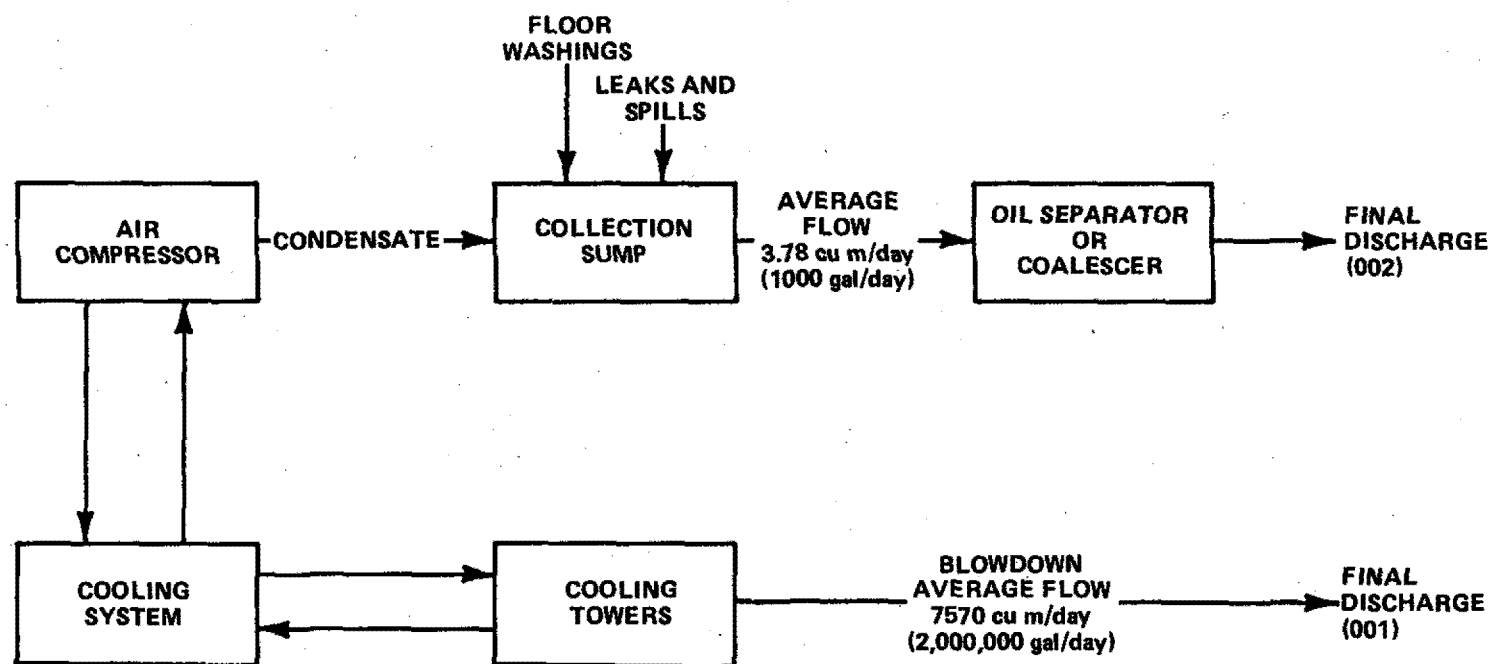
### Pretreatment

The use of pretreatment technology has been employed by the nitrogen and oxygen manufacturing industry to some degree since the inception of the industrial process of air separation. The level of treatment has been dependent on both the volume and waste characteristics of the process waters produced. Oily compressor condensate has been, and continues to be, the only significant process contact water produced which may be part of the total plant discharge. Most manufacturers, however, do not consider this to be a major problem in plant operation. Early efforts were made to physically contain the process water in a holding pond or ditch. Some plants employed a slightly more advanced technology using oil skimmers or weirs and dams, in conjunction with holding ponds, to separate the oil/water mixture. This produced a more acceptable effluent. In fact, various modifications of this type of oil separation still constitute the most widely practiced technology. Oil emulsifiers and coalescers are also utilized to some extent as a means to treat oily wastes.

In most contemporary air-separation plants, the flow of oily condensate waste water appears to be a major determining factor in the type of waste treatment employed. For example, Plant 13103 produces only about 7.5 liters (2.0 gallons) of compressor condensate per day. This small volume is easily handled, and the treatment consists of completely collecting the waste stream in large drums, which are removed once a month by a contractor.

Plant 13102 discharges directly to a surface stream and employs an oil separator consisting of a series of holding ponds with oil skimmers. The daily average flow, as indicated in Figure 53 is approximately 3.78 cubic meters (1,000 gallons). The treated effluent is discharged separately from the cooling-tower blowdown (although, in many plants, it is common practice to combine the two streams prior to discharge). The oil and grease concentration of the separator effluent ranges from 10 to 15 mg/l, which is well below any potentially harmful concentration for this pollutant. This effluent would be considered acceptable for either direct or indirect discharge.

Figure 53. FLOW DIAGRAM SHOWING PRETREATMENT OF WASTEWATER IN PRODUCTION OF NITROGEN AND OXYGEN (PLANT 13101)



Plant 13101 is currently discharging to a POTW and producing an effluent with an average oil and grease concentration of 9.0 mg/l. The type of pretreatment system employed by this plant is representative of another type of oil separator. A flow diagram for this treatment system is given in Figure 54. The average daily flow handled by this system is approximately 22.5 cubic meters (5,950 gallons), but this can vary considerably over a 48-hour period, depending on chemical production and relative air humidity. The compressor condensate is contained in a central sump area, along with small volumes of equipment washdowns. This waste water is periodically pumped to one of two oilseparator holding tanks, which operate alternately. A chemical addition takes place when the terminal tank volume is reached. After a period of physical agitation, the tank contents are allowed to settle quiescently. The separated oil layer is skimmed off after approximately 3 hours of settling, and the treated effluent is drained from the tank and directed to the cooling-water discharge leaving the plant. The collected oil is placed in a large drum, which is periodically removed by a contractor.

An analysis of the efficiency of the treatment system is given in Table 26. Note that the effluent pH indicated is abnormally high, due to a miscalculation of the amount of caustic added on the day the sample was taken. Caustic is normally added to adjust the pH of the system after the initial addition of the acidic chemicals.

#### Compatibility with POTW

The wastewater generated from production of nitrogen and oxygen contains oil and grease from compressor condensate. The flows are generally small (from 1000 to 7000 gallons per day) and the amounts of oil and grease discharged will not interfere with POTW operation, and will be adequately removed by the POTW. No pretreatment is indicated.

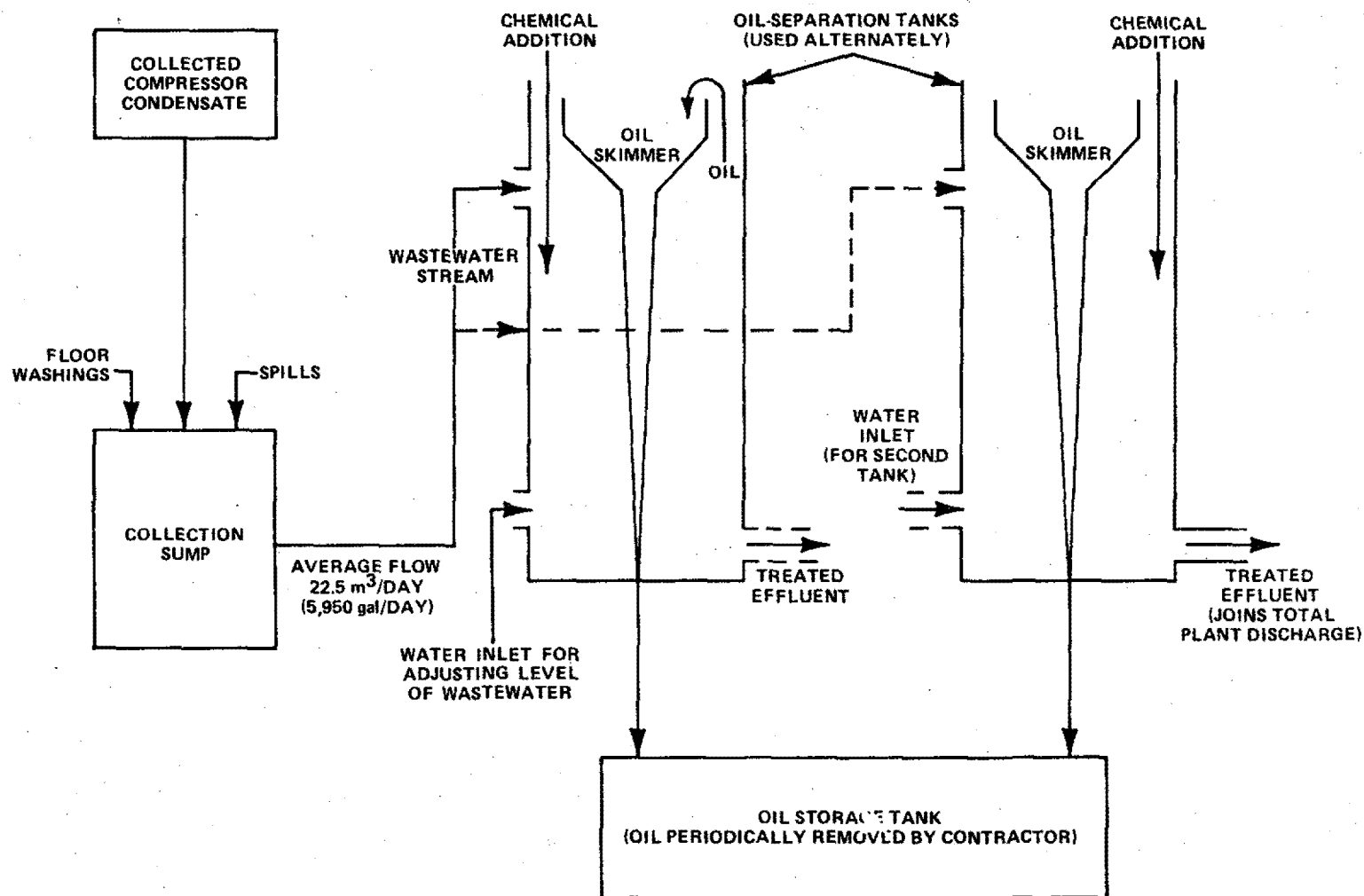
#### TYPICAL PRETREATMENT OPERATIONS FOR POTASSIUM DICHROMATE SUBCATEGORY

##### Control

As discussed previously in Section V, the manufacturing process employed at the single known plant in this subcategory does not generate a wastewater discharge. Water used in the process is either consumed by evaporation or recycled as steam condensate. Information concerning the reason for this recycle is not available.

Figure 54. FLOW DIAGRAM OF OIL-SEPARATION PROCESS FOR TREATMENT OF COMPRESSOR-CONDENSATE WASTEWATER IN PRODUCTION OF NITROGEN AND OXYGEN (PLANT 13101)

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**TABLE 26. CHEMICAL COMPOSITIONS OF AND WASTE LOADINGS FOR COMPRESSOR-CONDENSATE WASTEWATER FROM PRODUCTION OF NITROGEN AND OXYGEN BEFORE AND AFTER TREATMENT BY OIL-SEPARATION PROCESS (PLANT 13101)**

PARAMETER	OIL-SEPARATOR INFLUENT *			OIL-SEPARATOR EFFLUENT†		
	CONCENTRATION (ppm)	WASTE LOAD		CONCENTRATION (ppm)	WASTE LOAD	
		kg/1000 metric tons	lb/1000 short tons		kg/1000 metric tons	lb/1000 short tons
pH	6.4**	—	—	11.4**	—	—
TDS	560	24	48	1,400	58	116
TSS	780	33	66	22	0.94	1.88
Oil and Grease	1,960	84	168	9.0	0.38	0.76
Cd	< 0.01	< 0.00043	< 0.00086	< 0.01	< 0.00043	< 0.00086
Cr (total)	0.85	0.036	0.072	0.81	0.035	0.070
Cu	0.48	0.021	0.042	< 0.02	< 0.00086	< 0.0017
Pb	< 0.02	< 0.00086	< 0.0017	< 0.02	< 0.00086	< 0.0017
Hg	< 0.0002	< 0.00001	< 0.00002	< 0.0002	< 0.00001	< 0.00002
Zn	0.34	0.015	0.030	0.02	0.00086	0.0017

\*Analyses based on composite of four individual grab samples taken over 8-hour period.

†Analyses based on single grab sample taken approximately 4 hours after initiation of treatment.

\*\*Value in pH units.

If water is used at this plant for cleanup of spills or equipment, good housekeeping measures could be employed to reduce the volume of water required for these purposes. Such housekeeping measures would essentially be spill prevention precautions.

In the past, water used for cooling during the vacuum crystallization step of this process was contaminated with chromium. Plant officials reportedly planned to correct this problem during 1975 through the replacement of a barometric condenser with a noncontact heat exchanger.

#### Pretreatment

No known process-related waste water is present at Plant 19901. Assuming that the barometric condenser mentioned previously has been replaced with a heat exchanger the cooling water should no longer be contaminated with chromium. This being the case, this cooling water should require no treatment prior to discharge.

However, it is possible that water is used at this plant for the purpose of equipment washdowns and cleanup of spills. Should this be the case, it is likely that this water would be contaminated to a significant extent. Although the volume or character of such waste water is unknown it is expected that chrome would be the waste parameter of primary concern. In this case, it is possible that an applicable removal technology would be reduction of hexavalent chromium with sulfur dioxide ( $\text{SO}_2$ ) followed by lime precipitation of trivalent chromium.

#### Compatability with POTW

The wastes generated from potassium dichromate production could be contaminated by chromium, which in its hexavalent state is soluble and extremely toxic to biological treatment plant biota and to higher life forms. In addition, only incidental removal efficiencies insufficient to achieve effluent quality can be expected at the POTW. (See Table 21.) Therefore, pretreatment for control of chromium is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR POTASSIUM IODIDE SUBCATEGORY

##### Control

In this industry, waste water originates primarily as equipment and floor washdown and from the cleanup of spills.

Control measures applicable to these waste waters include simply good housekeeping and spill prevention precautions.

An in-process control measure is indicated in Figures 16, 17, and 18. This consists of mother liquor recycle for the purpose of recovering residual product values. Because waste solids generated in the manufacturing processes employed in this industry are typically landfilled, the practice of recycle of mother liquor results in no discharge of wastewater directly from these processes. The single exception is Plant 20103 which reportedly slurries the waste solids and discharges this slurry to a POTW.

### Pretreatment

Presently, only two of the four plants comprising this industry subcategory (Plants 20102 and 20103) discharge to POTWs. Neither of these plants practices pretreatment of its waste water prior to discharge. One of the two plants not discharging to a POTW (Plant 20101) is located on the West Coast and achieves zero discharge by use of an evaporation pond. The other plant (Plant 20104) treats waste water originating from a multitude of chemical manufacturing processes in a single, central treatment facility. The treatment technology employed includes pH adjustment, flocculation, and clarification.

As discussed previously in Section V, waste water generated in this industry subcategory includes equipment and floor washdown and cleanup of spills. Once-through, noncontact cooling water is also discharged. Plant 20102 daily discharges to a POTW an average of 32.6 cubic meters (8,600 gallons) of water used for noncontact cooling. With the exception of an elevation in temperature, the character of this water is expected to change little. POTWs which have established temperature requirements for waste waters received from industry have generally indicated a temperature limitation of 66°C (150°F). It is not expected that cooling water used once and discharged will approach or exceed this temperature.

At all plants in this industry subcategory, small quantities of water are used to clean up product or reagent spills and to wash down equipment, etc. Water used for these purposes will vary in degree of contamination. Raw materials and process products which such water will most likely contact at some time include: potassium iodide, potassium iodate, potassium hydroxide, potassium carbonate, and iron powder. Of these, the potassium hydroxide (a strong base) is of greatest concern from the viewpoint of compatibility with a POTW operation. Limitations established by POTWs require



the pH of water received from industry to be within the range of 6.0 to 9.0 in most instances and, in some instances, 5.5 to 10.5. Control of pH by use of neutralizing agents is a well-known technology. Such technology can be reasonably applied should pH of the waste water exceed the limits imposed by a POTW. However, in view of the small volumes of water being discharged, it is expected that the most effective and most economically desirable alternative is simply spill prevention and good housekeeping measures.

#### Compatability with POTW

Discharge from potassium iodide production generally consist solely of non-contact cooling water, and extremely small quantities of water used for equipment washdown or cleanup of spills. The wastes will not adversely affect POTW performance, and any pollutants picked up during the washdown process (oil and grease, suspended solids) will receive adequate treatment in the POTW. Therefore, no pretreatment is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR SILVER NITRATE SUBCATEGORY

##### General

Wastewater generated during silver nitrate production includes: evaporator condensate, chemical-purification waste water, NO<sub>x</sub> emissions-control scrubber water, and floor and equipment wash water. These waste streams are combined and sent to a silver-recovery unit, where 99+% of the silver present in the waste water is removed. The resultant waste water is discharged to a treatment system.

