EMISSION TESTING REPORT

PROJECT NUMBER 72 MM 05

STAUFFER CHEMICAL COMPANY

TARPON SPRINGS, FLORIDA

FINAL

PEDCo ENVIRONMENTAL

ENVIRONMENTAL SPECIALISTS, INC.
PEDCO
CINCINNATI, OHIO

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I. INTRODUCTION

Atmospheric emissions of fluorides, phosphorus pentoxide, total particulate, and sulfur dioxide from Stauffer Chemical Company's elemental phosphorus plant at Tarpon Springs, Florida, were sampled to form a data base for New Source Performance Standards as authorized by the Clean Air Act of 1970.

Tests were made to determine fluoride and phosphorus pentoxide concentrations before and after the venturi scrubber serving a furnace slag tapping operation. Fluoride, phosphorus pentoxide, total particulate, and sulfur dioxide concentrations before and after the spray chamber serving the feed nodulizing kiln were also measured. In addition, the fluoride and P_2O_5 concentrations in the air return line and the CO line leading to the kiln were measured. All field testing was conducted by PEDCo-Environmental Specialists, Inc. and all sample analyses were performed by the Environmental Protection Agency's Office of Air Quality and Planning. Table 1 summarizes the test locations, dates, and the measurements made. In addition, Stauffer Chemical Company conducted fluoride tests at the nodulizing kiln spray chamber outlet during this test series using both manual and continuous bubbler systems.

This test series was interrupted by Hurricane Agnes. Sampling therefore occurred during two different periods.

TABLE 1.

SUMMARY OF PROGRAM MEASUREMENTS MADE AT STAUFFER CHEMICAL COMPANY IN TARPON SPRINGS, FLORIDA

DATE 1972	TEST NO.	TEST SITE	STACK GAS PARAMETERS			EMISSIONS
6/13	1AK	Kiln Spray	Velocity	Temp.	% H_2O	Fluorides & P_2O_5
6/14	2AK	Chamber Inlet	↓	↓	↓	↓
7/18	3AK	↓				
7/20	1					Particulate & SO_2^c
7/21	2					↓
7/21	3	↓	↓			
6/13	1BK	Kiln Spray	a			Fluorides & P_2O_5
6/14	2BK	Chamber Outlet, B	↓			↓
7/18	3BK	↓				
6/13	1CK	Kiln Spray				
6/14	2CK	Chamber Outlet C				
7/18	3CK	5.7' Above Site B				↓
7/20	1	Kiln Spray				Particulate
7/21	2	Chamber Outlet, B				↓
7/21	3		↓	↓	↓	
6/15	1-CO	CO Line	b			Fluorides & P_2O_5
7/19	1,2,3	Air Return Line	Velocity	↓	↓	↓
6/16	1S	Slag Tap Scrubber Inlet	↓			Fluorides & P_2O_5
6/21	2S					↓
6/21	3S	↓				
6/16	1S	Slag Tap Furnace Outlet				
6/21	2S					
6/21	3S	↓	↓	↓	↓	↓

a) Velocity too low to measure and was calculated based on gas volume measured at inlet site and dilution air drawn into duct.

b) No velocity measured due to dangerous conditions (explosion) and small sampling port.

c) Also sampled for SO_2 on July 19 at inlet and outlet site

In all cases, the tests were run to determine average emission concentrations and rates under normal operating conditions. Whenever possible, testing was conducted during normal operating conditions.

Slag Tapping Operation

At this plant, the slag tapping ports in the electric arc furnace were covered by a movable hood system which vented fumes during slag tapping through a venturi scrubber and out the stack. Stack gases were sampled before and after the scrubber as shown by Points E and F in Figure 1. For the three test runs sampling was conducted only during the tapping operation to determine concentrations of fluoride and phosphorus pentoxide (P_2O_5). Samples of the scrubber water were also collected at Points g and h as shown in Figure 1.

Nodulizing Kiln

Gases from the feed nodulizing kiln pass through cyclone collectors and then a large diameter spray chamber which also serves as the exit stack. Stack gases were sampled before and after the spray chamber at Points A, and B and C, respectively, as shown in Figure 1. The C location was 5.7 ft. above Site B and was sampled to determine the effect of additional residence time of the gaseous emissions in the

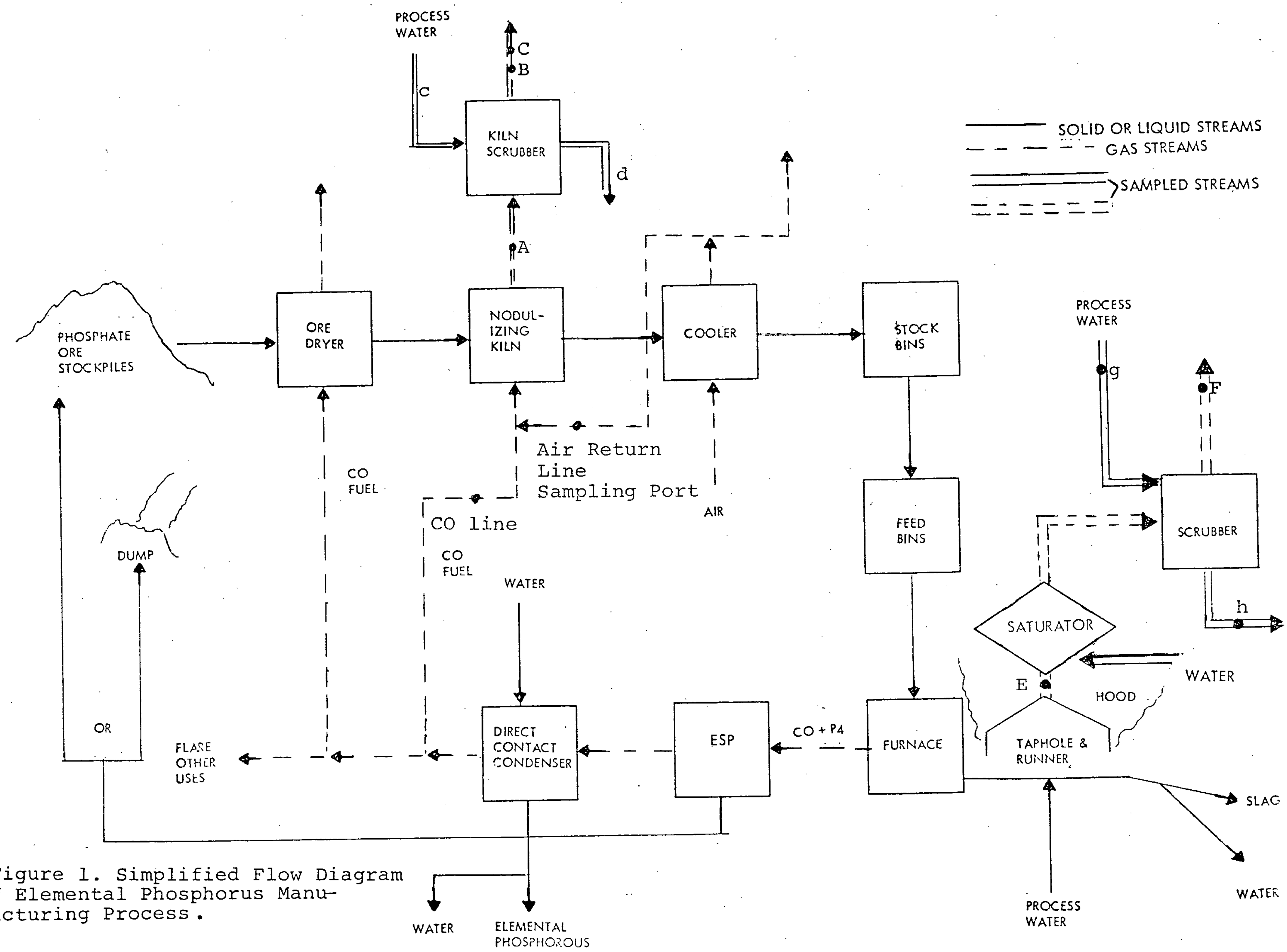


Figure 1. Simplified Flow Diagram of Elemental Phosphorus Manufacturing Process.

large stack. Sampling site A was located before the spray chamber. Scrubber water samples were taken at Points c and d.

Simultaneous testing was done at the three emission test sites, A, B, and C to determine concentrations of fluoride and P_2O_5. Triplicate tests were made. Simultaneous tests were performed at two test sites, A and B, to determine concentrations of particulate and sulfur dioxide. Triplicate tests were made for these constituents. During the fluoride and particulate tests, gas samples were also taken for molecular weight determinations.

Raw material and product samples were also collected during the test periods and analyzed for fluorides, P_2O_5, and trace metals. Complete analysis of these samples is included in EMB file 72-MM-05.

II. SUMMARY AND DISCUSSION OF RESULTS

Slag Tapping Operation

Slag tapping was an intermittent operation which occured approximately every 70 minutes. Each tap lasted for approximately 12 minutes. Sampling was conducted simultaneously before and after the venturi scrubber only during the tapping periods to determine the concentrations of fluorides and P_2O_5.

Tables 2, 3, and 4 summarize the stack gas and scrubber water data obtained during these tests. Sampling procedures are described in Section V. More detailed sampling and analytical results are included in the appendices to this report. Emission data are reported on a concentration (grains per standard cubic foot) basis, and also as pounds per hour emitted during the slag tapping periods.

The higher gas flows measured at the outlet site indicate leakage of outside air into the duct system around the fan. Measured moisture content of the outlet stream showed that the gas was not saturated with water. This may be due to some reheating of the gas because of the hot slag being dumped near the duct leading to the outlet site, and also incomplete saturation in the venturi scrubber.

