CONTROL TECHNIQUES FOR FLUORIDE EMISSIONS

PHOSPHORIC ACID
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3

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U.S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Public Health Service
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CONTROL TECHNIQUES FOR FLUORIDE EMISSIONS

SUMMARY

SOURCES OF FLUORIDE AIR POLLUTANTS

Fluorine, which is 13th among the elements in order of abundance, occurs in nature principally as fluorspar, (CaF_2), containing 49 percent fluorine, and as fluorapatite ($Ca_{10}(PO_4)_6F_2$), containing 3 to 4 percent fluorine. Fluorspar is the source of essentially all the fluorine and fluorine derivatives used in commerce, including the synthetic cryolite used in aluminum manufacture. Fluorspar is also used directly as a fluxing agent in the metallurgical and ceramic industries. Fluorapatite, more commonly known as phosphate rock, is the source of all phosphate fertilizers and of elemental phosphorus and its derivatives. The fluorine present in phosphate rock represents a potential air pollutant. The mineral form of fluorine in phosphate rock affects the evolution of fluorides when the rock is thermally processed. The substituted fluorapatite, $(Ca,Na,Mg)_{10}(PO_4)_{6-x}(CO_3)_xFy(F,OH)_2$, has more fluoride than normal fluorapatite and its fluoride is driven off more readily.[a] Both forms of fluorapatite are found in deposits of phosphate rock.[b] The use and processing of fluorspar and fluorapatite are the predominant sources of fluoride air pollutants.

A relatively unknown source of fluoride air pollutants is the use of clay in the brick and ceramic industries. Clay contains 0.02 to 0.3 percent fluorine.

Another relatively unknown source of fluoride emissions is the burning of coal containing 0.001 to 0.019 percent fluorine and an average of 0.008 percent fluorine.

Naturally occurring cryolite (Na_3AlF_6), containing 54 percent fluorine, is of limited commercial significance since it is available from only one deposit.

A summary of fluoride emissions is presented in Table S-1.

[a] Barber, J.C. and Thad D. Farr, Fluoride Recovery from Phosphorus Production. Tennessee Valley Authority, Muscle Shoals, Alabama Paper presented at the Meeting of the American Institute of Chemical Engineering at

[b] McClellan, G.H. and James R. Lehr. American Mineralogist, 54: 1374-1391, September-October, 1969.

Table S-1 1968 ESTIMATED SOURCES OF FLUORIDE EMISSIONS[a,b] IN UNITED STATES

	Released in process, tons/yr	Atmospheric emissions, tons/yr
Phosphate rock processing		
Fertilizers		
Normal superphosphate	53,000	9,700
Wet process phosphoric acid		
Digestion	20,000	100
Evaporation	178,000	-
Gypsum waste ponds	1,900	1,900
Handling, Shipping and Unloading	1,000	1,000
Superphosphoric acid		
Vacuum evaporation	3,800	-
Submerged combustion	1,700	-
Triple superphosphate	30,500	300
Diammonium phosphate	2,600	100
Elemental phosphorus	37,300	5,500
Defluorination animal feed	21,600	100
Sub total	351,400	18,700
Aluminum manufacture	100,000	16,000
Fluorspar fluxing		
Steel manufacture		
Open hearth furnace	19,300	16,800
Basic oxygen furnace	39,300	8,400
Electric furnace	16,600	14,900
Iron foundries	-	Negligible
Welding coatings	2,700	2,700
Non-ferrous foundries	4,000	4,000
Sub total	81,900	46,800
Brick and tile products	18,500	18,500
Glass and frit	3,000	2,700
Coal Combustion	16,000	16,000
Total	570,800	118,700

[a] In addition to the above, 302,000 tons of hydrogen fluoride were produced from fluorspar for conversion to fluorine, fluorocarbons, synthetic cryolite, and aluminum fluorides, with negligible fluoride emission.

[b] Based on 1968 Data

MAJOR SOURCES

Phosphate Rock Processing

Phosphate rock is the source of all phosphate fertilizers as well as the source of elemental phosphorus and various phosphate derivatives used in commerce. This mineral form is readily attacked by acids and although its fluorine content makes the rock the world's largest fluorine reserve, very little fluorine is recovered from this source for commercial purposes because it evolves principally as silicon tetrafluoride (SiF_4) and separation from silicon is difficult.

Of the 41 million tons of marketable phosphate rock mined in the United States in 1968, 25 million tons containing about 875,000 tons of fluorine was processed in the United States to phosphate fertilizers, elemental phosphorus, and animal feeds. The fluoride evolved during processing was estimated to be about 351,000 tons.

The fluoride emitted to the atmosphere was estimated to be about 18,700 tons. Fluoride recovered as fluosilicic acid amounted to about 20,000 tons.

Aluminum Manufacture

Aluminum is manufactured by the electrolytic reduction of aluminum oxide dissolved in a fused bath of cryolite and aluminum fluoride. The fluoride evolved during the manufacture of primary aluminum in 1968 amounted to about 100,000 tons. The fluoride emitted to the atmosphere amounted to about 16,000 tons.

Fluorspar Use in Manufacture of Hydrogen Fluoride and Fluorine Derivatives

Fluorine derivatives are important products of commerce and are prepared from hydrofluoric acid, which is almost exclusively produced from fluorspar. Table 1 shows the production of hydrogen fluoride (HF) and its distribution among the consuming industries.

Table S-2 PRODUCTION AND CONSUMPTION OF HF[c,d]

	1957	1959	1961	1963	1968
HF production, tons/Yr.	140,000	132,600	190,000	188,400	302,000
Fluorspar consumption, tons/Yr.	318,000	300,000	430,000	425,000	660,000
HF utilization, %[e]					
Fluorinated Organics	28	30	40	40	40
Aluminum	40	39	33	35	40
Atomic energy	12	13	12	10	-
Petroleum	4	5	4	5	20
Stainless steel	5	3	3	3	-
Other	11	10	8	7	-

[c] Estimated from 1957-1968 Minerals Yearbook. U.S. Dept. of Interior, Bureau of Mines. Washington, D.C.

[d] Current Industrial Reports, Inorganic Chemicals and Gases Series: M28A (68)-13. U.S. Dept. of Commerce, Bureau of the Census, Washington, D.C., April 15, 1970. p20.

[e] Kirk-Othmer Encyclopedia of Chemical Technology, Vol. IX, New York, Interscience Publishers. 1966. p624.

Although some fluoride emissions may occur from leaks and spills during production and use of hydrogen fluoride and derivatives, precautions should be exercised to virtually eliminate fluoride emissions to the atmosphere.

Fluorspar Fluxes in Metallurgy

Of the 1,240,000 tons of fluorspar consumed in 1968, about 560,000 tons was used directly as a fluxing agent in the metallurgical industries. The fluoride evolved during this use approached 50 percent of the contained fluorine and amounted to about 81,900 tons. The fluoride emitted to the atmosphere was estimated to be 46,800 tons.

Brick and Tile Products Manufacture

Clay deposits contain from 0.02 to 0.3 percent fluorine occurring as a replacement for the hydroxyl ion in the aluminum silicate structure. Under the firing conditions used in producing brick and clay products, practically all of the fluorine present is released into the atmosphere. The amount emitted in 1968 was estimated to be 18,500 tons.

Glass and Frit

Nearly 29,000 tons of fluorspar was used in 1968, as a fluxing agent in glass and frit manufacture. The fluorine equivalent in the fluorspar amounted to 15,000 tons. About 20 percent evolves during melting of the glass and an estimated 2,700 tons was emitted into the atmosphere.

Combustion of Coal

Coal mined in the United States contains an average of 0.008 percent fluoride as fluorapatite. The concentration of fluoride in the stack gases from coal combustion is estimated to be about 5 parts per million, (ppm). The total emitted during 1968 amounted to about 16,000 tons.

CONTROL METHODS

Dust Separation

Dusts are generated during the mining, handling, crushing and grinding, and calcining of phosphate rock. Techniques for abating dust are presented in the Control Techniques for Particulate Air Pollutants, AP-51. Commonly, dry cyclones are combined with bag filters to give collection efficiencies of 99.5 to 99.9 percent. Electrostatic precipitators with 98 to 99.5 percent efficiencies may also be used but are not usually favored because of higher costs.

Wet Scrubbers

Off-gases from the processing of phosphate rock in fertilizer manufacture contain gaseous fluorides as well as particulates. A variety of wet scrubbing equipment is available for limiting emissions. A high degree of removal, up to 99.9 percent, has been effected in a southern state by staging or combining several types of equipment. Particulates are removed in the first stage. Subsequent stages are designed with certain parameters in mind: The volume of off-gases, the concentration and nature of the fluoride gases, and the degree of separation or recovery that is desired. Types of wet scrubbing equipment include: venturi, impact and cyclonic-spray scrubbers, and spray towers (vertical and cross-flow).

Other Control Methods

The aluminum industry has two basic systems for controlling evolved fluorides from reduction cells. In the first system, individual cells may be hooded, with captured fluorides being removed by dry cyclones and by spray towers or wet scrubbers with an efficiency of 90 to 95 percent. The capture of fluorides from the cells varies from 85 to 95 percent. The cell fluorides not captured by the hoods are released into the cell room and frequently pass to the atmosphere from the roof monitors of the cell room. The other basic system uses general ventilation for the cell room. Ambient air is admitted through louvers on the sides of the cell room below cell level and is swept across the cells to the roof monitors, where fluorides are removed by spray towers with about 90 percent efficiency.

An alternate dry cleaning system recently available by licensing can be used to absorb the evolved, captured fluorides with activated alumina in a fluidized bed or by alumina-coated fabric filters. The alumina on which the fluorides are absorbed is recycled to the reduction cells. The control of all fluoride emissions is as high as 95 percent, depending on the efficiency of the capture of fluoride emissions from the cells. Some European plants have reported dual scrubbing systems that provide greater than 95 percent efficiency. A dual system uses scrubbers having about 96 percent efficiency for cleansing the captured emissions from the cells, and scrubbers with about 87 percent efficiency for cleaning the emissions from the roof monitors of the cell room.[f]

f) Brenner, E.M., Gas Collection, Cleaning, and Control at Soko, Sundsvall Works. TMS-AIME Paper No. A70-14. Presented at the Annual Meeting of The Metallurgical Society and American Institute of Mining, Metallurgical and Petroleum Engineers. Denver, Colorado. February 16-19, 1970.

Buffer Zone

A buffer zone surrounding a primary aluminum plant is sometimes used to monitor plant emissions, even when the control efficiency for all fluorides is 90 percent or more. The accumulation of fluorides in certain vegetation provides visual and analytical methods for studying short-and long-term exposures to fluorides that result from process upsets and/or excessive emissions.

1. INTRODUCTION

Pursuant to authority delegated to the Commissioner of The National Air Pollution Control Administration, Control Techniques for Fluoride Emissions is issued in accordance with Section 107c of the Clean Air Act (42 U.S.C. 1857c-2bl).

Airborne fluorides are known to accumulate in agricultural plants and in forage for livestock, which, in turn, produce vegetation damage and livestock fluorosis.[a,b,c]

Reduction of emissions of this class of pollutants is important to any effective air pollution abatement program in areas where fluoride emissions are prevalent. Fluoride pollutants originate from a variety of sources, and the emissions vary in physical and chemical characteristics. Similarly, the available control techniques vary in type, application, effectiveness, and cost.

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[a] Shupe, J.L., Fluorine Toxicosis and Industry, American Industrial Hygiene Association Journal, p.240-247, March-April, 1970.

[b] Hill, A. Clyde, Air Quality Standards for Fluoride Vegetation Effects. APCA Paper No. 68-165. Presented at the Annual Meeting of APCA, St. Paul, Minnesota, June 24-27, 1968.

[c] Suttie, J.W., Air Quality Standards for the Protection of Farm Animals from Fluorides, APCA Paper No. 68-166. Presented at Annual Meeting of APCA, St. Paul, Minnesota, June 24-27, 1968.

The control techniques described herein represent a broad spectrum of information from many engineering and technical fields. Many of the devices, methods, and principles have been developed and used over many years, and much experience has been gained in their application. They are recommended as the techniques generally applicable to the broad range of fluoride emissions control problems.

The proper choice of a method, or combination of methods, to be applied to any specific source depends on many factors other than the characteristics of the source itself. While a certain percentage of control, for example, may be acceptable for a single source, a much higher degree may be required for the same source when its emissions blend with those of others. This document provides a comprehensive review of the approaches commonly recommended for controlling the sources of fluoride emissions. It does not review all possible combinations of control techniques that might bring about more stringent control of each individual source.

The many commercial, and industrial, processes and activities that generate fluoride air pollutants are described individually in this document.

The various techniques that can be applied to control emissions of fluorides from these sources are reviewed and compared. Sections on source evaluations, equipment costs and cost-effectiveness analysis, and current research and development are also included. The bibliography comprises important reference articles, arranged according to applicable processes.

Although some data are presented on quantities of fluorides emitted to the atmosphere, the subject of the effects of fluorides on health and welfare will be considered in detail in a companion document, Air Quality Criteria for Fluoride Emissions.

2. BACKGROUND INFORMATION

2.1 Definitions

This section contains general definitions of the terms used in this document.

Alumina (Al_2O_3)	Compound (aluminum oxide) obtained by refining bauxite ore. Primary aluminum is manufactured by the electrolytic decomposition of alumina.
Aluminum reduction cell	An electrolytic cell for the reduction of alumina composed of a thermally insulated carbon crucible that serves as cathode, and of carbon anodes. Prefabricated carbon blocks are the anodes in prebaked anode cells, whereas in continuous anode (Soderberg) cells, the anode is replenished with component materials during operation.

Animal feed supplement	Element (or compound), such as calcium, potassium, and phosphorus, added to animal feeds to enhance their nutritional value. Phosphorus is generally added in the form of defluorinated phosphate rock.
Basic oxygen furnace	Steel-making, basic-lined vessel into which oxygen is blown through a lance onto the surface of the molten steel.
Control device	One or more pieces of equipment used to remove air pollutants from gas streams.
Cross-flow packed scrubber	A scrubber in which the gas stream moves horizontally through the packing while the scrubbing liquid flows by gravity vertically through the packing. Usually has a

	spray section ahead of packed section and a demister tail section.
Cryolite (Na_3AlF_6)	Used as a solvent for alumina in fused electrolysis reaction in aluminum reduction cells.
Cyclone Scrubber	A contacting device in which the gas stream contacts a fine spray of liquid. The gas flow is cyclonic during the scrubbing action.
DAP	Diammonium phosphate; compound made by reacting anhydrous ammonia with wet-process phosphoric acid.
Den	Chamber in which phosphate rock is acidulated for the production of normal superphosphate.
Electric furnace	Electrically heated furnace employed in the manufacture of elemental phosphorus and steel.

Electrostatic precipitator	A device that separates particles suspended in a gas stream by means of an electrostatic field that causes the charging of dust particles and their subsequent migration to a collection surface.
Emission of fluorides	Any fluoride-containing gas stream that is emitted to the atmosphere, from a process or from an air pollution control device.
Evolution of fluorides	Any fluoride-containing gas stream arising from the process prior to the application of controls.
Fabric filter	A device for removing particulates from gas streams by filtration through fabric media.

Floating-bed scrubber (Fluidized bed, fluid bed, floating bed, etc.)	A device having one or more beds packed with low-density polyethylene or polypropylene spheres about 1.5 inches in diameter. These spheres are continually in motion between the upper and lower retaining grids while gas flows downward through the bed.
Fluorapatite ($Ca_{10}(PO_4)_6F_2$)	The main phosphorus-bearing component of phosphate rock. A variety of apatite, which is the tenth most abundant mineral.
Fluoride	As used in the text, the term fluoride refers to any compound of fluorine which appears in the various process streams or effluents, e.g., HF, SiF_4, H_2SiF_6, AIF_3, CaF_2, Na_3AlF_6, etc.

Fluorine (F)	Restricted to describing quantity of fluoride ion in a specific compound.
Fluosilicic acid (H_2SiF_6)	Compound formed when scrubbing water reacts with gaseous silicon tetrafluoride (SiF_4) found in offgases from the manufacture of wet-process phosphoric acid and superphosphate.
Fluorspar	A mineral composed principally of calcium fluoride (CaF_2) that is used as a fluxing agent in the metallurgical and ceramic industries and for the production of other chemicals.
Frit	Produced by quenching a melt of minerals to yield a mass of friable, glassy particles.

	Used in compounding ceramic coatings.
Gypsum ($CaSO_4 2H_2O$)	Common name for calcium sulfate dihydrate.
Gypsum pond	A large pond, commonly unlined, used to dispose of gypsum from various phosphate conversion processes. Also acts as a source for fluoride scrubber water, which is commonly recycled to the scrubbers.
Hydrogen fluoride (HF)	Evolved as a gas in the processing of phosphate rock, manufacturing of aluminum, cement and steel and the combination of coal.
Impingement scrubber	A device, such as the Doyle scrubber, that impinges a gas at high velocity onto a liquid surface, and reverses it 180° on exit.

Integral scrubber	A device that combines several scrubbing operations in one piece of equipment.
NSP	Normal superphosphate; made by reacting phosphate rock with concentrated sulfuric acid. Contains 20 percent P_2O_5.
Open Hearth furnace	Steel-making furnace in which pig iron and scrap are oxidized on a hearth.
Packed scrubber	A conventional tower packed with plastic or ceramic rings, tile, etc., to effect contact and mass transfer between liquid and gaseous phases. Usually, the scrubbing liquid flows by gravity down counter-current to the rising gas stream in the tower.

P_2O_5	Phosphorus pentoxide, or phosphoric oxide. The strength of phosphate fertilizers is rated on the basis of P_2O_5 equivalent.
Phosphate rock	The only commercial ore of phosphorus, widely distributed over the world and containing many trace impurities. See apatite.
Phosphoric acid (H_3PO_4)	Orthophosphoric acid, the main phosphorus-bearing component of wet-process acid.
Transfer unit	A transfer unit is a measure of the difficulty of separation or absorption of the components of a mixture in a rectification process; the more difficult the separation or absorption, the higher the value of the transfer unit.

	The number of transfer units increases with the required degree of reduction in pollutant concentration and with reduction in the driving force for absorption.
TSP	Triple superphosphate; made by treating phosphate rock with wet-process phosphoric acid.
Venturi scrubber	A scrubber in which the scrubbing liquid is introduced at right angles to gases passing at high velocity through a constricted throat (vena contracta).

2.2 Costs

Cost considerations for air pollution equipment described in this document include definitions of alternative control systems and identification of costs.

2.2.1 Definitions of Alternative Control System

The process of selecting a control system should begin with identification of the total control needs of a plant. Usually more than one problem exists, and attacking the combined pollution problem is more economical than trying to handle each one separately. The advantages and disadvantages of the substitution of fuels or raw materials, and the modification or even replacement of the processes can best be assessed with the total needs in view, since these methods tend to alleviate or eliminate more than one problem. Such methods also tend to have an effect on solid waste disposal and water pollution problems. If process alternatives or substitutions are not feasible, then effluent control equipment is necessary. In most cases, the problems can be remedied in several ways. The cost analysis of the different ways is one approach to the selection of the best method for a given problem. Other considerations are the effects that the emissions may have on the company's relations with the public and on the growth potential of the plant or process.

An important factor in choosing among control equipment alternatives is the degree of reduction of emissions required to meet emission standards. The degree of emission reduction or collection efficiency required depends upon the reduction required to bring actual levels of emission down to desired levels. The usual ranges of collection efficiencies for various type of control equipment are discussed in this document.

Factors to be considered next are the process stream characteristics: flow rate, temperature, moisture content, explosiveness, particle content, odor, corrosiveness, and ignition point. The temperature modifications (heat transfer) necessary if adsorption is to be applied must be defined. The conditions for absorption must be determined. Power requirements for pumps, compressors, or blowers must be estimated. Space required for the control system is often an important consideration.

Plant facilities should be planned to include equipment for waste water treatment, product recovery, and heat recovery.

Each alternative that meets all requirements can then be evaluated in terms of cost.

2.2.2 Identification of Costs

Cost estimates, useful in comparing alternative control systems, are best developed using techniques available for preliminary capital cost estimating. The costs in this document were developed by a contractor using techniques developed by experience over many years. The updating to October 24, 1969, of equipment bids from vendors are done by using M and S Equipment Cost Index given in Chemical Engineering on October 24, 1969.

The definable control costs are those that are directly associated with the installation and operation of control systems. These expenditures can be broken down for accounting purposes as follows:

1. Purchase Cost

Vendors bids for large equipment such as scrubbers, spray towers, fabric filters, duct work, piping, tanks, blowers, pumps, motor, and special materials of construction.