##### Control

The silver nitrate production industry makes great use of recycling as a way to recover quantities of valuable silver and as a waste water control technology. Plant 20201 recycles evaporator condensate back to the nitric acid recovery unit. In addition, large quantities of noncontact condensate are used in the operation of boilers and turbines. Plant 20202 recycles centrifuge washwater back to the filtration step to recover additional silver nitrate.

Neither Plant 20201 nor Plant 20202 recycles equipment and floor washings back to the process. These washings are undoubtedly high in suspended solids, and the potential for recycle within the process without some settling is doubtful. Both plants direct these waste streams to silver recovery

units, thus reducing pollutant loads without reducing wastewater volume.

#### Pretreatment

Plant 20201 combines the waste water from the silver-recovery unit with waste water from other inorganic-chemical processes, with sanitary wastes, and with storm runoff. These combined waste streams are then directed to the company's industrial waste water-treatment plant. The treatment plant is a biological-treatment system consisting of primary clarification, neutralization, an activated-sludge process, trickling filters, secondary clarification, and chlorination.

Highly toxic levels of silver are present in the waste water generated during silver nitrate production. However, the concentration of silver is reduced by a factor of 1000 due to dilution by other streams entering the treatment system. This dilution allows large quantities of silver to enter the treatment plant without creating adverse effects on the biota.

The chemical characteristics of the discharge from Plant 20201's biological-treatment system are presented in Table 27. Note that significant reductions in metals are shown.

The waste water generated from silver nitrate production by itself is not amenable to biological treatment. In addition, significant removal of metals cannot be predicted from a biological-treatment system. Therefore, use of more conventional physical/chemical pretreatment technology is recommended. Figure 55 illustrates a batch pretreatment system.

Lime is added to form insoluble hydroxides, and polyelectrolyte is added to enhance flocculation. The resultant slurry is fed to a plate and-frame filter press to remove suspended material. Filtrate is recycled until the desired effluent quality is achieved and then discharged. Sludge is removed from the filter and landfilled.

#### Compatibility with POTW

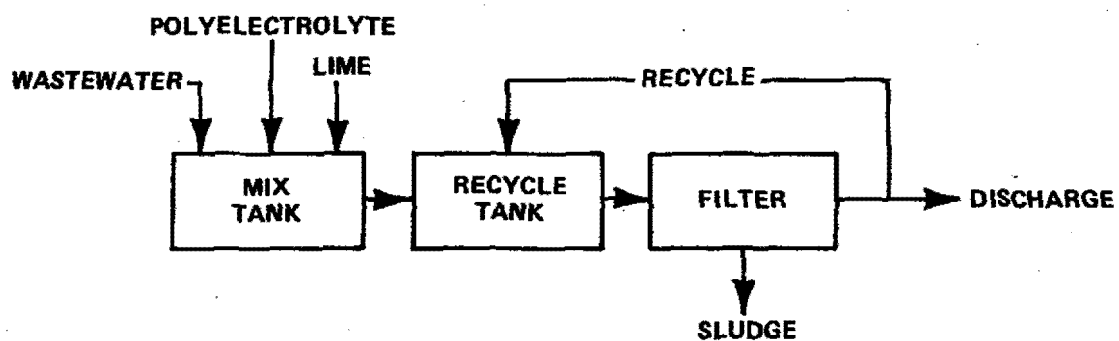
The waste streams generated from silver nitrate production can contain silver in quantities which exceed the quantities prescribed by most treatment plants. (See Table 25.) Silver in concentrations greater than 5 mg/l will inhibit biological treatment processes. In addition, only incidental removal efficiencies insufficient to achieve acceptable effluent quality can be expected at the POTW.

**TABLE 27. CHEMICAL COMPOSITION OF TREATED WASTEWATER  
DISCHARGED FROM PRODUCTION OF SILVER NITRATE  
(PLANT 20201)**

PARAMETER	CONCENTRATION (mg/l)
pH	7.1*
TSS	70
Ag	0.15
Ba	0.90
Cd	0.19
Cu	0.11
Fe	1.7
Pb	0.16
Mn	1.2
Hg	< 0.0001
Ni	0.11
Zn	1.0

\*Value in pH units.

**Figure 55. FLOW DIAGRAM SHOWING WASTEWATER PRETREATMENT USED IN PRODUCTION OF SILVER NITRATE (PLANT 20201)**



(See Table 21.) Therefore, pretreatment to reduce silver concentrations is indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR SODIUM BICARBONATE SUBCATEGORY

##### General

As discussed in Section V of this document, there are several sources of process waste water from the manufacture of sodium bicarbonate. Control and pretreatment technologies employed within the industry are discussed below for the following process waste water:

- (a) Recycle-liquor overflow
- (b) Filter backwash
- (c) Spills, leaks, and washdowns

Of these, recycle-liquor overflow (the combined waste water generated from slurry-thickener overflow and dryer emissions-control scrubber water) is the most significant from the standpoint of pretreatment in the sodium bicarbonate industry.. The volume and pollutant content of this process waste water far exceed those of other process-waste water sources for the industry.

Little information on waste water generated from the cleaning of filter media during backwash is available for the sodium bicarbonate industry. Observations made in this section on this waste water source are based upon the general nature of the waste water.

Wastewater generated from the spillage and leakage of raw materials and product from the sodium bicarbonate manufacturing process is not considered to be a major problem.

The discussions which follow treat, in turn, each of the waste water sources tabulated above.

##### Control

Recycle-Liquor Overflow. One of the three sodium bicarbonate producers has achieved zero discharge of sodium bicarbonate process waste water through impoundment. This facility, Plant 12103, has a favorable water balance, which allows sufficient evaporation to occur during waste water impoundment.

One plant presently plans to use slurry-thickener overflow as a source of liquid for the product-dryer scrubber.

Recycling this liquid to concentrate it with respect to sodium carbonate will enable it to be reused in the process. These process changes will eliminate the discharge of process waste water.

Filter Backwash. The purpose of filtration is to physically remove particulate matter from solution, and the purpose of backwashing the filter is to remove the accumulated particulate matter from the filter. Thus, the resulting backwash waste water contains large amounts of suspended solids. To recycle or reuse this water, the solids must be settled. The amount of use this control technique receives within the sodium bicarbonate industry is not known at this time.

Spills, Leaks, and Washdowns. Plants 12101, 12102, and 12103 all produce a refined, food-grade sodium bicarbonate product. It is mandatory for such facilities to employ good housekeeping procedures and thereby keep the quantity of this waste water small.

#### Pretreatment

Recycle-Liquor Overflow. Plants 12101 and 12102 are presently treating process waste waters by settling prior to discharge to surface water bodies. Untreated slurry-thickener overflow is combined with waste water from other segments of the complex in the settling basin. The degree of treatment achieved at these plants is shown in Table 28.

Both plants claim 99+% suspended-solids removals in their settling ponds, and Plant 12102 is aiming for a residual TSS concentration of 15 mg/l by the use of polyelectrolytes as settling aids.

Filter Backwash. Plant 12101 presently combines filter-backwash water with other sodium bicarbonate process waste water and discharges these wastes to a settling basin prior to discharge to a surface water body. Total suspended-solids removals of 99+% in the settling basin are claimed. Similar TSS removal efficiencies are reported at Plant 12102.

Spills, Leaks, and Washdowns. Plants 12101 and 12102 presently combine this waste water with other wastes generated within the complexes and settle the combined waste stream prior to discharge. Suspended solids, which are the major constituent of this waste water, are removed to a large degree in the settling basins.

**TABLE 28. EFFECTS OF TREATING WASTEWATER BY SETTLING IN PRODUCTION OF SODIUM BICARBONATE (PLANTS 12101 AND 12102)**

PARAMETER	RANGE OF CONCENTRATION (mg/l) IN SETTLING-POND OVERFLOW	
	Plant 12101*	Plant 12102
pH	10.6 to 11.5 <sup>†</sup>	—
TSS	26 to 1,784	20 to 30
TDS	34,227 to 87,046	—

\*Company monthly monitoring data for period November 1972 through April 1973.

<sup>†</sup>Value in pH units.

Plant 12103 presently discharges plant runoff directly to a surface water body.

#### Compatibility with POTW

The various waste streams generated from sodium bicarbonate production contain high levels of suspended solids (TSS) and dissolved solids (TDS). The wastes do not contain any substances which would be likely to upset POTW performance. Suspended solids would receive adequate treatment in a POTW. The dissolved solids would pass through a POTW without treatment. There is, however, no existing practicable technology for TDS removal, and the TDS in question pose no hazard to the environment. Pretreatment for this subcategory is not indicated.

#### TYPICAL PRETREATMENT OPERATIONS FOR SODIUM FLUORIDE SUBCATEGORY

##### General

There are several sources of process waste water in the sodium fluoride manufacturing industry, including:

separated silicate liquor,  
clarifier supernatant,  
scrubber blowdown ,  
washdown .

All of these sources may produce a waste water containing varying amounts of fluoride, suspended solids, and dissolved solids at different pHs. Consequently, it is more advantageous to combine these process waste water streams and treat them simultaneously rather than to treat each of the individual process waste water streams for the removal of the same pollutants. Control and treatment technologies employed by potential POTW dischargers are essentially the same for all process waste streams, and the discussion which follows centers around the removal or reduction of selected pollutant parameters from the process waste water as a whole.

From a pretreatment standpoint, the single most important pollutant present in process waste water from the manufacture of sodium fluoride is fluoride ion. It is incompatible with the operation of a POTW at the concentrations found in untreated process waste effluent.



## Control

Two of the three sodium fluoride producers have achieved zero discharge of fluoride-containing process waste water through the use of water recycle. Depending upon the manufacturing process employed and the chemical characteristics of the process waste water to be recycled, treatment may or may not be required prior to reuse of the water.

The manufacturing process employed at Plant 20301 is such that the process waste water is actually unreacted raw material in solution. This process waste stream is fairly homogeneous and can simply be recycled to the reactor without treatment.

Plant 20302 employs a different manufacturing process, using caustic soda and sodium silicofluoride as raw materials. The process waste water at this plant consists of separated silicate liquor, which is not a desirable input to the batch reactor and cannot be recycled without treatment. Therefore, this process waste stream is combined with other plant wastes and piped to a solids-retention pond, where neutralization and sedimentation occur. The plant has recently installed a surge pond to retain the solids-retention pond runoff during heavy rains. Effluent from the surge pond is recycled to the plant complex. A treatment system flow diagram for Plant 20302 is shown as Figure 56.

## Pretreatment

Plant 20303 is the only sodium fluoride manufacturer characterized which is not achieving zero discharge of sodium fluoride process waste water. At Plant 20303, untreated sodium fluoride process waste water is combined with the waste streams from the manufacture of various other inorganic and organic chemicals. This combined waste water is treated at a central treatment facility. The treatment facility is basically a lime-precipitation, flocculation, and sedimentation operation employing aeration, partial recirculation, and multiple pH adjustment. A simplified flow schematic of the central waste water treatment facility at Plant 20303 is shown as Figure 57. The degree of treatment achieved at this plant is enumerated in Table 29. The treatment-plant effluent is of neutral pH, with a low residual TSS content. The total dissolved-solids content of the combined waste stream remains nearly unchanged in passing through the treatment sequence. Fluoride effluent concentrations of 20 mg/l have been reported using lime treatment.

**Figure 56. FLOW DIAGRAM OF WASTEWATER-TREATMENT SYSTEM USED  
IN PRODUCTION OF SODIUM FLUORIDE (PLANT 20302)**

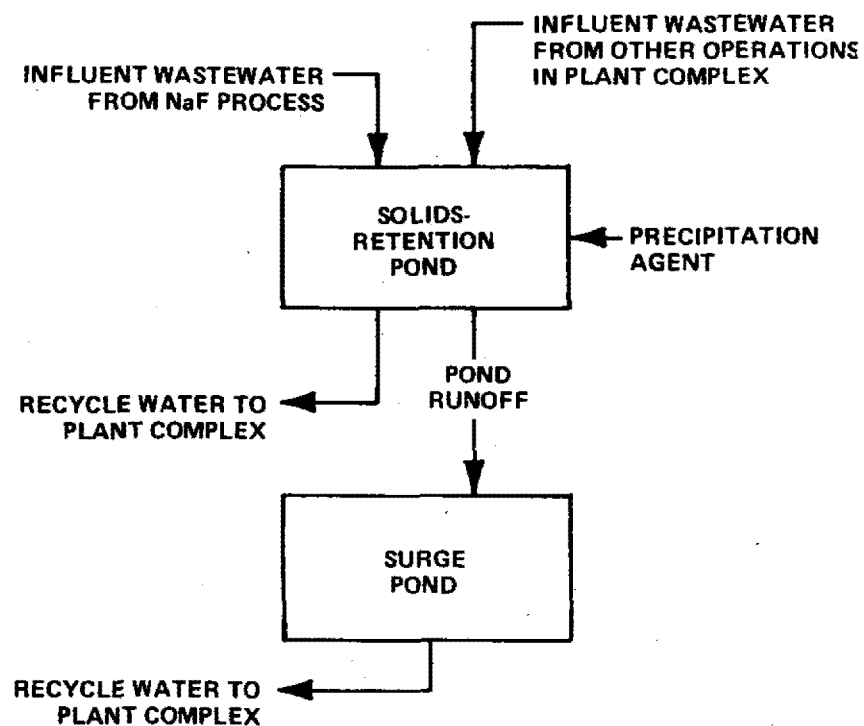
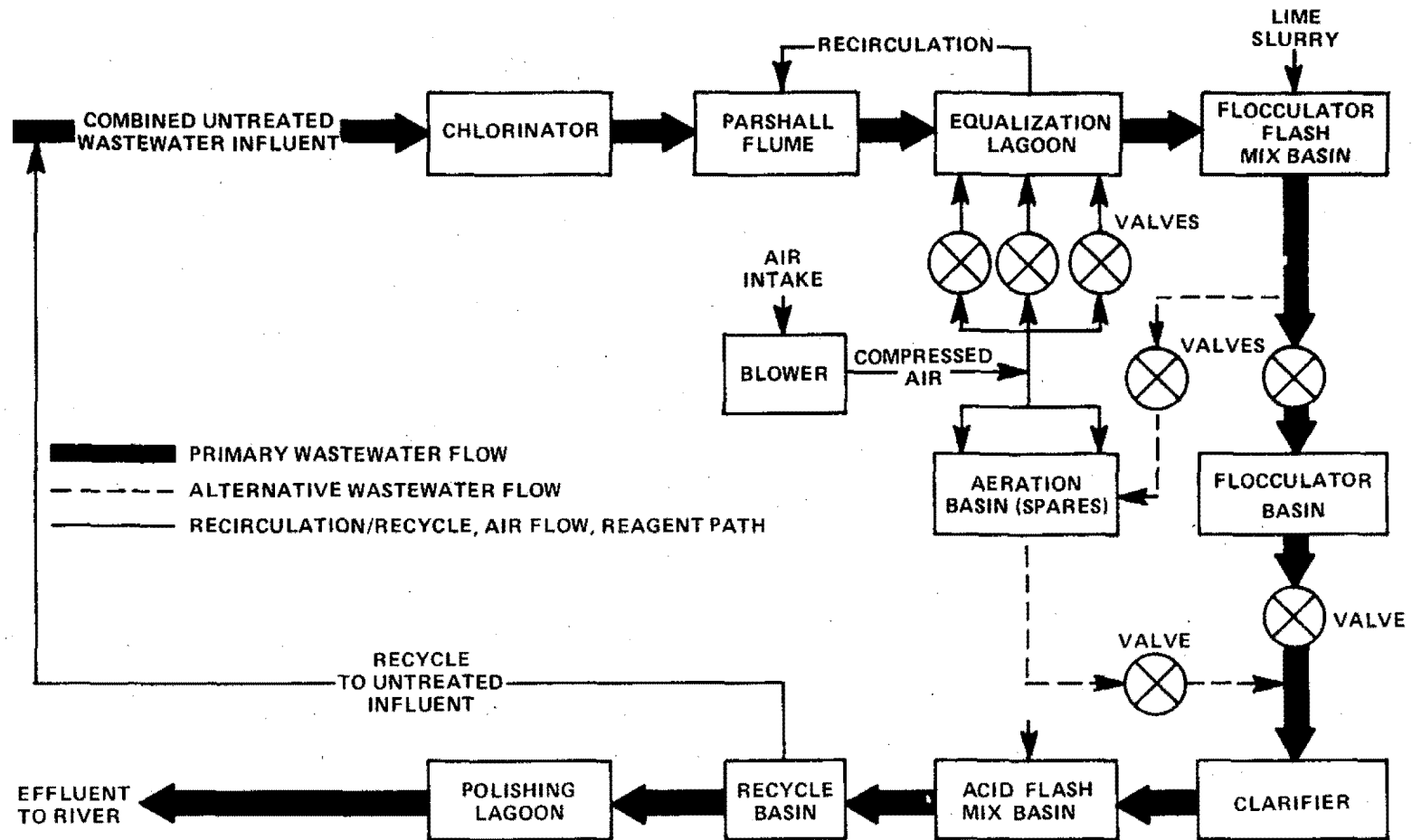


Figure 57. FLOW DIAGRAM OF CENTRAL WASTEWATER-TREATMENT SYSTEM USED IN PRODUCTION OF SODIUM FLUORIDE (PLANT 20303)



**TABLE 29. CHEMICAL COMPOSITIONS OF RAW  
AND TREATED WASTEWATERS FROM  
PRODUCTION OF SODIUM FLUORIDE  
AND OTHER CHEMICALS (PLANT 20303)**

PARAMETER	CONCENTRATION (mg/l)*	
	INFLUENT	EFFLUENT
pH	6.2 <sup>†</sup>	7.1 <sup>†</sup>
TDS	870	900
TSS	36	8.7
Fluoride	N/A	N/A

\* Combined wastewater influent from production of sodium fluoride and numerous other inorganic and organic chemicals; average values based on company monitoring data.

