

REPORT ON AIR POLLUTION MEASUREMENTS

11

FROM

ROCKY MOUNTAIN FERTILIZERS, INC.

CASPER, MONTANA

AUGUST 18-22, 1964

By

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**In cooperation with the
Montana State Board of Health**

**U.S. Public Health Service
Division of Air Pollution
Technical Assistance Branch**

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SUMMARY

Rocky Mountain Phosphates, Inc. operates a plant at Garrison, Montana, which produces defluorinated phosphate rock for use in animal feed supplement. Stack emissions from this plant have resulted in numerous complaints from local residents. To assess these complaints, the Montana State Board of Health requested the U.S. Public Health Service's assistance in conducting stack sampling at the plant. Sampling was conducted in August 1964. The scrubber stack on the superphosphate mixing den and the kiln stack of the superphosphate-defluorinating kiln were sampled for fluorides and sulfur oxides. The Scrubber stack was found to contain 12,000 to 19,000 ppm fluorides. The kiln stack gases contained 1,500 to 2,200 ppm fluorides; 2,200 to 4,200 ppm sulfur dioxide; and 125 to 600 ppm sulfur trioxide.

INTRODUCTION

In July of 1963, discussions began between staff members of the Division of Air Pollution, U.S. Public Health Service, and representatives of the Montana State Board of Health concerning the operation of a phosphate defluorination plant at Garrison, Montana. This plant, owned by Rocky Mountain Phosphates, Inc., began operation in Garrison in July-August 1963. Shortly thereafter, the Montana State Board of Health received numerous complaints about the operation of this plant.

At the request of the Montana State Board of Health, the United States Public Health Service agreed to assist in performing analyses of the stack effluents from the plant. The agreement is outlined in a letter dated November 27, 1963 by D. F. Walters, Public Health Service, to Dr. John S. Anderson, Executive Officer of the Montana State Board of Health. Briefly, the agreement was as follows:

1. The U.S. Public Health Service will provide the equipment suitable for obtaining the necessary stack samples and will loan this equipment to the Montana State Board of Health.
2. The Montana State Board of Health will make an arrangement for entering the plant and for providing the necessary test holes and scaffolding.
3. The Technical Assistance Branch of the Division of Air Pollution, U.S. Public Health Service, will supply two men to assist in conducting the stack tests.

4. The necessary laboratory analyses of the samples will be done by the Montana State Board of Health.

Following court proceedings in June and July 1964, a formal request was received by the Public Health Service to initiate the stack test work as outlined above. This request was contained in a letter dated July 15, 1964, from Dr. John S. Anderson.

The stack test team consisting of Richard W. Gerstle, Roger Shigehara, John S. Henderson, and Don R. Goodwin (all of the United States Public Health Service) arrived in Helena, Montana, on August 17, 1964. Stack sampling at Rocky Mountain Phosphates, Inc. began on August 18, 1964.

Mr. Ben Wake, Industrial Hygiene Engineer, Montana State Board of Health, assisted in the stack testing. All analyses of samples were performed at the Montana State Board of Health laboratory by Mr. Ludwig Champa, Chief Chemist.

THE PRODUCTION OF DEFLUORINATED PHOSPHATE ROCK

GENERAL COMMENTS

Rocky Mountain Phosphates, Inc. is engaged in defluorinating Montana phosphate rock to make it suitable for use in animal feed supplement. As a fertilizer, it is not essential that fluorine be completely eliminated; however, for use as a mineral supplement in livestock and poultry feeds, fluorine must be almost completely eliminated. Montana phosphate rock as used in this plant contains on the order of 3.5 percent to 4.2 percent fluorine. The plant specification on the fluorine content of defluorinated rock product is 0.18 percent fluoride.

Several methods are available for the reduction of fluoride content of phosphate rock. Rocky Mountain Phosphates liberates part of the fluoride by mixing phosphate rock, sulfuric acid, water, and phosphoric acid to form triple superphosphate. This mix, after aging a minimum of 24 hours, is calcined in a rotary kiln at temperatures up to $2,400^{\circ}\text{F}$; this substantially volatilizes all the fluorine. Sulfate compounds formed in the superphosphate reaction also decompose in the kiln, evolving considerable quantities of sulfur oxides (sulfur dioxide and sulfur trioxide).

The flow diagram and plant layout are shown on sketch 1 and sketch 2, respectively.

SUPERPHOSPHATE PRODUCTION

The raw phosphate rock is mined within 30 miles of the plant. After being reduced in size, (65 percent through 200 mesh) it is delivered to the plant in trucks. Three vertical silos are used to store the raw rock. Screw conveyors remove the ground rock from the storage silos and discharge it to a belt feeder. The belt feeder discharges into a small feed hopper above the mixing den.

Sulfuric acid and phosphoric acid are received in railroad tank cars and are stored in horizontal storage tanks. The sulfuric acid is normally about 96 percent sulfuric acid made from smelter off-gas in Anaconda, Montana. The 52 percent phosphoric acid is purchased from J. R. Simplot of Pocatello, Idaho. In the formation of the superphosphate, the sulfuric acid, phosphoric acid, water, and phosphate rock are mixed in a TVA mixing cone. The cone is 2 ft in diameter by 20 inches high with a 4 inch outlet in the bottom. The acids are metered into the cone

through rotameters. Flow is initiated by air pressure on the acid storage tanks. Phosphate rock is fed at a rate of 16 tons/hr by a screw conveyor. The resulting slurry falls into the 20 ft x 40 ft x 20 ft high concrete structure called a den. The reaction continues in the den for 6 to 12 hours. After this time, the material is removed by a rubber-tired, front-bucket truck loader and is transferred by a belt conveyor to the storage shed. If the superphosphate is not removed within 12 hours, it "sets up" and becomes very difficult to remove.

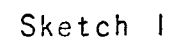
Vent gases (containing fluorides) are removed from the den by a blower and are passed through a vertical open-tower water scrubber to the atmosphere. The scrubber is a 10 ft diameter tower about 17 ft high with a 5-1/2 ft diameter by 15 ft high stack. Water is pumped from a small pond (80 ft x 50 ft x 3 ft deep) to the scrubber sprays. The water returns to the pond by gravity. Occasionally, lime is added to the pond to neutralize the pond water. In the top of the scrubber, above the sprays, a steel grating supports a 4 to 6 inch layer of stone and lime. Fluorides are removed from the vent gases by reacting them with this lime.

DEFLUORINATION OF SUPERPHOSPHATE

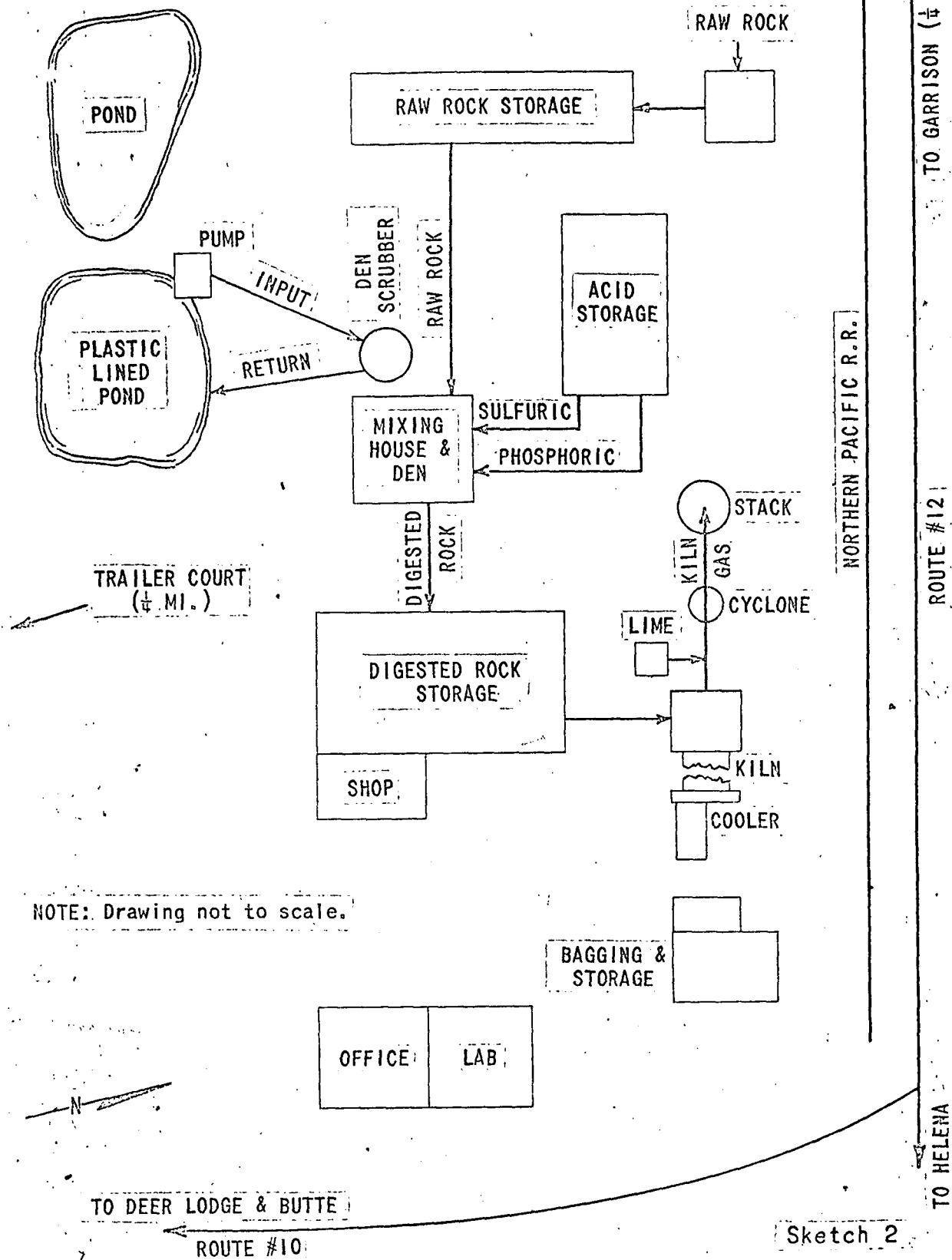
The superphosphate is allowed to age a minimum of 24 hours before being introduced into the rotary kiln. Depending on the age of the superphosphate produced, the fluorine content will average between 1.5 to 2 percent fluoride. The feed to the kiln is on a semicontinuous basis. Actually, charging is accomplished by a front-bucket truck loader at the rate of one load every 15 minutes. Each load weighs about 1 ton, and the plant assumes, therefore, a feed rate of 4 tons/hr. The crude