TABLE 2. SLAG TAPPING - SCRUBBER INLET
FLUORIDE & P_2O_5 EMISSIONS SUMMARY

Run Number	1	2 Composite	3	Weighted Average
Date	6-16-72	6-21-72	6-21-72	
Volume of Gas Sampled - DSCF[a]	29.78	26.00	20.10	25.29
Percent Moisture by Volume	2.60	1.82	2.15	2.19
Average Stack Temperature - F	219	173	189	194
Stack Volumetric Flow Rate - DSCFM[b]	14,000	14,600	13,100	13,900
Stack Volumetric Flow Rate - ACFM[c]	18,900	18,200	16,900	18,000
Percent Isokinetic	75.8	107	113	98.6
Percent by Volume CO_2	<1	<1	<1	<1
Percent by Volume O_2	21.0	21.0	21.0	21.0
Percent by Volume CO	<1	<1	<1	<1
Percent by Volume N_2	79.0	79.0	79.0	79.0
Fluoride Emissions - water soluble				
mg Collected	107	42.4	35.5	61.6
gr/DSCF	0.0555	0.0251	0.0272	0.0376
gr/ACF	0.0410	0.0201	0.0212	0.0289
lb/hr[d]	6.66	3.14	3.06	4.48
Fluoride Emissions - total				
mg Collected	107.1	44.2	35.8	62.4
gr/DSCF	0.0555	0.0262	0.0275	0.0381
gr/ACF	0.0410	0.0209	0.0213	0.0293
lb/hr[d]	6.66	3.28	3.08	4.53
Fluoride Emissions, % insoluble	0.093	4.07	0.838	1.28
P_2O_5 Emissions - water soluble				
mg Collected	509	453.2	527.6	496.6
gr/DSCF	0.264	0.269	0.405	0.303
gr/ACF	0.195	0.215	0.316	0.234
lb/hr	31.7	33.6	45.4	36.1
P_2O_5 Emissions - total				
mg Collected	509.6	465.8	532.3	502.4
gr/DSCF	0.264	0.276	0.408	0.306
gr/ACF	0.195	0.221	0.318	0.235
lb/hr[d]	31.7	34.5	45.8	36.5
P_2O_5 Emissions, % insoluble	1.18	2.71	0.883	1.16

[a] Dry standard cubic feet at 70 F, 29.92 in. Hg.

[b] Dry standard cubic feet per minute at 70 F, 29.92 in. Hg.

[c] Actual cubic feet per minute.

[d] During slag tapping only.

TABLE 3. SLAG TAPPING - SCRUBBER OUTLET
FLUORIDE & P_2O_5 EMISSIONS SUMMARY

Run Number	1	2	3	Weighted Average
Date	6-16-72	6-21-72	6-21-72	
Volume of Gas Sampled - DSCF[a]	28.95	27.29	26.71	27.65
Percent Moisture by Volume	7.56	5.62	5.86	6.35
Average Stack Temperature - °F	121	120	119	120
Stack Volumetric Flow Rate - DSCFM[b]	18,800	17,200	17,200	17,900
Stack Volumetric Flow Rate - ACFM[c]	22,500	20,000	20,000	20,800
Percent Isokinetic	106	107	105	106
Percent by Volume CO_2	<1	<1	<1	<1
Percent by Volume O_2	21.0	21.0	21.0	21.0
Percent by Volume CO	<1	<1	<1	<1
Percent by Volume N_2	79.0	79.0	79.0	79.0
Fluoride Emissions - water soluble				
mg Collected	3.21	1.70	1.40	2.10
gr/DSCF	0.00171	0.000960	0.000808	0.00117
gr/ACF	0.0143	0.000824	0.000692	0.000995
lb/hr[d]	0.276	0.142	0.119	0.179
Fluoride Emissions - total				
mg Collected	4.25	2.43	1.58	2.75
gr/DSCF	0.00227	0.00137	0.000912	0.00153
gr/ACF	0.0189	0.00118	0.000781	0.00130
lb/hr[d]	0.365	0.202	0.134	0.233
Fluoride Emissions, % insoluble	24.5	30.0	11.4	22.0
P_2O_5 Emissions - water soluble				
mg Collected	57.5	61.3	82.1	67.0
gr/DSCF	0.0307	0.0346	0.0474	0.0376
gr/ACF	0.0256	0.0298	0.0406	0.0325
lb/hr	4.94	5.11	6.98	5.68
P_2O_5 Emissions - total				
mg Collected	63.8	62.4	83.9	69.9
gr/DSCF	0.0340	0.0352	0.0484	0.0390
gr/ACF	0.0256	0.0298	0.0406	0.0325
lb/hr[d]	5.48	5.21	7.14	5.94
P_2O_5 Emissions, % insoluble	9.87	1.76	2.15	4.15

[a] Dry standard cubic feet at 70 °F, 29.92 in. Hg.
[b] Dry standard cubic feet per minute at 70°F, 29.92 in. Hg.
[c] Actual cubic feet per minute.
[d] During slag tapping only.

TABLE 4. SCRUBBER WATER ANALYSIS - SLAG TAP PROCESS VENTURI SCRUBBER

Date 1972	Test No.	Soluble Fluorides mg/liter		P_2O_5 mg/ml		pH	
6/16	1 - Discharge	282		1.4		2.78	
		366	avg = 375	1.7	avg = 1.7	2.50	avg = 2.53
		477		1.9		2.32	
6/21	2 - Discharge	365		1.7		2.62	
		340	avg = 359	1.6	avg = 1.6	2.75	avg = 2.75
		373		1.4		2.88	
6/21	3 - Discharge	596		2.5		2.15	
		452	avg = 491	1.8	avg = 1.9	2.43	avg = 2.40
		426		1.5		2.61	
6/21	Slag Pit[a]	243		1.4		3.48	
6/21	Slag Pit[a]	238		1.0		3.56	

a) This water is used for scrubber water make-up.

Flexible Teflon® tubing was used between the probe and first impinger for all tests at both the inlet and outlet sites.

Fluoride Data Evaluation - The measured values for the slag tapping appear to be representative of process emissions except for Test 1 (inlet and outlet) which has approximately twice the emission rate as compared to Tests 2 and 3. The following are possible reasons for the high fluoride measurement on Test 1:

1. During the first slag tap the sampling crew on the inlet side was driven off the platform by the high concentration of acid-gas fumes (probably escaping from under the furnace fume hood). The EPA Project Officer, John Wilkens, had delayed the first slag tap for approximately two hours.

2. The analytical results in Appendix E, show that for the inlet Test 1 the soluble fluorides were 107 mg/sample as compared to 42.4 mg/sample and 35.5 mg/sample of soluble fluorides respectively for Tests 2 and 3. Sample volumes were approximately the same for all three tests.

3. The percent isokinetic for Test 1 inlet was only 76% as compared to 107% and 113% for Tests 2 and 3. This would result in the possibility of a higher grain loading. Only four traverse ports were used during Test 1 at the inlet. During Tests 2 and 3 16 traverse points were used. The P_2O_5 concentration was however not out-of-line for this run.

Based on these observations, Test 1 inlet does not appear to be representative of normal operation. Water soluble fluoride emissions were in the range of 0.025 to 0.027 grains/DSCF at the scrubber inlet and averaged 0.0012 grains/DSCF at the outlet. The scrubber collection efficiency, based on pounds of total fluoride emitted, averaged 95%.

P_2O_5 Data Evaluation - The Test 3 inlet concentration of 0.405 grains/DSCF for the water soluble P_2O_5 is approximately 35% higher than the concentration measured in Tests 1 and 2. However, no reason is apparent for this, and an average of 0.303 grains/DSCF on the inlet appears to be representative of normal operation. The outlet concentrations, averaging 0.038 grains/DSCF and ranging from 0.031 to 0.048 grains/DSCF are also considered in the range of normal operation. Average scrubber collection efficiency for water soluble P_2O_5 was 88%.

Nodulizing Kiln Operation

Tables 5 to 13 summarize the data obtained on the nodulizing kiln spray chamber. Tests for fluorides, P_2O_5, total particulate, and sulfur dioxide were conducted before and after the spray chamber which was used to reduce atmospheric emissions. Since the outlet flow from the spray

TABLE 5. NODULIZING KILN TESTS - STACK GAS VOLUMETRIC FLOW RATES

RUN NO.	DATE	INLET		OUTSIDE TEMPERING AIR		OUTLETS		
		GAS VELOCITY FPM[a]	GAS VOLUME SCFM[b]	GAS VELOCITY FPM[a]	GAS VOLUME SCFM[b]	PORT SITE	GAS VELOCITY FPM[a]	GAS VOLUME SCFM[b]
Fluoride 1	6/13/72	6,490	23,900			Lower (B)	86.4	26,400
						Upper (C)	80.0	26,400
Fluoride 2	6/14/72	6,230	24,300			Lower (B)	94.7	26,800
						Upper (C)	91.9	26,800
	6/22/72			2,730	2,520			
Fluoride 3	7/18/72	6,800	24,300	2,730	2,520	Lower (B)	95.9	26,800
						Upper (C)	85.8	26,800
Particulate 1	7/20/72	4,700	18,100			Lower (B)	81.2	25,200
		5,960[c]	22,700[c]					
Particulate 2	7/21/72	5,440	20,700			Lower (B)	81.6	24,700
		5,840[c]	22,200[c]					
Particulate 3	7/21/72	5,230	20,200			Lower (B)	74.1	23,200
		5,390[c]	20,700[c]					

[a] Feet per minute, stack conditions.

[b] Standard cubic feet per minute, dry basis at 70°F, 29.92 in. Hg.

[c] Represents flow measurements determined by performing a separate pitot traverse before or after each particulate run. Normal inlet sampling covered only 12 traverse points and was considered not as representative as the separate pitot traverses that covered 24 points.

TABLE 6. FLUORIDE & P_2O_5 EMISSION DATA SUMMARY
NODULIZING KILN - SCRUBBER SPRAY CHAMBER INLET

Run Number	1 Composite	2	3	Weighted Average
Date	6-13-72	6-14-72	7-18-72	
Volume of Gas Sampled - DSCF[a]	64.03	28.65	32.70	41.79
Percent Moisture by Volume	19.9	19.1	20.7	19.9
Average Stack Temperature - °F	702	653	729	695
Stack Volumetric Flow Rate - DSCFM[b]	23,900	24,300	24,300	24,200
Stack Volumetric Flow Rate - ACFM[c]	67,000	64,300	70,200	67,200
Percent Isokinetic	102	105	120	109
Percent by Volume CO_2	1.7	12.4	16	
Percent by Volume O_2	20.3	13.3	8	
Percent by Volume CO	0.87	<1	2.2	
Percent by Volume N_2	77.1	74.3	73.8	
Fluoride Emissions - water soluble				
mg Collected	7300.8	3201.5	5401.4	5301
gr/DSCF	1.76	1.72	2.54	1.95
gr/ACF	0.626	0.651	0.880	0.703
lb/hr[d]	360	358	530	405
Fluoride Emissions - total				
mg Collected	8171.1	3382.6	5546.2	5700
gr/DSCF	1.97	1.84	2.61	2.10
gr/ACF	0.703	0.694	0.898	0.757
lb/hr[d]	404	382	540	434
Fluoride Emissions, % insoluble	10.7	5.35	2.61	6.68
P_2O_5 Emissions - water soluble				
mg Collected	85.1	243.1	317.5	215
gr/DSCF	0.0205	0.131	0.150	0.0795
gr/ACF	0.00731	0.0528	0.0516	0.0293
lb/hr	4.18	27.2	31.1	16.5
P_2O_5 Emissions - total				
mg Collected	149.6	466.7	d	-
gr/DSCF	0.0360	0.251	d	-
gr/ACF	0.0128	0.100	d	-
lb/hr[d]	7.36	52.2	d	-
P_2O_5 Emissions, % insoluble	43.1	47.9	d	-

[a] Dry standard cubic feet at 70 °F, 29.92 in. Hg.