<sup>†</sup> Value in pH units.

N/A Data not available.

Comparative laboratory and pilot-plant tests have shown that the use of calcium chloride with lime may have advantages over classic lime treatment (Reference 16).

Residual fluoride concentrations after lime treatment are mainly dependent upon:

- (1) maintenance of high soluble calcium-ion concentrations at pH 11 to 12 or higher,
- (2) long retention times of precipitated calcium fluoride to encourage postprecipitation, and
- (3) exclusion of interfering ions.

Both methods of treatment depend upon the availability of soluble calcium ion when either lime or lime and calcium chloride are fed to fluoride-bearing waste water streams. Insoluble calcium fluoride that is precipitated can be separated by sedimentation, filtration, or combinations of the two. The reaction is:



The solubility product of calcium fluoride at 18°C (64°F) suggests that residual fluoride levels of 7.8 mg/l may be attained.

The solubility of calcium hydroxide at 20°C (68°F) is 1.69 g/l, compared to the higher solubility of calcium chloride of 745 g/l at 20°C. The theory is that the more soluble calcium chloride provides higher soluble calcium-ion concentrations than lime alone and that, therefore, lower residual fluoride concentrations will result. At the same time, by using lime with calcium chloride, rather than calcium chloride alone, costs can be reduced, since calcium chloride is the more expensive of the two reagents.

#### Compatibility with POTW

Wastewater generated from the production of sodium fluoride can contain concentrations of fluoride which exceed the limits prescribed by most POTW. (See Table 25.) Fluoride concentrations in raw process water of 16000 mg/l have been reported. Fluoride is recognized as being extremely toxic to fish, wildlife, livestock, and humans. It would pass thorough a POTW without being treated or removed. Therefore, pretreatment for control of fluoride is indicated.

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## SECTION VIII

### COST, ENERGY, AND IMPLEMENTATION

#### INTRODUCTION

Capital and annual costs for waste water-pretreatment processes prior to discharge to POTWs are presented for selected inorganic chemical manufacturing operations. The costs are expressed in 4th-quarter 1975 dollars.

The following chemicals are considered:

Aluminum chloride (two options)	Nickel sulfate
Aluminum sulfate (two options)	Nitrogen and oxygen
Calcium carbide	Potassium dichromate
Calcium chloride	Potassium iodide
Copper (cupric) sulfate	Silver nitrate
Iron (ferric) chloride (two options)	Sodium bicarbonate
Lead monoxide	Sodium fluoride

The costs, cost factors, and costing methodology used to derive the capital and annual costs are documented following consideration of the control costs for each chemical manufacturing subcategory. For the aluminum chloride, aluminum sulfate, and iron (ferric) chloride subcategories, additional costs are presented which reflect options available to reduce the costs of pretreatment. Clearly, use of these alternative pretreatment technologies will result in less reduction of pollutants than the primary pretreatment technologies.

The types of costs shown for each model plant are:

- (a) capital costs
- (b) annual costs
- (c) cost per metric ton of product

The capital and annual costs are total costs. The actual additional costs a plant would incur in implementing the described treatment processes depend on current treatment practices.

The price per metric ton of product and the percentage that the treatment cost is of the product (selling) price area also shown. The latter value provides an initial estimate of the potential economic impact of implementing the treatment system on the manufacturing operation.

The plants are assumed to operate 24 hours per day, 350 days per year, except where noted otherwise.

Pretreatment costs for chemical manufacturing operations are based on estimates of daily waste water flows, concentrations of chemicals in the waste water (as described in Section VII), and annual production. Manufacturing plants are assumed to be single-product plants.

The pretreatment processes for which costs are developed do not necessarily represent optimum systems, with respect either to removal or reduction of hazardous chemicals or to economic efficiency. Rather, the selected pretreatment processes are representative of the types of systems and activities which may be required.

Industry costs are based on model-plant characteristics and treatment processes specified for each manufacturing operation. Treatment costs for a specific manufacturing operation are primarily a function of the magnitude of the waste water flow. Available data indicate that flows can vary significantly among plants manufacturing the same product. To the extent possible, extrapolation of industry costs from model-plant costs should be based on flow, rather than on production capacity.

#### CONTROL COSTS FOR ALUMINUM CHLORIDE SUBCATEGORY (TABLES 30 & 32)

The treatment processes proposed are:

- Metal precipitation/neutralization
- Settling
- Filtration
- Discharge to POTW/sanitary landfill

Caustic soda (sodium hydroxide) is added to the waste stream at the rate of 2.16 g/l (18 lb/1000 gal) of waste water and forms 1.4 g (dry weight) of solids per liter (12 lb/1000 gal) of waste water. Settling tanks sized for 24-hour retention are provided, yielding an underflow containing 3% solids. The underflow is pumped through a plate-and-frame filter. The resultant sludge contains about 10% solids and has a calculated specific gravity of 1.06. The sludge is benign and can be disposed of in a sanitary landfill. The treatment cost is relatively large compared to the product price, amounting to about 3.5% of the latter.

Alternative treatment processes include metal precipitation/neutralization and discharge to POTW. Caustic soda (sodium hydroxide) is added to the waste stream at the



TABLE 30. MODEL-PLANT CONTROL COSTS FOR ALUMINUM CHLORIDE INDUSTRY

## a. Proposed Pretreatment

PROCESS: <u>Metal Precipitation, Neutralization, Settling and Filtration,</u> <u>Discharge to POTW, and Sanitary Landfill</u>			
	PLANT A	PLANT B	PLANT C
PLANT ANNUAL CAPACITY IN METRIC TONS*:	10,500	7,000	
PLANT DAILY WASTEWATER FLOW IN LITER <sup>†</sup> :	53,000	35,300	
CAPITAL COST (\$)			
FACILITIES			
Wastewater sump/sludge pit	6,700	5,300	
EQUIPMENT			
Metal-precipitation/neutrali- zation system	9,000	8,700	
Settling tank	14,300	10,100	
Filter	20,000	15,000	
Pumps	900	900	
Piping	900	900	
Installation	44,200	34,700	
CONTINGENCY AND CONTRACTOR'S FEE	19,200	15,100	
TOTAL CAPITAL INVESTMENT	115,200	90,700	
ANNUAL COST (\$)			
AMORTIZATION	18,780	14,780	
OPERATION AND MAINTENANCE (O&M)			
OPERATING PERSONNEL	21,000	12,600	
FACILITY REPAIR AND MAINTENANCE	200	160	
EQUIPMENT REPAIR AND MAINTENANCE	4,470	3,520	
MATERIALS	17,030	11,350	
TAXES AND INSURANCE	4,610	3,630	
SLUDGE DISPOSAL	1,300	860	
ELECTRICITY	1,280	1,020	
TOTAL ANNUAL COST	68,670	47,920	
TREATMENT COST/METRIC TON OF PRODUCT**	6.54	6.85	
PRICE/METRIC TON OF PRODUCT**		198	
% TREATMENT COST OF PRODUCT PRICE	3.3	3.5	

\*To convert to short tons, multiply value shown by 1.1.

<sup>†</sup>To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

TABLE 31. MODEL-PLANT CONTROL COSTS FOR ALUMINUM CHLORIDE INDUSTRY

## b. Alternative Pretreatment

PROCESS: <u>Metal Precipitation, Neutralization, Discharge to POTW</u>			
	PLANT A	PLANT B	PLANT C
PLANT ANNUAL CAPACITY IN METRIC TONS*:	10,500	7,000	
PLANT DAILY WASTEWATER FLOW IN LITERS†:	53,000	35,300	
CAPITAL COST (\$)			
FACILITIES			
Wastewater sump	5,500	4,400	
EQUIPMENT			
Metal precipitation/neutralization			
System	9,000	8,700	
Pump	500	400	
Piping	900	900	
Installation	9,500	9,100	
CONTINGENCY AND CONTRACTOR'S FEE	5,100	4,700	
TOTAL CAPITAL INVESTMENT	30,500	28,200	
ANNUAL COST (\$)			
AMORTIZATION	4,970	4,600	
OPERATION AND MAINTENANCE (O&M)			
OPERATING PERSONNEL	8,400	4,200	
FACILITY REPAIR AND MAINTENANCE	170	130	
EQUIPMENT REPAIR AND MAINTENANCE	1,000	960	
MATERIALS	17,030	11,350	
TAXES AND INSURANCE	1,220	1,130	
SLUDGE DISPOSAL	---	---	
ELECTRICITY	1,080	830	
TOTAL ANNUAL COST	33,870	23,200	
TREATMENT COST/METRIC TON OF PRODUCT**	3.23	3.31	
PRICE/METRIC TON OF PRODUCT**		198	
% TREATMENT COST OF PRODUCT PRICE	1.6	1.7	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

rate of 2.16 g/l (18 lb/1,000 gal) of waste water. The treatment cost is about 1.6% of the product price.

CONTROL COSTS FOR ALUMINUM SULFATE SUBCATEGORY (TABLES 32 & 33)

The treatment processes proposed are:

- Metal precipitation/neutralization
- Thickening
- Filtration
- Discharge to POTW/sanitary landfill

Each liter of waste water is treated with 11.2 g (0.024 lb) of hydrated lime, which forms 30 g (0.07 lb) of solids (dry weight). The thickeners are sized for 8-hour retention and yield an underflow which contains 15% solids. The use of rotary vacuum filters thickens the sludge to 40% solids. This sludge has a specific gravity of 1.3. Approximately 23 cubic meters (6,100 gallons) and 2 cubic meters (530 gallons) are generated by Plants A and B, respectively. The treatment costs range from about 2% to 4% of the product price.

Alternative treatment processes include metal precipitation/neutralization and discharge to POTW. Each liter (1.6 quarts) of waste water is treated with 11.2 g (0.24 lb) of hydrated lime. The treatment costs range from about 0.5% to 1.9% of the product price.

CONTROL COSTS FOR CALCIUM CARBIDE SUBCATEGORY

No pretreatment of waste water appears necessary for plants which manufacture calcium carbide.

CONTROL COSTS FOR CALCIUM CHLORIDE SUBCATEGORY

No pretreatment of waste water appears necessary for plants which manufacture calcium chloride.

CONTROL COSTS FOR COPPER (CUPRIC) SULFATE SUBCATEGORY (TABLE 34)

The treatment processes proposed are:

- Metal precipitation/neutralization
- Settling
- Discharge to POTW/chemical landfill

Hydrated lime is added at a rate of 1.2 g per liter (10 lb/1000 gal) of waste water. This results in the formation

TABLE 32. MODEL-PLANT CONTROL COSTS FOR ALUMINUM SULFATE INDUSTRY

## a. Proposed Pretreatment

<b>PROCESS:</b> Metal Precipitation, Neutralization, Thickening, Discharge to POTW and Sanitary Landfill			
	<b>PLANT A</b>	<b>PLANT B</b>	<b>PLANT C</b>
<b>PLANT ANNUAL CAPACITY IN METRIC TONS*:</b>	64,000	40,000	
<b>PLANT DAILY WASTEWATER FLOW IN LITERS†:</b>	400,000	34,000	
<b>CAPITAL COST (\$)</b>			
<b>FACILITIES</b>			
Wastewater sump/sludge pit	32,800	6,300	
<b>EQUIPMENT</b>			
Metal precipitation/neutralization system	15,000	8,500	
Thickener	36,000	12,500	
Filter	65,000	26,500	
Pumps	1,500	900	
Piping	6,000	900	
Installation	117,500	48,400	
<b>CONTINGENCY AND CONTRACTOR'S FEE</b>	54,800	20,800	
<b>TOTAL CAPITAL INVESTMENT</b>	328,600	124,800	
<b>ANNUAL COST (\$)</b>			
<b>AMORTIZATION</b>	53,560	20,340	
<b>OPERATION AND MAINTENANCE (O&amp;M)</b>			
OPERATING PERSONNEL	33,600	25,200	
FACILITY REPAIR AND MAINTENANCE	980	190	
EQUIPMENT REPAIR AND MAINTENANCE	12,050	4,880	
MATERIALS	84,700	7,200	
TAXES AND INSURANCE	13,140	4,990	
SLUDGE DISPOSAL	52,500	4,460	
ELECTRICITY	11,870	2,550	
<b>TOTAL ANNUAL COST</b>	262,400	69,810	
<b>TREATMENT COST/METRIC TON OF PRODUCT**</b>	4.10	1.74	
<b>PRICE/METRIC TON OF PRODUCT**</b>		98	
<b>% TREATMENT COST OF PRODUCT PRICE</b>	4.2	1.8	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

TABLE 33. MODEL-PLANT CONTROL COSTS FOR ALUMINUM SULFATE INDUSTRY

## b. Alternative Pretreatment

PROCESS: <u>Metal Precipitation, Neutralization, Discharge to POTW</u>			
	PLANT A	PLANT B	PLANT C
PLANT ANNUAL CAPACITY IN METRIC TONS*:	64,000	40,000	
PLANT DAILY WASTEWATER FLOW IN LITERS†:	400,000	34,000	
<b>CAPITAL COST (\$)</b>			
<b>FACILITIES</b>			
Wastewater sump	21,200	4,300	
<b>EQUIPMENT</b>			
Metal precipitation/neutralization			
System	15,000	8,500	
Pumps	1,000	500	
Piping	6,000	900	
Installation	16,000	9,400	
CONTINGENCY AND CONTRACTOR'S FEE	11,800	4,700	
TOTAL CAPITAL INVESTMENT	71,000	28,300	
<b>ANNUAL COST (\$)</b>			
AMORTIZATION	11,570	4,610	
<b>OPERATION AND MAINTENANCE (O&amp;M)</b>			
OPERATING PERSONNEL	12,600	4,200	
FACILITY REPAIR AND MAINTENANCE	640	130	
EQUIPMENT REPAIR AND MAINTENANCE	1,900	970	
MATERIALS	84,700	7,200	
TAXES AND INSURANCE	2,840	1,130	
SLUDGE DISPOSAL	---	---	
ELECTRICITY	2,810	890	
TOTAL ANNUAL COST	117,060	19,130	
TREATMENT COST/METRIC TON OF PRODUCT**	1.83	0.48	
PRICE/METRIC TON OF PRODUCT**		98	
% TREATMENT COST OF PRODUCT PRICE	1.9	0.5	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

**TABLE 34. MODEL-PLANT CONTROL COSTS FOR COPPER (CUPRIC)  
SULFATE INDUSTRY**

<b>PROCESS:</b> <u>Metal Precipitation, Neutralization, Settling, Discharge to POTW, and Chemical Landfill</u>			
	<b>PLANT A</b>	<b>PLANT B</b>	<b>PLANT C</b>
<b>PLANT ANNUAL CAPACITY IN METRIC TONS*:</b>	21,000	12,500	
<b>PLANT DAILY WASTEWATER FLOW IN LITERS†:</b>	33,000	19,600	
<b>CAPITAL COST (\$)</b>			
<b>FACILITIES</b>			
Wastewater sump/sludge pit	4,900	4,000	
<b>EQUIPMENT</b>			
Metal-precipitation/Neutrali-			
zation system	8,500	8,200	
Settling	9,700	7,000	
Pumps	900	900	
Piping	900	900	
Installation	19,100	16,100	
<b>CONTINGENCY AND CONTRACTOR'S FEE</b>	8,800	7,400	
<b>TOTAL CAPITAL INVESTMENT</b>	52,800	44,500	
<b>ANNUAL COST (\$)</b>			
<b>AMORTIZATION</b>	8,610	7,250	
<b>OPERATION AND MAINTENANCE (O&amp;M)</b>			
OPERATING PERSONNEL	8,400	8,400	
FACILITY REPAIR AND MAINTENANCE	150	120	
EQUIPMENT REPAIR AND MAINTENANCE	1,960	1,660	
MATERIALS	760	450	
TAXES AND INSURANCE	2,110	1,780	
SLUDGE DISPOSAL	6,980	4,150	
ELECTRICITY	640	640	
<b>TOTAL ANNUAL COST</b>	29,610	24,450	
<b>TREATMENT COST/METRIC TON OF PRODUCT**</b>	1.41	1.96	
<b>PRICE/METRIC TON OF PRODUCT**</b>		835	
<b>% TREATMENT COST OF PRODUCT PRICE</b>	0.2	0.2	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

of 2 g of dry solids per liter (17 lb/1000 gal) of waste water. The overflow from the settling tanks, sized for 24-hour retention, is discharged to a POTW. The underflow is sent to a secure landfill. The treatment costs represent 0.2% of the product price.