superphosphate is elevated by a bucket elevator to a breaker in which large lumps are reduced in size and are metered onto a kiln feed belt by a Syntron feeder. The feed rate to the belt is uniform but not continuous. Quite often, the feed hopper is empty before the 15 minute charge period has elapsed. The kiln is fired with natural gas and has a maximum temperature of $2,400^{\circ}$ to $2,500^{\circ}$ F. The retention time of material in the kiln is about 4 hours. Stack gases from the kiln are discharged into an 8 ft diameter x 210 ft high stack. Air is used to cool the deflucrimated product as it passes to storage. The product is sold in bulk or bags. Vertical steel silos are provided for bulk storage, and bagging machines are provided for bagged product.

9/21/64



ROCKY MOUNTAIN PHOSPHATES, INC.
GARRISON, MONT.
PLANT LAYOUT



CONTROL DEVICES

SUPERPHOSPHATE PRODUCTION

In the defluorination of phosphate rock as conducted by Rocky Mountain Phosphates, Inc., superphosphate production is the initial step. Sulfuric acid, phosphoric acid, water, and phosphate rock are mixed and aged. Normally in superphosphate production, 15 to 40 percent of the input fluorine is emitted from the mixer and den. The fluorine is usually in the form of silicon tetrafluoride (SiF_4). Other constituents of the effluent stream would be carbon dioxide, steam, and some sulfur dioxide.

A commonly used abatement device to remove the fluorine from the mixing den effluent gas is a high intensity scrubber using copious quantities of water or fluosilicic acid up to about 20 percent by weight. Rocky Mountain Phosphates utilizes an open-tower scrubber as a control device. The scrubber is a 10 ft diameter vertical tower divided into four quadrant-type passes by baffles made of 2-inch lumber. It is an open tower without packing or grids. Gas flow is arranged so that flow is cocurrent in two passes and countercurrent in the other two passes. Approximately 32 spray nozzles are provided, 8 in each pass. Visual observations made during the stack sampling showed some deficiencies in design and operation of the scrubber:

1. All vertical baffles have about 6 inches of clearance between the bottom of the baffle and the base of the scrubber. The liquid outlet from the scrubber is a 6-inch pipe installed flush with the bottom of the scrubber.

Since no weir or any other method of sealing the bottom of

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THE LIME BED IN TOP OF SCRUBBER (P-4)

the wooden baffles is provided, gas stream bypassing will occur; thus, the full effect of a four-pass scrubber would not be obtained. The velocity traverse of the scrubber stack indicated that bypassing was occurring.

2. Physical inspection of one pass of the scrubber showed three of the eight nozzles to be completely covered with a crystalline deposit, indicating that these spray nozzles were not functioning.

3. Total water flow rate to the scrubber was approximately 50 gpm.

DEFLUORINATION OF SUPERPHOSPHATE

Superphosphate feed to the defluorinating kiln usually averaged 1.5 to 2 percent fluorine. Practically all of this fluorine, down to at least 0.18 percent, must be removed before the product is suitable for animal feed supplement. This is accomplished by subjecting the superphosphate to temperatures up to about 2,400° F. There is also an apparent decomposition of calcium sulfate, resulting in the formation of sulfur oxides.

The method of emission control applied by Rocky Mountain Phosphates is lime injection into the exhaust gas stream from the kiln. Subsequently, the exhaust gas stream is passed through a cyclone separator. The theory is that the lime will react with the pollutants and form solid particulate compounds, which can be removed in the cyclone-type separators. Variations of this technique are used in similar situations. Some deficiencies were noted in this system:

1. Considerable amounts of the lime dust settle out in the duct between the kiln and the cyclone separator. Doors have been provided, and the ducts are cleaned at regular intervals. This would indicate poor contact between the lime and the pollutant compounds and, therefore, incomplete reaction.
2. Samples of the solids collected in the cyclone were analyzed and found to contain less than 1 percent fluoride. This would indicate poor contact and reaction between lime and fluorine.
3. The cyclone provided at the plant is 10 ft in diameter by 10 ft straight side with a 15 ft high conical bottom. Inlet velocity to the cyclone averages between 25 to 40 ft/sec. Inlet velocities should normally be at least 50 ft/sec.
4. The bottom outlet of the cyclone was only partially sealed. The actual opening was donut-shaped and was 18 inches in diameter by about 2 inches across. Periodically, dust fell to the ground from this opening, but, most of the time, air was drawn into the cyclone by the stack draft. Air entering the cyclone through this opening interfered with the dust collecting efficiency of the cyclone operation.

SAMPLING PROGRAM

Every effort was made to conduct sampling when the plant was operating continuously and at a uniform feed rate. This, it developed, was practically impossible. The feed rate is based upon batch addition of superphosphate to the kiln. This is accomplished by using a rubber-tired tractor with a front-end loader. The plant management assumes this vehicle, when loaded normally, to hold 2,000 lbs. One load from this truck is placed into the kiln feed hopper every 15 minutes, resulting in a feed rate of about 4 tons/hr. In actual practice, the capacity of this loader can vary greatly. During the sampling, a typical truckload of kiln feed was weighed and found to contain only 1,250 pounds. Later during the week, two other truckloads of feed were weighed. These two loads weighed 1,750 pounds and 2,440 pounds, respectively. From the kiln feed hopper, the superphosphate passed through a bucket elevator, breaker, hopper, Syntron feeder to a belt feeder. The capacity of this equipment was greater than that provided by the normal four loads per hour. The result was that material was not fed to the kiln continuously. Usually, 10-12 minutes would be required to feed one truckload through this equipment. Until the next load was placed in the feed hopper, no material was added to the kiln.

Feed rate to the kiln was also affected by frequent equipment failures. During the week of sampling, there were usually several breakdowns per day. On most occasions, repairs were instituted quickly so that the feed could be started in about an hour. If repairs were not too difficult, the kiln continued to operate. During these mechanical

failures, sampling was continued. For major repairs requiring over 1 hour to complete, it was usual practice to stop the kiln and reduce the fuel feed rate to the kiln. At these times, sampling was delayed until operating conditions returned to normal.

It was also normal plant practice to cease operating the kiln if the meteorological conditions were such that the kiln stack plume was blowing toward a nearby trailer court or toward Garrison. For the first 3 days of the stack sampling, the weather was cool, and the wind was strong from the northwest. During this time, no shutdowns were made because of meteorological conditions; however, on the last 2 days of the test, three shutdowns were made because of pollution in Garrison or the trailer court. The frequency of these shutdowns is shown on table 5. During the first 23 days of August, the plant stopped kiln feed 26 times because of pollution being transported to one of these inhabited areas.

Another factor which made uniform sampling difficult was the age of the kiln feed. Digested material from the mixing den is aged a minimum of 24 hours before being fed to the kiln. Fresh material will normally contain higher percentages of fluorine. Efforts were made during the sampling to feed the kiln with freshly digested material. This was not always possible since there was also a supply of 60-day-old material in the storage building.

Lime is normally added to the kiln stack gases. This lime is thought to react with fluorine compounds to form particulate calcium fluoride, which can be removed from the stack gas and thereby reduce fluoride emissions. The plant log indicates that the rate of lime

addition varies considerably, and, during the week of the sampling, it was higher than for any week of the month of August. These data are tabulated in table 5.

Initial sampling was conducted on the rotary kiln stack gases. A sampling hole was provided 11 ft above the stack inlet at an elevation of between 30 and 35 ft above the base of the stack. During the initial test, lime was added continuously to the stack gases leaving the kiln; this is normal operating procedure. The sampling was conducted on August 18, 19, and 20. Velocity traverses were made on the 18th and 20th. Three samples were collected for fluoride and three, for sulfur oxides. The samples were collected in the sequence: fluoride, sulfur oxides, fluoride, sulfur oxides, etc. This resulted in a set (fluoride and sulfur oxide) of samples being taken on each of three successive days.