2. Installed Cost

Purchase cost times 2.95, a factor developed by a contractor, includes engineering studies, design costs, land, structural modifications, construction overhead, dismantlement, rearrangement, control hardware, auxiliary equipment, erection, insulating material, transportation of equipment, site preparation, classifiers, and liquid treatment.

3. Annualized Cost

Annualized costs include fixed costs plus variable costs, where fixed costs include 10 years depreciation of installed cost, at 10 percent per year; interest at 8 percent per year; and taxes and insurance at 2 percent per year; and where variable costs include cost of water, power, and maintenance at 2 percent per year.

Hence, the annualized cost is composed of the cost of power, the cost of water, and the installed cost times 0.22. No additional operating labor is included since some control installations will utilize present personnel while other installations will need one or more operators. Each proposed installation of control equipment will require an estimate of additional labor requirements, the cost of which must be included in annualized cost.

REFERENCE FOR SECTION 2

a. Personal communication from J. Schlesinger,
Cost Department, Singmaster & Breyer,
235 East 42nd Street, New York, N.Y. 10017.
October 13, 1969.

2.3 LEGISLATIVE TRENDS

Several philosophies prevail in the establishment of regulations for the control of fluoride contaminants in ambient air. One philosophy selects a fluoride level in ambient air which shall not be exceeded. Another philosophy selects an emission rate for fluorides which shall not be exceeded. A third embraces features of the other two philosophies.

2.3.1 Ambient Air Standards

Control of fluoride air concentrations by ambient air standards is difficult to enforce. If there is more than one source of fluoride emissions, the enforcement is almost impossible. One air pollution control agency uses ambient air sampling on the downwind side of the offending source. Vagaries of the wind make plume clearing frustrating and sometimes useless in obtaining adequate evidence of pollution. However, ambient air standards are useful in setting goals for achieving air quality which precludes or reduces the adverse impact of a pollutant on an area.

Several states have set ambient air qualities for control of fluoride at the boundaries of the emitting plant. These states also use the accumulation of fluoride in forage, (grasses and pasture vegetation eaten by livestock) as an indicator of the fluoride emitted since the measurement of ambient fluoride in the parts per billion (ppb) range is difficult. The use of calcium formate papers exposed in standard housing is another method of measuring ambient concentration of fluorides. The papers are exposed for 28 days and the fluoride pickup is determined. Tables 2-1, 2-2 and 2-3 present these regulations for several states and the data are representative of only the states mentioned since many states have not passed fluoride regulations.

2.3.2 Emission Standards

Regulations limiting the amount of fluoride emissions from individual sources provide effective methods for reducing ambient fluoride concentration. The air pollution control agency to enforce emission standards needs the right to enter the offending plant and to test its emissions by stack sampling. Several states having the entry and testing rights have set fluoride emission standards, as shown in

TABLE 2.3 1970 STATE CALCIUM FORMATE PAPER STANDARDS FOR FLUORIDES

State	Source Measured	Distance from Source	Maximum increase of fluoride micrograms/Cm^2/28 days
Montana	Pond, basin	18 to 48 inches	108
Florida	Pond, plant	as decided by tester	No limit, used as a monitoring technique

TABLE 2.1 1970 STATE AMBIENT AIR STANDARDS FOR FLUORIDES

State	Type Fluoride in ambient air	Time in consecutive units and concentrations in ppb by volume					Methods used for collection & analysis
		12 hours	24 hours	7 days	30 days	March 1 through Oct. 3 of any year	
Washington	Gaseous as HF	4.5	3.5	2.0	1.0	0.6	$NaHCO_3$ tube Technician auto analyzer
Montana	Total as F		1.0				
Florida	Total as F		1.0				
Texas	Gaseous as HF	4.5	3.5	2.0	1.0		

TABLE 2.2 1970 STATE FORAGE STANDARDS FOR FLUORIDES

State	Type Fluoride in Forage	Time in consecutive units and concentration in ppm by weight			
		12 months	2 months	Maximum in 2 months	Cured Forage
Washington	Total F, dry basis	40	60	80	40
Montana	Total F dry basis	35			
Florida	Total F dry basis	40			
Idaho	Total F dry basis	40	60	80	

Table 2.4. The regulations are representative of only the states mentioned since many states have no fluoride regulations. Some states as Florida and Montana uses the ambient air regulations to back up fluoride emission standards. One mile from fertilizer plants in Florida, the ambient air should not exceed 1.0 ppb. fluoride.

The presented information is not intended to be a summary of all state and local regulations for fluorides but are samples of the regulations passed by some states aware of the fluoride problem.

TABLE 2.4 1970 STATE OR COUNTY EMISSION STANDARDS FOR FLUORIDES FROM VARIOUS INDUSTRIES

State	Industry Controlled	Emission Standard
Washington	Primary aluminum	15 lb/hours of particulates, no fluoride standard
Montana	Primary aluminum	0.06 lb.F/hour/cell, maximum 38 lb F/hr.
	Elemental phosphorus, enriched phosphate, phosphoric acid, defluorinated phosphate, and phosphate fertilizers.	1 lb HF/933 lbs F evolved
Florida	Enriched phosphate, phosphate fertilizer, phosphoric acid, defluorinated phosphate. Each plant site is a unit even if several operations occur at one site	0.40 lb F/ton product calculated as P_2O_5
Mantee County, Florida	Enriched phosphate, phosphate fertilizer, phosphoric acid, defluorinated phosphate. Each plant site is a unit even if several operations occur at one site.	0.20 lb F/ton product calculated as P_2O_5.

3. MAJOR SOURCES OF FLUORIDE EMISSIONS

Fluorides, as hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4) gases and as dusts, are generated during the industrial use or processing of fluoride-bearing minerals. Two minerals, fluorapatite ($Ca_{10}F_2(PO_4)_6$), or phosphate rock, and fluorspar (CaF_2), are the predominant sources of fluoride emissions. The magnitude of the fluoride evolution during processing of these minerals is such that control must be exercised, and of the roughly 570,800 tons per year evolved during 1968, an estimated 118,700 tons were emitted to the atmosphere. Little or no control is exercised over fluorides emitted during production of brick and tile products from clays which may contain from 0.02 to 0.3 percent fluorine. Table 3-1 presents the estimated fluorides evolved in the United States for 1968. The nature, concentration, and amount of these emissions affect their impact on the area around the source. The industries are listed in Table 3-1 in probable order of fluoride impact on areas around these sources. Aluminum manufacture has the second most severe impact on an area since its emissions are about 50 percent gaseous fluoride, which are more reac-

Table 3-1 1968 ESTIMATED SOURCES OF FLUORIDE EMISSIONS[a,b] IN UNITED STATES

	Released in process, tons/yr	Atmospheric emissions, tons/yr
Phosphate rock processing		
Fertilizers		
Normal superphosphate	53,000	9,700
Wet process phosphoric acid		
Digestion	20,000	100
Evaporation	178,000	-
Gypsum waste ponds	1,900	1,900
Handling, Shipping and Unloading	1,000	1,000
Superphosphoric acid		
Vacuum evaporation	3,800	-
Submerged combustion	1,700	-
Triple superphosphate	30,500	300
Diammonium phosphate	2,600	100
Elemental phosphorus	37,300	5,500
Defluorination animal feed	21,600	100
Sub total	351,400	18,700
Aluminum manufacture	100,000	16,000
Fluorspar fluxing		
Steel manufacture		
Open hearth furnace	19,300	16,800
Basic oxygen furnace	39,300	8,400
Electric furnace	16,600	14,900
Iron foundries	-	Negligible
Welding coatings	2,700	2,700
Non-ferrous foundries	4,000	4,000
Sub total	81,900	46,800
Brick and tile products	18,500	18,500
Glass and frit .	3,000	2,700
Coal Combustion	16,000	16,000
Total	570,800	118,700

[a] In addition to the above, 302,000 tons of hydrogen fluoride were produced from fluorspar for conversion to fluorine, fluorocarbons, synthetic cryolite, and aluminum fluoride, with negligible fluoride emission.

[b] Based on 1968 Data

tive than the particulate fluoride. Emissions from fluorspar fluxing brick and tile production, glass and frit manufacture, and coal combustion contain more particulate than gaseous fluorides and thus have less impact on surrounding areas. Moreover, fluoride emissions from coal burning in large power plants are often emitted from high (400-foot) stacks and are more diffused when they impact on surrounding areas.

3.1 GEOGRAPHIC DISTRIBUTION OF FLUORIDE EMISSIONS

3.1.1 Phosphate Rock Processing

In 1968, about 25,000,000 tons of phosphate rock was processed domestically.[1] About 80 percent was mined in Florida and 45 percent processed there, principally to wet-process phosphoric acid and triple superphosphate fertilizer, with some production of elemental phosphorus. Fluoride emissions amounted to about 4,000 tons.

In the Texas-Louisiana region, about 13 percent of the phosphate rock was processed to wet-process phosphoric acid and to normal and triple superphosphate, with fluoride emissions of about 1,700 tons.

Tennessee processed about 8 percent of the phosphate rock to elemental phosphorus (42.5 percent of the U.S. elemental phosphorus production), with fluoride emissions amounting to about 2,400 tons.

The mid-continent region, including the Rocky Mountain Area, processed about 28 percent of the rock to wet-process acid, superphosphate fertilizers, and elemental phosphorus. Fluoride emissions were about 6,300 tons.

Only about 4 percent of the rock was processed on the Pacific Coast to normal superphosphate fertilizer, with fluoride emissions amounting to about 2,800 tons.

About 2 percent of the rock was processed to normal superphosphate fertilizers in the northeastern states, with fluoride emissions of about 1,500 tons.

TABLE 3-2 GEOGRAPHIC DISTRIBUTION IN UNITED STATES OF PHOSPHATE ROCK PROCESSING AND ESTIMATED FLUORIDE EMISSIONS IN 1968[1,7]

Location	Phosphate Rock Processing Tons/Yr	Atmospheric Emissions Tons/Yr
Florida	11,300,000	4,000
Texas - Louisiana	3,200,000	1,700
Tennessee	2,000,000	2,400
Mid-continent - Rocky Mountain	7,000,000	6,300
Pacific	1,000,000	2,800
Northeast	500,000	1,500
	25,000,000	18,700

3.1.2 Aluminum Manufacture

Table 3-3 gives the geographic distribution of primary aluminum production and its associated fluoride emissions.

TABLE 3-3 GEOGRAPHIC DISTRIBUTION IN UNITED STATES OF ALUMINUM PRODUCTION AND ESTIMATED FLUORIDE EMISSIONS FOR 1968[1,7]

Location	Aluminum Production Tons/Yr	Atmospheric Emissions Tons/Yr
Pacific Northwest	1,155,000	5,600
Gulf Coast	820,000	4,000
TVA Region	530,000	2,600
Ohio Valley - New York State	750,000	3,800
Total	3,255,000	16,000

3.1.3 Fluorspar-Consuming Industries

Of the 1.24 million tons of fluorspar consumed in 1968, nearly 659,500 tons were processed to hydrofluoric acid.[2] A large proportion of this acid was used as aluminum fluoride in the production of aluminum. The remainder was used for the production of aerosol propellants, refrigerants, plastics, coatings, etc., and in the production of fissionable materials. This usage does not result in significant fluoride emission except in case of leakage or accident spillage.

The remaining 560,000 tons of fluorspar is utilized as a flux in steel, glass, and ceramics manufacture. Geographically, consumption is concentrated at major population centers and the total emissions of nearly 47,000 tons per year are distributed among these sources.

3.1.4 Processing of Clays and Shale

Essentially all of the fluoride present in clays and shales (0.02 to 0.3 percent) is volatilized during processing of these materials into brick and tile. Total fluoride emissions from these materials amount to about 18,500 tons per year and are distributed geographically among the major population centers. Refractory, pottery, stoneware, lime, cement, and other kiln plants can contribute fluoride fines to the atmosphere.[6]

3.1.5 Combustion of Coal

Although the average fluoride content of coal amounts to only 0.008 percent, total emissions from combustion of coal amounted to about 16,000 tons in 1968. Emissions from an individual 500-megawatt generating station would amount to about 60 tons per year, for a concentration in ambient effluents of 5 ppm.[8] These emissions from older power plants are distributed roughly in proportion to population density in those areas in which coal is used as a fuel. Emissions from newer plants are distributed differently, since these plants are usually built near the source of coal. Savings in coal transportation have accentuated the trend of building mine-mouth, large coal-fired, electric generating stations at sites away from population centers.

3.2 Projected Increase in Fluoride Emissions

The projected increase in fluoride emissions at present degrees of control (Figure 3-1) can be related conservatively to the growth of the economy, since the major sources are found in established segments of industry. A growth rate of four to five percent will apply particularly in production of phosphate fertilizer, and ceramic and heavy clay products,although the consumption of phosphate fertilizers shows an erratic year-to-year pattern. However,

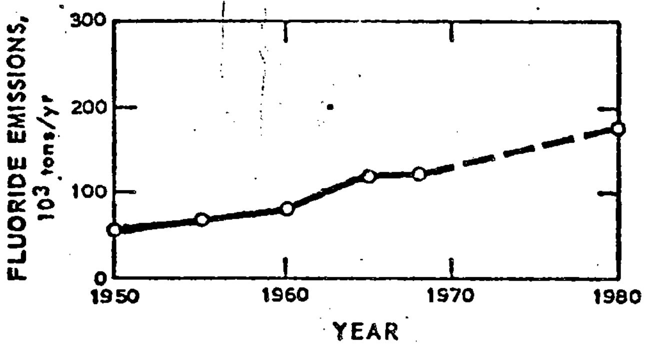

Figure 3-1. Projected increase in fluoride emissions with present degree of control.

aluminum output in the last ten years has been expanding a vigorous 7.5 percent per year.[9] Another exception has been the growth in industrial phosphorus compounds, which in 1950 represented 15 percent of the total phosphates and in 1965 were more than 30 percent.[3] A third exception is the use of fluorspar by the steel industry,[2,4] with the increased use of the basic oxygen process consuming 12.6 pounds fluorspar per ton steel versus 3.3 pounds for open hearth steel. In 1969, production of steel from basic oxygen furnaces exceeded the production of open hearth steel.[5]

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4. FERTILIZER MANUFACTURE

4.1 INTRODUCTION

Although phosphate rock and phosphate fertilizers are thought of synonymously, the non-agricultural use of phosphate derivatives has significantly increased, and in 1968 amounted to nearly 24 percent of the total output.[3] All phosphorus products are derived from phosphate rock. About 37 million tons of marketable rock were produced in the United States in 1968, of which 12 million tons were exported and 25 million tons were processed domestically.[2,3]

About 14.7 percent of the domestic rock output in 1968 appeared as normal superphosphate; 24.2 percent as elemental phosphorus, most of which was converted to derivatives; and 37.8 percent as wet process phosphoric acid; and 15.3 percent as triple superphosphate. The balance, or 8.0 percent of the rock, was used to produce nitrophosphates, direct application to the soil; animal feed; fertilizer filler and other uses.[3] Approximately 99 percent of the wet-process acid was used in fertilizer products and the remainder was used for industrial derivatives.

The fluorine contained in the domestically processed rock in 1968 amounted to 875,000 tons. An estimated 351,400 tons was evolved during processing, principally as silicon tetrafluoride (SiF_4). The balance was either retained in the product or discarded with waste. An estimated 18,700 tons of fluoride was emitted to the atmosphere. Less than 20,000 tons of the fluorine evolved during processing was recovered as fluosilicic acid.

A detailed breakdown of the distribution of phosphate to various phosphate products in 1965 is illustrated in Figure 4-1.[1] Phosphate fertilizers in 1965 accounted for 75 percent, whereas animal feed supplements accounted for about 5 percent and industrial phosphate products amounted to about 20 percent. Approximately 19 percent of the product mix was derived from elemental phosphorus, an amount almost equal to industrial phosphate products. Actually, about 15 percent of the elemental phosphorus was converted into fertilizer, while an equivalent amount of wet process phosphoric acid was converted into industrial phosphate products. Approximately 17 percent of the phosphate rock is lost during handling, drying, calcining, and beneficiation, and an additional 7.5 percent is lost during processing to final product.[4]

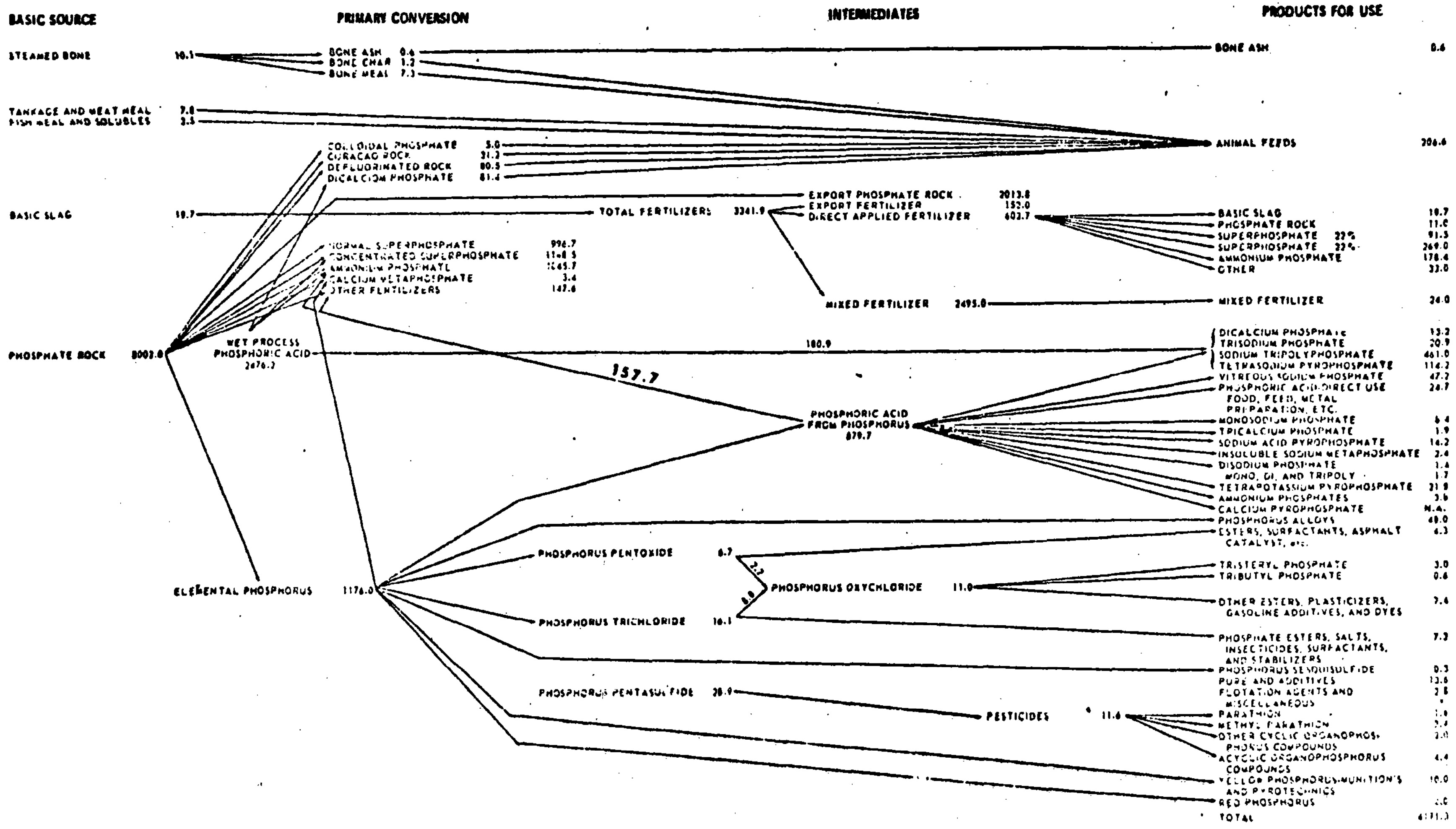

Figure 4-1. U.S. utilization of phosphorus products in 1965. Numbers correspond to million pounds of phosphorus equivalents. (Prepared by Paul Logue, Monsanto Corp.)[1]

4.2 NORMAL SUPERPHOSPHATE

4.2.1 Introduction

Normal superphosphate refers to a fertilizer produced by the acidulation of natural phosphatic material with sulfuric acid. Acidulated rock (or acidulated bone) was the earliest synthetic fertilizer and was originally mixed by hand at the point of use. Until about 1950, normal superphosphate was almost the exclusive source of phosphate in fertilizer. Its use has declined steadily, and in 1968 amounted to about 20 percent of the total phosphate fertilizer market. Further decline is expected because of increasing freight costs and greater acceptance of diammonium phosphate and triple superphosphate.[95]

The usual phosphoric oxide (P_2O_5) content of this product is in the neighborhood of 20 percent. In the United States, the starting material is phosphate rock containing fluorine to the extent of three to four percent on a dry-weight basis.[93] For normal superphosphate, 20 to 42 percent of this bound flourine volatilizes as gaseous silicon tetrafluoride (SiF_4) during and after acidulation of the phosphate rock.[94] The balance of the fluoride remains in the product.