CONTROL COSTS FOR IRON (FERRIC) CHLORIDE SUBCATEGORY (TABLES 35 & 36)

The treatment processes proposed are:

- Metal precipitation/neutralization
- Settling
- Centrifuging
- Discharge to POTW/recycle

The addition of 9 g of hydrated lime per liter (75 lb/1000 gal) of waste water forms 10 g of solids (dry weight) per liter (83 lb/1000 gal) of waste water. The waste stream is directed to a settling tank, sized for 24-hour retention. The underflow from the settling tank (10% solids) is centrifuged. The resultant sludge is about 30% solids and is recycled. The sludge has an estimated specific gravity of 1.28. Approximately 1.3 cubic meters (340 gallons) and 0.23 cubic meter (61 gallons) of sludge, respectively, are recycled daily from Plants A and B. The cost of the proposed treatment is significant, amounting to 2 to 6% of product price.

Alternative treatment processes include metal precipitation/neutralization and discharge to POTW. Treatment consists of the addition of 9 g of hydrated lime per liter (75 lb/1,000 gal) of waste water. The cost of the proposed treatment amounts to 1.3% to 2.6% of product price.

CONTROL COSTS FOR LEAD MONOXIDE SUBCATEGORY (TABLE 37)

The treatment processes proposed are:

- Metal precipitation/neutralization
- Settling
- Discharge to POTW/recycle to lead smelters

The waste stream is treated with 0.35 g of hydrated lime per liter (2.9 lb/1000 gal) of waste water. This forms about 2.5 g of solids (dry weight) per liter (21 lb/1000 gal) of waste water. The settling tanks are sized for 4-hour retention. The sludge, after settling, is estimated to be about 50% solids with a specific gravity of 1.6. The daily amount of sludge recycled from Plant A is 1.4 cubic meters (370 gallons); from Plant B, 1.1 cubic meters (290 gallons).

**TABLE 35. MODEL-PLANT CONTROL COSTS FOR IRON (FERRIC)  
CHLORIDE INDUSTRY**

**a. Proposed Pretreatment**

<b>PROCESS:</b> Metal Precipitation, Neutralization, Settling, Discharge to POTW, and Chemical Landfill			
	<b>PLANT A</b>	<b>PLANT B</b>	<b>PLANT C</b>
<b>PLANT ANNUAL CAPACITY IN METRIC TONS*:</b>	19,600	5,000	
<b>PLANT DAILY WASTEWATER FLOW IN LITERS†:</b>	51,100	13,000	
<b>CAPITAL COST (\$)</b>			
<b>FACILITIES</b>			
Wastewater sump/sludge pit	7,300	4,800	
<b>EQUIPMENT</b>			
Metal-precipitation/neutrali- zation system	8,800	8,200	
Settling	8,200	3,400	
Centrifuge	20,000	20,000	
Pumps	900	900	
Piping	900	900	
Instillation	37,900	32,500	
<b>CONTINGENCY AND CONTRACTOR'S FEE</b>	16,800	14,100	
<b>TOTAL CAPITAL INVESTMENT</b>	100,800	84,800	
<b>ANNUAL COST (\$)</b>			
<b>AMORTIZATION</b>	16,430	13,820	
<b>OPERATION AND MAINTENANCE (O&amp;M)</b>			
OPERATING PERSONNEL	8,400	4,200	
FACILITY REPAIR AND MAINTENANCE	220	140	
EQUIPMENT REPAIR AND MAINTENANCE	3,840	3,300	
MATERIALS	8,860	2,250	
TAXES AND INSURANCE	4,030	3,390	
SLUDGE DISPOSAL			
ELECTRICITY	1,320	740	
<b>TOTAL ANNUAL COST</b>	43,100	27,840	
<b>TREATMENT COST/METRIC TON OF PRODUCT**</b>	2.20	5.56	
<b>PRICE/METRIC TON OF PRODUCT**</b>		100	
<b>% TREATMENT COST OF PRODUCT PRICE</b>	2.0	5.6	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.



TABLE 36. MODEL-PLANT CONTROL COSTS FOR IRON (FERRIC) CHLORIDE INDUSTRY

## b. Alternative Pretreatment

PROCESS: Metal Precipitation/Neutralization, Discharge to POTW			
	PLANT A	PLANT B	PLANT C
PLANT ANNUAL CAPACITY IN METRIC TONS*:	19,600	5,000	
PLANT DAILY WASTEWATER FLOW IN LITERS†:	51,100	13,000	
CAPITAL COST (\$)			
FACILITIES			
Wastewater sump	5,400	2,300	
EQUIPMENT			
Metal precipitation/neutralization			
System	8,800	8,200	
Pump	500	400	
Piping	900	900	
Installation	9,300	8,600	
CONTINGENCY AND CONTRACTOR'S FEE	5,000	4,100	
TOTAL CAPITAL INVESTMENT	29,900	24,500	
ANNUAL COST (\$)			
AMORTIZATION	4,870	3,990	
OPERATION AND MAINTENANCE (O&M)			
OPERATING PERSONNEL	8,400	4,200	
FACILITY REPAIR AND MAINTENANCE	160	70	
EQUIPMENT REPAIR AND MAINTENANCE	980	910	
MATERIALS	8,860	2,250	
TAXES AND INSURANCE	1,200	980	
SLUDGE DISPOSAL	---	---	
ELECTRICITY	830	570	
TOTAL ANNUAL COST	25,300	12,970	
TREATMENT COST/METRIC TON OF PRODUCT**	1.29	2.59	
PRICE/METRIC TON OF PRODUCT**		100	
% TREATMENT COST OF PRODUCT PRICE	1.3	2.6	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

TABLE 37. MODEL-PLANT CONTROL COSTS FOR LEAD MONOXIDE INDUSTRY

PROCESS: <u>Metal Precipitation, Neutralization, Settling, Discharge to POTW, and Sludge Recycle</u>			
	PLANT A	PLANT B	PLANT C
PLANT ANNUAL CAPACITY IN METRIC TONS*:	20,000	15,900	
PLANT DAILY WASTEWATER FLOW IN LITERS†:	437,700	348,200	
CAPITAL COST (\$)			
FACILITIES			
Wastewater sump/sludge pit	22,700	19,900	
EQUIPMENT			
Metal-precipitation/neutrali-			
zation system	16,000	14,000	
Settling	17,600	14,500	
Pumps	1,200	1,000	
Piping	900	800	
Installation	34,800	29,500	
CONTINGENCY AND CONTRACTOR'S FEE	18,600	15,800	
TOTAL CAPITAL INVESTMENT	111,800	95,500	
ANNUAL COST (\$)			
AMORTIZATION	18,220	15,570	
OPERATION AND MAINTENANCE (O&M)			
OPERATING PERSONNEL	12,600	8,400	
FACILITY REPAIR AND MAINTENANCE	680	600	
EQUIPMENT REPAIR AND MAINTENANCE	3,530	2,990	
MATERIALS	2,950	2,350	
TAXES AND INSURANCE	4,470	3,820	
SLUDGE DISPOSAL			
ELECTRICITY	3,060	2,550	
TOTAL ANNUAL COST	45,510	36,280	
TREATMENT COST/METRIC TON OF PRODUCT**	2.28	2.28	
PRICE/METRIC TON OF PRODUCT**		530	
% TREATMENT COST OF PRODUCT PRICE	0.4	0.4	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

The cost of treatment represents only 0.4% of the product price.

CONTROL COSTS FOR NICKEL SULFATE SUBCATEGORY (TABLE 38)

The treatment processes proposed are:

Metal precipitation/neutralization  
Settling  
Discharge to POTW/chemical landfill

Plant A operates 8 hours per day, 42 days per year; Plant B, 16 hours per day, 250 days per year. The amount of waste water generated is very small. It is directed to a mixing/settling tank, sized for 24-hour retention, where hydrated lime in the amount of 0.5 g per liter (4 lb/1000 gal) of waste water is added manually. Gravity flow is assumed.

Solids formed in the process have an estimated dry weight of 0.7 g per liter (5.8 lb/1000 gal) of waste water. The underflow from the settling tanks consists of about 5% solids and has a specific gravity of about 1.1. The amount of sludge collected daily from Plant A is 0.072 cubic meter (19 gallons); from Plant B, 15 cubic meters (3,960 gallons). The treatment cost represents 0.2 to 1.3% of the product price.

An alternative treatment process includes, in addition to the above treatments, directing the overflow from the settling tanks through a sand filter prior to discharge to a POTW. The incremental capital and annual costs of this process are:

	Plant A	Plant B
Capital	\$11,900	\$11,900
Annual Cost	\$4,680	\$3,180

Sand filtration would be required only for about 2 hours per day in Plant A, and for 30 minutes per day in Plant B. The treatment cost per metric ton (per short ton) of product would be increased by \$2.06 (\$1.87) in Plant A and by \$41.84 (\$37.95) in Plant B. The very large increase in Plant B is due to the limited annual production. The percent of treatment cost of product price with sand filtration is 0.3% for Plant A and 3.8% for Plant B.

CONTROL COSTS FOR NITROGEN AND OXYGEN SUBCATEGORY (TABLE 39)

The treatment processes proposed are:

TABLE 38. MODEL-PLANT CONTROL COSTS FOR NICKEL SULFATE INDUSTRY

PROCESS: <u>Metal Precipitation, Neutralization, Settling, Discharge to POTW, and Chemical Landfill</u>			
	PLANT A	PLANT B	PLANT C
PLANT ANNUAL CAPACITY IN METRIC TONS*:	2,270	76	
PLANT DAILY WASTEWATER FLOW IN LITERS†:	5,680	1,135	
<b>CAPITAL COST (\$)</b>			
FACILITIES			
Sludge pit	300	300	
EQUIPMENT			
Mixing/settling tank	4,500	1,400	
Pump	500	500	
Piping	400	400	
Installation	5,000	1,900	
CONTINGENCY AND CONTRACTOR'S FEE	2,100	900	
TOTAL CAPITAL INVESTMENT	12,800	5,400	
<b>ANNUAL COST (\$)</b>			
AMORTIZATION	2,090	880	
OPERATION AND MAINTENANCE (O&M)			
OPERATING PERSONNEL	3,000	250	
FACILITY REPAIR AND MAINTENANCE	10	10	
EQUIPMENT REPAIR AND MAINTENANCE	520	210	
MATERIALS	60	10	
TAXES AND INSURANCE	510	220	
SLUDGE DISPOSAL	910	30	
ELECTRICITY	270	10	
TOTAL ANNUAL COST	7,370	1,620	
TREATMENT COST/METRIC TON OF PRODUCT**	3.25	21.32	
PRICE/METRIC TON OF PRODUCT**	1,672		
% TREATMENT COST OF PRODUCT PRICE	0.2	1.3	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

**TABLE 39. MODEL-PLANT CONTROL COSTS FOR NITROGEN AND OXYGEN INDUSTRY**

<b>PROCESS:</b> <u>Coalescing, Discharge to POTW, and Chemical Landfill</u>			
	<b>PLANT A</b>	<b>PLANT B</b>	<b>PLANT C</b>
<b>PLANT ANNUAL CAPACITY IN METRIC TONS*:</b>	250,000	165,000	36,000
<b>PLANT DAILY WASTEWATER FLOW IN LITERS†:</b>	26,500	17,500	3,800
<b>CAPITAL COST (\$)</b>			
<b>FACILITIES</b>			
Wastewater sump	3,800	2,700	1,000
<b>EQUIPMENT</b>			
Coalescer	1,400	1,400	1,400
Pumps	500	500	500
Piping	400	400	400
Installation	1,900	1,900	1,900
<b>CONTINGENCY AND CONTRACTOR'S FEE</b>	1,600	1,400	1,000
<b>TOTAL CAPITAL INVESTMENT</b>	9,600	8,300	6,200
<b>ANNUAL COST (\$)</b>			
<b>AMORTIZATION</b>	1,560	1,350	1,010
<b>OPERATION AND MAINTENANCE (O&amp;M)</b>			
OPERATING PERSONNEL	2,500	1,870	1,250
FACILITY REPAIR AND MAINTENANCE	110	80	30
EQUIPMENT REPAIR AND MAINTENANCE	210	210	210
MATERIALS	---	---	---
TAXES AND INSURANCE	380	330	80
SLUDGE DISPOSAL	500	330	70
ELECTRICITY	60	60	60
<b>TOTAL ANNUAL COST</b>	5,320	4,230	2,710
<b>TREATMENT COST/METRIC TON OF PRODUCT**</b>	0.02	0.03	0.08
<b>PRICE/METRIC TON OF PRODUCT**</b>		40††	
<b>% TREATMENT COST OF PRODUCT PRICE</b>	0.05	0.08	0.2

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

††Nitrogen only.

Coalescer  
Discharge to POTW/chemical landfill

Flow through the coalescer is estimated to reduce the pollutants by about 97%. The daily amount of oil and grease recovered is very small, only about 29 l (7.6 gal) for the largest plant considered. The treatment cost is not significant.

An alternative treatment process is considered for Plant B.

Water from the waste water sump flows into an adjacent sump (sized for 12-hour retention), where the oil is skimmed from the surface. This process is estimated to remove 90% of the oil.

Costs for Model-Plant B are:

Capital Cost	\$6,200
Annual Cost	\$3,020
Cost/Metric (Short) Ton of Product	\$0.02 (\$0.018)
% Treatment Cost of Product Price	0.05

CONTROL COSTS FOR POTASSIUM DICHROMATE SUBCATEGORY (TABLE 40)

The treatment processes proposed are:

Chemical chromate removal  
Neutralization  
Thickening  
Filtration  
Discharge to POTW/chemical landfill

Chromate removal and neutralization are achieved by the addition of 0.25 g (0.0006 lb) of sulfur dioxide, 0.25 g (0.0006 lb) of sulfuric acid, and 0.3 g (0.0007 lb) of hydrated lime to each liter (0.26 gal) of waste water. Resulting solids amount to 0.96 g (dry weight) per liter (0.008 lb/gallon) of waste water.

The thickeners employed are sized for 8-hour retention and form an underflow containing 5% solids. The underflow is pumped through a precoated, rotary vacuum filter. Approximately 1 kg (2.2 lb) of precoat (diatomaceous earth) is consumed for each 4 kg (8.82 lb) of filter cake. The latter contains 20% solids and has a specific gravity of 1.1.

**TABLE 40. MODEL-PLANT CONTROL COSTS FOR POTASSIUM  
DICHROMATE INDUSTRY**

<b>PROCESS:</b> Chromate Removal, Neutralization, Thickening, Filtration, Discharge to POTW, and Chemical Landfill			
	<b>PLANT A</b>	<b>PLANT B</b>	<b>PLANT C</b>
<b>PLANT ANNUAL CAPACITY IN METRIC TONS*:</b>	3,600		
<b>PLANT DAILY WASTEWATER FLOW IN LITERS†:</b>	164,000		
<b>CAPITAL COST (\$)</b>			
<b>FACILITIES</b>			
Wastewater sump/sludge pit	13,000		
<b>EQUIPMENT</b>			
Chemical chromate-removal system	19,800		
Metal-precipitation/neutrali- zation system	11,000		
Thickener	25,000		
Filter	22,000		
Pumps	1,700		
Piping	2,500		
Installation	79,500		
<b>CONTINGENCY AND CONTRACTOR'S FEE</b>	34,900		
<b>TOTAL CAPITAL INVESTMENT</b>	209,400		
<b>ANNUAL COST (\$)</b>			
<b>AMORTIZATION</b>	34,130		
<b>OPERATION AND MAINTENANCE (O&amp;M)</b>			
OPERATING PERSONNEL	16,800		
FACILITY REPAIR AND MAINTENANCE	390		
EQUIPMENT REPAIR AND MAINTENANCE	8,040		
MATERIALS	8,130		
TAXES AND INSURANCE	8,380		
SLUDGE DISPOSAL	12,530		
ELECTRICITY	3,910		
<b>TOTAL ANNUAL COST</b>	92,310		
<b>TREATMENT COST/METRIC TON OF PRODUCT**</b>	25.71		
<b>PRICE/METRIC TON OF PRODUCT**</b>	1,254		
<b>% TREATMENT COST OF PRODUCT PRICE</b>	2.1		

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

Daily, Plant A generates about 1,200 l (317 gal) of sludge, and Plant B, 700 l (185 gal) of sludge, which are disposed in a chemical landfill. The treatment cost amounts to approximately 2% of the product price.