On August 20, an attempt was made to obtain a particulate sample from the kiln stack. After 10 minutes of sampling, the flow through the sample train had practically ceased. This was thought to be due to coating of the sample train filter by the white, pasty material encountered in this stack. Additional heat was applied to the filter, and all sampling was stopped. After about 15 minutes, sampling was resumed, but again the sample flow rate was extremely low. Sampling was stopped, and the equipment was dismantled. Examination revealed the filter had been coated with a white, pasty precipitate. Apparently, this material is formed in the upper regions of the stack and falls into the base of the stack. Doors had been provided in the bottom of the stack to remove this material periodically. At the time of the test, this sludge was 2 ft deep in the

bottom of the stack. Because of this condition, particulate sampling was considered to be impossible and was discontinued.

Following the stack test with the plant operating normally an attempt was made to determine the effectiveness of lime addition by sampling without lime addition. Four samples were taken under these conditions--two samples of fluoride and two samples of sulfur oxides. All of these samples were taken on the afternoon of August 21.

On August 22, the plant operated the superphosphate producing facilities. The capacity of these facilities is considerably greater than the defluorination kiln capacity so that they are only operated every other day for a period of 6 hours. Feed conditions during the mixing are uniform. The rock is fed at a uniform rate by a screw feeder while sulfuric acid, phosphoric acid, and water feed rates are metered by indicating flow meters and are controlled by hand valves.

Gases evolved from the superphosphate den are exhausted by a blower and discharged into an open-tower liquid scrubber. The sample connection was located in the upper part of the scrubber above the sprays.

The major pollutants from the den are fluorine compounds. After the mixing den had been operating about one-half hour, a sample was collected for fluoride analysis. Following this, a sample was collected and analyzed for sulfur dioxide and sulfur trioxide. Significant emissions of sulfur oxides were not encountered. Following the sulfur oxide sample, two samples were taken for fluoride analysis.

One velocity traverse was made on the scrubber stack.

RESULTS

VELOCITY TRAVERSE

Data on the velocity traverses are given in table 1. Three velocity traverses were made on the kila stack; the first two were made when the plant was operating normally with lime addition. These data were collected on August 18 and August 20. The results were 24,800 acfm and 25,600 acfm. During the check of the effectiveness of lime addition, the velocity traverse gave a stack velocity of only 14,400 acfm. The reasons for this lower value are not clear. Some reduction in gas flow is due to the fact that the lime-addition blower was not operating. It is doubtful if this can explain completely the lower stack velocity. It is more likely that the reduction is caused by variation in plant operating conditions: i.e., fuel gas rate to kila.

FLUORIDE EMISSIONS

All fluorine emission data throughout this report includes both particulate and gaseous fluorine emissions, which are expressed as fluoride ion (F^-). The results of the fluorine sampling are given on table 2. Highest concentrations were found in the effluent gas from the superphosphate den. Three samples were analyzed. The first, after only one-half hour of operation, indicated a fluoride stack gas concentration of 12,000 ppm. The second and third samples were taken after 2-1/2 and 6 hours of operation. By this time, the concentration of fluoride in the scrubber stack had reached 18,430 ppm and 19,320 ppm, respectively.

Because of the physical arrangement of the piping, it was impossible to sample upstream of the scrubber and thereby check the efficiency of the fluoride removal in the scrubber. For this reason, a fluoride balance was made around the superphosphate den.

Fluoride in feed material:

$$1. \text{ Rock: } 16 \text{ tons/hr} \times 2,000 \text{ lb/ton} \times 4.2\% \text{ fluoride} = 1,340 \text{ lb/hr}$$

$$2. \text{ Phosphoric acid:}$$

$$4 \text{ tons/hr} \times 2,000 \text{ lb/ton} \times 1\% \text{ fluoride} = \underline{80 \text{ lb/hr}}$$

$$\text{Total input fluoride } 1,420 \text{ lb/hr}$$

Fluoride in den product:

$$30 \text{ tons/hr} \times 2,000 \text{ lb/ton} \times 1.9\% \text{ fluoride} = 1,140 \text{ lb fluoride/hr}$$

Calculated fluoride evolved in the den would be:

$$1,420 \text{ lb/hr} - 1,140 \text{ lb/hr} = 280 \text{ lb/hr}$$

The stack analysis (table 2) shows that the average emission rate of fluoride was 284 lb/hr. This rate indicates little, if any, fluoride is removed in the scrubber. The fluoride balance is only an approximation, but it does indicate relatively low efficiency for the den scrubber.

Table 2 indicates fluoride concentrations in the kiln stack gases; however, it must be remembered that the kiln stack emissions are on a 24-hr/day basis while the superphosphate den emissions are for only the limited time which the den operates--usually 6 hr/batch. When operating with lime addition in what is considered normal operation, the kiln stack samples analysed 2,070; 1,500; and 2,200 ppm fluoride. The average of the three samples resulted in an emission of 142 lb/hr fluoride. An

*

approximate efficiency check on the lime addition and cyclone as a control device was made using a material balance.

Fluoride in kiln feed:

$$3.6 \text{ tons/hr (raw rock)} \times 2,000 \text{ lb/ton} \times 1.9\% \text{ fluoride} = 137 \text{ lb/hr}$$

Fluoride in kiln product:

$$1.8 \text{ tons/hr (product)} \times 2,000 \text{ lb/ton} \times 0.18\% \text{ fluoride} = 6 \text{ lb/hr}$$

Fluoride in exhaust gases: $137 \text{ lb/hr} - 6 \text{ lb/hr} = 131 \text{ lb/hr}$ from kiln to control device.

Since the three stack samples averaged $1\frac{1}{2}$ lb/hr fluoride emitted, little advantage can be credited to the control device. Analysis of the particulate collected in the cyclone was about 1 percent fluoride. Both the Montana State Board of Health laboratory and Rocky Mountain Phosphates, Inc. laboratory agree on this concentration. This low concentration of fluoride in the cyclone product would indicate low fluoride collection efficiency.

Data available from a similar plant in Florida shows the efficiency of their control device to be slightly over 90 percent.

SULFUR OXIDE EMISSIONS

Sulfur dioxide and sulfur trioxide emissions are given in table 3 and table 4, respectively. Significant emissions of sulfur oxides were not expected in the den scrubber. This assumption was substantiated by one sample, and no additional samples were taken.

When operating normally, with lime addition, the kiln stack samples analyzed 4,200; 2,285; and 2,480 ppm sulfur dioxide. The average of the three samples gives an approximate emission of 741 lbs/hr

sulfur dioxide. Two samples were analyzed without lime addition. These analyzed 6,070 and 2,600 ppm or an average of 608 lb/hr sulfur dioxide.

With lime addition, the three sulfur trioxide samples analyzed 125, 4473, and 596 ppm or approximately 123 lb/hr. With lime injection into the stack gases, the results were 667 and 1,020 ppm sulfur trioxide. This would be about 148 lb/hr of sulfur trioxide. Apparently, the lime does remove some of the sulfur oxides.

Table 1. STACK FLOW CONDITIONS
 ROCKY MOUNTAIN PHOSPHATES, INC. GARRISON, MONTANA

Date	Location	Plant operating condition	Volume at stack condi- tions, cfm	Velocity ft/sec	Stack temperature	Volume, cfm at std conditions 70°F, 29.92" Hg
8-18-64	Kiln stack	Normal	46,600	15.5	385° F	24,800
8-20-64	Kiln stack	Normal	50,500	16.7	418° F	25,600
8-21-64	Kiln stack	Without line	29,900	9.9	440° F	14,900
8-22-64	Scrubber stack	Normal	7,600	-	112° F	5,950

**Table 2. FLUORIDE EMISSIONS
ROCKY MOUNTAIN PHOSPHATES, INC.
GARRISON, MONTANA**

Sample No.	Date	Sampling location	Operating conditions	Emission concentration,*			Emission, lb/hr
				ppm	lb/scf	mg/m ³	
19-1	8-19-64	Kiln stack	Normal	2,070	0.102×10^{-3}	1,630	153
20-3	8-20-64	Kiln stack	Normal	1,500	0.074×10^{-3}	1,180	110
21-1	8-21-64	Kiln stack	Normal	2,200	0.108×10^{-3}	1,730	162
21-4	8-21-64	Kiln stack	Without lime addition	3,150	0.155×10^{-3}	2,480	132
21-6	8-21-64	Kiln stack	Without lime addition	2,620	0.123×10^{-3}	2,050	111
22-1	8-22-64	Scrubber stack	Normal	12,000	0.589×10^{-3}	9,430	206
22-4	8-22-64	Scrubber stack	Normal	18,430	0.905×10^{-3}	14,500	317
22-6	8-22-64	Scrubber stack	Normal	19,320	0.945×10^{-3}	15,100	330

* Ten percent moisture assumed in kiln stack gases. Normal variations in moisture content will not have an appreciable effect on magnitude of the emissions.

Scrubber stack gases are assumed to contain 5 percent moisture (saturated conditions at 110° F stack temperature).

All concentrations are on a wet basis and at standard conditions of 70° F and 29.92 inches of mercury.

Table 3. SULFUR DIOXIDE EMISSIONS
ROCKY MOUNTAIN PHOSPHATES, INC. - GARRISON, MONTANA

Sample No.	Date	Sampling location	Operating conditions	Emission concentration, *		Emission, lb/hr
				ppm	lb/scf	
19-2	8-19-64	Kiln stack	Normal	4,200	0.695×10^{-3}	1,041
20-6	8-20-64	Kiln stack	Normal	2,285	0.378×10^{-3}	566
21-2	8-21-64	Kiln stack	Normal	2,480	0.410×10^{-3}	615
21-5	8-21-64	Kiln stack	Without lime addition	6,070	1.004×10^{-3}	852
21-8	8-21-64	Kiln stack	Without lime addition	2,600	0.430×10^{-3}	365
22-2	8-22-64	Scrubber stack	Normal	380	0.063×10^{-3}	22

* Ten percent moisture assumed in kiln stack gases. Normal variations in moisture content will not have an appreciable effect on magnitude of the emissions.