The current control practice in normal superphosphate plants is to remove the fluorides in the off-gases by scrubbing with water in spray towers, cyclonic-spray scrubbers, or ejector-venturi scrubbers.

Based on the 1968 usuage of 1,452,000 tons of normal superphosphate (expressed as P_2O_5) the emission of fluorides to the atmosphere has been estimated at 9,700 tons of fluorine (F) per year.[3]

4.2.2 Process Description

Normal superphosphate is produced as a screened material containing powdery and coarse particles, (referred to as run-of pile by the industry) in continuous or batch fashion, by acidulating dried and ground phosphate rock containing 31 to 35 percent P_2O_5[93] with sulfuric acid (54 to 56 °Be) or 68 to 71 percent H_2SO_4.

A batch operated process produces normal superphosphate in approximate one ton batches using a mixer-to-den method. The batch mixture (slurry) is dumped directly into a den which usually has a capacity of 50 tons. The entire mix is allowed to solidify for about 25 minutes after the last batch is added. One side of the den is removed and the movable floor of the den feeds the normal superphosphate into a vertical cutter. In some plants the cutter is movable and the den is stationary. The product is conveyed to bulk storage and allowed to cure for about 30 days. The cutting operation usually requires about 25 minutes. The total time cycle (mixing, curing, and cutting) is approximately one hour. The cured product usually has a P_2O_5 content of 16 to 18 percent.[5] A typical diagram for a batch operation for normal superphosphate manufacture is shown in Figure 4-2.

For the continuous process, acidulation takes place in a continuous acidulation mixer and den. A weigh feeder is used for the continuous flow of ground and dried phosphate rock which reacts with a continuous feed of sulfuric acid (54 to 56 °Be). The reaction slurry flows to a continuous den and cutter; the green superphosphate is subsequently transferred to the curing pile. A typical flow diagram for the continuous process is shown as Figure 4-3.[27]

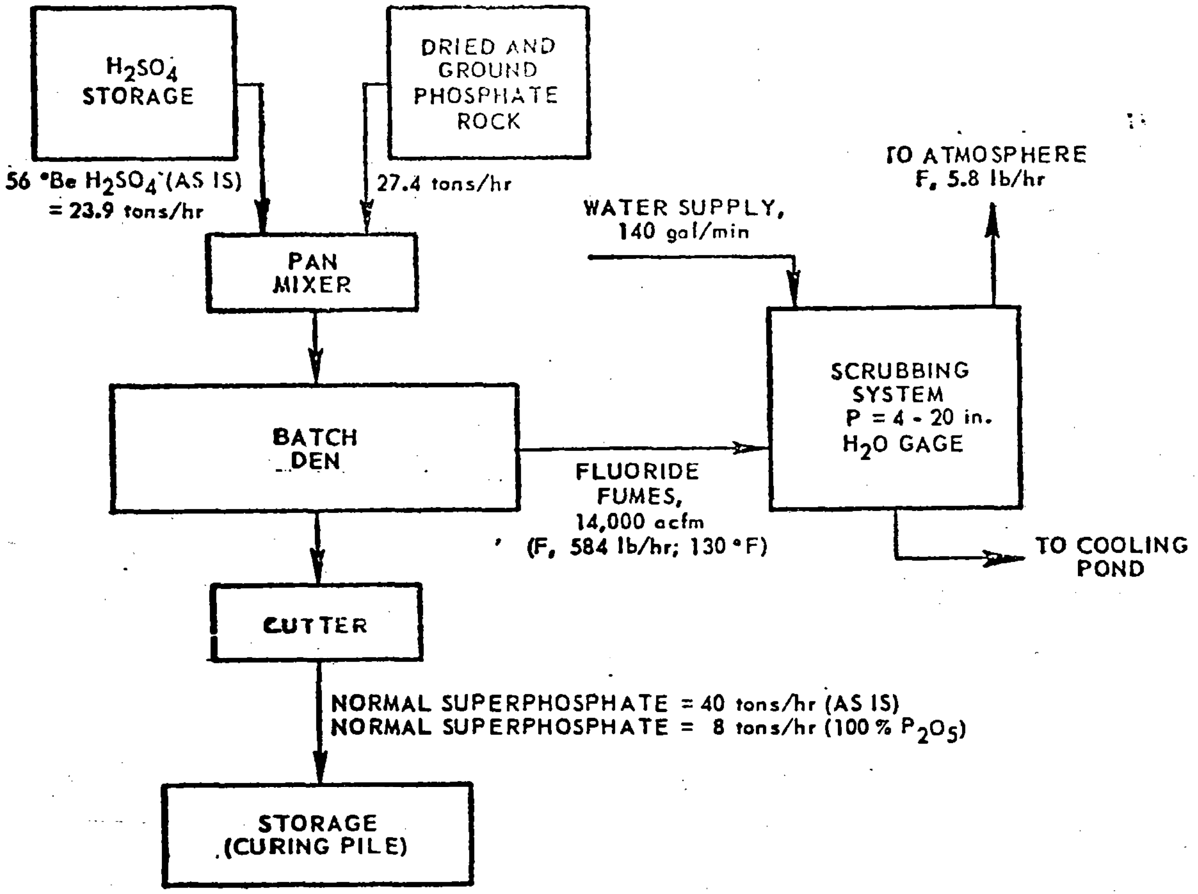

Figure 4-2. Batch process for normal superphosphate (as-is basis); typical capacity of 40 tons/hr.[9]

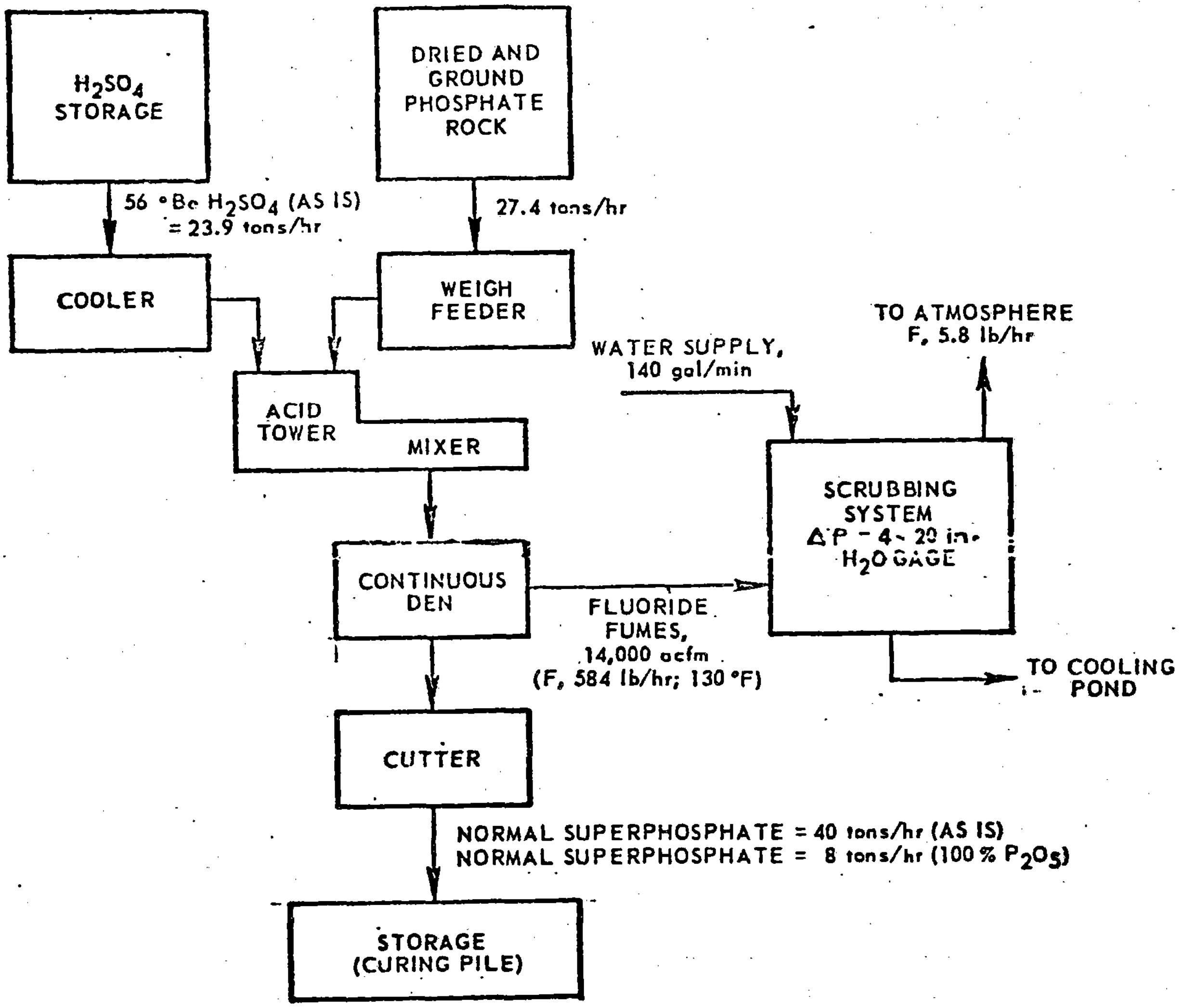

Figure 4-3. Continuous process for normal superphosphate (as-is basis); typical capacit 40 tons/hr.[27]

4.2.3 Fluoride Emissions

The emissions of particulates containing fluorides are principally in the form of dust generated in the drying and grinding of phosphate rock and in the reclaiming, screening, and handling of the cured normal superphosphate. Dusty conditions, which result from equipment leakage or from spillage, cause an industrial hygiene problem inside the plant and an air pollution problem outside the plant. Fluoride dusts are reduced by good housekeeping and attention to equipment.[6] Approximately 2 pounds of rock dust per ton of normal superphosphate (100% P_2O_5) is emitted after the control equipment from the rock grinding and drying operations.[26]

TABLE 4-1A SCRUBBER COLLECTION EFFICIENCY FOR DUST FROM PHOSPHATE ROCK DRIER (ROTARY KILN)[104]

Scrubber[x] Type	Years Operated	Inlet gas flow CFM at 100°F	Inlet dust loading gr/scf	Outlet dust loading	Collection efficiency %
Dynamic	2	100,000	3.5	0.05	98.5

[x] 12 cyclone collectors followed by twin size, 120 dynamic scrubber.

Gaseous fluorides evolved in the reaction between phosphate rock and sulfuric acid present a potential air pollution problem. The evolution of fluorides occurs as SiF_4[7] during the mixing of the acid and the phosphate rock and during the temporary residence of the fresh superphosphate in the den.

Apparently there is little further emission of fluoride to the atmosphere after the fresh superphosphate is cut from the den.[8] Normal superphosphate curing sheds are generally provided with natural ventilation, i.e., openings in the upper structures to release fumes and in the lower structure to create a draft.[6,19]

Table 4-1 shows the evolution of fluorine obtained in the regular manufacture of normal superphosphate using Florida and Tennessee phosphate rock. Aprroximately 70 pounds of fluoride is evolved per ton of P_2O_5 in normal superphosphate which is equivalent to 20 to 42 percent of the fluorine present in the rock. Normal superphosphate plants with inadequate fluoride collection and control equipment for the mixer, den, and cutter probably emit 500 pounds of fluoride per day.

Table 4-1. FLUORINE EVOLUTION FROM MANUFACTURE OF NORMAL SUPERPHOSPHATE[9]

Phosphate rock		Sulfuric acid		Acid/Rock Ratio	Time in den	Fluorine evolved
P_2O_5,%	F,%	°Be	°F	Acid as used		F in rock, %
Florida land pebble						
32.87	3.84	54.5	100	0.857	1-2 hr	25.7
33.17	3.62	55.0	120	0.861	50 min	29.8
33.43	3.88	54.8	111	0.836	16 hr	26.0
33.54	3.84	56.5	140	0.820	1 hr	26.6
33.80	3.68	55.0	140	0.818	6 hr	37.8
36.33	3.90	56.0	151	0.830	20 min	22.7
Tennessee brown rock						
32.44	3.47	55.0	120	0.881	20 min	42.1
33.53	3.92	55.2	135	0.910	1 hr	36.2
33.65	3.59	55.0	96	0.829	2 hr	42.1
33.90	3.70	55.0	109	0.876	5.5 hr	35.7
34.53	3.16	54.5	120	0.889	2 hr	32.6
34.96	3.79	54.7	120	0.899	10 min	28.1

The factors influencing the evolution of fluorides for both batch and continuous normal superphosphate processes other than the fluoride content of the rock itself, are:

1. Acid to rock ratio; fluorine evolution increases with the degree of acidulation and with increased acid concentrations.
2. Temperature; higher temperatures evolve more gaseous fluorides.
3. Grade of phosphate rock; fluorine volatilization decreases with an increase in P_2O_5 content in the phosphate rock.[9]

The literature indicates that the volume of gaseous effluent from the mixer-den system varies widely for a given plant capacity. The volume of evolved gases from normal superphosphate plants of a given capacity can vary considerably in accordance with plant design, tightness of the equipment, and the number of pieces of equipment being vented. The ranges in flow rates of gaseous effluents from various sizes of normal superphosphate plants are shown in Table 4-2:

Table 4-2. NORMAL SUPERPHOSPHATE PRODUCTION CAPACITY AND VOLUME OF GASEOUS EFFLUENT

Normal superphosphate capacity, tons/hr[a]	Flow rate of gaseous effluents, acfm
6 - 10 [20,16]	3,000 - 7,000
14 - 20 [21,22]	5,000 -12,000
25 - 40 [21,17]	9,500 -35,000

[a] Tons as-is of product containing 20 percent P_2O_5.

The literature indicates that the concentration of SiF_4 in the combined gaseous effluent from acid and rock mixing and from the den also varies over a wide range. The concentration of SiF_4 reportedly ranges from 2000 ppm to over 200,000 ppm.[8,10,11]

The undiluted effluent from mixing and from the den may also contain from 0.09 to 0.15 grains particulate per cubic foot, consisting mainly of phosphate rock dust carried over from mixing.[10] (Fluorides in mist and particulate matter from this operation have not been discussed as an operating problem.)

The undiluted effluent is generally mixed with air vented from the area of the cutter and from the conveyors before going to a scrubber. Typically, in a flow of 10,000 cubic feet per minute of undiluted effluent, SiF_4 is present to the extent of 23,000 parts per million (ppm). Dilution with 4,000 cubic feet per minute additional air reduces the concentration to about 16,000 ppm for batch operation. For continuous superphosphate production, the SiF_4 concentration may be as low as 2,000 ppm in the gas stream to the scrubbers.

4.2.3.1 Geographical Distribution of Fluoride Emission from Normal Superphosphate Production

Figure 4-4 shows the location of normal superphosphate-producing facilities in the United States. Some of the plants shown in Figure 4-4 have been shut down temporarily or perhaps permanently[12] due to the decrease in demand for normal superphosphate and the generally poor, current fertilizer market (see Section 4.2.1). Most of the normal superphosphate plants that are located along the eastern coast will be permanently closed.[13]

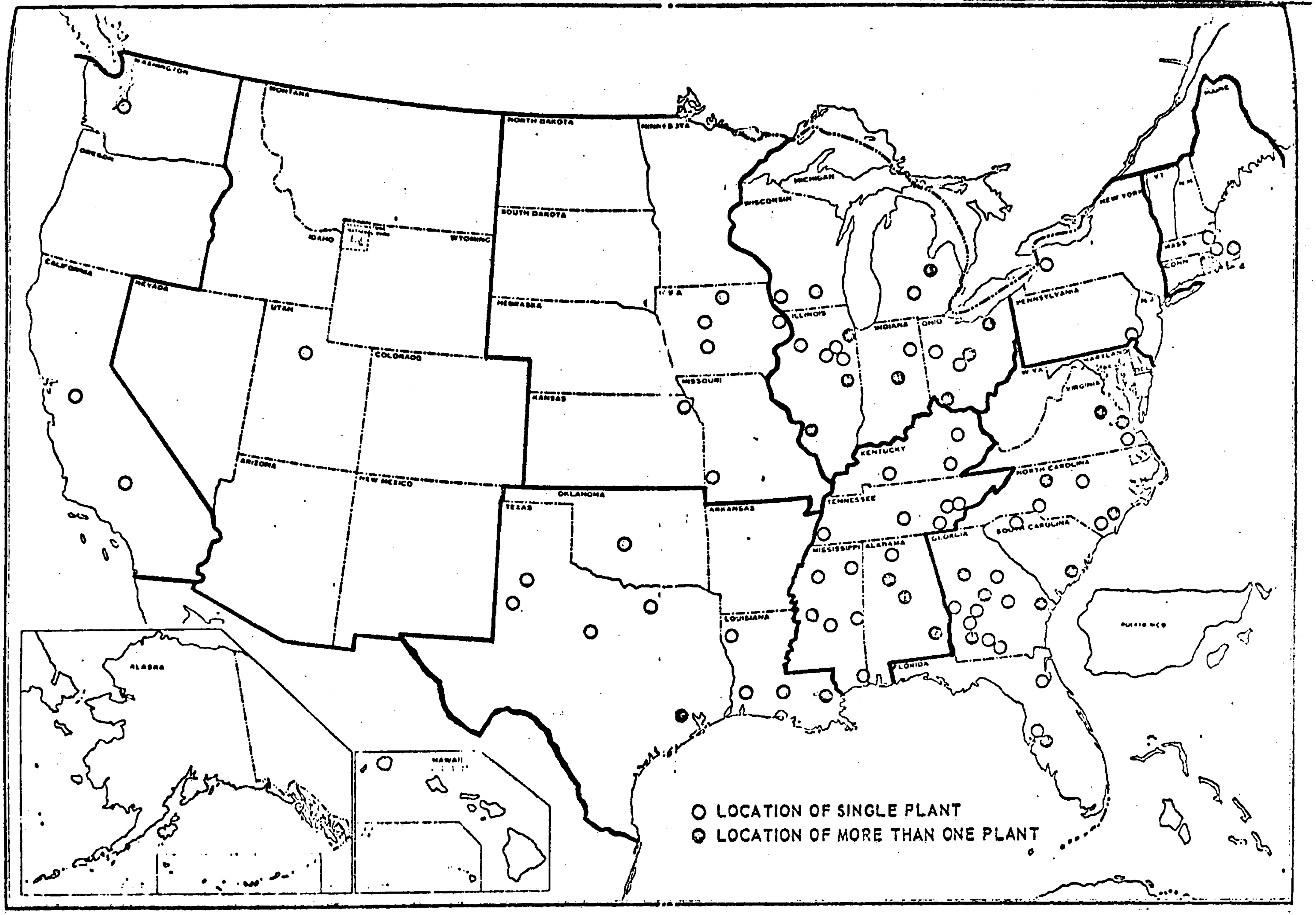

Figure 4-4. Distribution of normal superphosphate plants.12

Normal superphosphate is usually produced for a local market and is shipped over short distances. Consumption figures therefore closely approximate the production for the general area including nearby areas of adjacent states. Table 4-3 shows the domestic consumption of normal superphosphate by region, the estimated evolution of fluorides from the acidulation and denning operations, and the estimated atmospheric emissions of fluorides after the control equipment.

Table 4-3. NORMAL SUPERPHOSPHATE CONSUMPTION[14,15,28] ESTIMATED FLUORIDE EVOLUTION, AND ATMOSPHERIC EMISSIONS, USA (1968)

	Normal superphosphate consumption, tons/yr (P_2O_5)[a]	Estimated Evolution tons/yr[b]	Atmospheric emissions, tons/yr[b]
Direct application by region			
Northeast	13,000	500	100
Middle Atlantic	68,000	2,500	500
South Atlantic	58,000	2,100	100
East-North Central	54,000	2,000	400
West-North Central	116,000	4,200	800
East-South Central	82,000	3,000	600
West-South Central	82,000	3,000	600
Mountain	13,000	500	100
Pacific	156,000	5,700	1,100
Subtotal	642,000	23,500	4,300
Commercial mixtures			
	810,000	29,500	5,400
Total	1,452,000	53,000	9,700

[a] Basis is normal superphosphate (NSP) production for local market and short distance shipping. (100% P_2O_5 basis).