#### CONTROL COSTS FOR POTASSIUM IODIDE SUBCATEGORY

A preliminary analysis indicates that no pretreatment of small waste water flows appears necessary for plants which manufacture potassium iodide.

#### CONTROL COSTS FOR SILVER NITRATE SUBCATEGORY (TABLE 41)

The treatment processes proposed are:

- Metal precipitation/neutralization
- Flocculation
- Filtration
- Discharge to POTW/recycle

Material additions to the waste stream consist of 0.2 g (0.0004 lb) of hydrated lime and 2 mg of polyelectrolyte per liter of waste water. This material is added manually to the waste water in a mixing tank. In addition, about 1 kg (2.2 lb) of Filter Aid (diatomaceous earth) is used each week.

The waste water is recirculated through a plate-and-frame precoated filter until the filtrate appears clear. The amounts of solids produced are very small, amounting to about 1.1 liters (0.29 gallon) per day in Plant A and 0.1 liters (0.03 gallon) in Plant B.

The treatment cost is not significant when compared to the value of the product manufactured.

#### CONTROL COSTS FOR SODIUM BICARBONATE SUBCATEGORY

No pretreatment of waste water appears necessary for plants which manufacture sodium bicarbonate.

#### CONTROL COST FOR SODIUM FLUORIDE SUBCATEGORY (TABLE 42)

The treatment processes proposed are:

- Metal precipitation/neutralization
- Flocculation
- Settling
- Filtration
- Discharge to POTW/chemical landfill



**TABLE 41. MODEL-PLANT CONTROL COSTS FOR SILVER NITRATE INDUSTRY**

<b>PROCESS:</b> Metal Precipitation, Neutralization, Flocculation, Filtration, Discharge to POTW, and Recycle			
	<b>PLANT A</b>	<b>PLANT B</b>	<b>PLANT C</b>
<b>PLANT ANNUAL CAPACITY IN METRIC TONS*:</b>	3,200	350	
<b>PLANT DAILY WASTEWATER FLOW IN LITERS†:</b>	10,600	1,170	
<b>CAPITAL COST (\$)</b>			
<b>FACILITIES</b>			
Wastewater sump	2,100	400	
<b>EQUIPMENT</b>			
Mixing tank	1,300	800	
Recycle tank	1,100	700	
Filter	12,000	8,000	
Pumps	900	900	
Piping	500	300	
Installation	15,300	10,400	
<b>CONTINGENCY AND CONTRACTOR'S FEE</b>	6,600	4,300	
<b>TOTAL CAPITAL INVESTMENT</b>	39,800	25,800	
<b>ANNUAL COST (\$)</b>			
<b>AMORTIZATION</b>	6,490	4,210	
<b>OPERATION AND MAINTENANCE (O&amp;M)</b>			
OPERATING PERSONNEL	12,600	4,200	
FACILITY REPAIR AND MAINTENANCE	60	10	
EQUIPMENT REPAIR AND MAINTENANCE	1,560	1,060	
MATERIALS	20	10	
TAXES AND INSURANCE	1,590	1,030	
SLUDGE DISPOSAL			
ELECTRICITY	260	190	
<b>TOTAL ANNUAL COST</b>	22,580	10,710	
<b>TREATMENT COST/METRIC TON OF PRODUCT**</b>	7.06	30.60	
<b>PRICE/METRIC TON OF PRODUCT**</b>	90,000		
<b>% TREATMENT COST OF PRODUCT PRICE</b>	0.007	0.03	

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

TABLE 42. MODEL-PLANT CONTROL COSTS FOR SODIUM FLUORIDE INDUSTRY

PROCESS: Metal Precipitation, Neutralization, Flocculation, Settling, Filtration, Discharge to POTW, and Chemical Landfill			
	PLANT A	PLANT B	PLANT C
PLANT ANNUAL CAPACITY IN METRIC TONS*:	3,200		
PLANT DAILY WASTEWATER FLOW IN LITERS†:	18,000		
CAPITAL COST (\$)			
FACILITIES			
Wastewater sump/sludge pit	4,300		
EQUIPMENT			
Metal precipitation/neutralization			
System	8,200		
Flocculation system	1,600		
Settling tank	6,700		
Filter	22,000		
Pumps	500		
Piping	500		
Installation	39,000		
CONTINGENCY AND CONTRACTOR'S FEE	16,600		
TOTAL CAPITAL INVESTMENT	99,400		
ANNUAL COST (\$)			
AMORTIZATION	16,200		
OPERATION AND MAINTENANCE (O&M)			
OPERATING PERSONNEL	25,200		
FACILITY REPAIR AND MAINTENANCE	130		
EQUIPMENT REPAIR AND MAINTENANCE	3,930		
MATERIALS	15,720		
TAXES AND INSURANCE	3,980		
SLUDGE DISPOSAL	11,450		
ELECTRICITY	1,810		
TOTAL ANNUAL COST	78,420		
TREATMENT COST/METRIC TON OF PRODUCT**	24.51		
PRICE/METRIC TON OF PRODUCT**	640		
% TREATMENT COST OF PRODUCT PRICE	3.8		

\*To convert to short tons, multiply value shown by 1.1.

†To convert to gallons, multiply value shown by 0.264.

\*\*To convert to cost or selling price/short ton of product, multiply value shown by 0.9.

Materials added to the waste water consist of calcium chloride, at a concentration of 26.4 g/l (220 lb/1,000 gal), and polyelectrolyte at a concentration of 10 mg/l (0.83 lb/1,000 gal). The resulting solids amount to 18 g (dry weight) per liter (150 lb/1,000 gal) of waste water.

The settling tank is sized for 24-hour retention. The underflow from the settling tank consists of 15% solids. This sludge is thickened in a rotary vacuum filter, which produces filter cake containing 40% solids. The estimated specific gravity of the filter cake is 1.24. The daily amount of waste sent to the landfill is about 650 liters (172 gallons).

The treatment costs represent 3.8% of product cost.

#### DEVELOPMENT OF COST DATA BASE

##### Scope

The costs, cost factors, and costing methodology used to derive the capital and annual costs are documented in this subsection.

Most of the equipment costs are based on vendor quotations. The names of vendors are deleted to avoid any implications of product endorsement. Vendor identification will be provided, on request, to EPA and others authorized by EPA.

The following categorization is used for presenting the costs:

##### Capital Cost

- Facilities
- Equipment
- Installation
- Contingency and Contractor's Fee

##### Annual Cost

- Amortization
- Operation and Maintenance
  - Operating Personnel
  - Facility Repair and Maintenance
  - Equipment Repair and Maintenance
  - Materials
  - Taxes and Insurance
  - Sludge Disposal
- Energy

### Capital Cost of Facilities

Concrete pits sized to contain a 24-hour flow of waste water are included with most treatment processes. In addition, concrete sludge-holding pits are provided, generally designed to hold a 7-day supply of sludge.

The pits are constructed of 20-centimeter (8-inch) reinforced base slabs and 40-centimeter (16-inch) walls. A general cost-estimating relationship was developed from Reference 18, resulting in a base slab cost of \$20/square meter (\$2/square foot) and a wall cost of \$300/cubic meter (\$8/cubic foot) of concrete in place. The costs include setup and layout, excavation, concrete, backfill, and cleanup.

For example, the cost of a 6-cubic-meter (212-square-foot) pit, measuring 3 m x 2 m x 1 m (9.8 ft x 6.6 ft x 3.3 ft) is computed as follows:

$$(3 \times 2 \times \$20) + (2 \times 3 \times 1 \times 0.4 \times \$300) + (2 \times 2 \times 1 \times 0.4 \times \$300) = \$1,320$$

### Capital Cost of Equipment

General. Certain types of equipment, such as metal-precipitation/neutralization systems, thickeners, tanks, and pumps, are widely used in the described treatment processes. Parametric cost curves are developed for such items to facilitate the cost computations.

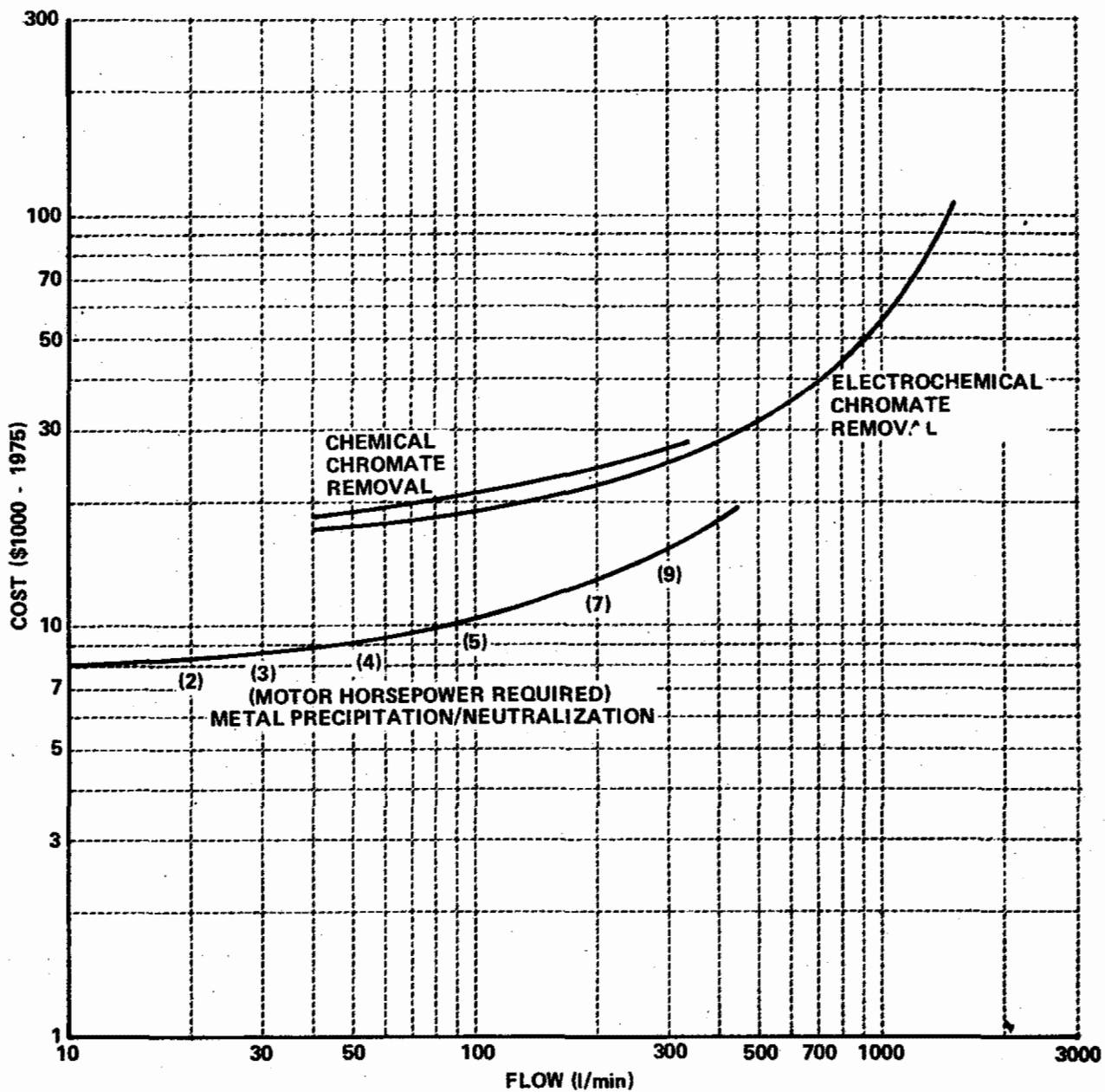
Chemical Chromate-Removal/Metal-Precipitation/Neutralization Systems. System costs as a function of waste water flow, expressed in liters (= 0.264 gallon) per minute, are shown in Figure 58. Costs are based on vendor quotations.

The costs represent packaged, factory-assembled units. The major system components are generally skid-mounted; interconnected; and include associated pumps, meters, and instrumentation.

Electrochemical chromate removal is applicable primarily to coolingtower washdown waste water--i.e., relatively large flows which contain small amounts of chromates. Chemical chromate removal is selected as the system of choice where applicable in this study.

Flocculant Feed Systems. The flocculant feed system consists of a tank, a feed pump (mounted under the tank), interconnecting piping with reliefreturn system, and

Figure 58. TREATMENT-SYSTEM COSTS



l/min x 0.2642 = gpm  
hp x 0.7457 = kW

stainless steel agitator. System design and costs were obtained from an equipment manufacturer. Costs are:

<u>Tank Size</u>	<u>Cost</u>
190-1 (50-gal)	\$1,600
570-1 (150-gal)	2,000
1,900-1 (500-gal)	3,500

Equipment is selected for employment at plant operations based on treatment flow requirements.

Holding/Settling Tanks. Costs, based on vendor quotations, are shown in Figure 59, as a function of capacity. The tanks are of steel construction.

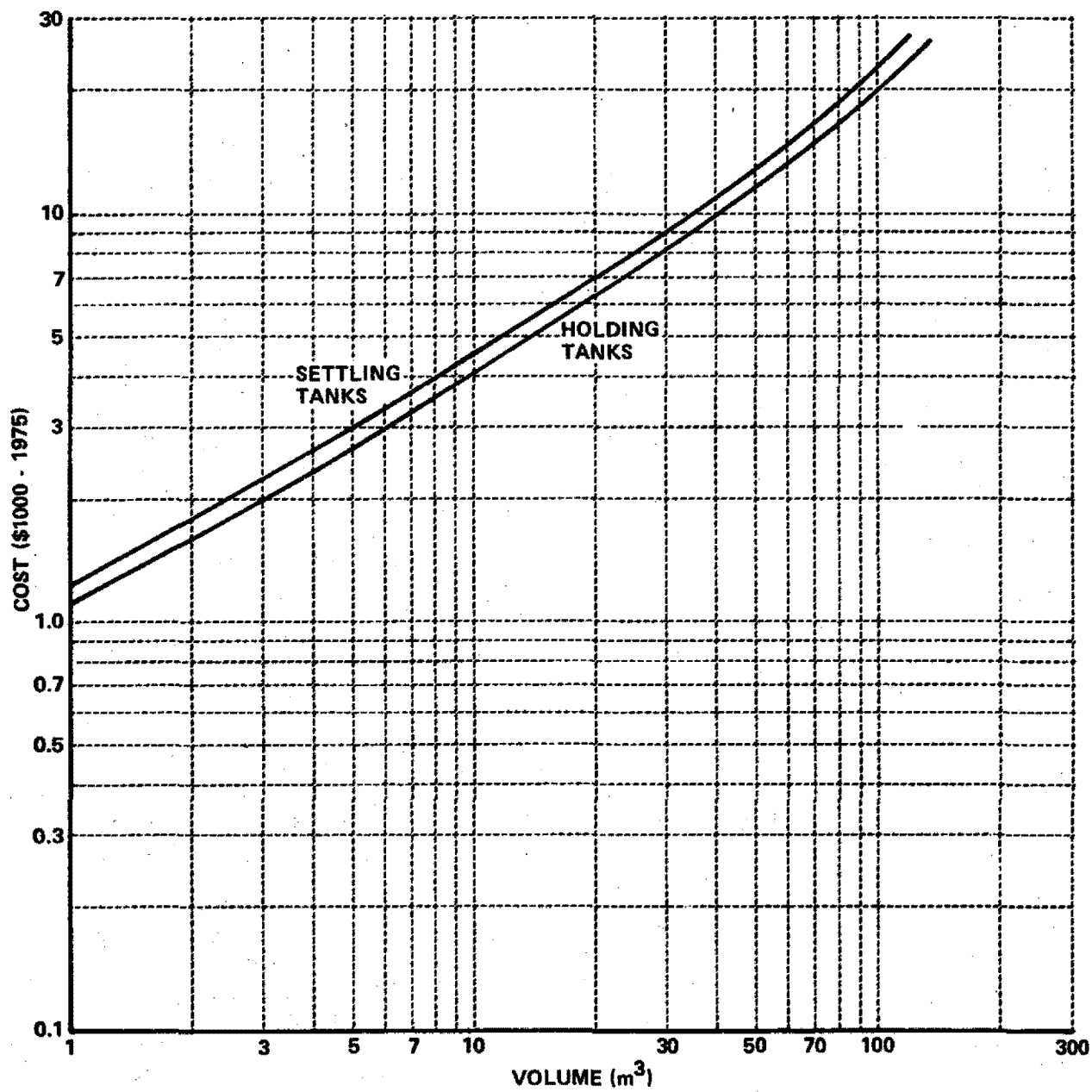
Thickeners. Costs for rake-type thickeners as a function of volume are shown in Figure 60. The costs represent vendor quotations. The thickeners are relatively small and are powered by electric motors ranging from about 0.4 to 6.5 kW (0.5 to 2 hp) in size. To illustrate the application of Figure 60, an operation with a daily flow of 100 cubic meters (26,000 gallons) of waste water requiring a thickener, sized for 6-hour retention, would require a 25-cubic-meter (6,600-gallon) thickener and would incur a cost of \$17,500.