Scrubber stack gases are assumed to contain 5 percent moisture (saturated conditions at 110° F stack temperature).

All concentrations are on a wet basis and at standard conditions of 70° F and 29.92 inches of mercury.

**Table 4. SULFUR TRIOXIDE EMISSIONS
ROCKY MOUNTAIN PHOSPHATES, INC. - GARRISON, MONTANA**

Sample No.	Date	Sampling location	Operating conditions	Emission *		Emission, lb/hr
				concentration, ppm	lb/sec	
19-3	8-19-64	Kiln stack	Normal	125	0.026×10^{-3}	39
20-7	8-20-64	Kiln stack	Normal	473	0.098×10^{-3}	147
21-3	8-21-64	Kiln stack	Normal	596	0.123×10^{-3}	184
21-6	8-21-64	Kiln stack	Without lime addition	667	0.138×10^{-3}	117
21-9	8-21-64	Kiln stack	Without lime addition	1,020	0.211×10^{-3}	179
22-3	8-22-64	Scrubber stack	Normal	129	0.027×10^{-3}	10

* Ten percent moisture assumed in kiln stack gases. Normal variations in moisture content will not have an appreciable effect on magnitude of the emissions.

Scrubber stack gases are assumed to contain 5 percent moisture (saturated conditions at 110° F stack temperature).

All concentrations are on a wet basis and at standard conditions of 70° F and 29.92 inches of mercury.

Table 5.
 OPERATING LOG FROM PLANT LOG
 ROCKY MOUNTAIN PHOSPHATES, INC. - GARRISON, MONTANA

AUGUST 1964

Date	Approximate hrs operated	No. of 50 lb bags of lime added to kiln stack gas	No. of times plant shut down because of pollutants blowing in Trailer court	Garrison
8-1	17.5	20	1	1
8-2	12.0	16	2	-
8-3	16.5	27	1	-
8-4	6.0	15	1	1
8-5	-	-	-	-
8-6	2.0	-	-	-
8-7	22.0	30	1	-
8-8	18.0	10	1	-
8-9	21.5	10	-	-
8-10	6.5	5	-	-
8-11	17.5	15	-	-
8-12	15.0	20	1	1
8-13	19.0	20	2	-
8-14	8.0	12	-	1
8-15	19.0	20	2	1
8-16	17.0	22	1	1
8-17	14.0	22	-	1
8-18	21.0	37	-	-
8-19	17.0	33	-	-
8-20	22.0	61	-	-
8-21	20.5	13	-	1
8-22	14.0	32	1	1
8-23	18.5	48	1	2

Average

15.7 hr/day

Grand total

26

Table 6. MISCELLANEOUS SAMPLES
 ROCKY MOUNTAIN PHOSPHATE, INC. - GARRISON, MONTANA

Sample number	Type of sample	Results of analysis
20-1	Kiln stack sludge	0.175% fluoride
20-2	Superphosphate (5-day-old)	1.5 % fluoride
20-3	Superphosphate (2-day-old)	1.96 % fluoride
20-4	Particulate collected in cyclone	0.95 % fluoride
20-8	Kiln stack particulate	0.042% fluoride
20-10	Superphosphate (60-day-old)	1.65 % fluoride
22-7	Raw phosphate rock	4.2 % fluoride
22-8	Phosphoric acid	0.95 % fluoride
22-8	Phosphoric acid	41 % P_2O_5
24-1	Den scrubber sludge	9.97 % fluoride

DETERMINATION OF SULFUR DIOXIDE AND SULFUR TRIOXIDE

SCOPE

When sampling stack gases for various concentrations of sulfur dioxide and sulfur trioxide, this method is used.

APPARATUS

Sampling Probe

Glass tubing (preferably Vycor or quartz, Pyrex) of suitable size with a ball joint at one end and a removable filter at the other. (One-half inch OD x 6 ft. long Pyrex tubing has been used.)

Filter

A Buchner filtering funnel with a coarse fritted glass to support a removable filter is required to remove any particulate or acid mist. Kaolin wool (resin-free), fritted quartz, or glass wool (Pyrex brand No. 3950) are suitable filters.

Adapter

Six plug-type connecting tubes, 24/40, one with a 90° bend with a socket joint.

Heating Tape

A heavy insulated heating tape with a variable voltage supply is needed to prevent condensation in exposed portions of the probe and adapter. Alternatively, glass wool or other suitable insulators may be used if temperature extremes are not too great.

Calibrated Tanks

Two evacuated tanks are required to provide an accurate sample volume measurement. One cubic foot tanks have been used satisfactorily.

Vacuum Source

A good vacuum source is needed to evacuate the calibrated tanks.
An absolute pressure of about 5 inches of mercury should be achieved.

Thermometer

Manometer

A 36 inch mercury manometer

Lamp Sulfur Absorber

Three ASTM D1266 lamp sulfur absorbers with coarse sintered plates

Filter Tube

Filter tube with a 40-mm diameter Corning medium sintered plate

Teflon Tubing

Teflon tubing, one-quarter inch ID, for connecting scrubbers
Alternatively, 8 mm Pyrex tubing with ball and socket connections may be used.

Ice-Water Bath

Burette

50-ml and 10-ml burettes

REAGENTS

Deionized Water

Deionized water should be used instead of distilled water.

Isopropyl Alcohol

80 Percent Isopropyl Alcohol

Dilute isopropyl alcohol with H_2O at a 4:1 ratio.

30 Percent Hydrogen Peroxide (Reagent Grade)

3 Percent Hydrogen Peroxide

Dilute 30 percent H_2O_2 with H_2O at a 1:10 ratio. Prepare fresh daily.

Barium Chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, Reagent Grade)

0.0100 N Barium Chloride

Dissolve 1.2216 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in ml H_2O and dilute to 1 liter with isopropyl alcohol.

Thorin Indicator O-(20hydroxy-3, 6-disulfo-1-naphthylazo)

Benzenearsonic acid disodium salt

0.2 Percent Thorin Indicator

Dissolve 0.2 gm Thorin indicator in 100 ml H_2O .

SAMPLING PROCEDURE

Set up the apparatus as shown in figure 1. Add 30 ml 80 percent isopropyl alcohol in the first scrubber and 10 ml in the filter tube. Add 50 ml 3 percent H_2O_2 to the third scrubber. A little silicone grease on the upper parts of the joints may be used to prevent leakage. Heat the probe so that no condensation occurs while sampling. Sample at a rate of about 2 cu ft per 30 minutes while sampling. Record the tank vacuum and temperature initially and at 10 minute intervals. Note the barometric pressure.

SAMPLE PREPARATION

Disconnect the probe, heating tape, and adapter and allow to cool. Connect the spare absorber and add 50 ml 3 percent H_2O_2 to act as an air filter. Replace the water in the ice-water bath with tap water. Draw

Draw air through the system for 15 minutes and remove the spare absorber.

Disconnect the third scrubber and transfer its contents and its water washings to a 250-ml volumetric flask. Dilute with water to the mark. Analyze this for SO_2 .

Stopper the first scrubber and apply suction to the filter end. Remove the suction line and allow the partial vacuum in the first scrubber to draw the solution from the filter. Rinse the filter tube with 80 percent isopropyl alcohol before the suction is lost. Transfer the contents of the first scrubber and its washings to a 250-ml volumetric flask and dilute to mark with 80 percent isopropyl alcohol. Analyze this for SO_3 .

ANALYTICAL PROCEDURE

Sulfur Trioxide

Pipet a suitable aliquot to a flask and dilute to 100 ml with 80 percent isopropyl alcohol. Add a few drops of Thorin indicator (enough to give a yellow color). Titrate with 0.01 N BaCl_2 to the pink end point. Make a blank determination in parallel.

Sulfur Dioxide

Transfer a suitable aliquot to a flask and add 4 times this volume of isopropyl alcohol. Dilute to 100 ml with 80 percent isopropyl alcohol, add enough Thorin indicator to give a yellow color, and titrate with standard 0.01 N BaCl_2 to the pink end point. Run a blank determination in parallel.