[b] Fluorine in both gaseous and particulate phases. Calculations based on 73 pounds of F per ton of normal superphosphate consumed (100% P_2O_5 basis).[25]

4.2.4 Control Techniques

Fluorides are removed from normal superphosphate off-gases by scrubbing with water in spray towers or various types of scrubbers. The typical performance characteristics of such systems are compared in Table 4-4.

Scrubbers for the removal of fluoride from the gaseous effluent of normal superphosphate plants are sometimes wooden towers that use water sprays to absorb fluorides. Fresh water is reportedly used for the scrubber sprays, and lime is occasionally used to neutralize the liquid effluent.[10] Efficiencies of 95 to 99 percent are reported for this type of fluoride scrubber.[18, 23] Twelve gallons of scrubbing water are used per 1,000 cubic feet of gas per stage.

Manufacturers of commercial scrubbing equipment report that cyclonic-spray scrubbers[16] and ejector-venturi scrubbers have been installed in recent years to increase scrubbing efficiency to as high as 99 percent overall.[17] The fluoride removal efficiency of two cyclonic-spray scrubbers in series is reported to be better than 99 percent. Water is used as the scrubbing liquid at a typical rate per stage

Table 4-4. TYPICAL PERFORMANCE CHARACTERISTICS OF GASEOUS EFFLUENT SCRUBBER SYSTEMS IN NORMAL SUPERPHOSPHATE PLANTS[8,11,16,17,18,20,103,104]

NSP plant size						
Capacity, tons/hr (as is)	15	40	15	40	15	40
Capacity, tons/hr (100% P_2O_5)	3	8	3	8	3	8
Scrubber system parameter	Spray towers		Ejector-venturi scrubbers		Cyclone-spray scrubbers	
Number of stages	2		2		2	
Effluent gas rate, acfm	7,500	14,000	7,500	14,000	7,500	14,000
SiF_4 in feed gas lbs/hr	790-2,100	790-2,100	790-2,100	790-2,100	790-2,100	790-2,100
SiF_4 in feed gas, ppm	6,000 to 16,000	6,000 to 16,000	6,000 to 16,000	6,000 to 16,000	6,000 to 16,000	6,000 to 16,000
gr/scf	12-32	12-32	12-32	12-32	12-32	12-32
Water flow per stage, gal/min	90	168	360 to 450[a]	670 to 840[a]	37.5	70
Water to gas ratio per stage, gal./1000 acf	12	12	48 to 60	48 to 60	5	5
Gas-phase pressure drop, in. H_2O/stage	0.1	0.1	0	0	2-10	2-10
SiF_4 in exit gas, ppm	300 to 600	300 to 600	180 to 480	180 to 480	60-120	60-120
gr/scf	0.6-1.2	0.6-1.2	0.36-0.96	0.36-0.96	0.12-0.24	0.12-0.24
Fluoride removal design efficiency%	95	95	97	97	99	99
Fluoride Removal Oper. Eff. Range %	90-98	90-98	92-98.9	92-98.9	98-99.6	98-99.6

[a] Recirculation pumping rate

of five gallons per 1000 cubic feet of gas. For two ejector-venturi scrubbers in series, the removal efficiency is reported to range from 92 to 97 percent.[10] A typical water rate of 50 gallons per 1000 cubic feet of gas is indicated. The fluoride removal efficiency of a single-stage venturi-separator scrubber is reported to range from 86 to 95 percent.[11]

One venturi-separator scrubber is reported to have been installed to produce fluosilicic acid at concentrations as high as 22 percent using recirculation.[24]

The general configuration of a two-stage ejector-venturi scrubber used in normal superphosphate plants is shown in Figure 4-5 and a cyclonic-spray scrubber is shown in Figure 4-6.

A typical operation for a normal superphosphate plant is two-shift operation at a product capcity range of 6 to 40 tons per hour using Florida phosphate rock as feed. The fluoride removal efficiency must be 98 to 99.5 percent in order to limit emissions to 30 pounds per day.

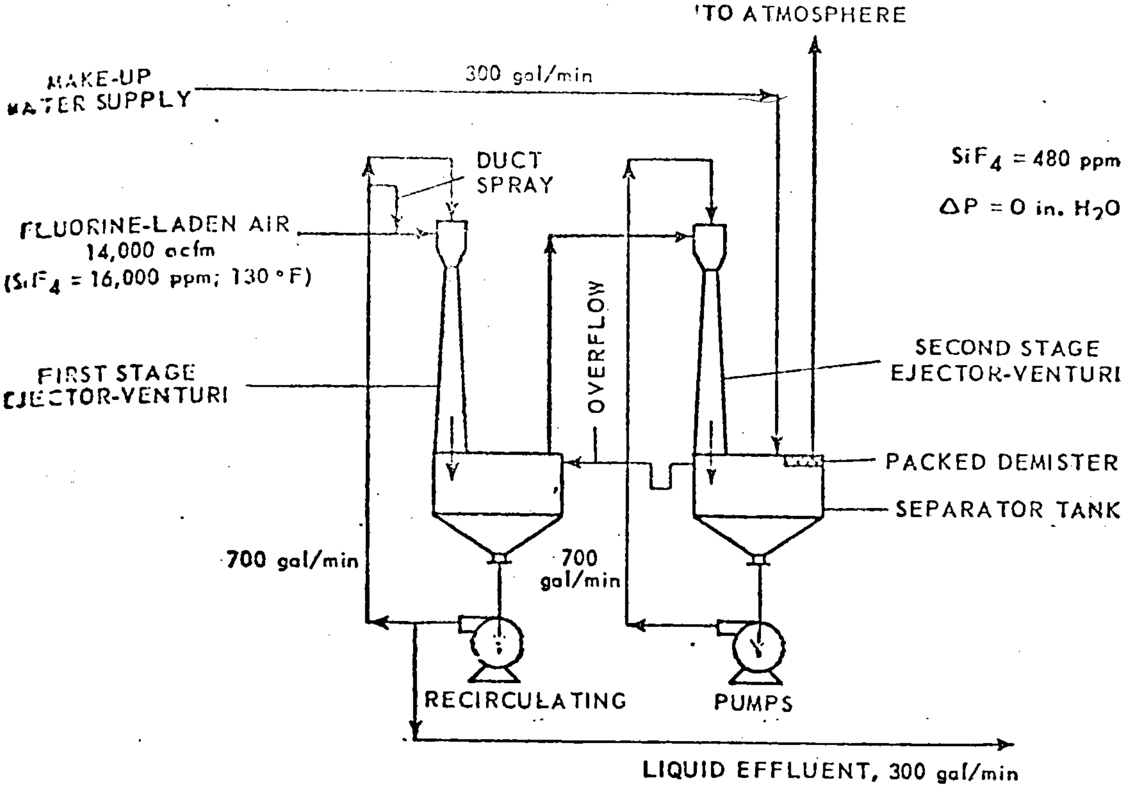

Figure 4-5. Two-stage ejector-venturi scrubber for normal superphosphate plant with capacity of 40 tons/hr, as-is basis.17

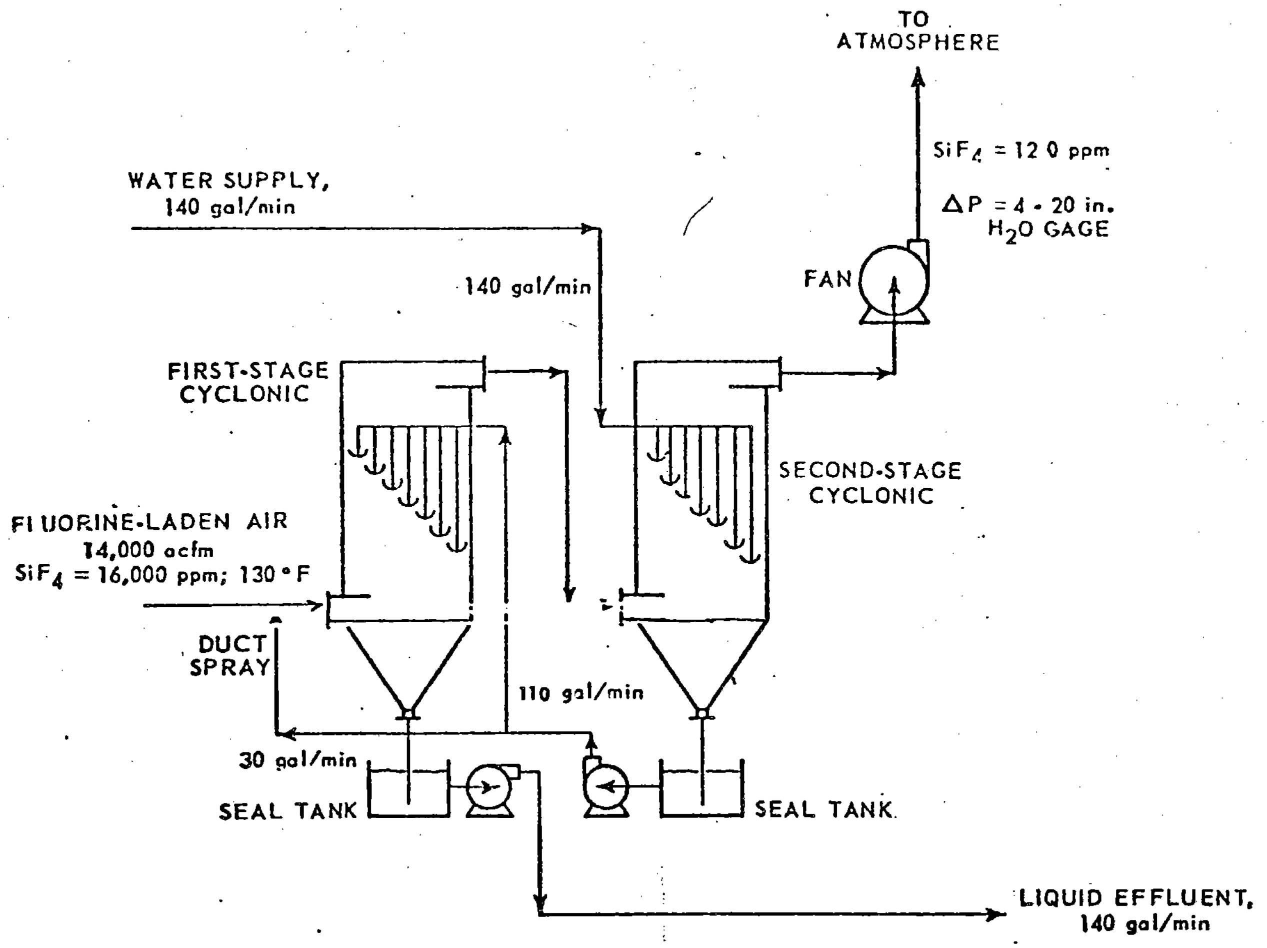

Figure 4-6. Two-stage cyclonic-spray scrubber for normal superphosphate plant with capacit of 4 0 tons/hr, as-is basis. [17]

4.2.5 Costs

The capital and operating costs of fluoride scrubbing systems in normal superphosphate plants are directly related to the volume of effluent gases which must be treated and to the overall fluoride removal efficiency of the scrubbing system.

As shown in Table 4-2, however, the flow rates of gaseous effluent from the mixer, den, cutter, and conveying equipment vary over a wide range for a given plant size. In order to develop a dust relationship between the plant size tons per hour and the costs of control, representative average flow rates for the effluent were used as a guide for the estimation of the size and cost of the pollution control system for a given plant.

The purchase, installed, and annualized costs are shown in Figures 4-7 to 4-12 for two scrubbing systems: two-stage cyclonic spray scrubbers, and two-stage ejector-venturi scrubbers. The costs are for plant capacities ranging from 10 to 60 tons per hour (as-is basis) and are based on the production and volumetric figures shown in Table 4-2, and are for commercially manufactured scrubbing

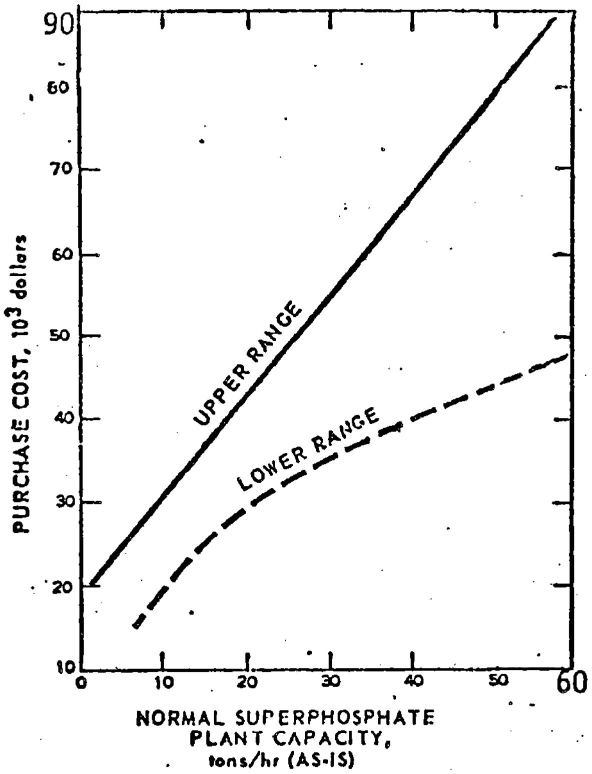

Figure 4-7. Two-stage cyclonic-spray scrubbers with 99 percent efficiency; purchase cost versus plant capacity.[99]

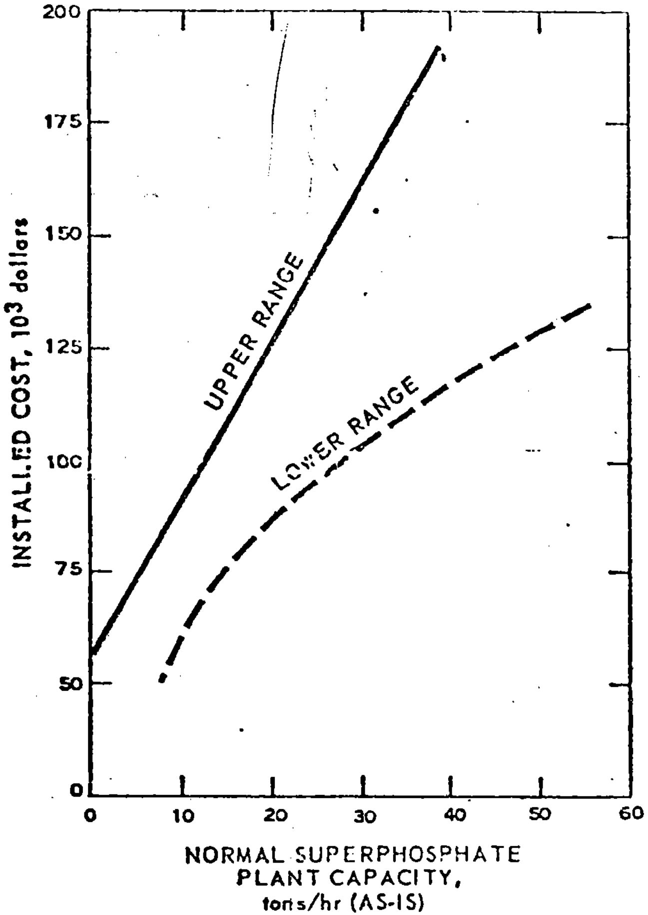

Figure 4-8. Two-stage cyclonic-spray scrubbers with 99 percent efficiency: installed cost versus plant capacity.[99]

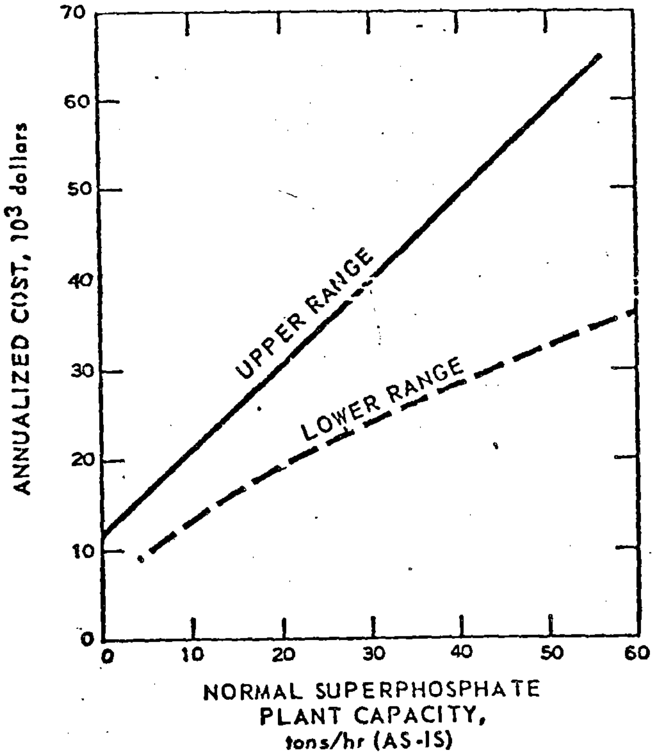

Figure 4-9. Two-stage cyclonic-spray scrubbers with 99 percent efficiency; annualized cost versus plant capacity.[99]

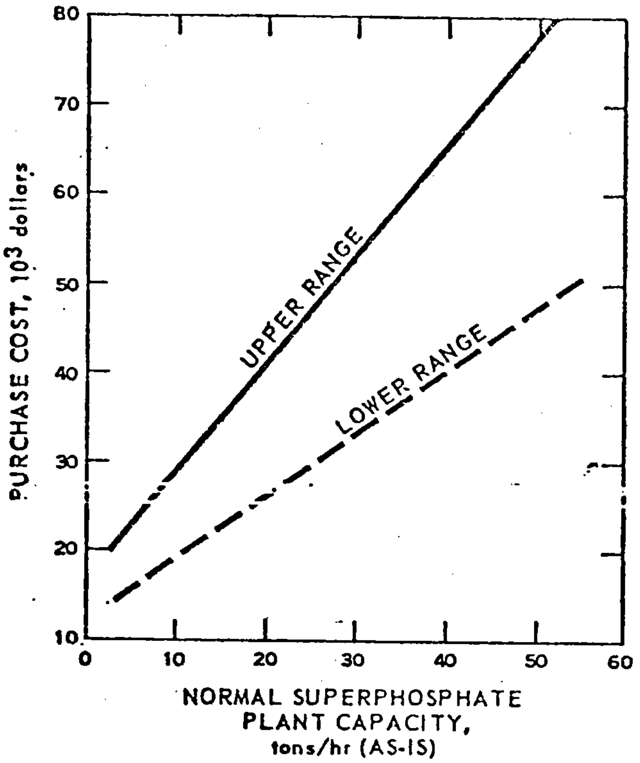

Figure 4-10. Two-stage ejector-venturi scrubber with 99 percent efficiency; purchase cost versus plant capacity.[99]

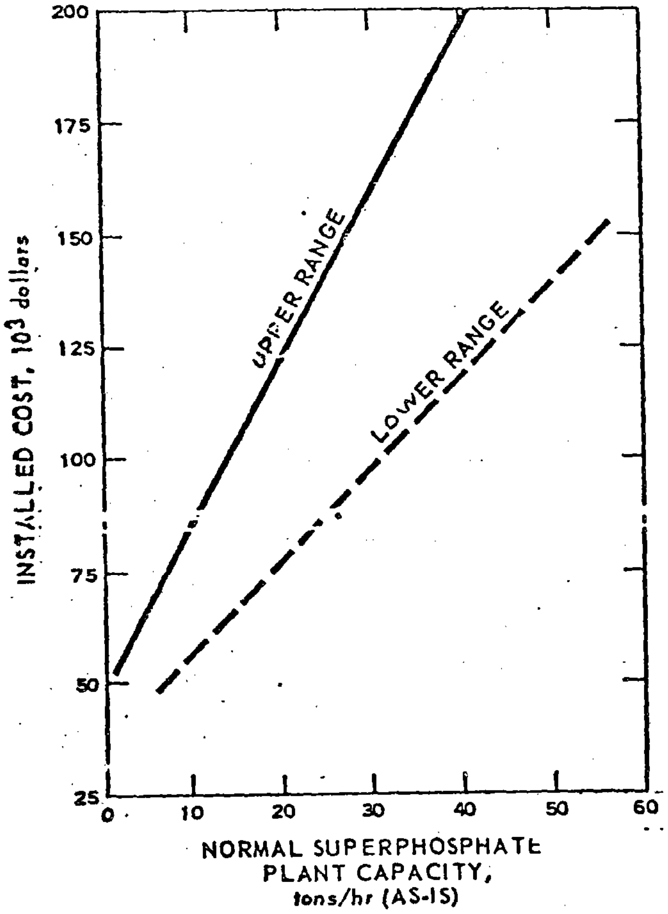

Figure 4-11. Two-stage ejector-venturi scrubber with 99 percent efficiency: installed cost versus plant capacity.[99]

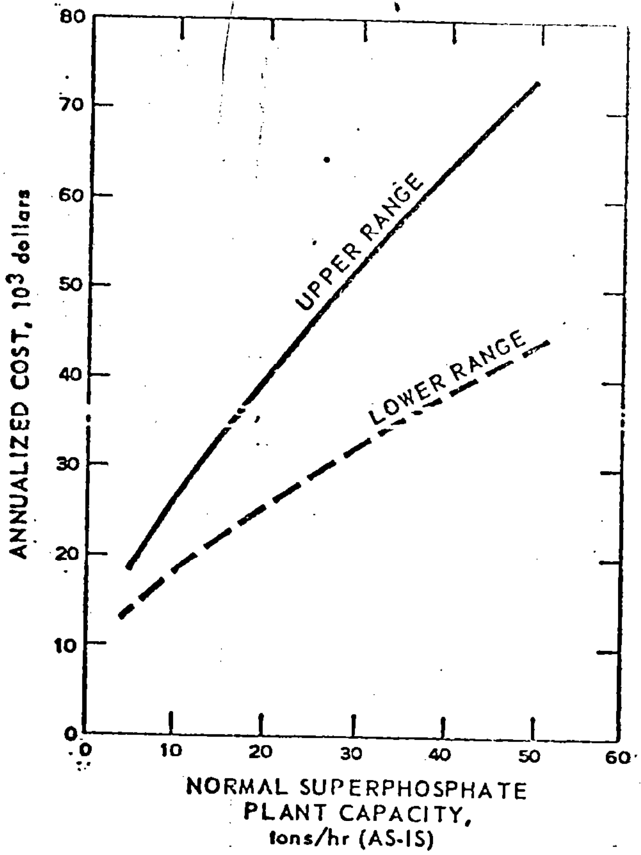

Figure 4-12. Two-stage ejector-venturi scrubber with 99 percent efficiency; annualized cost versus plant capacity.[99]

equipment. Many existing normal superphosphate plants are equipped with locally designed and fabricated scrubbing equipment. The installed costs include the cost of purchase of equipment from vendors plus the costs of erection, piping, instrumentation, engineering, etc. The annualized costs are comprised of the annual fixed charges and variable costs. The fixed charges include annual depreciation taken on a straight-line basis with ten years considered as the average useful life of the equipment. Taxes, insurance, and interest combined have been calculated at the annual rate of eight percent of the installed cost. Variable costs covering electric and water usage were also included; the costs of treating effluent waters from the plant were not included.