[b] Dry standard cubic feet per minute at 70°F, 29.92 in. Hg.

[c] Actual cubic feet per minute.

[d] Analysis of P_2O_5 insoluble portion impossible due to gel being formed when sodium hydroxide was combined with sample.

TABLE 7. FLUORIDE & P_2O_5 EMISSION DATA SUMMARY
NODULIZING KILN - SCRUBBER SPRAY CHAMBER OUTLET B

Run Number	1	2	3	Weighted Average
Date	6-13-72	6-14-72	7-18-72	
Volume of Gas Sampled - DSCF[a]	43.07	39.97	58.67	47.24
Percent Moisture by Volume	10.0	16.7	19.0	15.2
Average Stack Temperature - °F	138	140	135	138
Stack Volumetric Flow Rate - DSCFM[b]	26,400[d]	26,800[d]	26,800[d]	26,700[d]
Stack Volumetric Flow Rate - ACFM[c]	33,100	36,300	36,800	35,400
Percent Isokinetic	74.1	67.8	62.6	68.2
Percent by Volume CO_2	13.3	6.0		
Percent by Volume O_2	13.4	17.9		
Percent by Volume CO	0.2	<1		
Percent by Volume N_2	73.1	76.1		
Fluoride Emissions - water soluble				
mg Collected	8.8	4.7	24.5	12.7
gr/DSCF	0.00315	0.00181	0.00643	0.00414
gr/ACF	0.00251	0.00134	0.00468	0.00313
lb/hr[d]	0.689	0.404	1.47	0.947
Fluoride Emissions - total				
mg Collected	9.45	5.3	25.0	13.3
gr/DSCF	0.00338	0.00204	0.00656	0.00434
gr/ACF	0.00270	0.00151	0.00478	0.00328
lb/hr[d]	0.742	0.457	1.50	0.992
Fluoride Emissions, % insoluble	6.88	11.3	2.00	4.51
P_2O_5 Emissions - water soluble				
mg Collected	23.9	15.1	67.0	35.3
gr/DSCF	0.00855	0.00582	0.0176	0.0115
gr/ACF	0.00683	0.00431	0.0128	0.00859
lb/hr	1.94	1.33	4.04	2.64
P_2O_5 Emissions - total				
mg Collected	26.6	17.8	70.4	38.3
gr/DSCF	0.00951	0.00686	0.0185	0.0125
gr/ACF	0.00760	0.00508	0.0135	0.00933
lb/hr[d]	2.20	1.56	4.23	2.86
P_2O_5 Emissions, % insoluble	10.2	15.2	4.84	7.83

[a] Dry standard cubic feet at 70 °F, 29.92 in. Hg.

[b] Dry standard cubic feet per minute at 70°F, 29.92 in. Hg.

[c] Actual cubic feet per minute.

[d] Outlet volumetric flows based on inlet flow measurements plus additional tempering air entering prior to the outlet sampling site.

TABLE 8. FLUORIDE & P_2O_5 EMISSION DATA SUMMARY
NODULIZING KILN - SCRUBBER SPRAY CHAMBER OUTLET C

Run Number	1	2	3 Composite	Weighted Average
Date	6-13-72	6-14-72	7-18-72	
Volume of Gas Sampled - DSCF[a]	44.78	39.42	27.07	37.09
Percent Moisture by Volume	3.17	14.1	9.01	8.76
Average Stack Temperature - °F	136	140	138	138
Stack Volumetric Flow Rate - DSCFM[b]	26,400[d]	26,800[d]	26,800[d]	26,700[d]
Stack Volumetric Flow Rate - ACFM[c]	30,700	35,200	32,900	32,900
Percent Isokinetic	74.7	65.8	105	81.8
Percent by Volume CO_2	13.3	6.0		
Percent by Volume O_2	13.4	17.9		
Percent by Volume CO	0.2	<1		
Percent by Volume N_2	73.1	76.1		
Fluoride Emissions - water soluble				
mg Collected	4.1	6.4	11.1	7.20
gr/DSCF	0.00141	0.00250	0.00631	0.00299
gr/ACF	0.00122	0.00191	0.00514	0.00243
lb/hr[d]	0.320	0.576	1.45	0.684
Fluoride Emissions - total				
mg Collected	4.42	7.6	11.6	7.87
gr/DSCF	0.00151	0.00297	0.00660	0.00327
gr/ACF	0.00130	0.00226	0.00537	0.00266
lb/hr[d]	0.343	0.684	1.52	0.748
Fluoride Emissions, % insoluble	7.2	15.8	4.31	8.51
P_2O_5 Emissions - water soluble				
mg Collected	11.5	17.1	25.5	18.0
gr/DSCF	0.00395	0.00668	0.0145	0.00747
gr/ACF	0.00340	0.00510	0.0118	0.00605
lb/hr	0.898	1.54	3.33	1.72
P_2O_5 Emissions - total				
mg Collected	13.2	19.7	26.4	19.8
gr/DSCF	0.00454	0.00770	0.0150	0.00822
gr/ACF	0.00391	0.00588	0.0122	0.00662
lb/hr[d]	1.03	1.77	3.45	1.88
P_2O_5 Emissions, % insoluble	12.9	13.2	3.41	9.09

[a] Dry standard cubic feet at 70 °F, 29.92 in. Hg.

[b] Dry standard cubic feet per minute at 70°F, 29.92 in. Hg.

[c] Actual cubic feet per minute.

[d] Outlet volumetric flows based on inlet flow measurements plus additional tempering air entering prior to the outlet sampling site.

TABLE 9. PARTICULATE EMISSION DATA
NODULIZING KILN-SCRUBBER SPRAY CHAMBER INLET

RUN NUMBER	1	2	3	WEIGHTED AVERAGE
Date	7-20-72	7-21-72	7-21-72	
Volume of Gas Sampled-DSCF[a]	23.02	25.006	24.81	24.28
Percent Moisture by Volume	20.1	18.4	18.1	18.9
Average Stack Temperature-°F	652	682	670	668
Stack Volumetric Flow Rate-DSCFM[b]	18,100	20,700	20,200	19,700
Stack Volumetric Flow Rate-ACFM[c]	48,500	56,100	54,000	52,900
Percent Isokinetic	114	108	110	111
Percent Excess Air	167	39.4	44.7	83.7
Feed Rate-ton/hr				
Particulates-probe, cyclone, and filter catch				
mg	1069	1054.6	1114.5	1079
gr/DSCF	0.715	0.650	0.692	0.685
gr/ACF	0.266	0.240	0.259	0.254
lb/hr	111	115	120	116
Particulates-total catch				
mg	1382.9	1196.7	1347.9	1309
gr/DSCF	0.925	0.738	0.838	0.831
gr/ACF	0.345	0.272	0.313	0.309
lb/hr	143	131	145	140
Percent impinger catch	22.7	11.9	17.3	17.6

[a] Dry standard cubic feet at 70°F, 29.92 in. Hg.
[b] Dry standard cubic feet per minute at 70°F, 29.92 in. Hg.
[c] Actual cubic feet per minute

TABLE 10. PARTICULATE EMISSION DATA
NODULIZING KILN-SCRUBBER SPRAY CHAMBER OUTLET

RUN NUMBER	1	2	3	WEIGHTED AVERAGE
Date	7-20-72	7-21-72	7-21-72	
Volume of Gas Sampled-DSCF[a]	105.57	109.38	105.51	106.82
Percent Moisture by Volume	19.6	22.7	20.1	20.8
Theoretical Saturated percent moisture	12.0	13.5	11.5	12.5
Average Stack Temperature-°F	122	126	120	123
Stack Volumetric Flow Rate-DSCFM[b]	25,200	24,700	23,200	24,400
Stack Volumetric Flow Rate-ACFM[c]	31,200	31,300	28,400	30,300
Percent Isokinetic	119	127	130	125
Feed Rate-ton/hr				
Particulates-probe, and filter catch				
mg	386.4	417	300.3	368
gr/DSCF	0.0564	0.0587	0.0439	0.0531
gr/ACF	0.0455	0.0466	0.0360	0.0426
lb/hr	12.3	12.5	8.76	11.1
Particulates-total catch				
mg	634.5	799.3	630.2	688
gr/DSCF	0.0926	0.113	0.0922	0.0993
gr/ACF	0.0749	0.0892	0.0754	0.0797
lb/hr	20.1	23.9	18.4	20.8
Percent impinger catch	39.1	47.8	52.3	46.5

[a] Dry standard cubic feet at 70°F, 29.92 in. Hg.

[b] Dry standard cubic feet per minute at 70°F, 29.92 in. Hg.

[c] Actual cubic feet per minute calculated from saturated gas conditions.

NOTES: All outlet volumetric flows are based on inlet duct gas flow plus 2530 SCFM for dilution air entering the gas stream prior to the outlet sampling point.