Sludge-Dewatering Equipment. The use of such equipment may be dictated in large part by the economics of chemical landfill costs. This is illustrated in Figure 61, which demonstrates potential cost savings achievable by reducing the volume of sludge to be disposed. For example, an operation which generates 10 cubic meters (2,641 gallons) of sludge per day and is able to reduce this volume by 30% through settling/filtration reduces its sludge disposal cost of \$150. Specific sludge-dewatering equipment costs, based on vendor quotations, are presented.

Rotary Vacuum Filters. Characteristics and costs of rotary vacuum filters are shown in Table 43. Filter selection for specific operations is based on solid content in the waste stream which is expected to be separated by filtering.

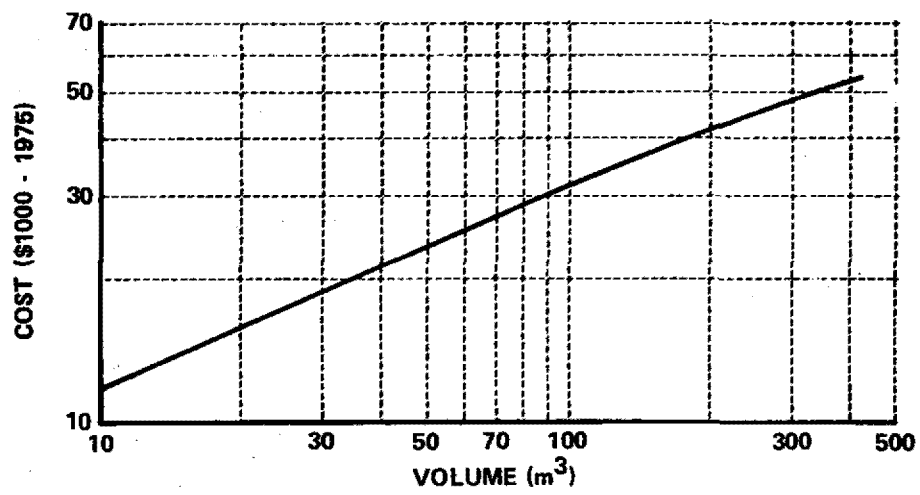
Centrifuges. Costs, as a function of weight of sludge generated per day, are shown in Figure 62. Power requirements for the size of centrifuges shown range from 25 to 18.6 kW (10 to 25 hp). The curve given in Figure 62 should not be extended beyond the lowest point shown, since this point represents the smallest applicable centrifuge manufactured. Costs are based on equipment-manufacturer quotations.

Figure 59. SETTLING/HOLDING-TANK COSTS



$m^3 \times 264.172 = \text{gal}$

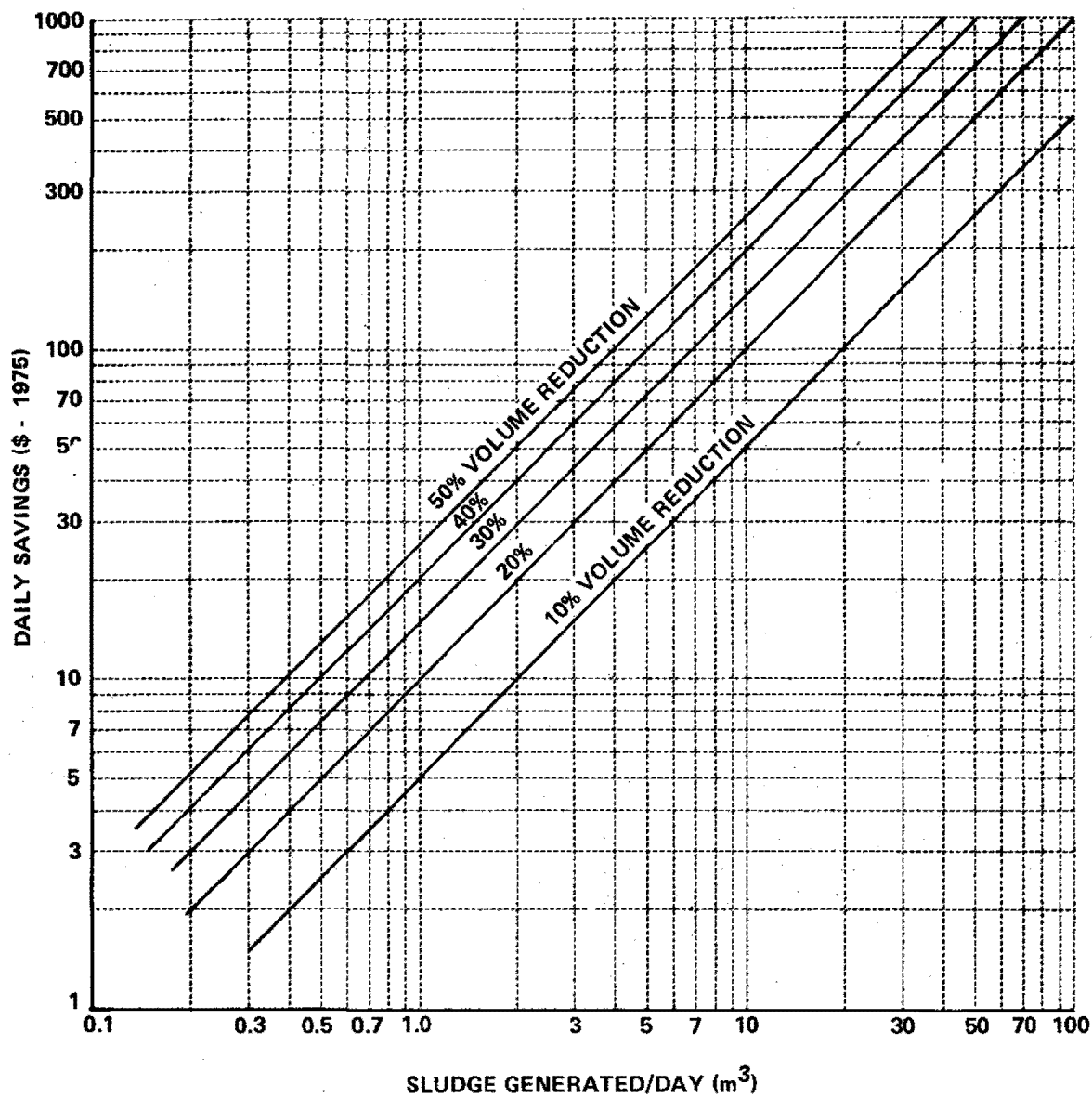
Figure 60. THICKENER COSTS



$$\text{m}^3 \times 264.172 = \text{gal}$$



Figure 61. DAILY SAVINGS ACHIEVED BY VOLUME REDUCTION OF SLUDGE  
 BASED ON DISPOSAL COST OF \$50/m<sup>3</sup> (\$38/yd<sup>3</sup>)



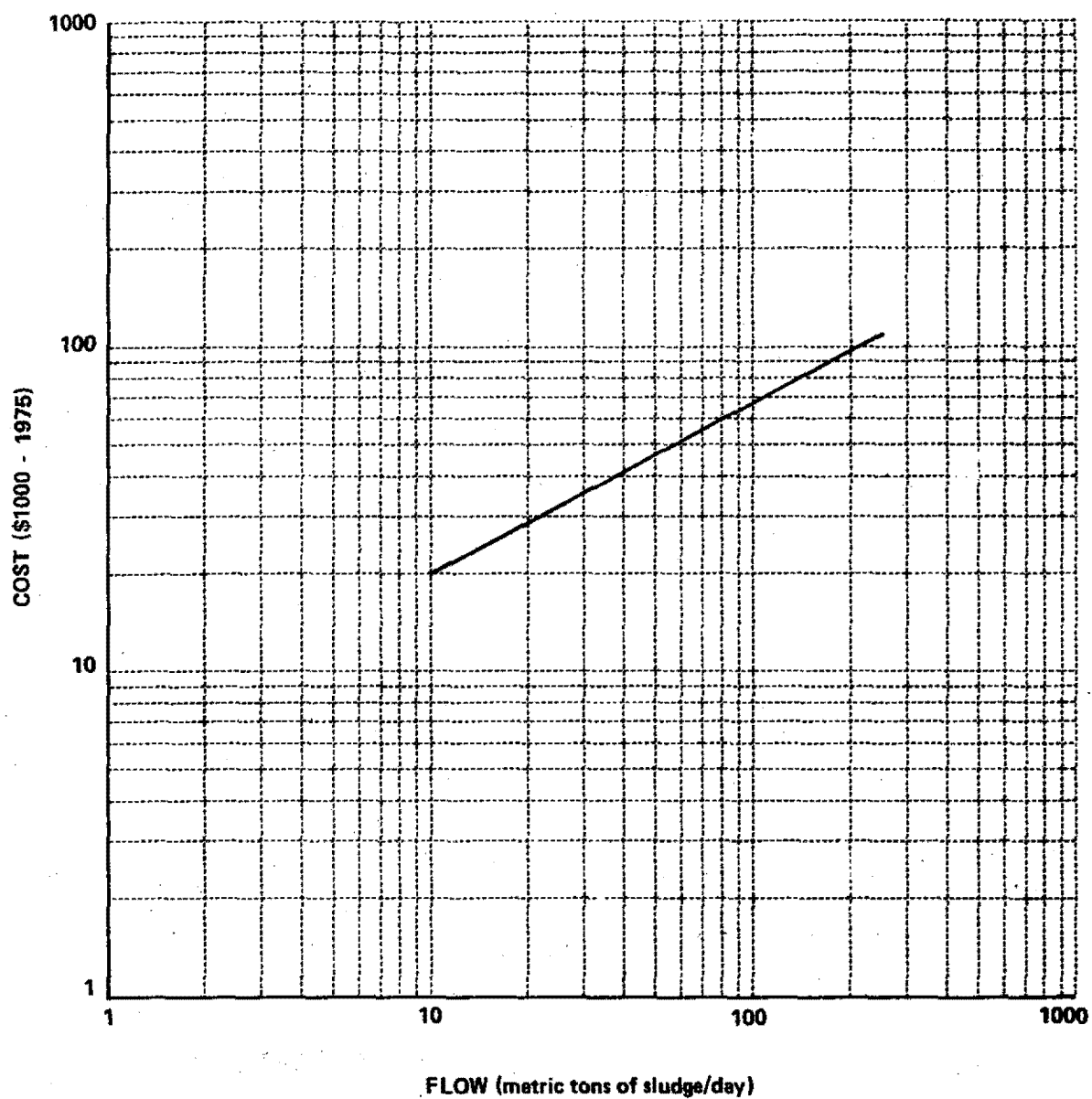
m<sup>3</sup> x 264.172 = gal

**TABLE 43. ROTARY VACUUM-FILTER COSTS**

FILTER DESIGNATION	FILTER AREA		COST	CAPACITY FOR DRY SOLIDS/HOUR		ENERGY REQUIREMENTS	
	m <sup>2</sup>	ft <sup>2</sup>		kg	lb	hp	kW
3 x 1	0.86	9.4	\$22,000	31.8	70	10	8
3 x 2	1.66	18.8	25,000	63.6	140	12	9
3 x 3	2.59	28.2	26,500	95.5	210	14	10
3 x 4	3.46	37.6	28,000	127.3	280	16	12
3 x 5	4.32	47.0	30,000	159.1	350	18	13

**SOURCE: EQUIPMENT MANUFACTURER**

Figure 62. CENTRIFUGE COSTS



metric tons x 1.1 = short tons

Sand Filters. Sand-filter costs are shown as a function of flow rate in Figure 63. The flow rate of the type of sand filters from which the costs are derived is 205 to 250 l/square meter/min (5 to 6 gal/square ft/min).

Plate-and-Frame Filters. Cost quotations were obtained from vendors for filters applicable to specific, postulated treatment processes. They are:

122-cm (48-inch)	30 plates	\$20,000
122-cm (48-inch)	20 plates	15,000
61-cm (24-inch)	24 plates	12,000
61-cm (24-inch)	4 plates	8,000

Mixing Tanks. Mixing-tank costs are shown in Figure 64. The tanks are of steel construction and include agitators and motors. Costs are based on a vendor quotation.

Coalescers. Vendor cost quotations obtained for water coalescers are:

19 to 38 l (5 to 10 gal)/min	\$1,400
42 to 87 l (11 to 23 gal)/min	1,600
76 to 152 l (20 to 40 gal)/min	1,800

Pumps. Pump costs, including motors, are shown in Figure 65 as a function of capacity, expressed in liters (=0.264 gallon)/minute. The types and sizes of pumps required for a particular activity can vary widely, depending on the characteristics of the material being pumped and the height and distance the material must be transported. The pump costs in Figure 65 are representative of centrifugal pumps capable of pumping to a head of about 6 m (20 ft).

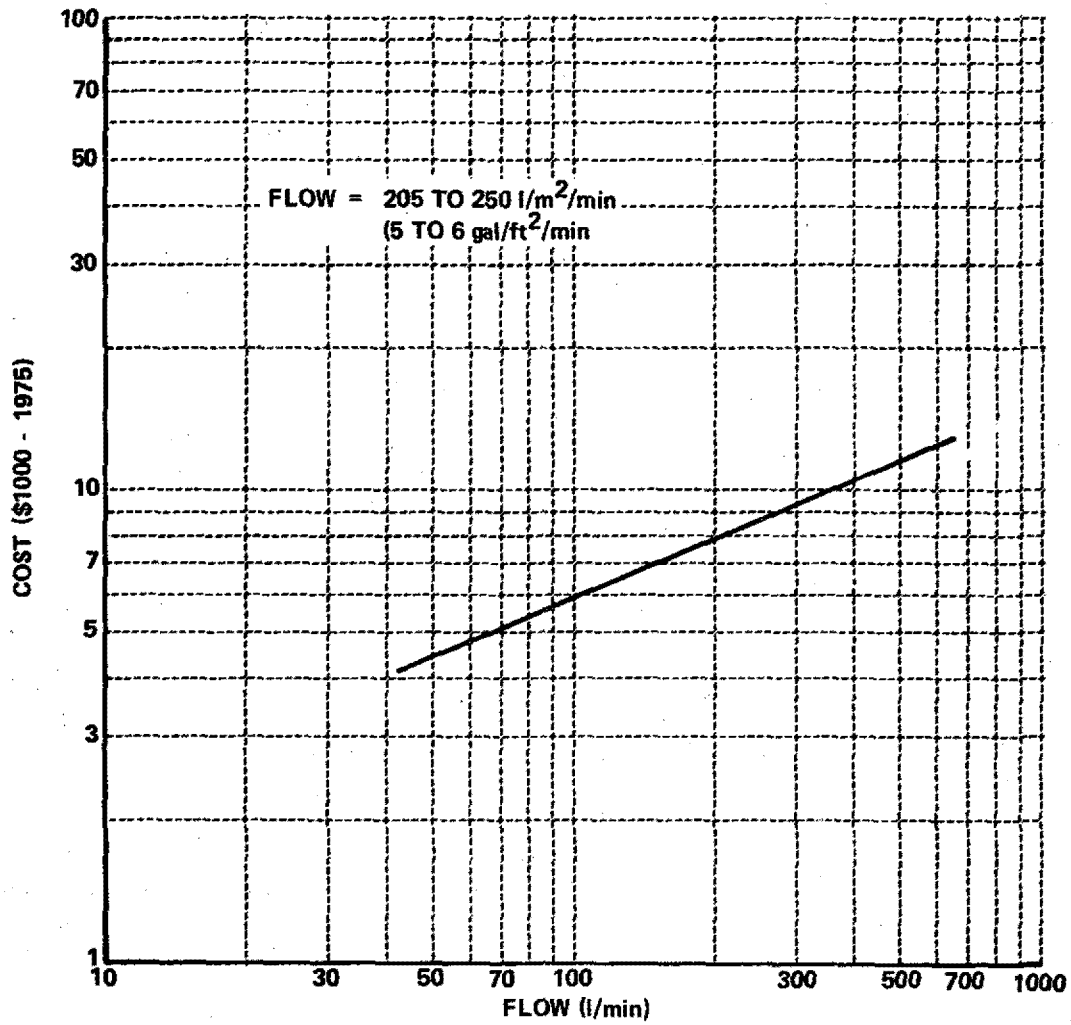
Pipes. Installed costs of several types of pipes are shown in Table 44. The basic costs are increased by 20% to account for ancillary items, such as connectors, tees, and valves. PVC piping is generally employed.