4.3 WET-PROCESS PHOSPHORIC ACID

4.3.1 Introduction

Approximately 39 percent of the phosphate rock produced in this country in 1968 was used to produce wet-process phosphoric acid.[3] Of the 333,000 tons of fluorine (3.5 percent) contained in this phosphate rock, about six percent, or 20,000 tons, was evolved in the digesters, and an estimated 100 tons was emitted to the atmosphere.[99] Approximately 77,000 tons of fluoride was discharged with the gypsum waste to settling ponds.[35] Evaporation of the product acid (32 percent P_2O_5 by weight) to a concentration of 54 percent P_2O_5 by weight released 178,000 tons of fluoride, which was absorbed in the barometric condensers, or in the scrubbers, and discharged to the gypsum settling ponds.[35] The balance of the fluorine was in the product acid.[39]

The wet-process phosphoric acid is reacted further with phosphate rock to produce triple superphosphate fertilizer or with ammonia to produce diammonium phosphate fertilizer. Essentially all of the wet-process phosphoric acid is used to produce various phosphate fertilizers.[102]

Various wet processes have been proposed or used commercially for the production of wet-process acid; however, the most commonly used is the dihydrate, or conventional, process in which gypsum is formed as a by-product. This process involves the continuous acidulation, or digestion, of phosphate rock with sulfuric acid which results in a slurry of gypsum and phosphoric acid. The acid produced is separated from the gypsum by filtration. The filtered product acid, at a strength of 28 to 32 percent P_2O_5 by weight, may then be concentrated to 40 or 54 percent P_2O_5, depending on the desired fertilizer end product.[71] In some instances the strong acid is aged and clarified to remove solids that could interfere in the production of certain fertilizer grades, or that would settle on shipment of the acid for consumption outside the plant. Filtered and washed reaction residue solids are transferred as an aqueous slurry to a disposal area, frequently a settling pond. Water is usually recycled to the wet-process acid plant after clarification and cooling in the settling ponds. In a few isolated cases, at plants which are located in coastal areas, sea water is used on a once-through basis in the vacuum cooler and evaporator condensers and the reaction solids are discarded directly into the sea.

The phosphate rock used in wet-process phosphoric acid manufacture is usually ground, and sometimes calcined, prior to the acidulation. Grinding of phosphate rock is required primarily because the rate of attack by acid is related to the surface area of the rock particles. Surface area increases with decreasing particle size. The degree of grinding required may also be influenced by the relative reactivity of the phosphate rock. Certain apatites require very fine particle size for proper digestion and reasonable recovery of P_2O_5 values. "Secondary" phosphate rock for use in the manufacture of triple superphosphate (TSP) is also finely ground.

Calcination of phosphate rock is sometimes used to reduce the level of certain impurities in the rock. Some sedimentary phosphate rocks contain organic impurities that cause odor and foaming problems and may hamper the filtration and concentration steps of the process; also, high carbonate content in the rock is undesirable since carbon dioxide is liberated in the digestion reactions which induces foam generation.

A typical process flow diagram for wet-process phosphoric acid production, 500 tons per day (P_2O_5) is shown in Figure 4-13.[25,33]

4.3.2 Emissions

Fluorides are emitted from virtually all manufacturing operations that involve phosphate rock. Dust particles are released in the handling and treatment of the rock prior to actual processing. Gaseous fluorides are evolved in the manufacture and concentration of phosphoric acid. Mists with dissolved fluorides and phosphoric acid may be released from evaporators and scrubbers. Leaks or spillages of waste water solutions may occur. Most significant is the evolution of silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF) vapors from waste process water streams. These streams are fairly dilute water solutions of fluosilicic acid (H_2SiF_6) and its sodium and potassium salts.

The production of wet-process phosphoric acid in the United States in 1968 amounted to 2,979,000 tons P_2O_5, up 19.5 percent from 1966 and down 17.1 percent from 1967.[3] Based on this production rate and the emission factors stated in Section 4.3.3.2, an estimated 2,000 tons of fluorine was emitted in the gases released to the atmosphere

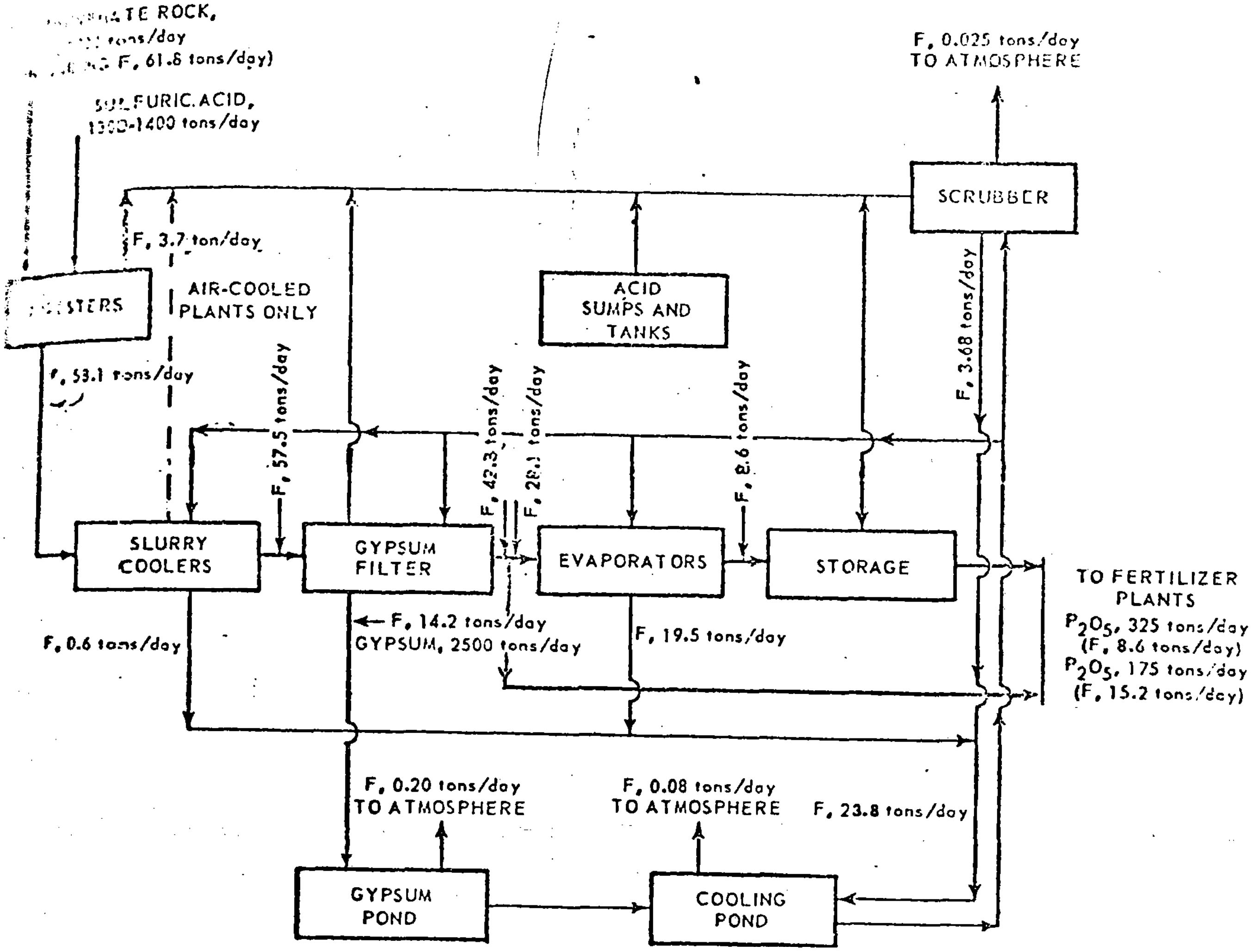

Figure 4-13. Block flow diagram for a wet-process phosphoric acid plant.[25 33]

from wet-process phosphoric acid plants and ponds in 1968.[4] The emission of fluoride particulates for the same year is estimated as follows: handling and treatment, 60 tons fluoride; and shipping and unloading, 923 tons fluoride (estimated as 0.2 percent of consumption of rock containing 3.5 percent F by weight).

The potential atmospheric emission of fluorides is much greater since the installed capacity of the wet-process phosphoric acid industry in 1968 was 6,881,000 tons P_2O_5.[37, 39, 46] Table 4-5 shows the geographical distribution of wet-process plants in the United States and the potential emissions from them.

4.3.2.1 Handling and Treatment of Phosphate Rock - Dusts containing three to four percent fluorine are released in the handling of ground and unground rock and in drying, grinding, and calcining operations. Fluoride as gaseous HF may also be released during high temperature calcining.[29] Dust losses in the shipment, unloading, and transfer of unground rock depend largely on the screen analysis of the rock as well as on the methods of handling employed, and normally amount to 0.1 to 0.5 percent of a shipment. Storage and reclamation of unground rock is virtually a

Table 4-5. WET PROCESS PHOSPHORIC ACID PLANTS IN THE UNITED STATES: LOCATIONS, CAPACITIES[37], POTENTIAL FLUORIDE EVOLUTION[39], AND EMISSIONS[46]

State	Capacity tons/yr P_2O_5	Potential Fluoride[c] evolution tons/yr[a]	Atmospheric Emissions tons/yr[b]
Arkansas	50,000	400	30
California	70,000	500	40
Delaware	33,000	200	20
Florida	3,165,000	23,000	1,930
Idaho	590,000	4,300	360
Illinois	658,000	4,800	400
Indiana	30,000	200	20
Iowa	170,000	1,200	100
Louisiana	960,000	7,000	600
Minnesota	30,000	200	20
Mississippi	120,000	900	70
Missouri	100,000	700	60
Oklahoma	30,000	200	20
North Carolina	375,000	2,700	230
Texas	400,000	2,900	240
Utah	100,000	700	60
	6,881,000	49,900	4,200

[a] Evolution based on 14.5 pounds F per ton P_2O_5. Assume no dust loss.

[b] Emissions based on 1.22 pounds F per ton P_2O_5 of which the uncontrolled emissions from gypsum and cooling ponds amounts to 1.12 pounds F per ton P_2O_5.

[c] Fluoride which is captured by water in barometric and vacuum condensers is not included.

dust-free operation when covered storage and fabric filters, designed for collecting two to four pounds of dust per ton of rock handled, are provided.[39] Dust from open storage in piles, however, may amount to several percent due to wind losses.[48]

Transfer, storage, and reclamation of ground rock are inherently dusty operations because of the fineness of grind and the frequent use of fluidized conveyors. Fabric filters used for this service are commonly designed to remove dust burdens of eight pounds per ton of rock handled, with dust loadings in the range of 30 to 60 grains per cubic foot of air effluent.[39]

Dust evolution from dryers and grinding mills after primary collection in dry cyclones is on the order of 10 to 30 pounds per ton of rock for dryers, and 15 to 40 pounds per ton of rock for grinding mills.[37,39]

Calcination for the beneficiation of phosphate rock takes place in rotary kilns or multi-hearth fluid bed calciners at temperatures of 1200 to 2000 °F with the normal range being 1400 to 1500 °F. At these temperatures, significant defluorination does not take place and fluorides are evolved only as dusts in the calciner off-gases at loadings in the range of 1.5 grains per cubic foot.[11,37]

Investigations have shown no evolution of fluoride gases during short residence time at 1500 °F. At 2000 °F, only three percent of the original fluorine evolves as a gas.[29] At temperatures greater than 2000 °F, thermal defluorination occurs and fluoride evolves principally as gaseous HF in concentrations of 23,500 to 94,000 ppm F by volume.[11] This effect is utilized in the defluorination of animal feeds and is described elsewhere in this report.

4.3.2.2 Manufacture of Wet-Process Phosphoric Acid - During the manufacture of wet-process phosphoric acid, from 3 to 12 percent of the fluorine present in the rock will appear in the gas streams as SiF_4 from the digesters, vacuum cooler tanks, and filter, while the balance of the fluorine will be distributed between the solids precipitated and the phosphoric acid generated by the acidulation reaction. Further evolution of fluoride occurs in the evaporators where the digester acid containing 28 to 32 percent P_2O_5 is concentrated to 40 to 54 percent P_2O_5.

The amount of fluoride evolved from the process is influenced by the type of rock consumed and the processing techniques applied. Typical fluorine content of phosphate rock varies from 1.3 to 6.7 percent by weight, depending on its origin, but for most phosphate rocks in this country the fluorine content range is 2.9 to 3.9 percent.[40] The distribution of fluorine among the reaction products is influenced by the concentration of the phosphoric acid product, the temperature at which acidulation takes place, and the presence of sodium and potassium salts in the digesters which may precipitate acid fluorides, and the amount of iron, aluminum and silica in the phosphate rock. At higher temperatures and acid concentration, fluoride evolution increases. Typical distribution among reaction products of the fluorine contained in rocks found in the United States is shown in Table 4-6.[31]

Other pollutants, primarily sulfur oxides, are emitted during the manufacture of phosphoric acid and normal superphosphate. The National Air Pollution Control Administration has published information on the control of sulfur oxide emissions.[69]

Table 4-6. 1968 DISTRIBUTION OF FLUORINE AMONG WET-PROCESS PLANT REACTION PRODUCTS (31,40)

	Total Fluoride Expressed as	
	F, lb/ton P_2O_5	F Distribution, % of Total
Rock[a]	236 - 258[b]	100
Reactor gases	9 - 20	4 - 8
Reaction solids	47 - 116	20 - 45
Product acid (30% P_2O_5)	118 - 177	50 - 75

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[a] Typical fluorine to P_2O_5 ratio for commercial rocks is 0.11 to 0.12.

[b] Based on 93 percent average P_2O_5 extraction from rock.

The concentration of fluoride in the reactor off-gases will depend on the type of cooling used in the plant. If the reactors are air-cooled the fluoride loading, as SiF_4, in the off-gases will range from 1900 to 3800 ppm,[38] whereas with vacuum flash cooling, the concentration range will be 9400 to 23,500 ppm.[11] Small amounts of unreacted rock are also present, normally in concentrations of 0.8 grains per cubic foot or less.[50]

Although the filtration and storage of wet-process acid releases very little SiF_4, vented effluents must be scrubbed in order to meet certain emission standards. Typical SiF_4 loadings of these gases are 500 to 1500 ppm for filtration and 150 to 500 ppm for tankage. Quantitatively, these sources amount to less than 1.0 percent of the fluorine content of the rock.[43] The fluoride appears as H_2SiF_6 in recirculated pond water.

4.3.2.3 Concentration of Wet-Process Acid - Wet-process phosphoric acid may be concentrated by vacuum evaporation, submerged combustion, or by hot gases in wetted wall or spray tower concentrators. The most common method used in this country is vacuum concentration, which is favored by the availability of byproduct steam from companion sulfuric acid plants.

Evaporation of wet-process acid from 30 to 40 or 54 percent P_2O_5 releases substantial quantities of fluoride as HF and SiF_4 gases. Vacuum concentration to 40 percent P_2O_5 may release up to 62 pounds of fluorine per ton of P_2O_5,[35] while evaporation to 54 percent P_2O_5 can release up to 120 pounds of fluorine per ton of P_2O_5,[35] or approximately 40 percent of the fluorine present in the rock. In the case of submerged combustion units, concentration to 54 percent P_2O_5 may release 130 to 150 pounds of fluorine per ton of P_2O_5 for a Florida rock acid.[51] The evolution of fluoride gases on evaporation of wet-process phosphoric acid is influenced by the fluosilicic acid content of the evaporator feed and by the desired concentration of the phosphoric acid produced. An increase of either factor favors the release of fluoride.

The loading of fluoride in the concentrator off-gases may vary from 0.1 to 5.0 percent[39] fluoride by weight for vacuum evaporators, depending on the number of stages of evaporation used and the concentration of the phosphoric acid in a given stage. For submerged combustion or hot gas evaporators on 54 percent P_2O_5 service, the effluent gas loading is usually on the order of 1.0 to 1.4 percent[39,52] fluoride by weight because the combustion products dilute the evaporator off-gases.

The balance of the fluorine remains in the concentrated acid and is partially volatilized in the further concentration of phosphoric acid to superphosphoric acid or in the manufacture of fertilizers.

4.3.2.4 Waste Disposal - Wet-process phosphoric acid plant wastes include filtered reaction solids, largely gypsum, and water effluents from coolers, condensers, evaporator condensers and scrubbers. The gypsum solids contain from 20 to 45 percent[40] of the fluorine in the phosphate rock mostly as sodium and potassium fluosilicates (Na_2 or K_2SiF_6). The water effluent normally contains, as H_2SiF_6, 30 to 60 percent[40] of the fluorine in the rock. If fluorine recovery is provided in the evaporators, however, the amount carried over into the water may drop to 5 to 15 percent.

As previously mentioned, plants located in coastal areas sometimes pump gypsum wastes directly into the sea and use sea water on a once-through basis for cooling, scrubbing, etc. Where tidal flows are favorable, this practice has not been reported as presenting a pollution problem. In the future, more stringent examination of this practice may lead to its prohibition. The majority of wet-process plants must utilize gypsum settling and cooling ponds which are operated separately or combined. Water is conserved by continuous recirculation from the ponds to the wet-process acid plant and associated fertilizer units. The fluoride content of these ponds, particularly that of gypsum ponds, increases steadily until values of 3000 to 5000[35,54] ppm F by weight in the liquid phase are reached at the end of three to five years. At this time the build-up ceases and the fluoride input is balanced largely by the precipitation of fluoride-calcium and fluoride-silica complexes. In addition, some seepage, adsorption by gypsum, and direct release of fluorides to the atmosphere takes place.[36,54] The dissolved fluorides in pond water exert partial pressures that have been estimated[11,54] as follows: partial pressure of SiF_4 = 0.00007 to 0.0001 mm Hg; and partial pressure of HF = 0.0008 to 0.001 mm Hg.