TABLE 11. NODULIZING KILN SUMMARY OF GASEOUS TESTING

A. CARRIER GASES[a]

RUN NO.	DATE	GAS COMPOSITION (VOLUME % DRY) CO_2	O_2	CO	N_2^b
Fluoride 1	6-13-72				
Inlet		1.70	20.3	0.87	77.1
Outlet		13.3	13.4	0.20	73.1
Fluoride 2	6-14-72				
Inlet		12.4	13.3	<1	74.3
Outlet		6.0	17.9	<1	76.1
Fluoride 3	7-18-72				
Inlet		16.0	8.0	2.2	73.8
Outlet					
Particulate 1	7-20-72				
Inlet		18.6	12.1	1.93	67.4
Outlet		-	-	-	-
Particulate 2	7-21-72				
Inlet		18.3	6.47	2.00	73.3
Outlet		12.2	10.7	2.90	74.2
Particulate 3	7-21-73				
Inlet		18.4	6.70	1.43	73.4
Outlet		11.3	10.8	2.30	75.6

B. SULFUR DIOXIDE EMISSIONS

RUN NO.	DATE	SPRAY CHAMBER INLET ppm SO_2^c	SPRAY CHAMBER OUTLET ppm SO_2^c
1	7-19-72	2540	144
2	7-20-72	2100	210
3	7-20-72	787	415
		Weighted Average 1610	Weighted Average 235

TABLE 11. Continued

C. FLUORIDE EMISSIONS
(CO LINE TO KILN)

RUN NO.	DATE	FLUORIDE EMISSIONS, (GR/DSCF[d]) WATER SOLUBLE	TOTAL
1	6-15-72	0.000630	0.000630

[a] Orsat analysis

[b] Determined by differences, includes other gases

[c] Parts per million by volume

[d] Grains per dry standard cubic feet

TABLE 12. AIR RETURN LINE
FLUORIDE & P_2O_5 DATA SUMMARY

Run Number	1	2	3	Weighted Average
Date	7-19-72	7-19-72	7-19-72	
Volume of Gas Sampled - DSCF[a]	5.73	5.72	5.62	5.68
Percent Moisture by Volume	2.90	3.36	3.26	3.18
Average Stack Temperature - °F	700	700	700	700
Stack Volumetric Flow Rate - DSCFM[b]	16,900	16,800	16,800	16,800
Stack Volumetric Flow Rate - ACFM[c]	36,400	36,400	36,400	36,400
Percent Isokinetic	-	See note	-	-
Percent by Volume CO_2	0	0	0)	Assumed values based on air
Percent by Volume O_2	21	21	21)	
Percent by Volume CO	0	0	0)	
Percent by Volume N_2	79	79	79)	
Fluoride Emissions - water soluble				
mg Collected	79.5[d]	42.6	63.4	61.8
gr/DSCF	0.214[d]	0.115	0.174	0.168
gr/ACF	0.0995[d]	0.0530	0.080	0.0775
lb/hr[d]	31.1	16.5	25.2	24.3
Fluoride Emissions - total				
mg Collected	79.6[d]	42.7	63.5	61.9
gr/DSCF	0.215[d]	0.115	0.174	0.168
gr/ACF	0.0996[d]	0.0531	0.080	0.0776
lb/hr[d]	31.1[d]	16.6	25.2	24.3
Fluoride Emissions, % insoluble	0.13[d]	0.23	0.16	0.16
P_2O_5 Emissions - water soluble				
mg Collected	1.2	1.3	1.4	1.3
gr/DSCF	0.00323	0.00350	0.00384	0.00352
gr/ACF	0.00149	0.00161	0.0018	0.00163
lb/hr	0.48	0.51	0.55	0.51
P_2O_5 Emissions - total				
mg Collected	1.7	1.9	2.0	1.9
gr/DSCF	0.00457	0.0051	0.0055	0.00506
gr/ACF	0.00211	0.0023	0.0025	0.00230
lb/hr[d]	0.68	0.74	0.79	0.74
P_2O_5 Emissions, % insoluble	29	31.6	30	31.6

[a] Dry standard cubic feet at 70 °F, 29.92 in. Hg.

[b] Dry standard cubic feet per minute at 70°F, 29.92 in. Hg.

[c] Actual cubic feet per minute.

[d] Observed interference in analysis (see Sampling & Analytical Procedures Section).

Note: Run not conducted using isokinetic sampling procedures due to small sampling port.

TABLE 13. SCRUBBER WATER ANALYSES - NODULIZING KILN SPRAY CHAMBER

Date 1972	Test No.	Soluble Fluorides mg/liter	Soluble P_2O_5 mg/ml	pH
6/13	1 - Intake	27.8	0.1	7.65
		38 avg = 32.3	0.02 avg = 0.05	9.25 avg = 8.50
		31	0.02	8.60
6/13	1 - Discharge	1200	0.04	2.12
		480 avg = 779	0.03 avg = 0.033	2.18 avg = 2.14
		657	0.03	2.12
6/14	2 - Intake	42	0.02	8.39
		40 avg = 41	0.02 avg = 0.02	8.80 avg = 8.73
		40	0.02	9.01
6/14	2 - Discharge	549	0.1	2.49
		610 avg = 602	0.05 avg = 0.10	2.34 avg = 2.39
		647	0.16	2.34
7/18	3 - Intake	21	0.01	5.50
		33 avg = 24	0.01 avg = 0.01	6.00 avg = 5.70
		18	0.01	5.60
7/18	3 - Discharge	976	0.09	2.40
		22 avg = 482	0.04 avg = 0.06	3.50 avg = 2.88
		447	0.05	2.75

chamber was too low to measure with a pitot tube, the value was calculated and based on the sum of the inlet flow and the outside tempering air which entered the duct just before the induced draft fan (see Table 5). Two outlet test sites were used to measure fluorides and P_2O_5. These sites, designated by test numbers BK and CK were 5.7 ft. apart near the top of the spray tower (see Figure 6 , Page 38). Sampling ports B, D, F, and H were associated with test site BK, and Ports A, C, E, and G were associated with the upper (downstream) site CK.

Table 5 summarizes the measured gas velocities at the inlet, and the calculated velocities and volumes at the outlet.

Fluoride Evaluation (Water soluble) - Tests 1 and 2 with inlet loadings of 1.76 grains/DSCF and 1.72 grains/DSCF, respectively, as seen in Table 6, seem to be representative of normal kiln operation. Carbon monoxide from the furnace supplying fuel to the kiln and residual fuel oil were normal during testing, and pH control of the scrubber water by addition of lime was controlled satisfactorily as shown by the data in Table 13. Testing was interrupted by inclement weather (Hurricane Agnes) and Test 3 was conducted a month later on July 18, 1972. The following observations are pertinent to Test 3:

1. Due to equipment limitations at the inlet site, four points on the 12 point traverse were not sampled and the remaining eight points were used in obtaining the stack sample (see Appendix C, Field Data).

2. Table 13 shows that the pH of the inlet scrubber water was not well controlled during Test 3. Measurements of 5.5 to 6.0 pH for Test 3 were obtained as compared to 7.65 to 9.00 pH measurements for Tests 1 and 2.

Inlet Test 3 is therefore not too representative of normal operation, but is indicative of emission control fluctuations which can be expected. Average grain loadings for the water soluble fluorides averaged 1.95 grains/DSCF before the spray chamber, and 0.0041 at the outlet. Total fluorides measured at the inlet site averaged 434 pounds/hour. The spray chamber was very effective in reducing fluoride concentrations and achieved an average collection efficiency of more than 99% with an average outlet loading of 0.99 pound/hour at site BK.

The attempt at relating increased residence time of the gas stream in the spray chamber to a reduction in emissions was not conclusive since only slightly lower values were measured on the average at the downstream sampling site. The close proximity of the downstream sampling site to the stack exit caused the flow and probably the pollutant concentrations to be affected by the wind.

P_2O_5 Evaluation - Outlet B, Tests 1 and 2 appear representative of normal operation with average water soluble P_2O_5 loadings of 0.0058 to 0.0086 grains/DSCF. Inlet loadings of 0.02 to 0.13 grains/DSCF were measured at this time. Carbon monoxide from the furnace supplying fuel to the kiln and residual fuel oil usage were normal during testing. The scrubber water pH was satisfactorily adjusted to an alkaline range to control emissions. For Test 3, the inlet total P_2O_5 loading is not reported. The insoluble portion consisted of a very large amount of particulate matter and upon fusion with sodium hydroxide in the analysis procedure a gel was formed. The soluble P_2O_5 for this test was slightly higher than for Tests 1 and 2.

Concentrations of water soluble P_2O_5 averaged 0.08 grains/DSCF at the inlet and 0.009 at the spray chamber outlet and appear to be representative of emissions for this unit over extended periods of time. The spray chamber collection efficiency for P_2O_5 removal was approximately 87% based on the data at Site B.

Table 8 summarizes the data obtained at the downstream outlet site, CK. Average values for both fluorides and P_2O_5 are approximately 25% lower than those measured at Site B.

However, one cannot state whether these lower concentrations are caused by the increased residence time in the spray chamber or by dilution with outside air which blew into the chamber.

Isokinetic sampling rates at the outlet were generally low for the fluoride runs. This was due to a variety of factors including; sampling rates so low that orifice pressure could not be read accurately; higher than expected moisture content; and not accounting for dilution air added to vent gas flow between inlet and outlet sites. This low isokinetic sampling rate would tend to bias the test results on the high side.

Particulate Evaluation - Tables 9 and 10 present the particulate emission data obtained for the inlet and outlet of the spray chamber. Only the lower (BK) outlet sampling site was used for particulate measurements and samples were taken at a single point approximately six feet into the stack at each port for a total of four sampling points. The definition of true particulate in this type of gas stream when sampled with a train using a glass probe and fiber glass filter is very difficult because of the re-activity of gaseous fluorides with the sampling equipment.

The inlet tests are representative of uncontrolled emission rates and agreed fairly well from test to test and averaged 0.69 grains/DSCF for the front portion of the sampling train (probe, cyclone, and filter). The "total particulate" concentration averaged 0.83 grains/DSCF. The outlet samples also agreed fairly well from test to test. All of these tests were run at a sampling rate which was approximately 25% too high; thus biasing the results on the low side. Outlet particulate concentrations averaged 0.053 and 0.099 grains/DSCF respectively for the front portion (probe and filter) and total train fractions. The impinger contents averaged 46.5% of the total particulate collected.

Excessively high moisture content of the stack gas confirms the observed presence of entrained water droplets.

The spray chamber removed an average of 90% of the particulate as determined by the front portion of the sampling train.

Sulfur Dioxide Evaluation - Table 11 presents the SO_2 data obtained at the spray chamber inlet and outlet. Inlet concentrations averaged 1610 ppm and the outlet averaged 235 ppm yielding a scrubber efficiency of approximately 85%. This efficiency was, however, very variable.

Presented in Table 11 also are the fluoride results from the CO line tests. Due to the high carbon monoxide content of this line, and the potential presence of trace amounts of phosphorus, a severe explosion hazard existed when the sampling port was opened. For this reason, only one test was run at this location. A very low fluoride concentration of 0.00063 grains/DSCF was found.

Air Return Line

Table 12 summarizes the data obtained on the air return line. These samples were taken by sampling at a constant rate with a straight probe since little, if any, visible particulate matter was present in this gas stream.

The concentrations of soluble fluorides in the air return line range from 0.115 to 0.214 grains/DSCF. Soluble phosphorus pentoxide concentrations range from 0.00323 to 0.00384 grains/DSCF.