#### Capital Cost of Installation

Many factors can impact on the cost of installing equipment modules. These include wage rates, whether the job is performed by outside contractors or regular employees, and site-dependent conditions (e.g., availability of sufficient electrical service).

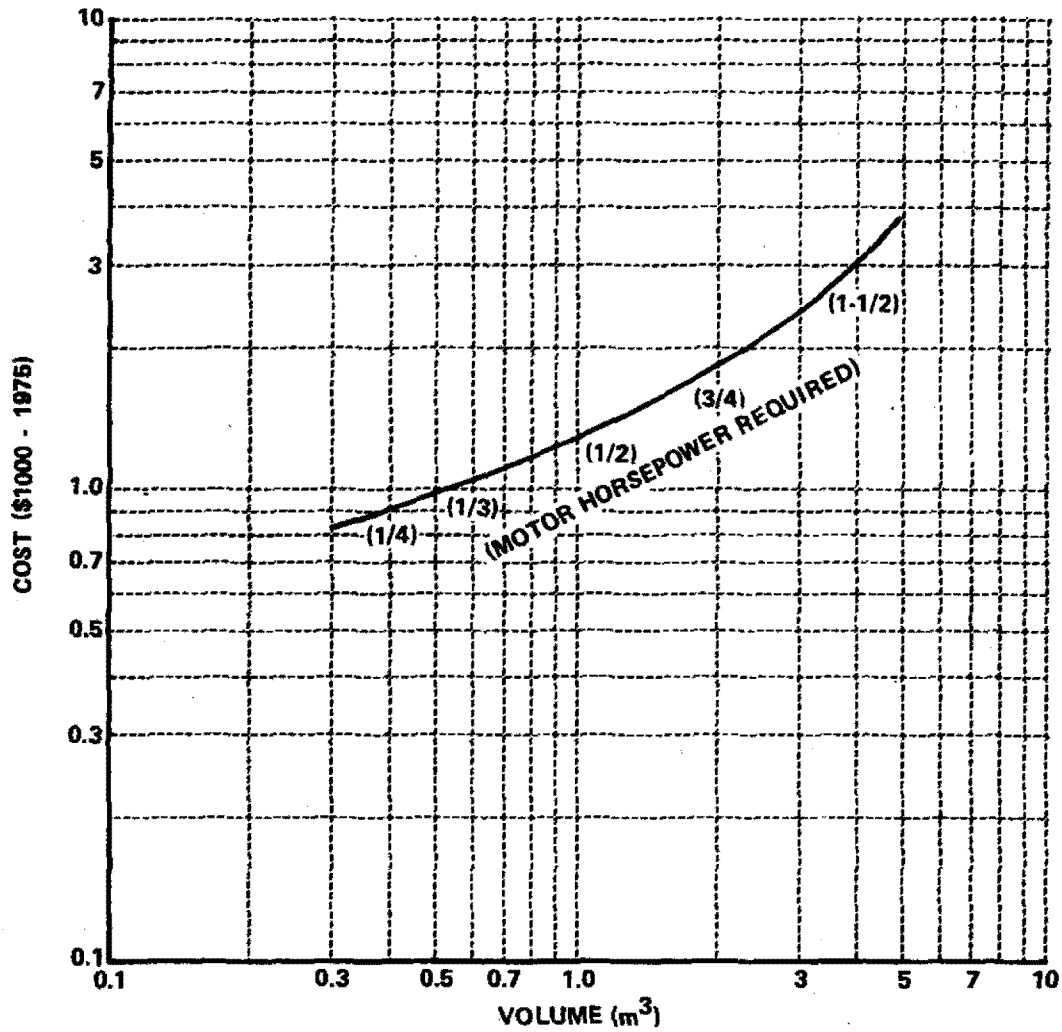
In this study, installation cost is computed as 100% of the cost of equipment which is installed, less piping. Note that the costs of major treatment-system components, such as metal-precipitation/neutralization equipment, are based on

Figure 63. SAND-FILTER COSTS



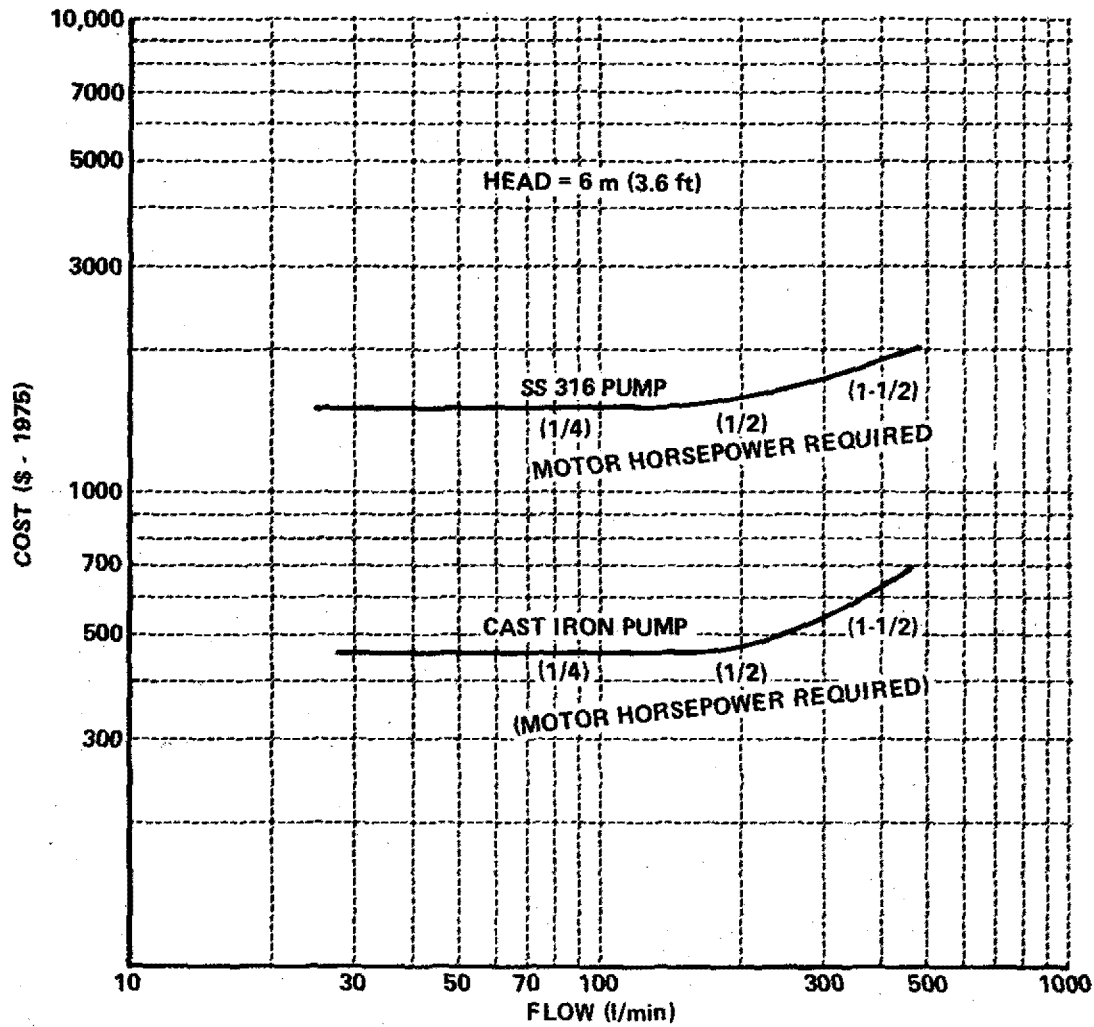
l/min x 0.2642 = gpm

Figure 64. MIXING-TANK COSTS



$\text{m}^3 \times 264.172 = \text{gal}$   
 $\text{hp} \times 0.7457 = \text{kW}$

Figure 65. PUMP COSTS



l/min x 0.2642 = gpm  
hp x 0.7457 = kW

**TABLE 44. INSTALLED-PIPE COSTS**

TYPE	DIAMETER		COST (\$)	
	cm	in.	PER METER	PER FOOT
ABS - PVC	3.8	1-1/2	17	5
	5.1	2	19	6
	7.6	3	25	8
	10.2	4	30	9
	15.2	6	60	18
STAINLESS STEEL #304, SCHEDULE 40	5.1	2	70	21
	7.6	3	125	38
	10.2	4	213	64
STAINLESS STEEL #316, SCHEDULE 40	5.1	2	82	25
	7.6	3	146	44
	10.2	4	250	75
STEEL, SCHEDULE 40	10.2	4	67	20
	12.7	5	98	29
	15.2	6	114	34
	20.3	8	160	48



factory-assembled, skid-mounted units. The use of such equipment generally entails considerably lower installation costs than if the entire system were field-assembled. Further, most of the equipment modules, (e.g., tanks and thickeners) are relatively small, which also tends to result in relatively low installation costs.

#### Capital Cost of Contingency and Contractor's Fee

This cost is computed as 20% of the sum of the costs for facilities and equipment, including installation.

#### Annual Cost of Amortization

Annual depreciation and capital costs are computed as follows:

$$CA = \frac{B(r)(1+r)^n}{(1+r)^n - 1}$$

where CA = Annual cost

B = Initial amount invested

r = Annual interest rate

n = Useful life in years

The computed cost is often referred to as the capital recovery factor. It essentially represents the sum of the interest cost and depreciation.

An interest rate of 10% is used. The expected useful life of facilities and equipment is 10 years. No residual or salvage value is assumed.

#### Annual Cost of Operation and Maintenance

General. Plant operations are assumed conducted 24 hours per day, 350 days per year.

Operating Personnel. Personnel costs are based on an hourly rate of \$12.00. This includes fringe benefits, overhead and supervision (Reference 18). Personnel are assigned for specific activities as required.

Facility Repair and Maintenance. Facility repair and maintenance are included as 3% of facility costs.

Equipment Repair and Maintenance. The cost of these activities is estimated as 5% of installed equipment costs.

Materials. The materials employed in the pretreatment processes and their costs are shown below.

Hydrated Lime (Calcium Hydroxide)	\$55/metric ton (\$50/short ton)
Flocculant	\$2/kg (\$4/lb)
Filter Aid (Diatomaceous earth)	\$0.264/kg (\$0.58/lb)
Calcium Chloride (80%)	\$75/metric ton (\$68/short ton)
Caustic Soda (Sodium Hydroxide)	\$425/metric ton (\$385/short ton)
Sulfuric Acid	\$55/metric ton (\$50/short ton)
Sulfur Dioxide	\$190/metric ton (\$170/short ton)

The cost of manufactured chemicals in \$/metric ton (\$/short ton) used to assess the potential economic impact of the pretreatment costs are:

Aluminum Chloride	\$198 (180)	Nickel Sulfate	\$ 1,672 (1,516)
Aluminum Sulfate	98 (89)	Nitrogen and Oxygen	40 (36)
Calcium Carbide	188 (170)	Potassium Dichromate	1,254 (1,137)
Calcium Chloride	60 (54)	Potassium Iodide	8,270 (7,500)
Copper (Cupric) Sulfate	835 (760)	Silver Nitrate	90,000 (82,000)
Iron (Ferric) Chloride	100 (90)	Sodium Bicarbonate	180 (163)
Lead Monoxide	530 (480)	Sodium Fluoride	640 (580)

The costs are based on vendor quotations and prices published in the Chemical Marketing Reporter.

Taxes and Insurance. The combined costs are included as 4% of the total investment cost.

Sludge Disposal. Disposal costs can vary widely. Chief cost determinants include the amount and type of waste, on-site vs. contractor disposal, size of the disposal operation, and transport distances. The following disposal costs are employed in this study.

Chemical landfill	\$0.05/l (\$0.19/gal)
Sanitary landfill	\$5.00/metric ton (\$4.55/short ton)

### Annual Cost of Electricity

Energy (electricity) costs are based on the cost per horsepower-year computed as follows:

$$Cy = 1.1 \frac{HP}{E \times P} \times 0.7457 \times Hr \times CkW$$

where

$$Cy = \text{Cost}$$

HP = Total horsepower rating of motors (1 hp=  
0.7457 kW)

E = Efficiency factor (0.9)

P = Power factor (0.9)

Hr = Annual operating hours (as applicable)

CkW = Cost per kilowatt-hour of electricity  
(\$0.03)

Note: 1.1 factor represents allowance for miscellaneous  
energy use.

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## SECTION IX

### BEST PRACTICABLE PRETREATMENT TECHNOLOGY

#### INTRODUCTION

The recommended pretreatment standards to be achieved are based on the ability of POTW to alter or remove certain waste water pollutants--most notably, pH and total suspended solids (TSS), respectively--and on the chemical producers' application of pretreatment technologies in keeping with the best practicable control technology currently available (BPCTCA) to remove pollutants which are not effectively treated within a POTW. For the 14 inorganic chemical subcategories covered by this document, these levels of technology are based on:

- (1) The average of the best existing performance of facilities of various sizes discharging to POTW;
- (2) The performance of facilities discharging directly to surface waters; and
- (3) The performance of similar treatment systems in other industries.

Consideration was also given to:

- (1) The total cost of application of technology in relation to the effluent-reduction benefits to be achieved from such application;
  - (2) Process employed;
  - (3) Engineering aspects of the application of various types of control techniques;
  - (4) Nonwater-quality environmental impact (including solid-waste generation and energy requirements);
  - (5) Incidental pollutant removals achieved within POTW;
  - (6) Toxicity of various pollutants relative to a POTW;
- and
- (7) Influent limitations imposed by POTW.

Pretreatment technology emphasizes treatment facilities at the end of chemical process. Excluded from this technology are control practices available to significantly reduce or

eliminate process waste water discharges. These control practices which include process controls, recycle, alternative uses of water, and recovery and reuse of some waste water constituents, are discussed in Section VII for each subcategory.

The remainder of this section discusses, for each chemical subcategory, the pollutant parameters determined to be significant, the recommended pretreatment standard for each of these pollutants, and the rationale for achievement of the recommended standards.

Within this section, each subcategory is treated separately for recommendation of pretreatment standards.

#### Aluminum Chloride Subcategory

This subcategory includes those plants producing hydrous and anhydrous aluminum chloride, except where the salt is produced as an intermediate for synthesis of other products. The significant pollutant parameter for this subcategory, and pretreatment standard for that parameter is shown below.

##### Effluent Characteristics

##### Effluent Limitations

pH                      Within the range 5.0 to 10.0

At anhydrous aluminum chloride plants using scrap aluminum as a raw material, zinc concentration can be expected to be similar to concentrations which occur in secondary aluminum scrubber waste water. Control of zinc may be required at the local level to protect POTW operation. As guidance for local POTW authorities, zinc limitations of 2.5 mg/l (30 day average) and 5.0 mg/l (daily maximum) are recommended. This limit can be met by lime treatment and settling.

Aluminum in the discharge from aluminum chloride producing plants is acceptable in municipal treatment systems when it occurs in low concentrations. At higher concentrations it can cause excessive sludge bulking in a POTW. Because aluminum is relatively insoluble at neutral pH, a pH limit from 5.0 to 10.0 has been established for the purpose of limiting aluminum discharges. The cost of this treatment is estimated at from 1.6 to 3.5 percent of product price.

#### Aluminum Sulfate Subcategory

This subcategory includes those plants producing solid and liquid aluminum sulfate (including iron-free alum) except plants where the alum is produced as an intermediate for

manufacture of other products. The significant pollutant parameter for this subcategory, and pretreatment standard for this parameter is shown below.

<u>Pollutant or Pollutant Property</u>	<u>Pretreatment Standard</u>
Maximum for any one day  _____	Average of daily values for thirty consecutive days <u>shall not exceed</u>
Zinc	2.5
5.0	mg/l

Zinc may be present in discharges from aluminum sulfate plants in sufficient amounts to interfere with POTW operation. The zinc standard can be met by pH adjustment and settling. Aluminum in the discharge from aluminum sulfate plants is acceptable when it occurs at low concentrations. High concentrations of aluminum can cause sludge bulking in a POTW. Pretreatment for control of zinc will also reduce aluminum concentrations to acceptable levels. The cost of this treatment is estimated at 0.5 to 4.8 percent of product price.

#### Calcium Carbide Subcategory

This subcategory includes the production of calcium carbide in open furnaces. The significant pollutant parameter is suspended solids in the range of 50 to 750 mg/l. Suspended solids at these levels will not interfere with POTW operation, and will receive adequate treatment. Since no suspended solids limit is imposed, there is no treatment cost.

#### Calcium Chloride Subcategory

This subcategory includes those plants producing calcium chloride from all sources. Since wastes contain only calcium and sodium brines that will not interfere with municipal systems, no limitations are established and no costs will be incurred.