Studies of the surface of a gypsum pond indicated a fluoride emission factor of at least 0.16 pounds of fluoride per acre per day.[36] Other studies indicate that the average fluoride emission factor is 1.60 pounds per acre per day and varies with temperature over a range of 0.41 to 1.82 pounds per acre per day.[68] Gypsum ponds are designed on the basis of at least 0.5 acre per ton of P_2O_5 produced daily;[55] thus the emission of fluorides that may be expected from gypsum ponds is estimated at 0.80 pound of fluoride per ton of P_2O_5, after the pond water is saturated with fluorides. Although no data are available on fluoride losses from associated cooling ponds, the emission factor may be assumed to be similar to that of gypsum ponds. Acreage requirement for cooling ponds is based on a minimum of 0.2 acres per ton of P_2O_5 per day[56] and are considered for weather conditions similar to Florida. This represents an additional emission of at least 0.32 pound of fluorine per ton of P_2O_5.

$\left(\frac{1\ \text{ton}\ P_2O_5}{.5\ \text{acre}}\right)\left(\frac{1.6\ \text{lb}}{\text{ton}\ P_2O_5}\right)$

$\frac{.5\ \text{acre}}{\text{ton}\ P_2O_5}$

In some special situations, normal soil conditions may be inadequate for the precipitation of the fluorides in the water percolating from gypsum settling and cooling water recirculation ponds. As noted in Section 4.3.3.4, the fluorides may be neutralized with limestone and lime. Occasionally, the water recirculated to the scrubbers is treated with limestone. Limestone treatment of wastes and scrubber water represents a significant operating expense. One plant indicates a fluorine evolution from their gypsum pond of approximatly 2.0 pounds of fluorine per acre at 80 °F.[68] The annual cost of liming an 80 acre pond, to pH 4 is estimated to be \$46,000.[68]

Liming to a pH of 9 is necessary to reduce the dissolved fluoride concentration to 1 ppm by weight. This neutralization, which is entirely for the purpose of avoiding water pollution, has an operating cost of about \$160,000 per year, in addition to the initial capital cost of \$300,000 per year for a plant producing 200 tons of P_2O_5 per day.[70]

4.3.3 Control Techniques

4.3.3.1 Phosphate Rock Dusts - The atmospheric emission of water-insoluble fluorides is not subject to stringent codes such as those applied to water soluble and gaseous fluorides emitted from fertilizer complexes. The control of dusts from the treatment and handling of phosphate rock is practiced in varying degrees from plant to plant to avoid an industrial hygiene problem inside the plant, an air pollution problem outside the plant, and to prevent the loss of a valuable raw material. Dry cyclones, fabric filters, and electrostatic precipitators are used either alone or in combination for the recovery of phosphate rock dust. Wet scrubbers are used to control the atmospheric emission of rock dust.

Dry cyclones are normally used in drying, grinding, and calcining plants only to separate coarse particles and reduce the dust loading going to fabric dust collectors. Dry cyclones, used alone, are inadequate for controlling dust emission.

Electrostatic precipitators used in some drying and calcining operations are normally preceded by dry cyclones. These units can be designed and operated at 98 to 99.5 percent efficiency but are not usually favored because of high installed cost.

Fabric filters are almost invariably used to collect dusts evolved from the transfer and storage of phosphate rock, and evolved in grinding operations. In the latter use, they are usually preceded by dry cyclones to reduce dust loading. These units are preferred because of their relatively low cost and their high efficiency for removing very fine (sub-micron) particles. Fabric filter collection efficeency is normally above 99.5 percent[41] and not uncommonly in the 99.9 percent range. These units are also used in modern grinding plants which combine drying and grinding into a single operation by introducing heated air into the grinding mill and venting the effluent air through the bag collector. The temperature limitation imposed by the bag fabric material precludes the use of fabric collectors in rotary dryers and calciners where the off-gas temperatures are excessive.

Wet scrubbers preceded by dry cyclones are normally used in calciners and dryers and have been used successfully in grinding operations. High-energy venturi scrubbers have the best collection efficiency among the wet scrubbers used for fine particles, usually 95 to 99 percent.[11,38,42]

Venturi scrubbers offer the advantages of handling hot effluent gases at the lowest relative installed cost, and absorbing any HF gas that may be evolved in calcining phosphate rock.

Dust emissions from the various operations involving phosphate rock follow:

Table 4-7. DUST EMISSIONS FROM PHOSPHATE ROCK

Operation	Control System	Efficiency; %	Emissions lb dust / ton rock	Ref.
Drying	Dust cyclones & high energy venturi scrubber	95 to 99	0.15-0.30	49
Grinding	Dust cyclones and fabric dust collectors	99.5 to 99.9	0.01-0.20	39,49
Transfer & Storage	Fabric dust collectors	99.5 to 99.9	0.004-0.010	39

No emission data were found for calciners but the emissions may be assumed to be similar to those for dryers since the process and equipment are similar.

4.3.3.2 Wet Process Plant Off-Gases - The emission of water-soluble and gaseous fluorides from new wet-process phosphoric acid plants that are not part of a fertilizer complex is limited by certain authorities to 0.05 pounds of fluorine per ton P_2O_5 produced, which is equivalent to 0.02 to 0.025 percent of the fluorine present in the phosphate rock.[84] For older plants, the emission factor is limited to a maximum of 0.1 pound of fluorine per ton P_2O_5 produced. When a wet-process plant is part of a fertilizer complex, the emission of fluorine from the complex is limited by certain authorities to 0.4 pound of fluorine per ton P_2O_5 produced. The owner of the fertilizer complex may choose to allow emissions from the wet-process acid portion of the plant to exceed 0.05 pound as long as the total emission from the complex is kept within limits. In order to meet statutory limitations, absorption efficiencies in excess of 99 percent are required.

Fluoride in effluent gases is normally absorbed in water recycled from gypsum or cooling ponds to prevent contamination of water supplies. In some cases, fluoride from effluent gases is absorbed by solutions of fluosilicic acid with strengths under 10 percent by weight in the first stage of a multiple-stage system.[57]

The number of transfer units required for the absorption of a gaseous substance in a lean system can be determined[11] by the equation: $N_{og} = \ln \dfrac{Y_1 - Y_e}{Y_2 - Y_e}$

where Y = concentration of substance in gas phase at inlet 1, and outlet 2, in mol percent, and

Y_e= concentration of substance in gas phase in equilibrium with absorbing liquor, mol percent.

N_{og}= number of transfer units based on an over-all-gas-phase driving force.

This equation is valid where there is no significant change in the liquor concentration as a result of absorption. As may be anticipated from the above equation, when recycled pond water is used as scrubbing liquor, the number of mass transfer units required, and particularly for high efficiencies of absorption, depends on the partial pressure of fluorides in the pond. As many as 8.0 transfer units have been required in some plants.[58] If the fluoride content of the pond is present largely as HF, the recycled water may require neutralization to achieve low fluoride concentrations in the stack gases.[58] Failure to reduce the fluoride content of the recycled water fed to the scrubbers can result in the stripping of fluorides from the recycled water and a subsequent increase in the fluoride content of stack gases.

Types of scrubbers that have been successfully used in wet-process phosphoric acid plants are venturi, wet cyclonic, duct sprays, packed bed, and combinations of two or more types. Table 4-8 lists the characteristics of these scrubbers, and Table 4-9 lists the relative power requirements of packed, spray, and venturi scrubbers for the absorption of SiF_4 and HF for a service of three transfer units.

Absorption efficiencies of 90 to 95 percent can be readily achieved by integral-type scrubbers, i.e., venturi, cyclonic, and spray types, since the number of transfer units required is 2.3 to 3.0. When pond water is used as the absorption medium, however, efficiencies in excess of 99 percent can only be met by series and combination systems. Combination systems, which are favored in recent practice, consist of an integral scrubber for primary contact, because of the high solids handling requirement, and of a secondary or tail-gas scrubber which may be either of the integral or of the packed differential type. Packed units may be favored, since the secondary scrubber requires a high number of transfer units because its inlet gas has a

Table 4-8. CHARACTERISTICS OF SCRUBBERS USED IN WET-PROCESS PLANTS[59]

Equipment	Pressure drop, in H_2O	Liquid requirement, gal/min-1000 cfm	Liquid pressure required, psig	Transfer units	Solids handling capacity
Venturi					
Gas-motivated					
Nozzle injection[a]	High, 10-50	3-15	15-40	2-3.5	High
Entrained liquid[b]	High, 10-50	3-15	1-3	2-3	High
Liquid motivated	Low, 0	3-15[c]	20-60	2-3	High
Cyclonic (wet)	Moderate, 2-10	5-15	40-100	2-3	High
Spray					
Crossflow	Low, 0.1	3-10	40-60	0.2-0.5	High
Cocurrent	Low, 0.1	3-10	40-60	0.3-0.7	High
Countercurrent	Low, 0.1	3-10	40-60	0.4-1.0	High
Packed section					
Crossflow	0.1-0.5/ft packing	1-5/ft packing	1-2	0.2-0.5/ft	Medium
Cocurrent	0.1-0.5/ft packing	7-15/ft	1-2	0.1-0.5/ft	Medium
Countercurrent	0.2-1.0/ft packing	10-20/ft	1-2	0.2-1.0/ft	None
Wetted pads	2-5/4-in. depth	2-15	10-20	2-3	Low
Turbulent contact (Floating ball)	Moderate, 3-15	10-15	2-15	2-4	Medium

[a] Liquid injected by spray nozzles.

[b] Liquid entrained by weir overflow.

[c] Liquid makeup requirement. Actual recirculation flow [illegible]

relatively low fluoride concentration. Packed demisters are usually used prior to the scrubbing system fan to eliminate the entrainment of pond water in the effluents to the atmosphere. Pressure drop across these demisters is normally in the range of 0.5 inches of water.

Table 4-9. RELATIVE POWER CONSUMPTION FOR ABSORPTION OF SiF_4 AND HF.[60]

Type of Equipment	SiF_4	HF
Packed	1	- *
Spray	1.5	1
Venturi	7	10

* No data available.

The number of transfer units that an integral-type scrubber may supply is limited to an economic maximum because of the dependence of absorption efficiency on power supplied to the liquid or gas phase. This economical maximum has been estimated to be at 3.0 transfer units for cyclonic scrubbers, 3.5 for venturis, and 4.0 for turbulent contact scrubbers.[30] Spray scrubbers used as primary scrubbers in combination or series systems are further limited to the countercurrent spray pattern which prevents the gas stream from bypassing the liquid contact area. Packed units, regardless of the type of packing, are limited to secondary scrubbing duty because of their low capacity to handle solids. They are further limited to cocurrent and cross-flow spray patterns because the deposition of silica, as a result of SiF_4 absorption, causes buildups in the support plate and packing.

The most significant operating problem common to all types of scrubbers in SiF_4 absorption service, particularly in the case of packed units, is that of the scaling and eventual plugging of the packed bed. When SiF_4 is absorbed in water, hydrated silica precipitates. The nature of the precipitate, in the presence of HF, depends on the temperature of absorption. Below 125 °F the precipitate may be in the form of a gel or soft fibers, but at higher temperatures it can be granular with particles cementing together and accumulating in the equipment. Packed scrubbers are commonly and successfully used for absorbing SiF_4 with careful attention to irrigation. Accumulated deposits of precipitated silica must be removed periodically from the packing and grids.

Plugging of spray nozzles due to solids in the scrubbing liquid is minimized with the use of strainers in the pond water feed lines to the scrubbers.

4.3.3.3 Concentration of Wet-Process Acid - The fluoride evolved in the concentration of wet-process phosphoric acid is absorbed by cooling water in the direct contact barometric condensers used in vacuum concentration, or removed by conventional scrubber systems in the case of submerged-combustion and wetted-wall units.

Vapors from concentrators are the most attractive source for recovery of fluoride from wet-process plants since as much as 35 percent of the fluorine (as SiF_4) in the rock is evolved.[50] In the case of vacuum concentration, up to 95 percent of the fluoride evolved may be recovered[33] as a usuable product by any one of several patented methods. The most frequently used process employs spray towers located between the concentrator and the barometric condensers with fluosilicic acid as the absorption medium.[32] Part of the spray liquid is withdrawn as product while the balance plus make-up water is recycled to the spray tower. The concentration of fluosilicic acid produced is in the range of 12 to 25 percent by weight, depending on its intended use. As far as is known there has been no recovery of fluoride as a by-product from submerged-combustion evaporator off-gases,[61] probably because the economical recovery of a concentrated fluosilicic acid would be made difficult by the dilution of fluoride vapors with combustion products.

Fluoride emissions from vacuum evaporators are negligible since virtually all the fluoride evolved is absorbed in the vacuum systems. The published data on emissions from hot-gas or submerged-combustion units are meager at best. However, calculations based on published values for stack loadings of 10 mg fluorine per cubic meter,[37] and material and heat balances for submerged combustion units[52] indicate emissions of 0.036 pound or more of fluorine per ton of P_2O_5 for natural gas-fired units, and 0.052 pound or more of fluorine per ton P_2O_5 for fuel oil-fired units. In order to limit emissions to these values, absorption efficiencies must exceed 99.9 percent and equipment design requires 7.6 to 8.1 transfer units, since 100 to 120 pounds of fluorine per ton of P_2O_5 are evolved when the acid is concentrated to 54 percent P_2O_5.

4.3.3.4 Gypsum Ponds - Fluoride pollution of surface waters due to the release of gypsum and cooling-pond water does not normally constitute a problem since these waters are treated with limestone and lime prior to release into streams.

The only satisfactory method of treatment for the complete removal of fluoride at present involves two steps, the neutralization and subsequent settling of the precipitated fluorides and phosphates. Lime or lime-slurry is normally used as a neutralizing agent, although finely ground limestone has been used in the first step of neutralization. The first stage of liming precipitates up to 75 percent of the fluorides present and raises the pH to 3 to 4. The second stage of liming precipitates phosphates and additional fluorides so that after settling,the clear effluent contains 10 to 20 ppm fluorides and has a pH of 5 to 6.[62]

Atmospheric pollution as a result of the partial pressures of fluorides in gypsum pond waters has been quantified only recently[36,68] and is not presently controlled.

4.3.4 Costs

The purchase, installed, and annualized costs of fluoride scrubbers for wet-process phosphoric acid plants vary proportionately with fluoride absorption efficiency and volumetric flow rate of gaseous effluents. An indication of the variation of these costs with fluoride removal efficiency is outlined in Table 4-10 for a typical scrubber installation with two wet cyclonic units. Since efficienies in excess of 99.4 percent are required to meet present emission standards,[84] the most significant scrubber cost factor is the volumetric gas flow rate. This factor is reduced to the lowest possible level in present process design techniques. Table 4-11 shows the design volumetric gas flow rate range encountered in plants of different design in which a wide range of gas flow rates is caused by the following factors:

1. Tightness extent of seals on openings in digestion tanks and launders (slurry transfer channels).
2. Size of gypsum filter hoods that may cover the filter entirely or partially.
3. Number of sumps and tanks vented to scrubbers.
4. Plant size; minimum design gas flow rates for plants in the 100 to 300 tons per day P_2O_5 range are slightly higher than those shown in Table 4-11.

The method of cooling digester slurries is particularly significant since vacuum cooling does not contribute to the scrubber gas-handling requirement whereas air cooling may double or triple the volume of gases to be scrubbed in a wet-process plant.

Table 4-10. VARIATION OF CYCLONIC SCRUBBER COSTS WITH ABSORPTION EFFICIENCY[67]

Absorption efficiency, %	Stages	Scrubber purchase cost, $/acfm	Liquid rate, gal/min/1000 acfm
95	1	0.45	4
99	2	0.75	8
99.9	2	1.20	12

Table 4-11. DESIGN DATA FOR WET PROCESS PLANT FLUORINE SCRUBBERS[34,39,66] (1968)

Source	Volumetric gas rate acfm/ton-day P_2O_5	Fluorine evolution lb/ton P_2O_5
Digestion	30 - 90	15 - 20
Filtration	30 - 90	0.6 - 1.5
Sumps and vents	10 - 50	0.05 - 0.10
Air cooling	140	9 - 15

Table 4-12 shows fluoride evolution from and volumetric gas flow rates for submerged-combustion evaporators. The gas rates were calculated from published data on heats of concentration and heat and material balances.[52]

In vacuum, flash cooled, phosphoric acid plants, the digestor off-gases contain a higher concentration of fluorine than gaseous effluents from other sources.[50] These digestor off-gases can be treated separately to reduce the size of the equipment and scrubbing liquor flow rates. Table 4-13 shows a comparison of capital costs and power requirements for a separate, or staged, scrubbing operation versus treatment of a blend of the same gaseous effluents based on total emission of ten pounds of fluorine per day.[11]

The purchase, installed and annualized costs of scrubbers for wet process plants shown in Figures 4-14, 4-15 and 4-16 are based on the staged treatment of gaseous effluents from a vacuum-cooled plant in two stages of wet cyclonic scrubbers for a fluoride absorption efficiency of 99.6 percent. In the development of these costs, it was assumed that the digestion gases to the staged scrubber constitute 40 percent of the combined digestion and filtration gaseous effluents.[34,39] The upper curves shown on Figures 4-14, 4-15

Table 4-12. DESIGN DATA FOR SUBMERGED COMBUSTION EVAPORATORS[39,52] (1969)

Source	Minimum volumetric gas flow rate, Acfm/tons-day P_2O_5		Fluoride evolution lb./ton P_2O_5
	Evaporator	Stack	
Natural gas, 30 tons/day of 54% P_2O_5	117	40	100 - 150
Fuel oil, 30 tons/day of 54% P_2O_5	134	56	100 - 150

Table 4-13. COMPARISON OF INSTALLED COSTS AND POWER REQUIREMENTS[11] BLENDED VERSUS STAGED OPERATION[a] (1969)

	Mass transfer units	Relative installed cost	Relative power requirement
Blended	7.0	1.5	1.7
Staged	8.0	1.0	1.0

[a] In staged operation, the digestor gas effluent is scrubbed separately, then blended with other gas streams and the mixture treated in a subsequent scrubbing stage.

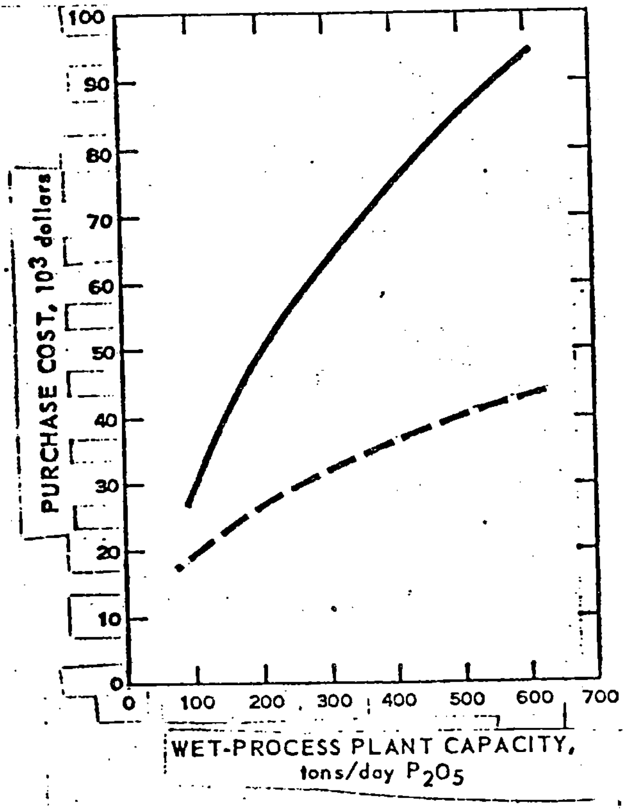

Figure 4-14. Two-stage cyclonic-spray scrubber with 99^+ percent efficiency; purchase cost versus plant capacity (1969).[34,66]

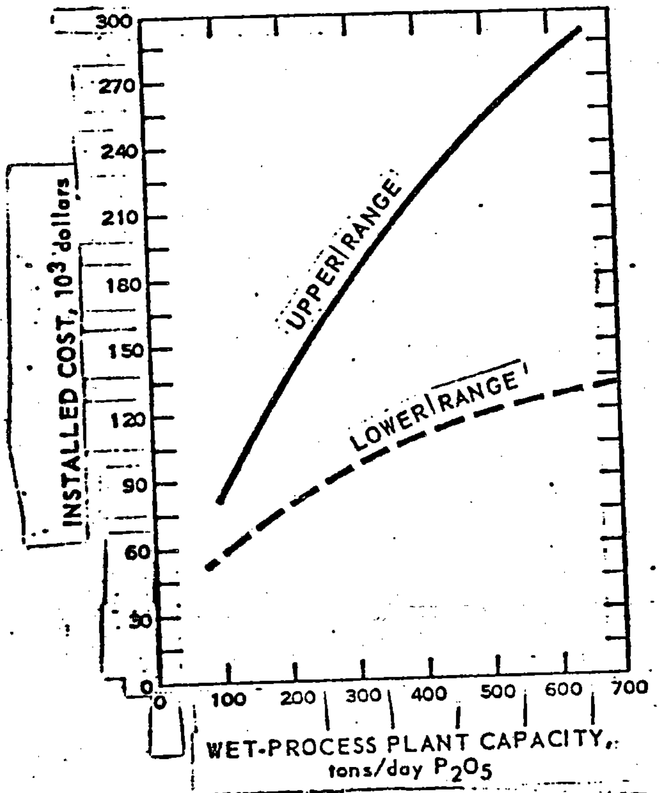

Figure 4-15. Two-stage cyclonic-spray scrubber with 99+ percent efficiency; installed cost versus plant capacity (1969; based on references 34 and 66).[83]

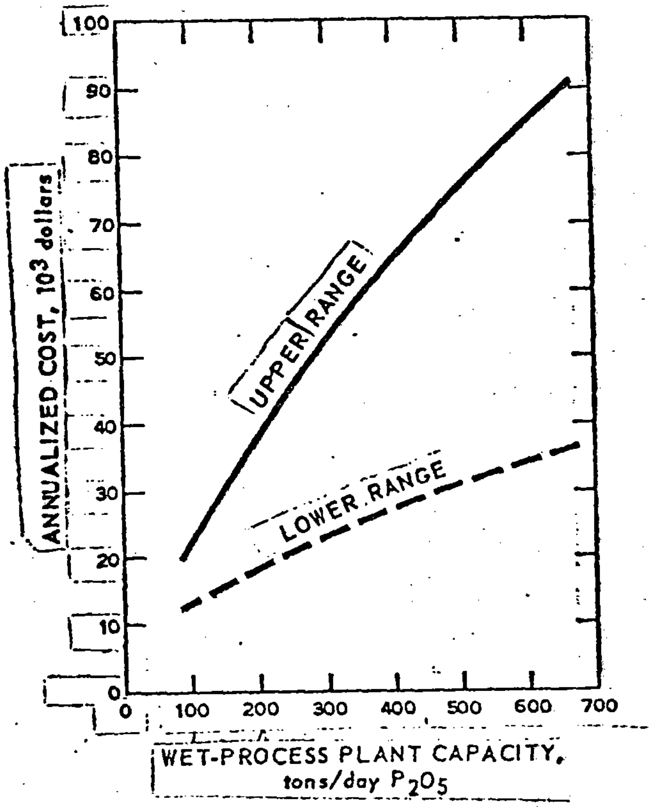

Figure 4-16. Two-stage cyclonic-spray scrubber with 99+ percent efficiency; annualized versus plant capacity (1969).[34,66]

and 4-16 are based on the maximum gas flow rates shown in Table 4-11, whereas the lower curves apply to the minimum gas flow rates given in the same table.