CALCULATIONS

$$\text{ppm SO}_2 \text{ or SO}_3 \text{ by volume} = \frac{6.8 \times 10^2 (A-B)(N)(F)}{V_t \frac{P_f}{T_1} - \frac{P_1}{T_1}}$$

(dry basis)

where

A = ml 0.01 N BaCl₂ used for titration of sample

B = ml 0.01 N BaCl₂ used for titration of blank

N = exact normality of BaCl₂

F = dilution factor

T_f = final tank temperature, °R

T_i = initial tank temperature, °R

V_t = volume of tank, liters

P_f = final absolute tank pressure, in Hg

$$(P_f = (P_b - \text{final vacuum}))$$

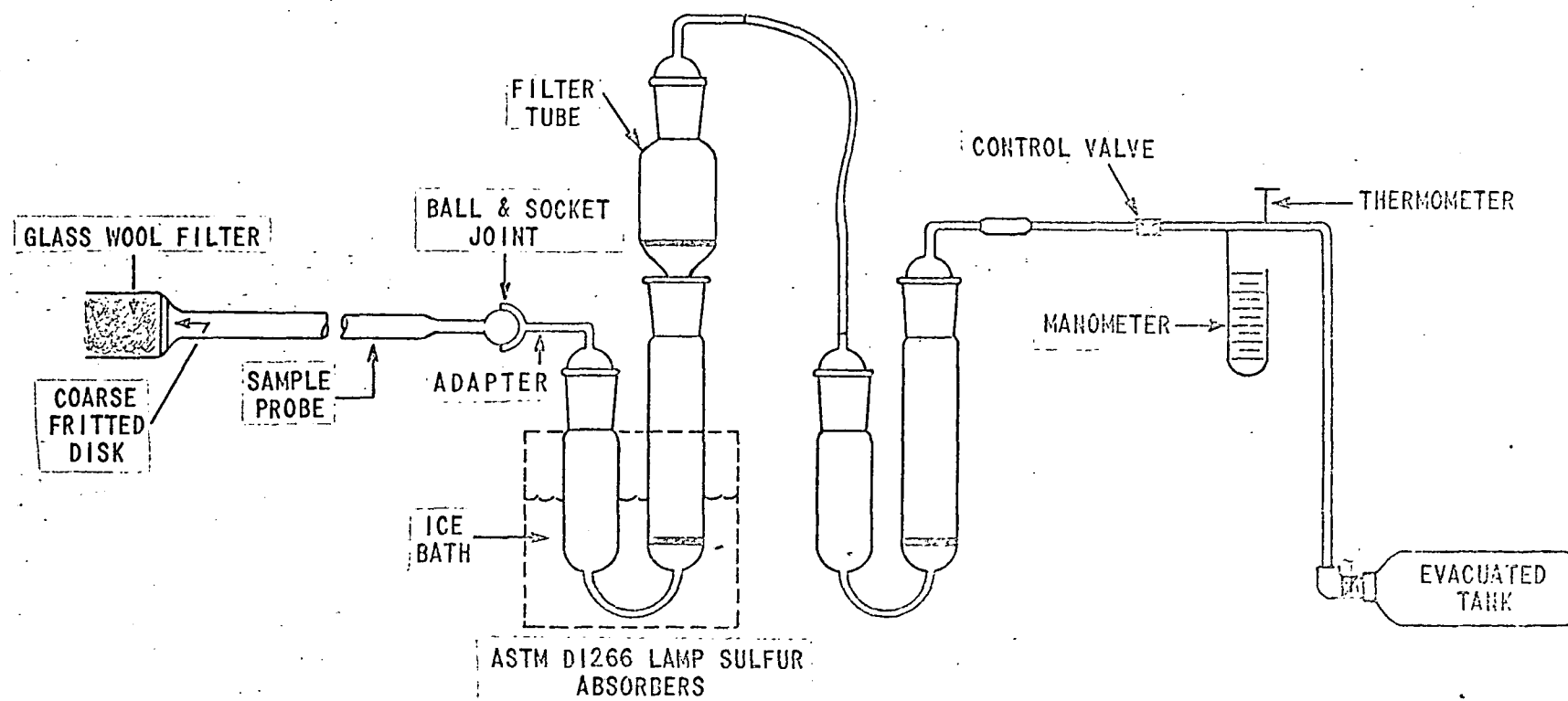
P_i = initial absolute tank pressure, in Hg

$$(P_i = (P_v - \text{initial vacuum}))$$

REFERENCES

Shell Development Company Analytical Department, "Determination of Sulfur Dioxide and Sulfur Trioxide in Stack Gases," Emeryville Method Series 4616/59a.

Figure 1. SAMPLING TRAIN FOR SULFUR OXIDES.



DETERMINATION OF SOLUBLE FLUORIDES
SPADNE-ZIRCONIUM LAKE METHOD

SCOPE

This method is used for the determination of soluble fluorides in stack gases. Accuracy within 0.02 mg/liter in the concentration range of 0.00 to 1.40 mg/liter is obtainable. The interferences from stack gases necessitate distillation of the samples.

APPARATUS

Sampling Probe: Glass tubing of suitable size (12 inch by 6 feet long Pyrex brand tubing has been used).

Impingers: Four standard Greenburg-Smith impingers.

Ice Bath: Ice bath with a suitable rack for holding impingers.

Dry Gas Meter: One cubic foot/revolution meter.

Manometer: A 36 inch Hg manometer.

Vacuum Pump: Pump with control valve.

Thermometers: 0-200° C and 0-180° F range.

Boiling Flask: One-liter, round bottom, long neck, Pyrex boiling flask with joint number 24/40.

Connecting Tube

Graham Condenser

Adapter

Receiver

Burner

Glass Beads: Two to three dozen

Spectrophotometer: Beckman model B.

REAGENTS

Sodium Hydroxide

1 N (Approximate) Sodium Hydroxide: Dissolve 40 gm NaOH pellets in H_2O and dilute to 1 liter.

Concentrated Sulfuric Acid.

Silver Sulfate

Spadns: 4,5-dihydroxy-3 (p-sulphophenylazo)- 2, 7-naphthalenedisulfonic acid trisodium salt.

Spadns Solution: Dissolve 0.959 gm Spadns in H_2O and dilute to 500 ml.

Zirconyl Chloride Octahydrate

Concentrated Hydrochloric Acid

Zirconyl Chloride Octahydrate Solution: Dissolve 0.133 gm $ZrOCl_2 \cdot 8 H_2O$ in 25 ml H_2O . Add 350 ml concentrated HCL and dilute to 500 ml with H_2O .

Reference Solution: Dilute 7 ml concentrated HCL to 10 ml with H_2O . Add 10 ml Spadns solution to 100 ml H_2O and add the HCL solution. Mix well. This solution is used to set the zero point and is stable indefinitely.

Mixed Reagent: Mix well equal parts of the Spadns solution and $ZrOCl_2 \cdot 8 H_2O$ solution. This reagent is stable for at least 3 months.

Sodium Fluoride (Reagent Grade).

Fluoride Standard: Dissolve 3.0947 gm dry NaF and dilute to 1 liter.

Dilute 1 ml of this solution to 1 liter. This final solution contains 1.4 $\mu g/ml$.

Pipet 0.0, 10.0, 20.0, 30.0, 40.0, and 50.0 ml standard NaF solution into separate 100-ml beakers. Add 50.0, 40.0, 30.0, 20.0, 10.0, and 0.0 ml H_2O , respectively, to the beakers. Then add 10 ml of mixed

reagent to each beaker. Mix thoroughly and read the absorbance at 570 m μ . Plot concentration vs absorbance on a rectangular graph paper.

At least one point should be run with each sample and each time that a new batch of mixed reagent is made. It is important that standards and samples be at the same temperature as each degree difference causes about 0.01 mg/liter error.

SAMPLING PROCEDURE

Set up the apparatus as shown in figure 1. Add 100 ml 0.1 N NaOH to each of the first two impingers, leave the third dry to catch any carry-over. Silica gel may be placed in the fourth impinger to absorb any additional moisture (this helps to protect the meter and pump). Put some ice in the bath. Draw the sample through the train at 1 cfm for 30 minutes or as suitable. Record water temperatures and pressures at 10 minute intervals during sampling and obtain an average. Record the barometric pressure.

SAMPLE PREPARATION

Transfer the solution and its H₂O washings from the three impingers to a 500-ml volumetric flask and dilute to the mark. Pipet a suitable volume (25 to 50 ml has been found adequate for 25 cu ft stack samples from power plants) and dilute to 300 ml with H₂O. This is used for the distillation.

DISTILLATION PROCEDURE

Use the method of Willard and Winter as described in "Standard Methods for the Examination of Water and Wastewater," 11th edition,

American Public Health Association, Inc., New York City, 1960, pages 123 to 125.

The fluoride was distilled with steam using sulfuric acid distilling over at 155° C. The distilling flask is known as the Aleco flask, which is used extensively by the aluminum companies for fluorine distillation. This is actually a Claisen flask with the neck to which the delivery tube is attached sealed off with glass.

ANALYTICAL PROCEDURE

Pipet a suitable aliquot and dilute to 50-ml. Add 10 ml of mixed reagent and read the absorbance at 570 mμ. If the absorbance falls beyond the calibration curve range, repeat the procedure using a smaller sample aliquot.