Scrubber Water Samples

Presented in Table 13 are the analytical results of the scrubber water samples, collected during the fluoride and P_2O_5 sampling at the nodulizing kiln spray chamber. The lower pH of the scrubber water intake during Run 3 (5.7

compared to 8.5 and 8.7 for Runs 1 and 2) did not result in any significant change in scrubber efficiency for fluorides and P_2O_5.

Three separate samples were taken during each test period at approximately one-hour intervals.

III. PROCESS DESCRIPTION AND OPERATION

Elemental phosphorus is produced from phosphate rock by reduction in an electric arc-furnace. Typical ores contain 10-13% phosphorus so that about 10 tons of rock must be processed per ton of phosphorus produced. Considerable quantities of coke, silica, and recycled materials are fed to the furnace with the beneficiated ore. Table 14 presents a typical analysis for the fluoride content of various materials used in the elemental phosphorus manufacturing process (see Figure 1).

Prior to being fed to the furnace, the ore is agglomerated and heat-hardened in a direct-fired rotary kiln. The partially fused product is cooled and crushed to a specified size before being fed to the electric-arc furnace. Aside from some particulates, the major emissions from this feed preparation step are fluorides.

At Stauffer's Tarpon Springs Plant, the rotary kiln is fired with a combination of CO from the phosphorus furnace and residual fuel oil. The gaseous kiln effluent is passed through low pressure drop cyclones, diluted with quench air, blown through a fan and scrubbed with water in a spray tower. The scrubber water has an inlet design pH of 7 to 7.5 which is maintained by lime addition. Particulate collected in the cyclones is recycled to the kiln feed.

TABLE 14. FLUORIDE CONTENT OF VARIOUS PROCESS STREAMS

PROCESS STREAM	FLUORIDE ANALYSIS mg/gram
Kiln Feed	
Coarse	35 - 45
Fine	32
Kiln Product	31
Furnace Phosphate	
Rock Feed	38
Residual Fuel Oil	0.06
Kiln Nodules	33
Coke	0.14
Silica Sand	0.06
Furnace Slag	28.5
Ferro Phosphorus	0.10
Phosphorus Condenser Water	276 mg/liter pH 1.63

Kiln operation is usually erratic. Not only do mechanical and operating problems affect its performance, but furnace problems are also reflected at the kiln. The kiln uses CO directly from the furnace as a partial fuel source. Because of the erratic furnace operation, the kiln did not operate smoothly during testing. However, this is representative of "usual" operating procedures and production rates were reasonably close to design capacity.

Rock fed to the kiln is of two types. The two materials are weighed (moist) into the kiln. An undetermined, variable amount of undersized product is returned to the kiln from the cyclone collectors.

The furnace feed is carefully proportioned with silica and coke before being transferred to feed bins directly above the furnace. The feed mixture then moves by gravity from the bins down into the furnace as the furnace feed is consumed.

The reaction within the furnace is approximated by the following equation:

$$2\ Ca_3\ (PO_4)_2 + 10\ C + 6\ SiO_2 \xrightarrow{(2300-2700°F)} P_4 + 10\ CO + 6\ CaSiO_3$$

Elemental phosphorus and carbon monoxide leave the furnace as a gas. Dust is removed from the stream by an electrostatic precipitator and the phosphorus vapor is condensed out in direct-contact water condensers. Waste CO gas is used as a fuel in the kiln operation or flared. Fuel oil is also used for kiln fuel when the furnace is down, or insufficient CO is available.

The non-gaseous by-products of slag and ferrophos (FeP_4) are periodically tapped from the furnace into open-pits and quenched with water. Ferrophos is tapped into molds.

Furnace tapping operations are a source of particulate emissions in the form of P_2O_5, coke smoke, and fluorides. Hooding over the front of the furnace and over the slag runner is satisfactory. However, the hood over the metal catch pot is unsatisfactory since it is too small and poorly placed. There is no hood over the ferrophos molds. Vent gases from the hood system pass through a water saturator and then through a venturi scrubber.

Make-up water for the scrubber is fed into the circulating pump discharge. Total instrumentation on this system is a pressure gauge on the water line to the venturi. The lack of instrumentation combined with the make-up water feed method makes estimates of the total water circulation rate difficult.

IV. LOCATION OF SAMPLING POINTS

Slag Tapping

Figures 2, 3, and 4 show the slag tapping scrubber inlet and outlet sampling sites. As shown, 16 points were used at the horizontal inlet duct (8 along each diameter), and 36 points (18 along each diameter) at the outlet site. Both ducts were circular.

Nodulizing Kiln

Figures 5, 6, and 7 show the sampling port locations on the kiln spray chamber inlet and outlet respectively for the Tarpon Springs Plant. The inlet site was located in a vertical round section leading down to the induced-draft fan. Twelve points were sampled along each diameter. The outlet sites were in the top of the spray chamber, approximately 78 feet above the inlet line. The two outlet sites were identical except that site CK was 5.7' downstream from site BK. Sixty sampling points were to be used at each outlet site. However, due to probe length limitations caused by the narrow platform, Point 15 in each port was not sampled.

Particulate was sampled only at the lower (BK) site at the spray chamber outlet, and since a rigid probe was used, only a single point approximately 6' into the chamber was sampled at each of the four ports.

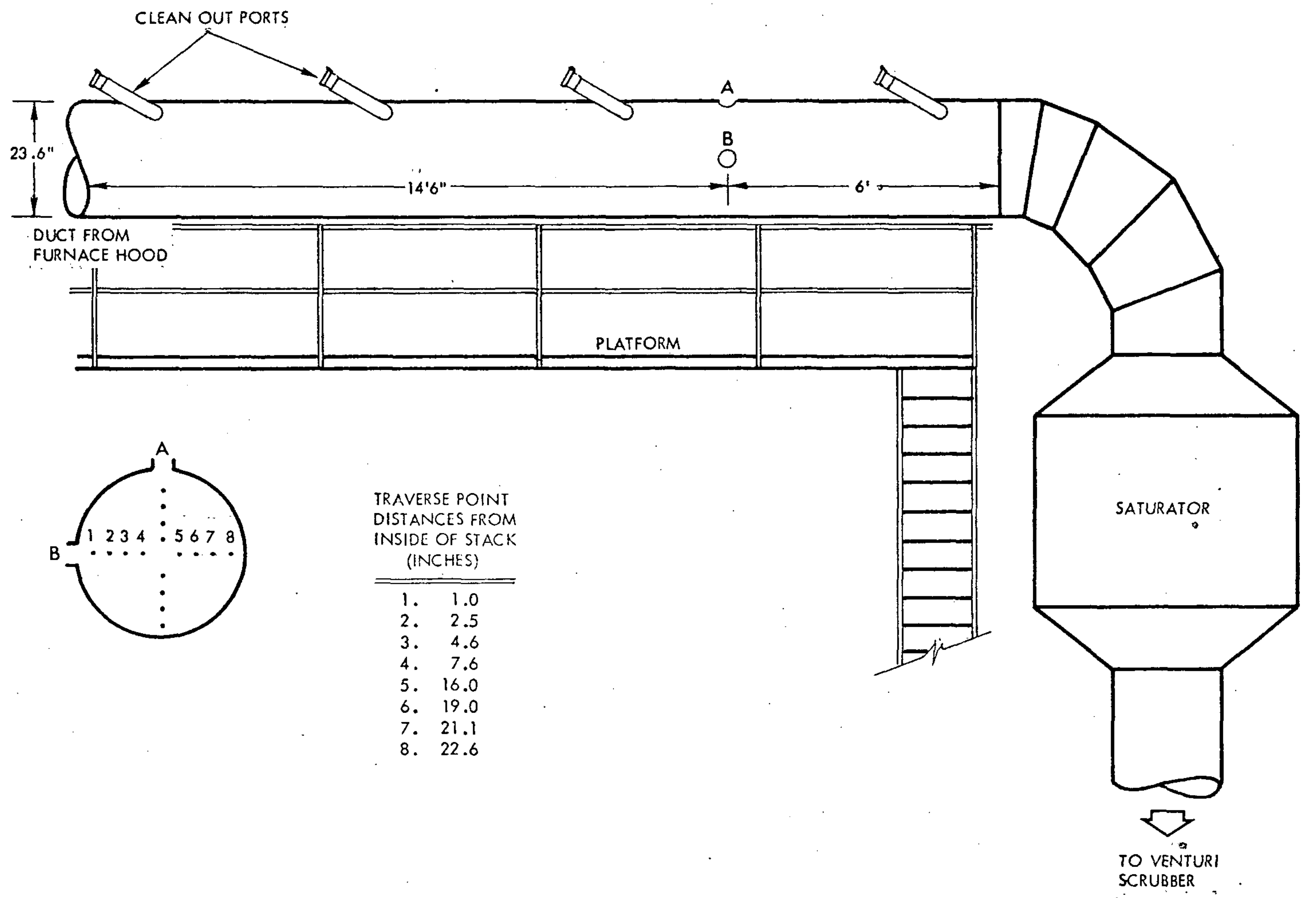
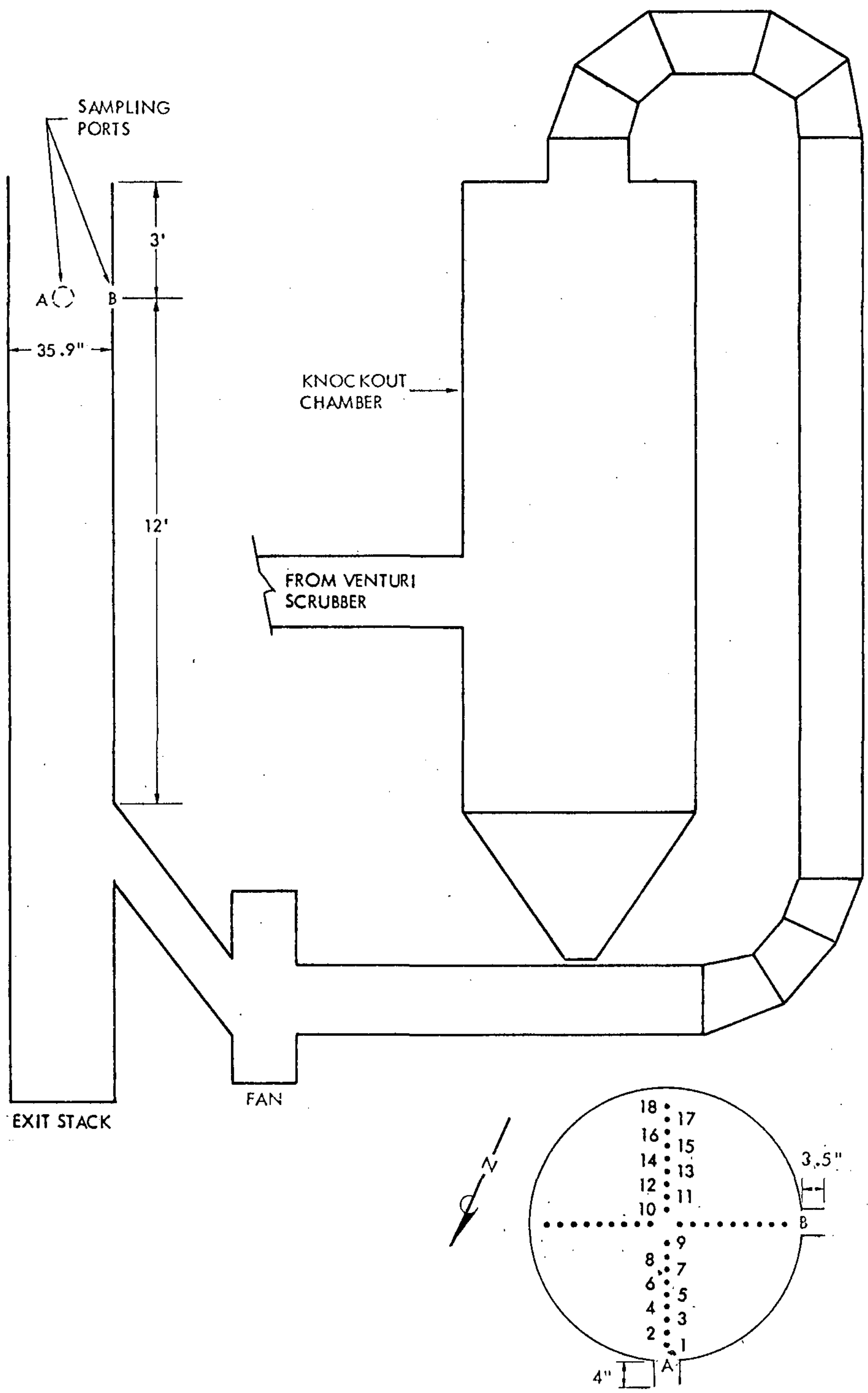