Since several combinations of scrubbers may be used to meet fluoride absorption efficiencies in excess of 99 percent, the purchase , installed and annualized costs shown in Figures 4-14, 4-15 and 4-16 can vary, depending on the particular system used. Table 4-14 lists the estimated relative installed and annualized costs for different scrubber systems operating at approximately 99.5 percent efficiency. More expensive systems with a second stage packed scrubber (differential-type) are advantageous because efficiencies in the 99.9 percent range can be easily achieved at little extra cost, and the system capacity can be moderately, but readily, expanded when required. Higher efficiencies and expanded service cannot be as readily and economically achieved by systems using integral-type scrubbers.

No cost data are given for submerged-combustion evaporators because few plants in this country use this method of evaporation, and their annual capacities are small.

Table 4-14. RELATIVE COSTS FOR DIFFERENT SCRUBBER SYSTEMS[67] (1969)

Type of scrubber		Relative cost	
First stage	Second stage	Installed	Annualized
Wet-cyclonic	Wet-cyclonic	1.0	1.0
Ejector-venturi	Ejector-venturi	.95 - 1.15	1.05-1.30
Wet-cyclonic	Packed, cross-flow	1.18 - 1.30	1.50-1.60
Sprays	Packed, cross-flow	1.30	2.0

4.4 SUPERPHOSPHORIC ACID

Phosphoric acid, in concentrations up to 69 percent P_2O_5 by weight, contains almost all of its phosphorous in the highest degree of molecular hydration, the ortho form.[101] As the P_2O_5 concentration is increased above the 69 percent level, however, molecular dehydration converts ortho molecules to pyro and longer chain forms. The term, "superphosphoric acid" is applied to those concentrated acids that contain a substantial fraction of phosphorus in the converted forms, and in particular to those acids which will flow at moderate temperatures and which contain 68 to 80 percent P_2O_5 by weight, although the more common strength is about 72 percent by weight.

Superphosphoric acid can be manufactured in one of two different ways: by evaporation of 54 percent P_2O_5 wet-process acid or by the control of the degree of hydration in the furnace-acid process.

4.4.1 Emissions

The evolution of fluoride in the production of superphosphoric acid takes place only in processes which involve the concentration of wet-process phosphoric acid, since the furnace method uses fluoride-free elemental phosphorus as raw material.

Two basic processes are used for the concentration of 54 percent P_2O_5 wet-process acid to superphosphoric acid strength: vacuum evaporation, in either forced-circulation or falling-film units, and submerged combustion.

Superphosphoric acids (72 percent P_2O_5), made from feed acids (54 percent P_2O_5) containing 0.5 to 0.8 percent fluoride by weight, usually contain 0.2 to 0.3 percent fluoride.[44,63]

Up to 75 percent of the fluoride present in the feed acid is released, an evolution of 13 to 22 pounds of fluoride per ton of P_2O_5. As in the case of the evaporation of filter acid to 40 or 54 percent P_2O_5, fluoride evolution is in the form of SiF_4 and HF gases, with a substantial portion as the latter. The amount evolved depends on the fluosilicic acid content of the feed acid and the final concentration of the phosphoric acid produced.

The loading of fluoride in the concentrator off-gases will depend on the evaporative process used. Based on the evolution stated above, fluoride loading in the off-gases of a vacuum evaporator has been calculated at 1.4 to 2.4 percent fluoride by weight. Fluoride loadings in the off-gases of a submerged-combustion unit were calculated at 0.35 to 0.65 percent fluoride by weight, based on the above mentioned evolution, with a heat requirement of 3.0 to 3.5 x 10^6 Btu per ton P_2O_5,[64] and the combustion of natural gas of a heat content of 1000 Btu per cubic foot with stoichiometric air.

The atmospheric emission of gaseous fluorides from superphosphoric acid plants is estimated to be an average of 4.0 tons fluoride per year based on the emission factor of 0.025 pound of F per ton P_2O_5 (See Section 4.4.2) and on the installed capacity of the industry as indicated in various sources.[39,27,47]

Table 4-15 shows the geographical distribution of superphosphoric acid plants in the United States and potential atmospheric emissions from them.

Table 4-15. GEOGRAPHICAL DISTRIBUTION OF ESTIMATED 1968 FLUORIDE EMISSIONS FROM SUPERPHOSPHORIC ACID PLANTS[27,39,47]

State	Capacity, tons/Yr.P_2O_5 Total	Capacity, tons/Yr.P_2O_5 Submerged Combustion	Potential emission, tons/yr F	Atmospheric Emissions tons/yr F[b]
Florida	264,000	204,000	1,700 - 2,900	2.6 - 3.9
Idaho	119,000	-	800 - 1,300	-
Illinois	102,000	51,000	650 - 1,100	0.6 - 1.0
North Carolina	102,000	-	650 - 1,100	-
Texas	17,000	-	110 - 190	-
Utah	51,000	-	330 - 560	-
	655,000[a]	255,000	4,240 - 7,150	3.2 - 4.9
		Average	5,500	

[a] Shutdown capacity in 1968: 51,000 tons per year P_2O_5.

[b] Emissions from submerged combustion evaporators only. Fluorides evolved during vacuum evaporation are totally absorbed in condenser water.

4.4.2 Control Techniques

Fluorides released during the vacuum evaporation of 54 percent P_2O_5 acid to superphosphoric grades are readily absorbed by the scrubbing action of the water in the barometric condensers of the vacuum systems with a negligible emission of fluoride to the atmosphere. Fluorides can be recovered in systems identical to those used for concentrating the 32 percent P_2O_5 digester product. The fluoride in the recovery solution contains approximately 75 percent fluoride as HF and 25 percent as H_2SiF_6.[61]

In the case of submerged-combustion evaporation, the off-gases are cleaned not only for fluoride abatement, but also for recovery of P_2O_5, which may be from 1.5 to 5 percent of the input to the concentrator.[65] Present practice favors the use of high efficiency scrubbers, such as venturis or wet cyclones, in series. The first stage recirculates weak phosphoric acid and the second uses water for fluoride removal. The fluoride content of stack gases has been reported to be from 10 to 15 ppm fluoride,[45,65] which represents an emission factor of at least 0.025 pound fluorine per ton P_2O_5. To achieve this emission factor a scrubber efficiency of 99.7 percent is required. Pilot plant tests with woven teflon mesh demisters indicate that they are also effective for the cleanup of gases downstream of scrubbers.[53] These demisters can be expected to exhibit a low pressure drop.

4.4.3 Costs

As in any scrubbing operation, purchased, installed and annualized costs are directly proportional to the efficiency of contaminant absorption and particulate removal, and to the volumetric capacity. The volume of gases from submerged-combustion evaporators depends on plant size, concentration of the feed and product acids, source of feed acid, and on the amount of excess air used in the combustion of fuel.

The dependence of scrubbing costs on fluoride removal efficiency alone cannot be clearly defined because the first stage of the scrubbing system normally recovers P_2O_5 entrained in the concentrator off-gases with only incidental fluoride absorption. The tail gas scrubber in the multistage system is used solely for fluoride removal.

Table 4-16 lists design loadings and volumetric flow rates for scrubbers on submerged-combustion, superphosphoric acid evaporator service. The volumetric flow rates were calculated on the same basis as the loadings and evolutions stated in Section 4.4.1.

The purchase, installed and annualized costs shown in Figures 4-17, 4-18 and 4-19 are based on a single-stage wet-cyclonic scrubber installation used as a tail scrubber in a multiple-stage system where the primary scrubber and associated equipment are considered a process requirement for the recovery of phosphoric acid. The fluoride removal efficiency of the multiple-stage system is calculated to be 99.7 percent, based on a fluoride loading of 15 ppm in the stack effluent.[45] The costs shown in Figures 4-17, 4-18 and 4-19 were developed from equipment capacities based on the volumetric stack-gas flow rates shown in Table 4-12.[67] These are minimum costs; other types of scrubbers, more expensive to install and operate, may be used for the service.

Table 4-16 DESIGN DATA FOR SUBMERGED-COMBUSTION, SUPERPHOSPHORIC ACID EVAPORATOR SCRUBBERS[44,45,63,64,65]

Gaseous effluent source	Minimum Volumetric Gas Flow Rate acfm/tpd P_2O_5	F loading in gases, ppm
Concentrator	80	3,500 - 6,500
Stack	32	10 - 15

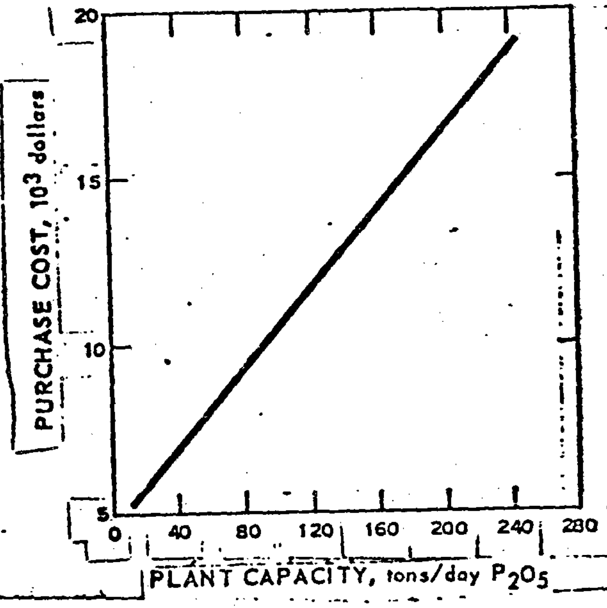

Figure 4-17. Single-stage cyclonic-spray scrubber, with 99 + percent efficiency (two stages), for submerged-combustion superphosphoric evaporators; purchase cost versus plant capacity (1969).[67]

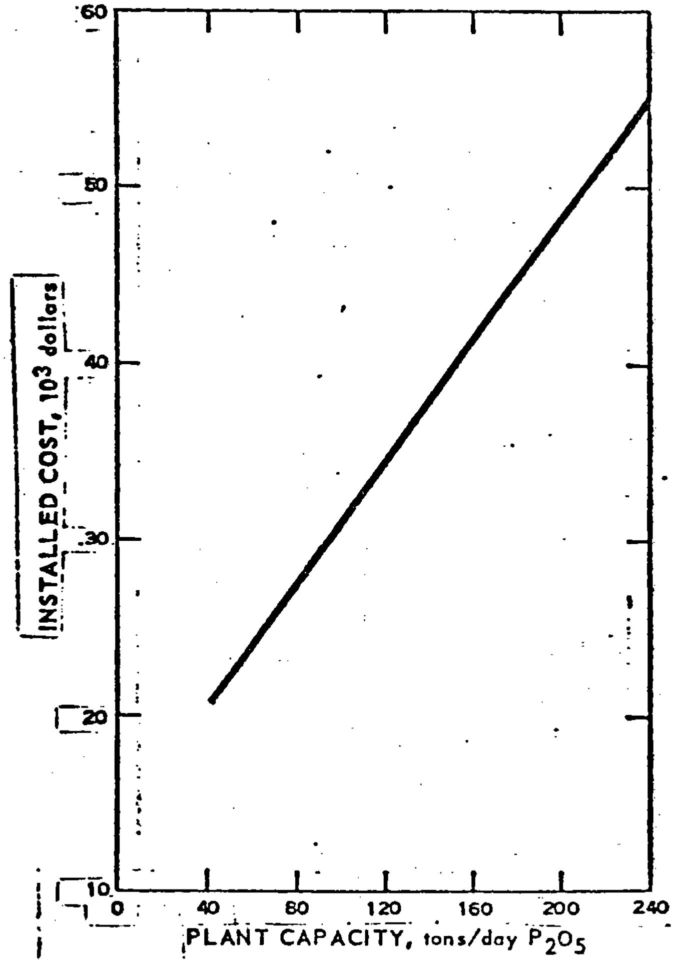

Figure 4-18. Single-stage cyclonic-spray scrubber, with 99+ percent efficiency (two stages), for submerged-combustion superphosphoric evaporators; installed cost versus plant capacity (1969).[67]

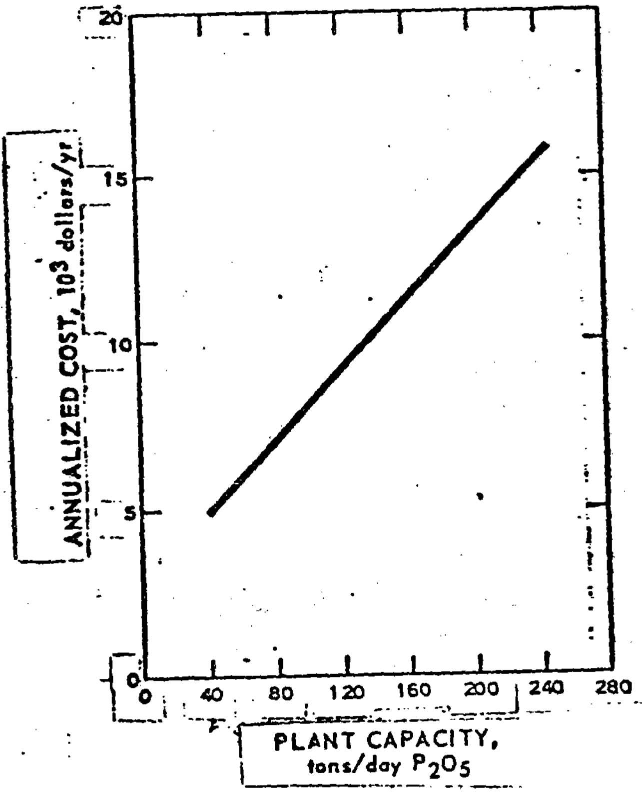

Figure 4-19. Single-stage cyclonic-spray scrubber, with 99+ percent efficiency (two stages), for submerged-combustion superphosphoric evaporators; annualized cost versus plant capacity (1969).[67]

4.5 TRIPLE SUPERPHOSPHATE

4.5.1 Introduction

Triple superphosphate refers to the fertilizer produced by the reaction of phosphate rock with wet-process phosphoric acid. The product contains 40 percent or more of available phosphoric oxide (P_2O_5).[96]

During the acidulation reaction, about 35 to 55 percent of the total fluorine bound in the phosphate rock and in the phosphoric acid is volatilized as gaseous silicon tetrafluoride (SiF_4).[97]

The fluoride (as SiF_4) in the off-gases from triple superphosphate production is removed by scrubbing with water in spray towers, cyclonic-spray scrubbers, and venturi scrubbers.

4.5.2 Process Description

Triple superphosphate, which is manufactured by acidulating phosphate rock with wet-process phosphoric acid, is produced as a granular, or as a pulverized, "run-of-pile" product with a P_2O_5 content of 45 to 47 percent.[96]

There are three principal methods of manufacturing triple superphosphate.[72,73]

1. The Tennessee Valley Authority (T.V.A.) cone process, shown in Figure 4-20, is a continuous process in which dried and ground phosphate rock and wet-process phosphoric acid with a concentration of 50 to 54 percent P_2O_5 are metered in the required proportions into a mixing cone.[25] The resulting slurry drops onto a hooded conveyor belt and rapidly solidifies into a porous mass. A disintegrator at the end of the hooded conveyor reduces the solid raw triple superphosphate into a friable material which is then conveyed to a storage pile to cure for two weeks or more to allow the reactions to approach completion. Cured run-of-pile triple superphosphate is sold in bulk or is granulated in an auxiliary facility.

2. The continuous slurry process, see Figure 4-21, for the manufacture of granular triple superphosphate utilizes wet-process phosphoric acid at approximately 40 percent P_2O_5 concentration.[25] The acid and phosphate rock (dried and ground) are metered into acidulator vessels in the required proportions. The resulting slurry is fed to a granulator along with triple superphosphate fines recycled from the screens.