CALCULATIONS

$$\text{ppm fluorides} = \frac{(2.53)(10^{-3})(C)(F_1)(F_2)(T_m)}{(V_m)(P_m)}$$

C = Concentration - μg

F₁ = Distillation dilution factor

F₂ = Sample dilution factor

T_m = Sample temperature

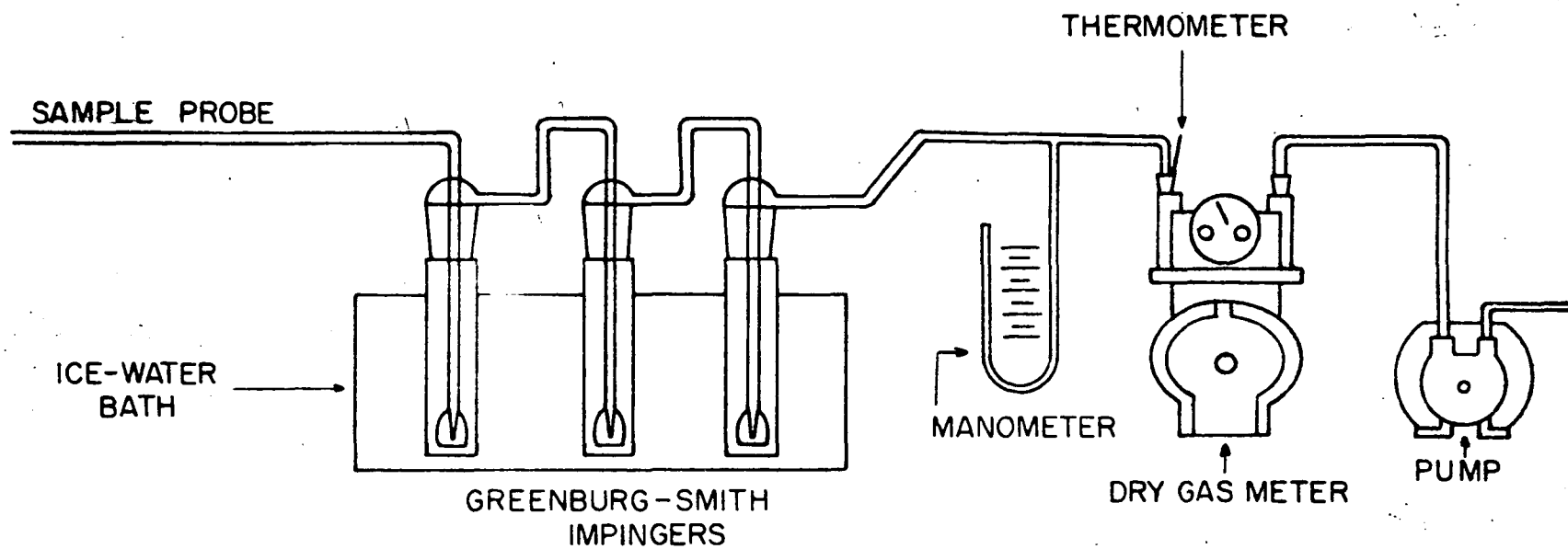
V_m = Volume of sample (at sampling conditions)

P_m = Pressure at sample meter

REFERENCES

Bellack, Ervin and Schoubbe, P. J., "Rapid Photometric Determination of Fluoride in Water." *Analytical Chemistry*, 30, 2032-34 (December, 1958).

Bellack, E., "Simplified Fluoride Distillation Method." *JAWWA* 50, 530-6 (April, 1958).



SAMPLING APPARATUS

FIGURE 1

DIFFUSION ESTIMATES FOR GARRISON, MONTANA

UNSTABLE TO NEUTRAL CONDITIONS

Ground-level concentrations beneath the plume axis were computed for various distances under the assumption that a plume traveling along the valley would spread (diffuse) in a manner subject to usual diffusion calculations for a distance up to 5 km (3.1 miles). These concentrations are tabulated for the kiln and scrubber separately, and a graph is prepared showing a distribution of concentration down wind, assuming the two sources to be immediately adjacent. Maximum values may not appear since computations were for specific distances only. The summed values reflect in nearly every case the contribution from one or the other source, and in no case are they significantly greater than from the greater source alone.

Plume center-line concentrations only were computed for stability class F since under stable conditions the plume may not lower to the valley floor but may impinge on valley sides with maximum concentrations approaching those within the plume itself. These concentrations are also tabulated.

All computations are based on the following emission rates:

Kiln	141 lb F ⁻ /hr	738 lb SO ₂ /hr
Scrubber	286 lb F ⁻ /hr	22 lb SO ₂ /hr

EFFECTIVE STACK HEIGHT

The Holland equation was used to estimate effective stack heights based on the following data:

	Kiln stack	Scrubber stack
Diameter	8' 0"	5' 6"
Height	210'	35'
Stack velocity	900'/min	600'/min
Stack temperature	400° F at 30'	112° F

Air temperature: 60° F, Pressure: 900 mb

Effective stack heights were found to be:

Wind speed	22 1/2 mph	11 mph	7 mph
Kiln stack	233 ft	256 ft	286 ft
Scrubber stack	39 ft	46 ft	49 ft

The Holland equation is considered relatively good for neutral atmospheric stability. Even under unstable conditions it appears that effluents from the scrubber stack will remain within the valley since the stack velocity and temperature are both very low.

GROUND LEVEL CONCENTRATIONS (gm/m³)

Stability class and wind speed		Source	Pollutant	1/16 mi	1/8 mi	1/6 mi	1/3 mi	.6 mi	1.25 mi	3.1 mi	
SUM PM UNSTABLE	A 7 mph	Kiln	F1	1.3×10^{-12}		5×10^{-7}	1.1×10^{-4}	1.4×10^{-5}			
			SO ₂	6.5×10^{-12}		2.6×10^{-6}	5.6×10^{-4}	7.1×10^{-5}			
		Scrubber	F1	4.7×10^{-3}		8.9×10^{-4}	2.8×10^{-4}	2.8×10^{-5}			
			SO ₂	3.9×10^{-4}		7.4×10^{-5}	2.3×10^{-5}	2.3×10^{-6}			
	SUM PM NEUTRAL	B 9 mph	Kiln	F1	2.3×10^{-19}	9.5×10^{-8}		9.5×10^{-5}	5.4×10^{-5}	1.3×10^{-5}	
				SO ₂	1.2×10^{-18}	4.9×10^{-7}		4.9×10^{-4}	2.8×10^{-4}	6.8×10^{-5}	
		Scrubber	F1	3.5×10^{-3}	3.1×10^{-3}		6.4×10^{-4}	1.4×10^{-4}	2.7×10^{-5}		
			SO ₂	2.9×10^{-4}	2.6×10^{-4}		5.3×10^{-5}	1.1×10^{-5}	2.3×10^{-6}		
SUM PM NEUTRAL	D 11 mph	Kiln	F1	9.0×10^{-22}	3.5×10^{-17}		1.8×10^{-6}	4.7×10^{-5}		3.0×10^{-5}	
			SO ₂	4.7×10^{-21}	1.8×10^{-16}		9.5×10^{-6}	2.4×10^{-4}		1.5×10^{-4}	
		Scrubber	F1	7.4×10^{-3}	4.5×10^{-3}		2.4×10^{-3}	9.4×10^{-4}		7.9×10^{-5}	
			SO ₂	6.2×10^{-4}	3.8×10^{-4}		2.0×10^{-4}	7.8×10^{-5}		6.6×10^{-6}	
PLUME CENTER-LINE CONCENTRATIONS (gm/m ³)											
SUM PM UNSTABLE	F 4 mph	Kiln	F1	5.1×10^{-1}	1.2×10^{-1}		2.0×10^{-2}	5.7×10^{-3}		5.1×10^{-4}	
			SO ₂	2.7	6.4×10^{-1}		1.0×10^{-1}	3.0×10^{-2}		2.7×10^{-3}	
		Scrubber	F1	1.0	2.4×10^{-1}		4.0×10^{-2}	1.1×10^{-2}		1.0×10^{-3}	
			SO ₂	8.5×10^{-2}	2.0×10^{-2}		3.3×10^{-3}	9.4×10^{-4}		8.6×10^{-5}	

FUMIGATION CONDITIONS THAT MAY BE EXPECTED:

Clark Fork valley, downstream (to northwest)

Valley volume was estimated by measurements of contour spacing at various points along the valley. The measurements were continued down-valley for a distance of about 4 miles (measured along the valley, not a straight-line distance), to the point where Warm Springs Creek enters Clark Fork. The effective top of the valley was estimated at 4,600 ft msl for these computations, and it is assumed for these purposes that the plumes would remain within this volume.

Assuming a drift of the plumes of 2 mph along the valley and emission rates (total from the two stacks) of 427 lb/hr of fluorine and 760 lb/hr of SO_2 fumigation conditions would produce a concentration within this valley area of $470 \mu\text{gm}/\text{m}^3$ of fluorine and $820 \mu\text{gm}/\text{m}^3$ of SO_2 .

Little Blackfoot valley, upstream (eastward)

A similar estimate of the valley volume was made, but it was limited to a distance of 2 1/2 miles upstream.