#### Copper (Cupric) Sulfate Subcategory

This subcategory includes the manufacture of copper (cupric) sulfate in crystal and solution form. Significant pollutant

parameters for this subcategory, and pretreatment standards for these parameters, are shown below.

<u>Pollutant or Pollutant Property</u>	<u>Maximum for any one day</u>	<u>Pretreatment Standard</u>
		<u>Average of daily values for thirty consecutive days shall not exceed</u>
	mg/l	
Copper	1.0	0.5
Nickel	2.0	1.0

The copper sulfate manufacturing industry recycles almost all process waste waters. The waste source is from plant spills and wash downs. The standards can be readily achieved by lime neutralization and settling as is shown in data from plant 19505. This plant achieves an average copper concentration of 0.48 mg/l. the cost of treatment for this system is estimated at 0.2 percent of the product price.

#### Ferric Chloride Subcategory

This subcategory includes plants which produce both ferric chloride solution and ferric chloride hexahydrate crystals from iron and steel pickling liquors. It does not include production of ferric chloride by passing chlorine gas over iron at red heat, or by oxidizing anhydrous ferrous chloride with chlorine. Significant pollutant parameters for this subcategory, and pretreatment standards for these parameters, are shown below.

<u>Pollutant or Pollutant Property</u>	<u>Maximum for any one day</u>	<u>Pretreatment Standard</u>
		<u>Average of daily values for thirty consecutive days shall not exceed</u>
	mg/l	
Total Chromium	1.8	0.9
Hexavalent Chromium	0.18	0.09
Copper	1.0	0.5



Nickel	2.0	1.0
Zinc	5.0	2.5

The major source of pollutants in waste water generated from ferric chloride production is the pickle liquor feed. The pickle liquor contains a variety of trace elements, including chromium, copper, nickel, and zinc, all of which may prove detrimental to POTW operation, and may pass through the treatment system without adequate removal. The standards can be achieved by lime neutralization and settling. The cost of treatment for this system is estimated to be from 2.0 to 5.6 percent of product price.

#### Lead Monoxide Subcategory

This subcategory includes all manufacturing operations which produce lead monoxide. The significant pollutant parameter selected for this subcategory, and pretreatment standards recommended for this parameter, is shown below.

<u>Pollutant or Pollutant Property</u>		<u>Pretreatment Standard</u>
	Maximum for any one day	Average of daily values for thirty consecutive days <u>shall not exceed</u>
	<hr/>	
	mg/l	
Lead	2.0	1.0

The best practicable control technology currently available for the control of waste water from this subcategory is no discharge of process waste water. This is currently being accomplished at most lead monoxide plants by dry dust control and cleanup practices. Only those plants employing wet washdown practices will produce a process waste water having the characteristics of high suspended-solids and lead concentrations. No limit is set on suspended solids concentrations, as suspended solids will be adequately removed in a POTW. Lead is toxic to plants and animals, and can inhibit POTW operations. Lead can be removed from solution by pH adjustment and settling. One lead monoxide manufacturing plant is achieving lead removals down to 0.9 mg/l using sulfate precipitation and settling. Lime is more commonly used for lead removal, and residual lead concentrations of about 1 mg/l are attainable using this

precipitating agent. The cost of treatment for this system is estimated to be 0.4 percent of product price.

#### Nickel Sulfate Subcategory

This subcategory includes those plants which produce nickel sulfate solution and nickel sulfate crystals from nickel, nickel oxide, and impure nickel-bearing materials. Significant pollutant parameters selected for this subcategory, and pretreatment standards recommended for these parameters are shown below.

<u>Pollutant or</u> <u>Pollutant Property</u>	<u>Pretreatment</u> <u>Standard</u>
Maximum for any one day	Average of daily values for thirty consecutive days <u>shall not exceed</u>
mg/l	
Nickel	2
Copper	1.0
	1
	0.5

Nickel and copper, the parameters of concern in nickel sulfate, can inhibit POTW operations, and can pass through the treatment plants without adequate treatment. Chemical precipitation, settling, and filtration will produce an effluent that meets the limits for copper and nickel. Nickel reductions to 0.5 mg/l have been reported using chemical precipitation with soda ash and settling. The cost of treatment for this system is estimated to be from 0.2 to 1.3 percent of product price.

#### Nitrogen and Oxygen Subcategory

This subcategory covers all industrial plants producing nitrogen and oxygen via air separation. Excluded are those plants utilizing the Linde process of molecular sieves, and also those plants (classified as "filling stations") which do not actually manufacture the gases but, rather, convert liquid nitrogen and oxygen to gaseous products for commercial distribution. Process wastes from this subcategory are characteristically small volumes of compressor condensate, which results when the water vapor portion of atmospheric air condenses within compressor. Oil and grease may become a part of this stream as the condensate comes into contact with the internally lubricated

parts of the compressor. The volume of water generated is usually less than 7000 gallons per day, and will not contain sufficient oil and grease to cause any adverse effects at a POTW. For this reason no limit is set for oil and grease. Since no pretreatment is required, there will be no cost to the industry.

#### Potassium Dichromate Subcategory

This subcategory includes production of potassium dichromate by reaction of sodium dichromate with potassium chloride. Significant pollutant parameters for this subcategory, and pretreatment standards for those parameters, are shown below.

<u>Pollutant or Pollutant Property</u>	<u>Pretreatment Standard</u>
Maximum for any one day	Average of daily values for thirty consecutive days <u>shall not exceed</u>
	mg/l
Hexavalent chromium	0.18 0.09
Total chromium	1.8 0.9

The pollutant of concern is chromium which is soluble and potentially very harmful in its hexavalent form. Treatment for chromium removal consists of treatment with sulfur dioxide to reduce the hexavalent chromium to its trivalent state and neutralization, precipitation, and solids separation to remove the trivalent chromium. Estimated cost for this treatment are 2.1 percent of product price.

#### Potassium Iodide Subcategory

This subcategory is composed of four domestic manufacturers. Three slightly varying production processes are employed by this industry, and these have been described in Section III of this document. No pretreatment standard is required for this subcategory as discussed below. Discharge from the industry subcategory generally consists solely of non contact cooling water, and extremely small quantities of water used for equipment washdowns or cleanup of spills. Because of the nature of the waste water and the small amount generated, no effluent limitations are necessary for

this subcategory and no costs will be incurred by the industry.

#### Silver Nitrate Subcategory

This subcategory includes all plants producing silver nitrate. The significant pollutant parameter for this subcategory, and the pretreatment standards for that parameter are shown below.

<u>Pollutant or Pollutant Property</u>	<u>Pretreatment Standard</u>
Maximum for any one day	Average of daily values for thirty consecutive days <u>shall not exceed</u>
_____	_____
mg/l	
Silver	0.5
1.0	

Silver is extremely toxic to microorganisms and can cause inhibition of the activated sludge process. Because of its toxicity, a limit of 1.25 mg/l (30 day average) is established. This is achievable by chlorination, chemical precipitation with lime and a flocculating agent, and settling or filtration. The cost of the treatment is estimated to be from 0.007 to 0.03 percent of the product price.

#### Sodium Bicarbonate Subcategory

This subcategory includes operations manufacturing sodium bicarbonate from either sodium carbonate or crude sodium bicarbonate. The pollutant of concern is total dissolved solids for which no practicable treatment is available at the present time. No limitations are established and thus, no costs are incurred.

#### Sodium Fluoride Subcategory

This subcategory includes all batch and continuous manufacturing operations which produce sodium fluoride. The significant pollutant parameter selected for this subcategory, and the pretreatment standards recommended for that parameter, are shown below.

Pollutant or  
Pollutant Property

Pretreatment  
Standard

Maximum for  
any one day

Average of daily  
values for thirty  
consecutive days  
shall not exceed

mg/l

Fluoride

50.0

25.0

Fluoride is recognized as a material potentially toxic to fish, wildlife, livestock, and humans. It would pass through a POTW without being treated or removed. Fluoride concentrations in excess of 10,000 mg/l are found in raw waste water from sodium fluoride production. Treatment technologies for fluoride removal include; precipitation/neutralization, flocculation, settling, and filtration. The cost of this treatment system is estimated at 3.8 percent of product cost.



## SECTION X

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## SECTION XI

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## SECTION XII

### GLOSSARY

Acetylene - A gas (chemical formula -  $C_2H_2$ ) which can be prepared by the action of water on calcium carbide. The starting material for large-scale synthesis of important organic compounds.

Activated-Sludge Process - A biological waste water-treatment process which involves the generation, under aerobic conditions, of organisms capable of decomposing organic material present in municipal waste water. The sludge produced is subsequently removed from the treated waste water by sedimentation and wasted or used as seed material in subsequent treatment.

Algicide - Any substance which kills algae or controls its growth.

Alum - Technically, a double sulfate of ammonium or a univalent or trivalent metal but commonly used to denote aluminum sulfate -  $Al_2(SO_4)_3$ .

Arc Furnace - A furnace heated by the "arc" produced between electrodes.

Atmospheric Crystallizer - Apparatus used to carry out crystallization under ambient pressure.

Baghouse - Apparatus for cleaning dusts and other particulates from a gas stream.

Barometric Condenser - A jet condenser in which water and the vapor to be condensed are in direct contact. The condenser is set sufficiently high so that the water drains from it by a barometric hot leg.

Bauxite - The principal ore of aluminum, composed of aluminum hydroxides and impurities in the form of free silica, clay, silt, and iron hydroxides.

Batch Process - Any discontinuous process which proceeds stepwise in a timed sequence, as opposed to a continuous process in which all steps proceed simultaneously without interruption.

Blowdown - The use of compressed air and/or liquid (usually, water) under pressure to remove liquids and solids from a

vessel (i.e., cooling towers, emission scrubbers, compressors, boilers).

Carbonation - The process by which a solution is impregnated with carbon dioxide to produce a carbonate or bicarbonate.

Caustic Soda - A common name for sodium hydroxide (NaOH).

Centrifugal Compressor - Type of non-lubricated compressor utilized in those processes requiring low-pressure conditions for effective compression.

Centrifugation - A physical operation involving the separation of suspended solids (such as crystals) from a mixture of liquid and suspended solids by centrifugal force.

Compressor Condensate - Moisture trapped within a compressor when the water-vapor portion of atmospheric air is subjected to high-pressure effects.

Cooling Tower - Towers which accomplish the cooling of water circulated in the tower by moving ambient air through the tower. The air/water contact causes some of the water to be evaporated by the air. Thus, through latent heat transfer, the remainder of the circulated water is cooled.

Crystallization - Process of forming crystals from a solution.

Decant - To remove the liquid portion of a settled mixture without disturbing the sediment.

Demagging - The process by which magnesium is removed from molten aluminum through techniques such as injection of chlorine.

Filter Backwash - The reversal of flow through a filter to wash clogged material out of the filter medium and reduce conditions causing loss of head.

Filter Cake - The dewatered sludge discharged from a filter. Contains 65 to 80% moisture, depending on the type of sludge, dewatering equipment, and the conditioning of the sludge.

Filter Press - An apparatus which separates a thick mixture into liquid (filtrate) and solids (filter sludge cake) by compressing the sludge.

Filtrate - The effluent or liquid portion of a mixture of solids and liquid removed by or discharged from a filter.

Fusion - The union of two chemical species by melting.

Heat Exchanger - A device providing for the transfer of heat from a fluid flowing in tubes to another fluid outside the tubes or the reverse.

Ion Exchange - Involves the displacement of ions of given species from insoluble exchange materials by ions of different species in solutions. The process can be used to remove ionic pollutants from waste water.

Double-Column Rectifier - System of fractional distillation employed in the air-separation process to effectively separate compressed, purified air into liquified components of nitrogen and oxygen.

Electric Furnace - A furnace heated by electric coils.

Electrolyte - Materials which, when placed in solution, make the solution conductive to electrical currents.

Evaporator - Apparatus used to reduce or remove water from a solution to concentrate the desired product.

Litharge - A common name for lead monoxide or yellow lead (PbO).

Linde Process (via molecular sieves) - An alternative technology employed for air separation which is particularly adaptable to those facilities having low product demand, such as waste water treatment plants and small industrial complexes. High-purity oxygen is produced by compressing air and then purifying and separating it through a series of vessels containing granular adsorbent (molecular sieve).

Mother Liquor - A concentrated solution substantially freed from undissolved matter by filtration, centrifugation, or decantation. Crystals are formed from the mother liquor.

Multi-Effect Evaporator - In chemical processing installations requiring a series of evaporations and condensations, the individual units are set up in series, and the latent heat of vaporization from one unit (or effect) is used to supply energy for the next.

Multi-Stage Separator - An apparatus used to physically separate several constituents or components of a solution based on density differences.

Noncontact Cooling Water - Cooling water which does not come into contact with the materials being cooled.

Oxidizing Tower - A process tank where oxidation reactions occur.

Pretreatment - The necessary processing given to materials before they can be properly utilized or treated in a process or treatment facility.

Primary Treatment - Major treatment, and sometimes the only treatment in a waste-treatment works, usually sedimentation and/or flocculation. Attains removal of a moderate percentage of suspended matter but little or no colloidal or dissolved matter.

POTW - Publicly Owned Treatment Works.

Reciprocating Compressor - Type of compressor which utilizes a rod-and-piston mode of operation for efficient compression of material. May be designed either single- or multi-stage, depending on compression needs. A distinguishing characteristic of this compressor is the need for oil lubrication of the cylinder compartments.

Reversing Exchangers - Heat-exchange unit which serves to purify compressed air by the removal of carbon dioxide and water vapor.

Screening - Process used to segregate solid material into various sizes.

Scrubber - Apparatus used in gas cleaning in which the gas is passed through packing or spray.

Secondary Treatment - Treatment of wastes by biological or chemical methods after primary treatment by flocculation/sedimentation. Secondary treatment depends primarily upon biological aerobic organisms for the biochemical decomposition of organic solids to inorganic or stable organic solids.

Sedimentation - The deposition of suspended matter in liquids, wastes, etc., by gravity. It is usually accomplished by reducing the velocity of liquid flow below the point where suspended material will be transported.

Settling Pond - A pond, natural or artificial, for recovering solids from an effluent.

Sludge - A viscous waste, with a high solids content, resulting from a number of waste water treatment processes (i.e., filtration, sedimentation, etc.).

Slurry - A watery mixture or suspension of solids (such as mud, lime, sludge).

Soda Ash - Common name for sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).

Solvay Process - This process for producing soda ash (sodium carbonate) involves a reaction (under pressure) between ammonia, brine (mostly  $\text{NaCl}$ ), and carbon dioxide to yield sodium bicarbonate. The sodium bicarbonate is heated to yield soda ash.

Sublimation - The process by which a solid transforms directly to its vapor without passing through the liquid state.

Supernatant - The liquid standing over a precipitate.

Vacuum Crystallizer - Apparatus for increasing the rate of crystallization through the use of pressure.

Venturi Scrubber - A device for the removal of particulates from a gas stream. The particulate-laden stream is directed through a venturi tube at a certain throat velocity. Water sprays are introduced just ahead of the venturi throat. The water and particles are then removed from the gas.

Washdown - Water resulting from cleaning of equipment, walls, floors, etc., within a plant.

Zeolite Process - An ion-exchange process for softening water. The zeolite exchanges sodium ions for hardness constituents (calcium, magnesium, etc.) in the water.

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# CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by	TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acres	ac	0.405	ha	hectares
acre - feet	ac ft	1,233.5	cu m	cubic meters
British Thermal Units	BTU	0.252	kg cal	kilogram - calories
British Thermal Units/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic inches	cu in.	16.39	cu cm (or cc)	cubic centimeters
cubic yards	cu y	0.76456	cu m	cubic meters
degrees Fahrenheit	°F	0.555 (°F-32) <sup>1</sup>	°C	degrees Celsius
feet	ft	0.3048	m	meters
flask of mercury	(76.5 lb)	34.73 <sup>1</sup>	kg Hg	kilograms of mercury
gallons	gal	0.003785	cu m	cubic meters
gallons	gal	3.785	l	liters
gallons/day	gpd	0.003785	cu m/day	cubic meters/day
gallons/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kW	kilowatts
inches	in.	2.54	cm	centimeters
inches of mercury	in. Hg	0.03342	atm	atmospheres
miles (statute)	mi	1.609	km	kilometers
million gallons/day	mgd	3,785 <sup>1</sup>	cu m/day	cubic meters/day
ounces (troy)	troy oz	31.10348	g	grams
pounds	lb	0.454	kg	kilograms
pounds/square inch (gauge)	psig	(0.06805 psig +1) <sup>1</sup>	atm	atmospheres (absolute)
pounds/square inch (gauge)	psig	5.1715	cm Hg	centimeters of mercury
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in.	6.452	sq cm	square centimeters
tons (short)	t	0.907	kg	metric tons (1000 kilograms)
tons (long)	long t	1.016	kg	metric tons (1000 kilograms)
yards	y	0.9144	m	meters

<sup>1</sup> Actual conversion, not a multiplier

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