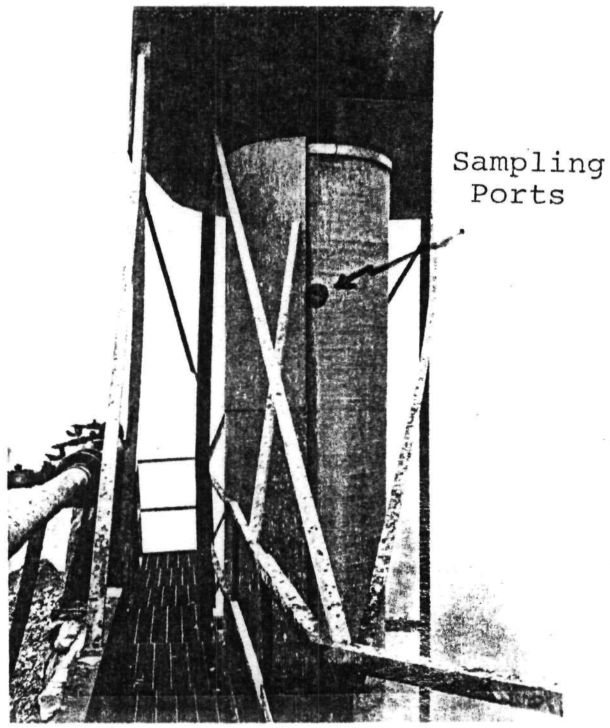
Figure 2. Slag tap scrubber inlet sampling site.



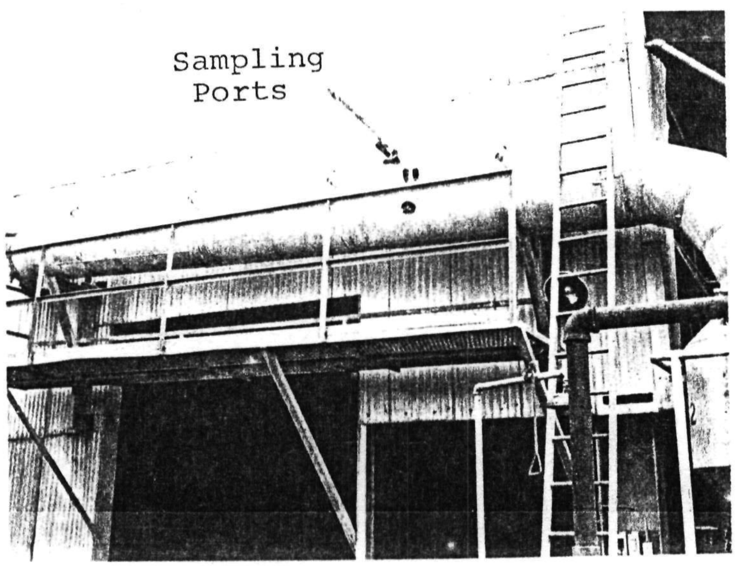
TRAVERSE POINT DISTANCE FROM INSIDE OF STACK (INCHES)

1.	1.0
2.	1.6
3.	2.7
4.	3.9
5.	5.2
6.	6.7
7.	8.4
8.	10.6
9.	13.7
10.	22.1
11.	25.2
12.	27.3
13.	29.1
14.	30.5
15.	31.9
16.	32.1
17.	34.3
18.	34.9

Figure 3. Slag tap scrubber outlet sampling site Stauffer Chemical Co., Tarpon Springs, Florida.

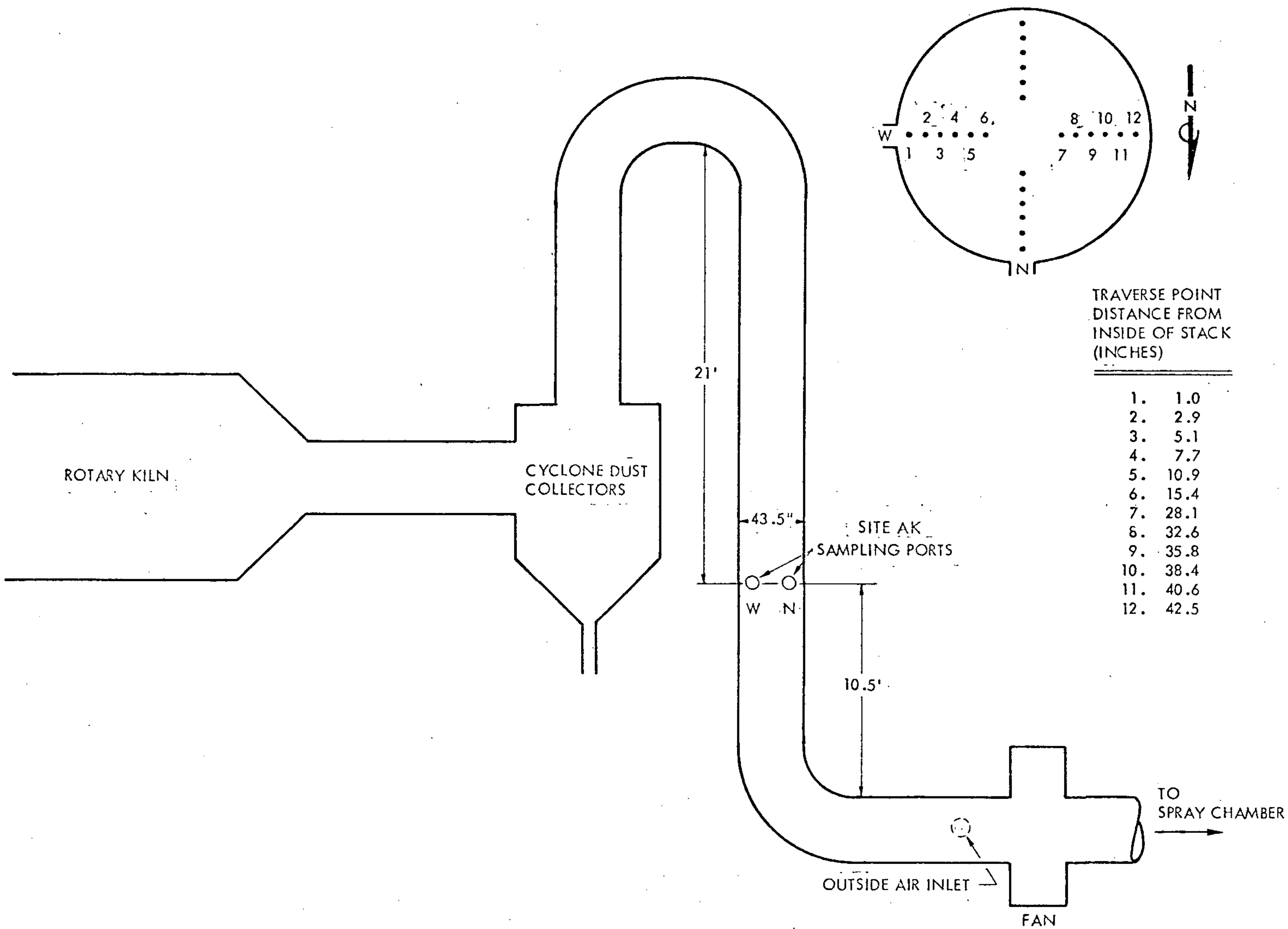


Outlet duct leading from venturi scrubber. Sampling ports were later installed 3' from top.



Inlet duct leading from hood inside building to saturator

Figure 4. Slag tapping sampling sites.



TRAVERSE POINT	DISTANCE FROM INSIDE OF STACK (INCHES)
1.	1.0
2.	2.9
3.	5.1
4.	7.7
5.	10.9
6.	15.4
7.	28.1
8.	32.6
9.	35.8
10.	38.4
11.	40.6
12.	42.5

Figure 5. Kiln scrubber inlet sampling site
Stauffer Chemical Co., Tarpon Springs, Florida.