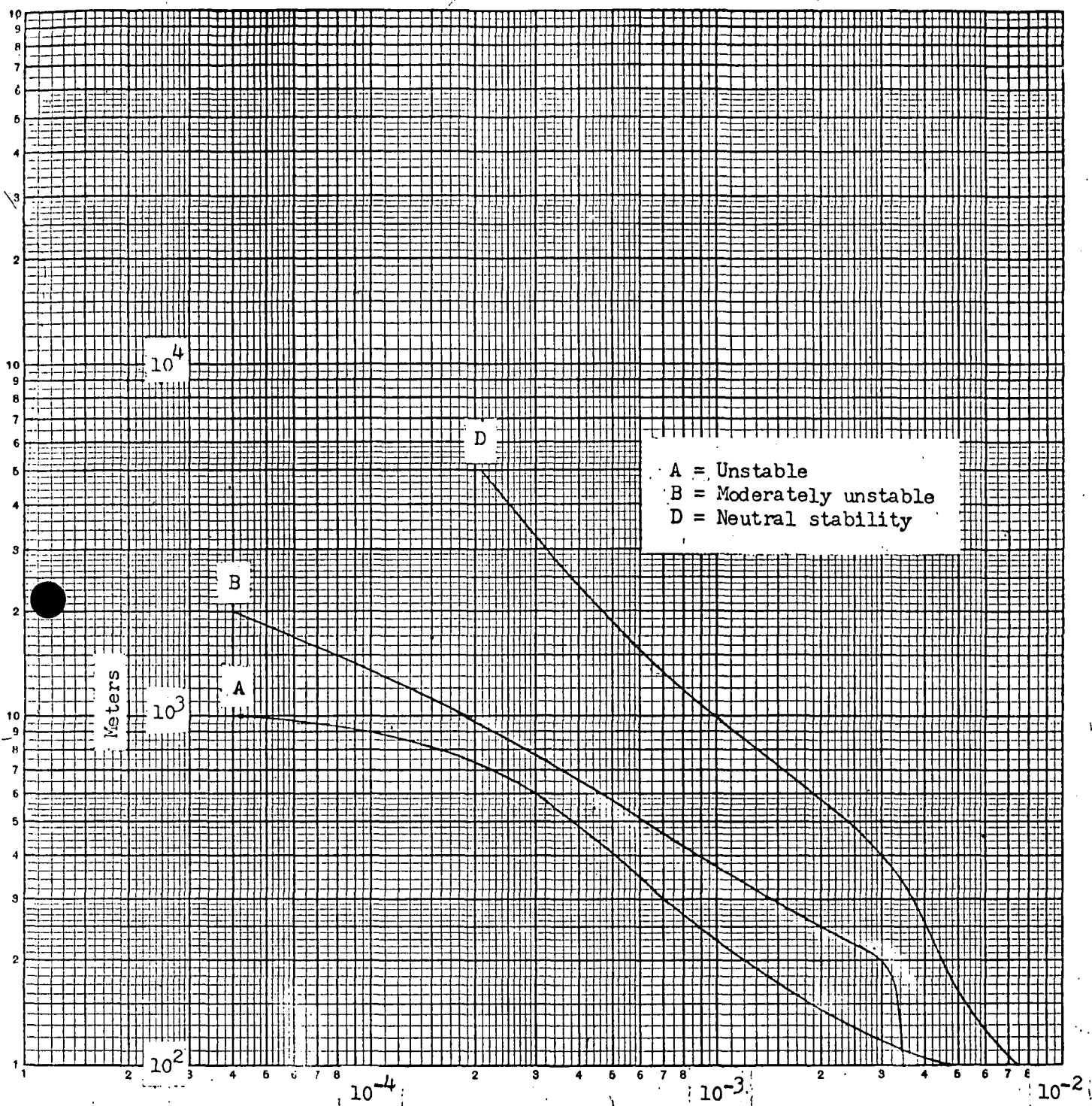
With the same assumptions, a fumigation concentration within this valley of $600 \mu\text{gm}/\text{m}^3$ of fluorine and $1050 \mu\text{gm}/\text{m}^3$ of SO_2 is obtained.

Clark Fork valley, upstream (southeastward)

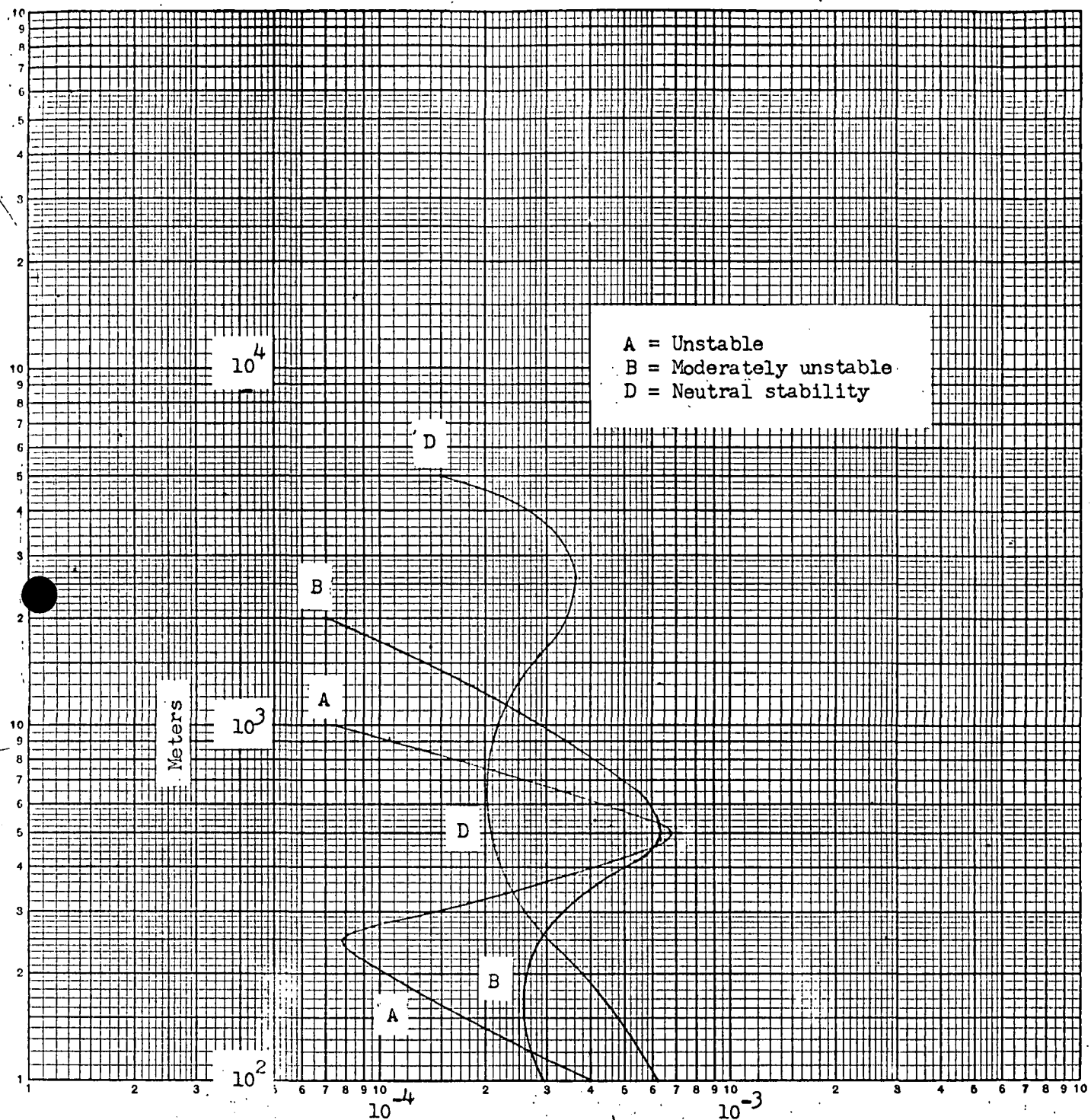
Map data is insufficient to provide a satisfactory estimate of valley volume for a significant distance upstream. However, the cross section of the valley within the first 1/2 mile or so suggests that similar concentrations would be found within this valley also.

The figures given above are rough estimates only and assume a uniform mixing within the entire portion of the valley used in the volume estimate. However, the valleys are of variable cross section and the concentrations under fumigation conditions will vary inversely as the cross section of the valley.

Under inversion conditions accompanied by light winds, it is possible that the plume from the kiln stack will not be trapped in the valley. If this plume escapes, the concentrations estimated for fumigations will be reduced for fluorine by about one-third; and for SO_2 , by over 95 percent. It is likely that this plume will be trapped or partially trapped most of the time, but meteorological data available is not sufficient to estimate the effective inversion heights with confidence.



Ground-Level Concentration of Fluorides
 (Total from both sources) gm/m³



Ground-Level Concentration of Sulfur Dioxide
(Total from both sources) gm/m³

GROUND LEVEL CONCENTRATIONS (ppm)

Stability class and wind speed	Source	Pollutant	300' 1/16 mi	600' 1/8 mi	800' 1/6 mi	1/3 mi	.6 mi	1.25 mi	3.1 mi
SUM PM UNSTABLE A 7 mph	Kiln	Fl	2.87×10^{-9}		7.17×10^{-4}	1.53×10^{-1}	2.01×10^{-2}		
		SO ₂	2.77×10^{-9}		1.10×10^{-3}	2.35×10^{-1}	3.02×10^{-2}		
	Scrubber	Fl	6.75		1.28	4.02×10^{-1}	4.02×10^{-2}		
		SO ₂	1.66×10^{-1}		3.15×10^{-2}	9.83×10^{-3}	9.83×10^{-4}		
SUM B 9 mph INTERMEDIATE	Kiln	Fl	3.30×10^{-16}	1.37×10^{-4}		1.37×10^{-1}	7.75×10^{-2}	1.87×10^{-2}	
		SO ₂	5.11×10^{-16}	2.08×10^{-4}		2.08×10^{-1}	1.19×10^{-1}	2.90×10^{-2}	
	Scrubber	Fl	5.02	4.45		9.13×10^{-1}	2.01×10^{-1}	3.88×10^{-2}	
		SO ₂	1.23×10^{-1}	1.10×10^{-1}		2.26×10^{-2}	4.68×10^{-3}	9.83×10^{-4}	
NEW YORK D 11 mph	Kiln	Fl	1.29×10^{-18}	5.52×10^{-14}		2.58×10^{-3}	6.75×10^{-2}		4.30×10^{-2}
		SO ₂	2.60×10^{-18}	7.66×10^{-14}		4.05×10^{-3}	1.02×10^{-1}		6.38×10^{-2}
	Scrubber	Fl	1.07x10	6.45		3.44	1.35		1.13×10^{-1}
		SO ₂	2.64×10^{-1}	1.62×10^{-1}		3.51×10^{-2}	3.32×10^{-2}		2.80×10^{-3}

PLUME CENTER-LINE CONCENTRATIONS (ppm)

INDICATION VIEW SARATOGA F 4 mph	Kiln	Fl	7.32×10^2	1.72×10^2		2.87×10	8.19		7.31×10^{-1}
		SO ₂	1.14×10^3	2.27×10^2		4.25×10	1.27×10		1.19
	Scrubber	Fl	1.44×10^3	3.44×10^2		5.74×10	1.58×10		1.44
		SO ₂	3.62×10	8.51		1.40	4.00×10^{-1}		3.66×10^{-2}

**SUGGESTED GUIDES FOR EMISSION STANDARDS AND AMBIENT AIR QUALITY CRITERIA
FOR ROCKY MOUNTAIN PHOSPHATES, INC. AND GARRISON, MONTANA**

FLUORIDE EMISSIONS

Fluorides in general and gaseous fluorides in particular are important as air pollutants, first because hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4) are toxic to some plants in concentrations as low as 0.1 part per billion and secondly, because fluorides, both gaseous and particulate, may be accumulated by vegetation. Animals which consume vegetation containing in excess of 30-50 ppm fluoride can develop fluorosis.