TRAVERSE POINT	DISTANCE FROM INSIDE OF STACK (INCHES)
1.	2.1
2.	6.9
3.	11.7
4.	16.4
5.	21.7
6.	26.1
7.	32.9
8.	38.7
9.	45.2
10.	52.2
11.	59.9
12.	68.4
13.	78.4
14.	90.1
15.	108.5

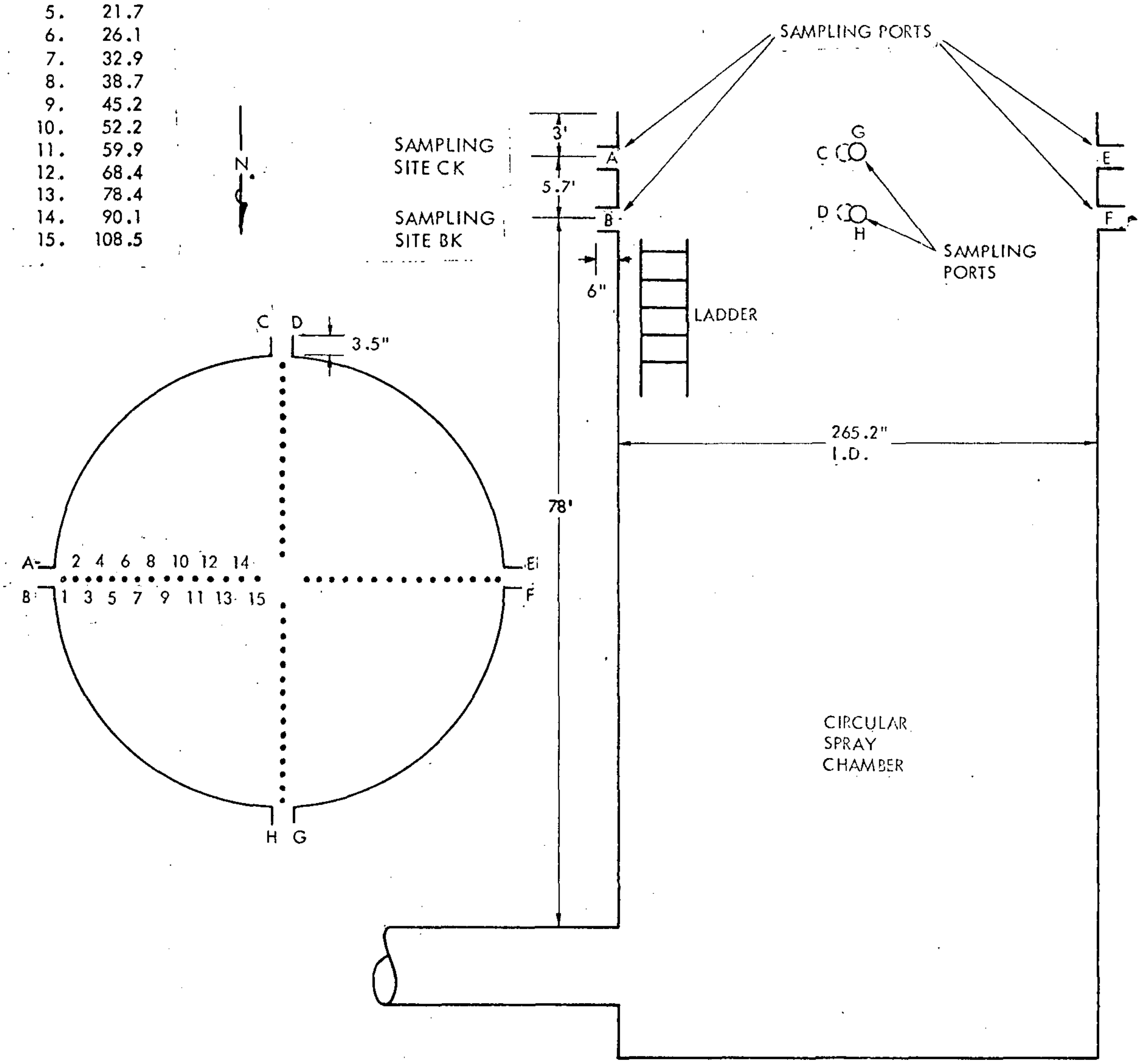
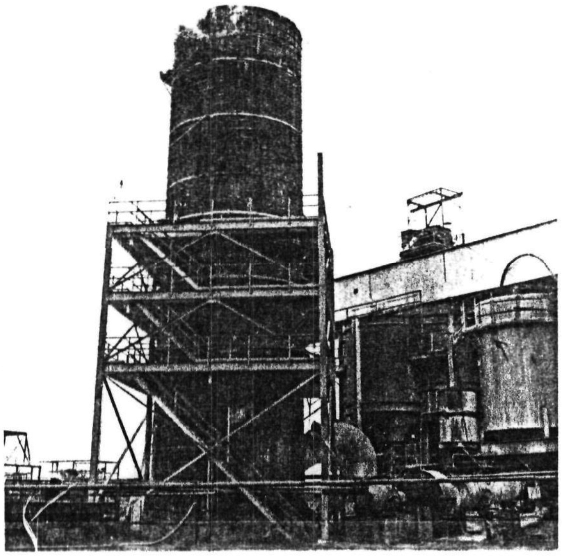
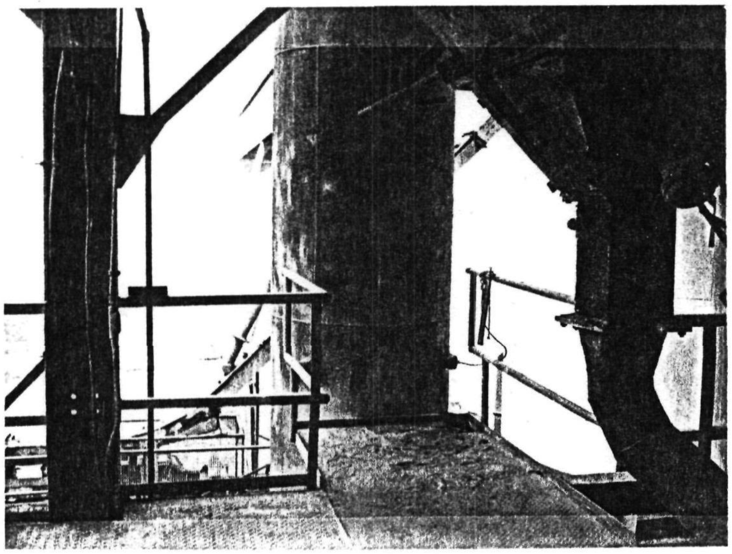


Figure 6. Kiln scrubber outlet sampling site Stauffer Chemical Co., Tarpon Springs, Florida.



Spray chamber. Outlet sampling ports were later located 3' and 8.7' from top of chamber



Inlet site showing existing ports near floor. Cyclone hoppers seen in right foreground

Figure 7. Spray chamber inlet and outlet sampling sites.

Gas samples taken for Orsat analyses were collected by traversing across the spray chamber inlet and outlet ducts. Sulfur dioxide samples were taken at a single point in the spray chamber outlet, and at two locations (one in each port) at the inlet.

V. SAMPLING AND ANALYTICAL PROCEDURES

All sampling procedures were selected by EPA prior to field sampling. All analyses of collected samples were also performed by EPA. Details of the sampling procedures are presented in Appendix D. At all sampling sites, narrow work space and poor accessibility hindered completion of the work. In addition, interruptions due to process malfunctions and thunderstorms further delayed the test program.

Velocity and Gas Temperature

All gas velocities were measured with a type S pitot tube and inclined draft gage. In all cases, velocities were measured at each sampling point across the stack diameter to determine an average value according to procedures described in the Federal Register[1] - Method 1. Temperatures were measured by long stem dial thermometers, except at the spray chamber outlet sites where a chromel-alumel thermocouple was used because of the large diameter.

Molecular Weight

An integrated sample of the stack gases was collected during each run by pumping gas into a Mylar[R] bag at the rate of approximately 0.5 liter per minute. This bag sample was then analyzed with an Orsat apparatus for CO_2, O_2 and CO.

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[1] Federal Register, Vol. 36, No. 247, December 23, 1971

Fluorides and P_2O_5

The basic train for all total fluorides and phosphorus pentoxide samples is shown in Figure 8 and consisted of three standard Greenburg-Smith impingers containing 100 ml each of 10% sodium hydroxide, one empty, straight tip impinger, a 3" or 4" unheated Whatman #1 paper filter, and an impinger containing approximately 200 grams of accurately weighed silica gel. The impingers were contained in an ice-water bath. A stainless steel nozzle and glass lined probe were used in all cases. A flexible Teflon® line, approximately 7' long, connected the probe to the first impinger when sampling at the slag tap inlet and outlet sites, and when sampling for fluorides and P_2O_5 at the kiln spray chamber outlet. A flexible connector was used since traversing with a rigid train was not possible at these sites.

In most cases sampling was conducted under isokinetic conditions either by calculating an average velocity and sampling rate,[a] or by monitoring the velocity with a pitot tube and adjusting the sampling rate accordingly.

Train clean-up consisted of measuring the volume increase of the impinger contents and silica gel weight gain, a triple water rinse of all components from nozzle tip to filter holder, and triple acetone rinse of all components. The impinger

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a) This was required at the kiln outlet where the sampling velocity was too low to measure.