There are no regulations applicable specifically to stack emission rates for fluorides in the United States. One such regulation, however, has been proposed for Polk-Hillsborough Counties in Florida. This regulation might not be directly applicable to the plant under study as it could be unnecessarily restrictive. The Florida proposed regulation is designed for use in an area where there is a large number of fluoride emitting plants. The proposal, however, is of interest as a reference point and as an indication of performance which can be achieved. The proposed Florida regulation would limit emissions of fluorides to 0.6 pounds per ton of P_2O_5 produced in the manufacture of phosphoric acid and calcined or defluorinated phosphate rock. In the manufacture of normal phosphate, superphosphate or normal superphosphate, the proposed emission limit for gaseous and/or water soluble fluorides (F^-) is 30 pounds per operating day per plant. Applying these standards to the Rocky Mountain Phosphate plant, gives the following

approximate results:

<u>Operation</u>	<u>Rocky Mountain Plant Average emission at time of stack analyses, pounds (F⁻)/hour</u>	<u>Allowable emissions per Florida proposal, pounds (F⁻)/hour</u>
Mixer and Den	284	1.25*
Kiln	<u>142</u>	<u>0.6</u>
Total	426	1.85

*24-hour/day operation

From the foregoing, it is obvious that a substantial reduction of emissions would be required at the Garrison plant, if the proposed Florida regulations were applied.

In view of the lack of fluoride emission standards, a more simplified approach must be taken to arrive at an allowable fluoride emission rate for this plant. One such approach would be the requirement that fluoride emissions be controlled to a degree that is usually attainable in similar processes. The emission from the mixer and den is the larger source of fluorides, and its effluent is discharged from a relatively low stack. Methods now in use to control similar emissions and processes include simple spray towers, packed towers, and various high energy devices, such as jet scrubbers and venturi scrubbers. Published data indicate that even multiple pass spray towers achieve fluoride removal efficiencies well above 90 percent--often as high as 99 percent. In Great Britain where industrial operations are generally controlled by the "chemical efficiency" that can be attained, the emission limitation for this same type of process is 0.143 grains F₂ per cubic ft. Applying this criteria to the plant under study, results in the following:

$$7,600 \text{ cfm} \times \frac{0.143 \text{ grains}}{\text{cf}} \times \frac{\text{lb}}{7,000 \text{ gr}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{19 \text{ lb F}^-}{38 \text{ lb F}_2} = 4.2 \text{ lb/hr}$$

$$\text{percent reduction: } \frac{284 - 4.2}{284} = 98.5 \text{ percent}$$

In view of the practical possibilities listed above, it is suggested that an average efficiency of 95 percent be specified and maintained for emissions from the mixer and den operation.

Assuming that the total fluoride emissions from the mixer and den operation were 95 percent controlled, the control of fluorides from the kiln would probably not have to exceed 90 percent because of the tall stack.

Applying 95 percent control to the mixer and den and 90 percent control to the kiln stack, the total fluoride emissions would be as follows:

$$\text{Kiln: } 142 \text{ lb/hr} \times 0.10 = 14 \text{ lb/hr}$$

$$\text{Den: } 284 \text{ lb/hr} \times 0.05 = \underline{14 \text{ lb/hr}}$$

$$28 \text{ lb/hr}$$

The 28 pounds per hour would be the total allowable emission regardless of production rates, control equipment efficiency, or specific source.

An indication of the improvement in air quality that might be achieved if fluoride emissions are reduced to 28 lbs/hour can be

estimated from meteorological dispersion calculations. While these calculations are not exact, they can serve as guidelines in air sampling and pollution control applications. Our calculations (attached) indicate the following maximum ground level concentrations for the conditions assumed:

1) Don emissions

Maximum concentration of approximately 10 ppm as F^- occurring with a near neutral atmosphere at a wind speed of 11 mph and at a distance of about 330 ft. from the scrubber discharge.

If current fluoride emissions were reduced 95 percent, this calculated maximum ground concentration would be reduced to an estimated 0.5 ppm.

Also of interest is the estimated ground level concentration of 6.5 ppm as F^- which could be expected at approximately 660 ft. from the scrubber discharge. This level would be reduced to about .3 ppm if the don emissions were reduced 95 percent.

2) Kiln emissions

The estimated maximum ground level of F from the kiln is expected to occur with an unstable atmosphere (looping plume) and a 9 mph wind. The concentration would approximate .14 ppm at a distance of about 1300 feet from the kiln stack. Reducing kiln emissions by 90 percent, would reduce this concentration to approximated .02 ppm.

For the morning inversion breakup (fumigation) case, which appears to be important in Garrison, the fluoride levels are estimated

at .05 ppm for current emission levels and .05 ppm if the proposed control efficiencies were achieved.

The plant's valley location with its numerous morning inversions and the lack of detailed meteorological data makes it impossible to accurately document the degree of control necessary to eliminate nuisance complaints and prevent excessive accumulation of fluoride in vegetation. It will, therefore, be necessary after a period of operating experience at the reduced emission rate to determine if adequate control has been realized or whether further reduction is needed. The basis for such determinations could be the analyses of freshly grown vegetation to determine if the fluoride content has been reduced to 40 ppm or less.

SULFUR DIOXIDE EMISSIONS

A number of communities have regulations limiting concentration of sulfur dioxide in emissions to 2000 ppm. The plant under study emits 2300-4200 ppm in the kiln stack gases which would be in violation of such regulations. Other regulations limit emission of sulfur dioxide on the basis of concentrations at ground level beyond the plant premises due to the emissions. A reasonable regulation of this type would limit ground concentrations to an average of 0.5 ppm for a one-hour period, not to be exceeded during more than two one-hour periods during any seven-day period and an average of 0.1 ppm for a 24-hour period, not to be exceeded during more than one 24-hour period in any three month period.

Again referring to the attached calculated ground level concentrations, it is estimated that the SO_2 concentration (from the den scrubber) reaches a maximum of 0.26 ppm at about 330 feet from the source, with a near neutral atmospheric stability and a wind speed of 11 mph.

The fumigation level is estimated at 0.45 ppm to which the kiln emission is the major contributor. Since this concentration is very close to the suggested level of 0.5 ppm for 1 hour, it is felt that the sulfur dioxide concentrations in the kiln effluent gases should be limited to 2000 ppm at stack conditions.

SULFUR TRIOXIDE EMISSIONS

Regulations applicable to emission of sulfur trioxide and sulfuric acid mist have been used by only a few agencies. The only one reasonably applicable is 0.3 grains per scf expressed as 100 percent sulfuric acid, a regulation of the San Francisco Bay Area Air Pollution Control District. The kiln stack of the plant in question was emitting gases containing 0.2 to 1.1 grains per standard cubic foot (an average of 0.7 grains per scf) when lime was being added to the kiln effluent gases.

Another way to view the emissions of sulfur trioxide is to estimate ground concentrations on the basis of emissions, stack height and meteorological dispersion formulas. In this manner, we estimate that ground concentrations of sulfur trioxide, calculated as 100 percent

sulfuric acid, could on occasion reach or exceed 0.3 mg/m^3 . While there are no ambient air quality standards for sulfuric acid mist in the United States, there is considerable expert opinion that if a peak concentration of 0.3 mg/m^3 is not exceeded, no detrimental effects on health will be observed. For this reason, it is suggested that SO_3 concentrations in the kiln stack be limited to .3 grains/standard cubic foot.

VISIBLE EMISSIONS

The stack sampling team was unable, because of process conditions in the stack, to measure total particulate emissions from the plant. However, it was obvious that there was considerable particulate matter in the plume. These emissions could be regulated on the basis of visual observations of the plume. Such a regulation would limit the discharge of any contaminant for a period of three minutes in any one hour, which would obscure an observer's view by greater than 40 percent. This type of measurement is based upon the Ringelmann chart which is also applied to black or gray smoke. A 40 percent equivalent opacity, which we are suggesting, for the Garrison standard is equivalent to No. 2 on the Ringelmann chart. This type of regulation is enforced in many areas of the United States.

Control devices applied to reduce other emissions may reduce the particulate emissions. Therefore, if the plant could demonstrate a solid particulate emission of 0.1 grain per standard cubic foot or less, the visible emission opacity regulation could be waived.