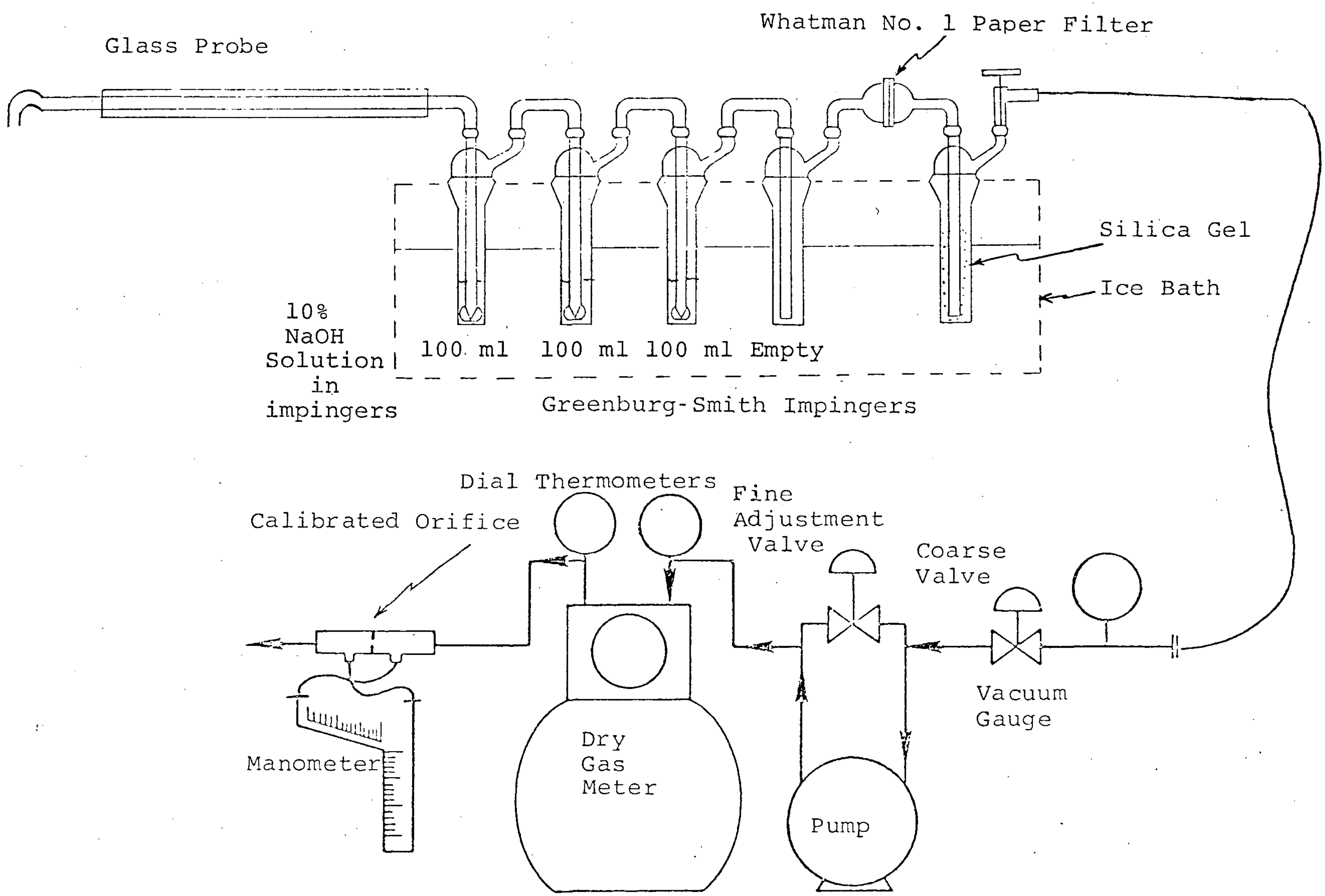

Figure 8. Fluoride and P_2O_5 sampling train.

contents, filter, and water rinse were combined in one glass sample jar and the acetone rinse was placed in a separate jar.

Particulates

Method 5 as described in the Federal Register, December 23, 1971, was used to measure particulate matter. This sampling train is shown in Figure 9. At the kiln inlet, a cyclone was used just before the filter and the duct was traversed for only six of the 12 points along each diameter. At the outlet site, one point was sampled in each of the four ports at the 'B' test site. This sampling point was about 6' inside the stack wall.

The train clean-up procedure included measuring the water collected and weighing the silica gel to determine moisture content. The probe, cyclone, and front half of the filter holder were then rinsed with acetone and placed in a container. The rear half of the train consisting of the rear half of the filter holder, impingers, and connectors was rinsed with water and the water then added to the impinger contents. The rear half of the train was then rinsed with acetone and the washings placed in a third sample jar. The filter was placed in a separate container.

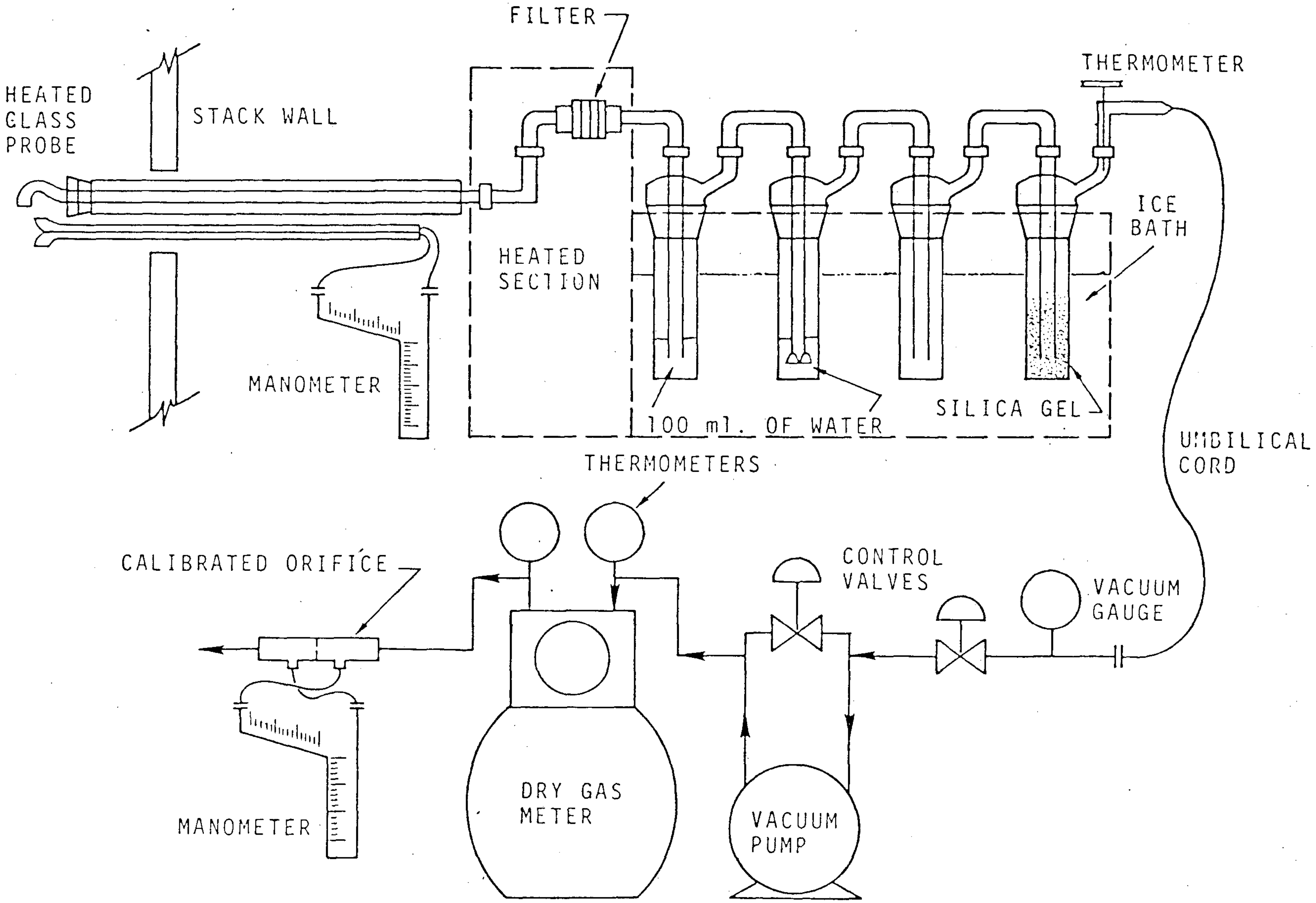

Figure 9. Particulate sampling train.

Sulfur Dioxide

EPA Method 6 in the Federal Register, December 23, 1971, was used to measure SO_2. The sampling train is shown in Figure 10 and consisted of a heated glass probe, a midget bubbler (fritted glass tip) containing 15 ml of 80% isopropyl alcohol, glass wool, two midget impingers containing 15 ml each of 3% H_2O_2, and a fourth dry impinger. The probe washings and the bubbler contents were discarded after each run. The midget impinger contents were placed in a glass sample container. These impingers were then rinsed with distilled water and the washings placed into this same container.

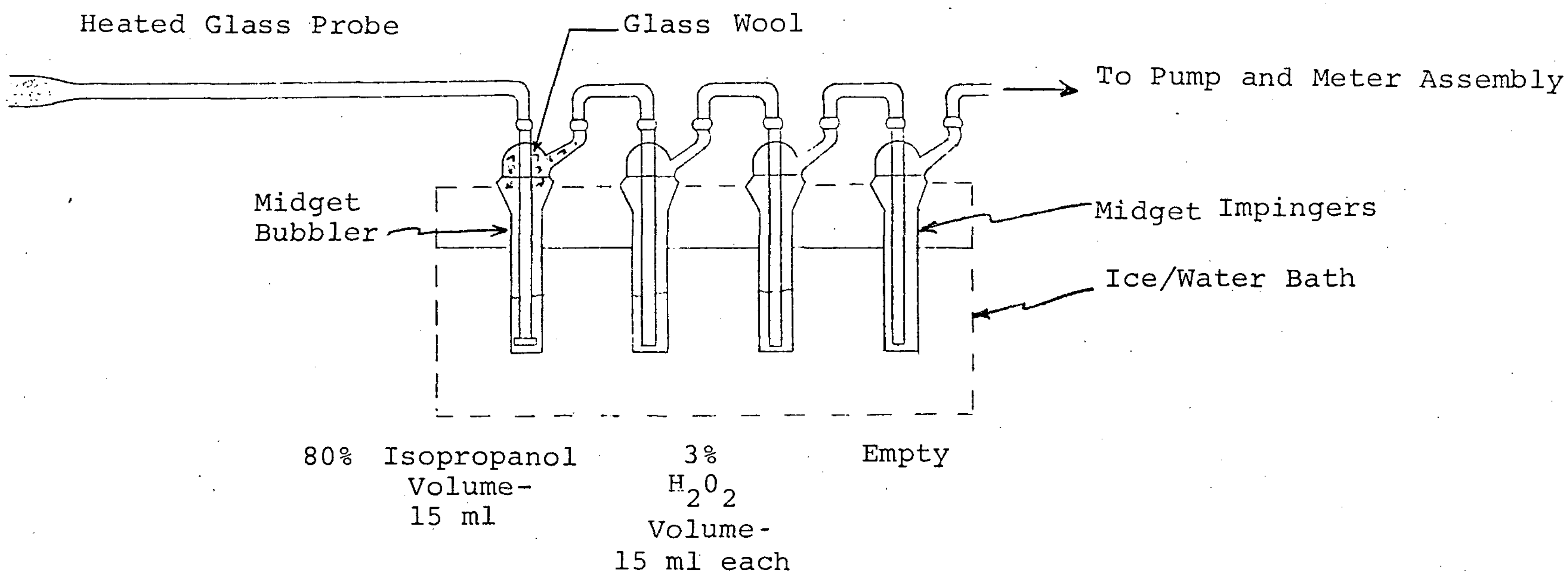

Figure 10. Sulfur dioxide sampling train.