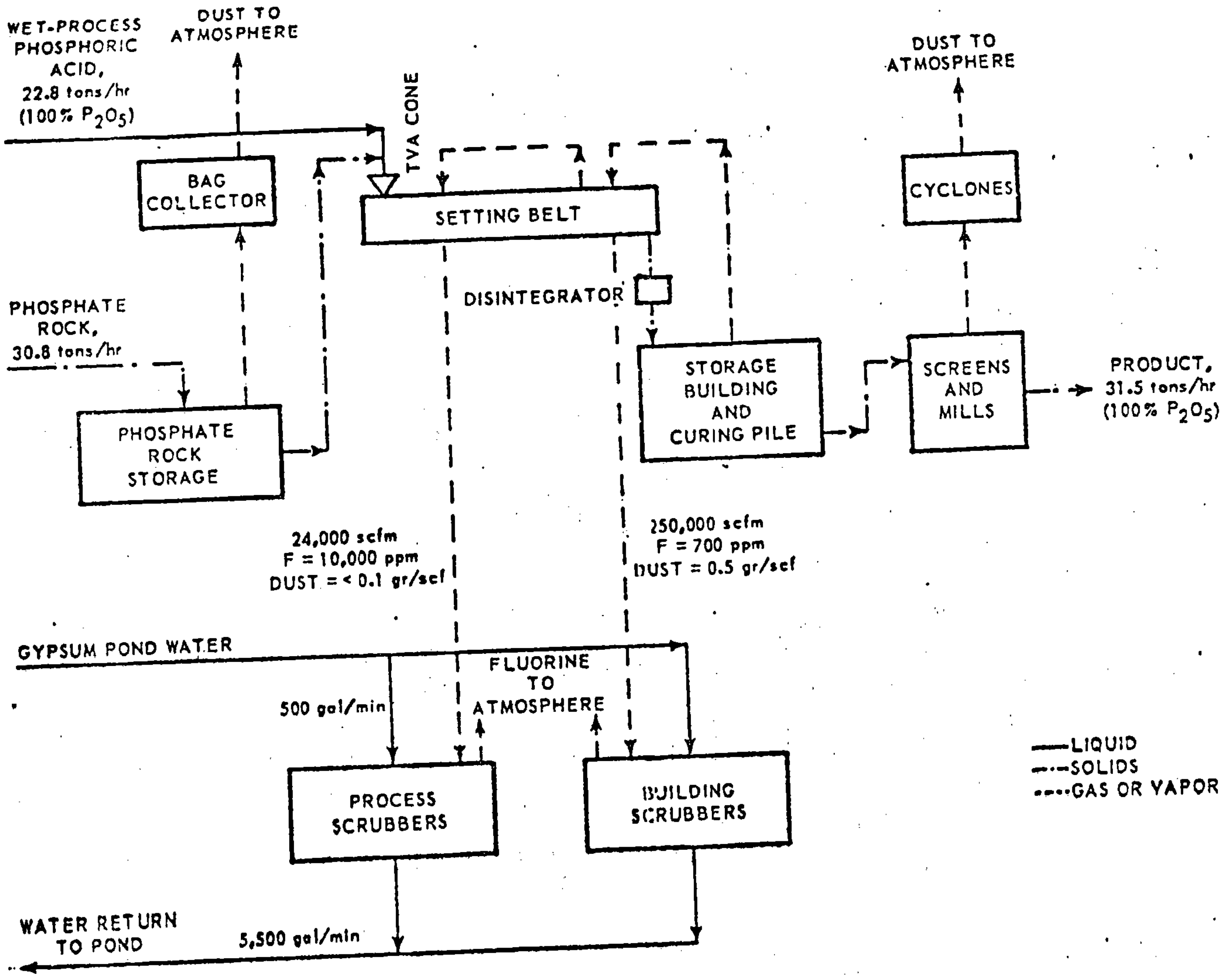

Figure 4-20. TVA cone and setting belt plant for production of run-of-pile triple superphosphate.[25]

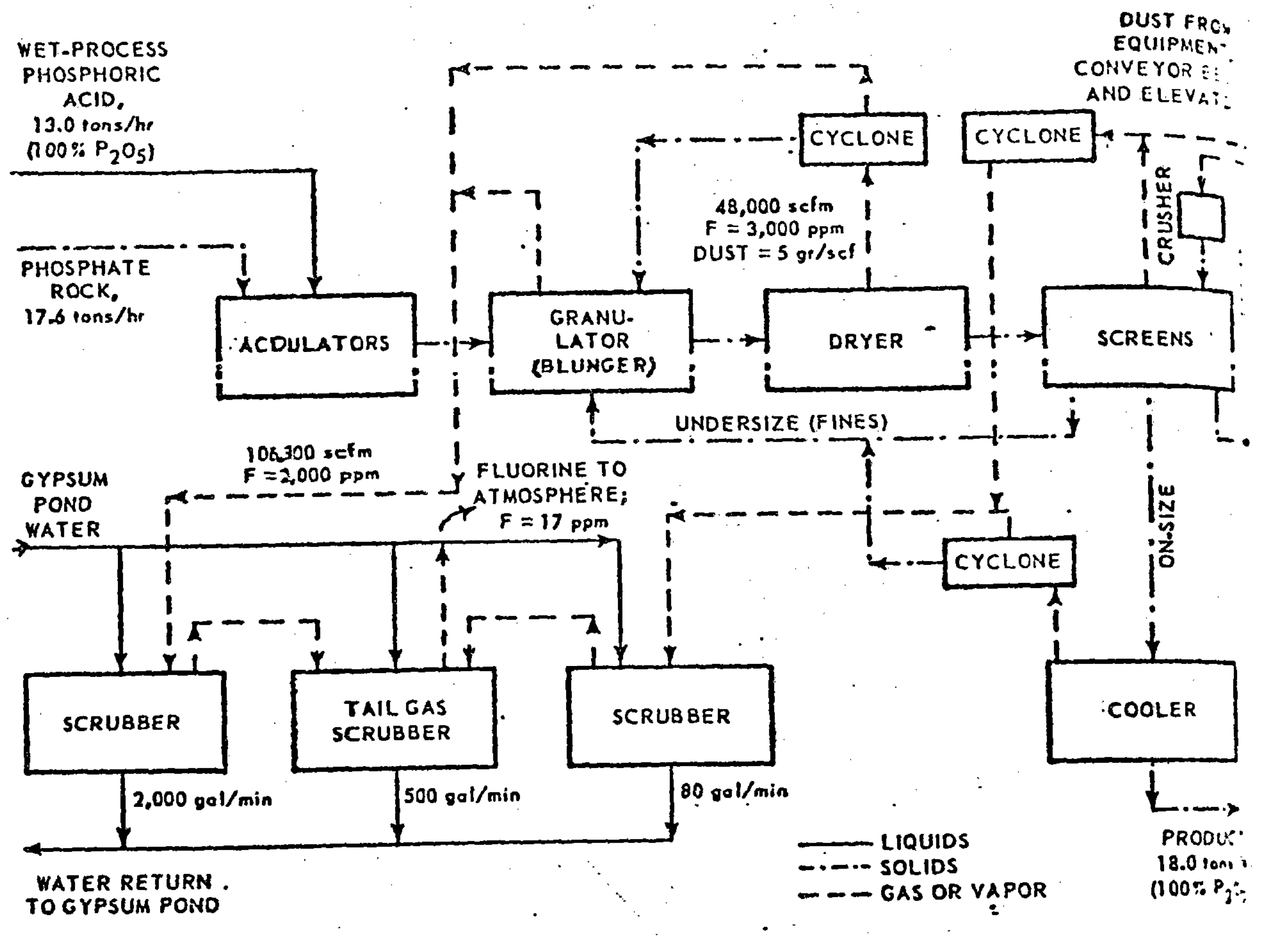

Figure 4-21. Plant for production of granular triple superphosphate.[25]

Uniform, moist granules of triple superphosphate are formed in the granulator. The granules are then dried, cooled, and screened to obtain a uniform product about 1/8 inch in diameter.

3. Triple superphosphate may also be manufactured in an ordinary normal superphosphate den. Unless a surfactant is used, however, the triple superphosphate solidifies into a very hard mass.

4.5.3 Evolution of Fluorides

The volatilization of fluorine as gaseous SiF_4 during the manufacture of triple superphosphate varies widely with the phosphate rock, phosphoric acid, and the process and operational conditions employed.

The greatest variation in the quantity of fluoride evolved from phosphate rock and phosphoric acid occurs at plants manufacturing granular triple superphosphate. The percentage of total fluorides evolved during processing in plants producing granular superphosphate is shown in Table 4-17. The striking disparity between the percentages of fluorine evolved during acidulation is attributable to a greater formation of an acid-soluble aluminum fluoride complex in the acid made from Tennessee rock.[67] A much lower proportion of the fluorine content of the rock is carried over into the superphosphate by acid made from Florida rock than by acid made from Tennessee rock.

Table 4-17. EVOLUTION OF GASEOUS FLUORIDES DURING THE MANUFACTURE OF GRANULAR TRIPLE SUPERPHOSPHATE[76,a]

	Fluorine in feed, %		
Volatilized during acidulation	Nil	-	13
Volatilized during product drying	14	-	38
Total volatilized	14	-	51
Remaining in final product	86	-	49
	100		100

---

[a] Based on total fluorine in rock and acid; 3.47 to 3.84 percent F in rock and 1.03 to 3.13 percent F in acid by weight.

Variations in operating conditions in TVA cone-type plants manufacturing run-of-pile triple superphosphate are much less than in the slurry granulation plants. Fluoride evolution from a typical TVA cone plant during the manufacture of run-of-pile triple superphosphate is shown in Table 4-18.

Table 4-18. EVOLUTION OF FLUORINE IN TVA CONE-TYPE PLANTS[77]

Operation	Superphosphate, % by Wt.	Total fluorine, %
Evolved on mixing and conveying	0.8 - 1.2	31.4 - 33.3
Evolved in storage curing, and reclaiming	0.05 - 0.10	2.0 - 2.8
Retained in final product	1.7 - 2.3	66.6 - 63.9
Totals	2.55 - 3.6	100.0 - 100.0

4.5.3.1 Points of Fluoride Evolution - Fluoride is evolved during the manufacture of triple superphosphate in the solid (particulate), liquid (mist), and gaseous phases.

The particulate pollution problem results from the handling of ground phosphate rock and the triple superphosphate product. Approximately 1.45 pounds of phosphate rock dust per ton of product is emitted from granular and run-of-pile triple superphosphate plants and, approximately 0.34 to 1.04 pounds of triple superphosphate dust per ton of product is emitted from run-of-pile plants.[11,25] Ground phosphate rock storage silos, conveyors, and weighing equipment are vented to fabric filters capable of removing more than 99 percent of the dust handled. Triple superphosphate dust generated during reclaiming, conveying, grinding in mills, and screening is generally collected by high efficiency cyclones. In granular plants, the dust-laden gases leaving the cyclones are sent to a wet scrubber for the removal of particulates. In some run-of-pile (ROP) plants, dust-laden gases leaving the cyclones are vented directly to the atmosphere; however, new ROP plants use a secondary wet scrubber to adequately remove dust from emissions to the atmosphere.

The principal points of gaseous fluoride evolution in triple superphosphate plants are:

1. Granular Plants
   - a. Acidulation of phosphate rock.
   - b. Granulator.
   - c. Dryer and Cooler.
   - d. Tank storage of wet-process phosphoric acid and fluosilicic acid obtained during scrubbing of fluoride fumes.
2. Run-of-Pile (TVA Cone) Plants
   - a. Acidulation of phosphate rock.
   - b. Curing belt and transfer points of green triple superphosphate conveyor belts.
   - c. Curing pile and reclaiming of cured run-of-pile triple superphosphate.
   - d. Tank storage of wet-process phosphoric acid and fluosilicic acid obtained during the scrubbing of fluoride fumes.

The average rate of fluoride evolution in both the gaseous and particulate phases from all sources in triple superphosphate plants (TSP) has been estimated at 48 pounds fluorine per ton TSP (100% P_2O_5 basis).[83]

Fluoride Emissions to Atmosphere - The amount of fluorides emitted to the atmosphere for a particular triple superphosphate plant is generally regulated by local or state air pollution control ordinances in effect in the geographical area in which the plant is located. One state limits the total allowable atmospheric pollutants from a combined wet-process phosphoric acid plant and triple superphosphate plant to 0.4 pound or less of elemental fluorine, as fluorides, per ton of P_2O_5 processed in the acid plant.[84]

One plant design is based on a fluoride concentration of 17 ppm in the stack effluent from process scrubbers and a concentration of 5 ppm in the effluent from storage building scrubbers.[85]

4.5.3.2 Distribution and Magnitude of Fluoride Evolution-

Polk and Hillsborough counties in Florida, east of Tampa, contain the greatest concentration of triple superphosphate manufacturing plants in this country: fourteen plants with a total rated capacity of 1,900,000 tons per year (100% P_2O_5 basis), representing about 70 percent of the triple superphosphate capcity of the United States and 95 percent of the capacity of the State of Florida.

The locations of triple superphosphate plants in the United States are shown in Table 4-19 and Figure 4-22. Table 4-19 also shows plant capacities, total potential fluoride evolution, and potential atmospheric emission of fluorides by location, on the basis of capacity operation of the plants.

Table 4-19. LOCATION AND CAPACITY OF TRIPLE SUPERPHOSPHATE PLANTS AND POTENTIAL EVOLUTION AND ATMOSPHERIC EMISSION OF FLUORIDES

States	Manufacturing capacity[74] tons/yr (100% P_2O_5)	Fluoride evolution[a] tons/yr F	Atmospheric emissions[a] tons/yr F
Southern			
Mississippi	138,000	3,310	33
North Carolina	138,000	3,310	33
Florida	2,130,000	51,180	512
Total	2,406,000	57,800	578
Mid-West			
Missouri	16,000	385	4
Mountain & Pacific			
California	78,000	1,870	19
Idaho	257,000	6,120	61
Utah	35,000	840	8
Total	370,000	8,830	88
U.S. Total	2,792,000	67,015	670

[a] Potential evolution and emission based on capacity operation. Actual operation in 1967 was at about 50 percent capacity. Evolution and emission include gaseous and particulate phases. Evolution based on 3.8 percent F in rock and 2 percent F in Wet-process phosphoric acid.

[b] Actual production in 1968 was 1,271,000 tons of triple superphosphate (100% P_2O_5) which is the basis for fluoride emission in Table 3-1.[3]

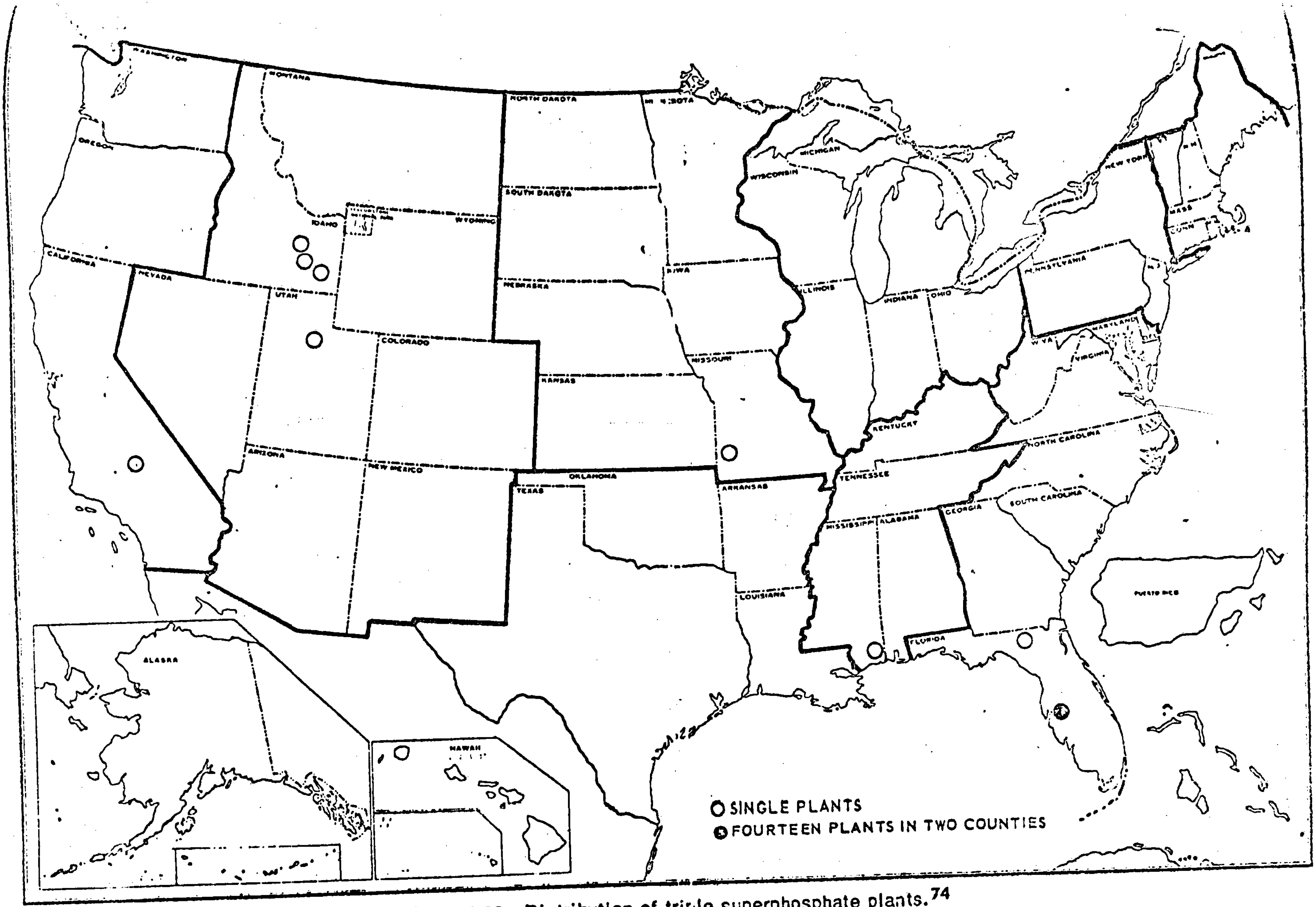

Figure 4-22. Distribution of triple superphosphate plants.[74]

4.5.4 Control Techniques

All points of fluoride evolution should be hooded or sealed and vented to a wet-scrubbing system. (Refer to Section 4.5.3.1). Run-of-pile triple superphosphate storage buildings are usually sealed and ventilated by approximately eight air changes per hour, equal to 200,000 to 300,000 cubic feet per minute of air or more,[78] to reduce the fluoride content of the air in the building to level that are safe for plant personnel.

The large volume of storage-building air is then exhausted through multiple wet-scrubbing systems operating in parallel or series.

The flow of ventilation air and the concentration of fluoride and dust from the various points of evolution in superphosphate plants are shown in Table 4-20.

Table 4-20. VENTILATION AIR FLOW RATES AND LOADINGS OF EVOLVED FLUORIDES

Location	TSP production, tons/hr. (100% P_2O_5)	Ventilation air flow scfm	Ventilation air flow °F	Air Loading Gaseous F, ppm	Air Loading Dust grains/scf	Air Loading Total F, lb/ton TSP
TVA process	31.5					
ROP, (run-of-pile)						
TVA cone curing belt,		24,000[a]	140	8,000	0.1	17-34
Conveyor belt				16,000[a]		
ROP storage building		250,000[a]	95	500-1000[a]	0.5	12-24
Total		274,000				29-58
Slurry process	18					
Reactor-Granulator		7,900	160	2350-4700[77]		2.9 - 5.8
Dryer		48,000	220	2800-4700[8]	3-10[11]	23 - 40
Cooler, Screens, Etc.		51,000	120	700-1400[8]	3-10	7.5 15.0
Total		106,900[17]				33.4 - 60.8
Multi-purpose type facility	18					
Reactor		7,000				
		9,000				
Screens, mills, etc.		30,000				
Dryer		68,000				
Cooler		48,000				
Total		162,000				

[a] ROP storage building effluent handled by two scrubbers in parallel. Volume per scrubber is 125,000 SCFM.[85]

The cleaning of stack gases from triple superphosphate plants is generally done with commercially fabricated scrubbers using fresh and recirculated water from a gypsum pond. These systems are usually custom-built, and are designed for estimated fluoride removal efficiencies of between 95 percent to 99 percent.[75]

Air pollution control equipment used in triple superphosphate plants have included the following scrubber types, generally operating in two stages of scrubbing:

1. Cyclonic-spray scrubber (tower).
2. Venturi scrubber with separator.
3. Ejector-venturi scrubber.[75]
4. Impingement-type scrubber.
5. Packed tower-stationary bed.[75]

The most widely used scrubber for triple superphosphate plants is the cyclonic-spray scrubber (tower), equipped with removable spray nozzles located in the cyclone body.

All scrubber types in triple superphosphate plants should be designed so that silica particles are easily and continuously removed from the scrubbing system. The buildup of silica inside the scrubber generally interferes with scrubbing efficiency and operation. The carry-over of scrubber liquid to the scrubbing system fan may cause the evaporation of liquid inside the fan, resulting in high fluoride emissions to the atmosphere. Good system design for the use of tail-gas demisters is required to avoid liquid evaporation and fluoride emission.

Fixed-bed, packed-tower scrubbers have been used as tail-gas scrubbers only to reduce further the concentration of fluorides in the effluent of other scrubbers.

Venturi scrubbers with separators are generally used to remove large quantities of dust present in stack gases or to collect fluoride as fluosilicic acid. The separator portion of the scrubber is cyclonic and may be equipped with spray nozzles to increase the scrubbing efficiency of the system.

The operation of the ejector-venturi, another scrubber used for fluoride removal, is based on the creation of a draft by means of a high rate of flow of water through a venturi throat. Fluoride-containing gases are drawn in and mixed with the water so that gaseous fluorides are absorbed.

In the impingement-type scrubber, fluoride-containing gases are impacted against a water surface so that gaseous fluoride is absorbed and particulates are removed from the gas stream.

The pressure drop and water to air ratio for typical fluoride scrubbers are shown in Table 4-4 in Section 4.2.

4.5.4.1 Evolution Inhibition - The evolution of fluorides from triple superphosphate in the storage pile is reported to be inhibited by the addition of nitrogen compounds such as ammonia or urea.[79] The amount of fluoride evolved during ventilation can be reduced about 88 percent by the addition of nitrogen equal to 0.4 to 1.25 percent of the weight of the triple superphosphate product.

A reduction in fluoride evolution during the acidulation of phosphate rock has been achieved by the addition of 0.075 to 0.41 mol of an alkaline earth metal compound per mol of fluorine in the phosphate. The reduction in fluoride evolution is reported to be 77 percent.[80]

4.5.5 Costs

The design capacity of triple superphosphate plants in the United States is generally 18 tons per hour (100% P_2O_5) for granular product manufactured in slurry-process plants or combined diammonium phosphate-triple superphosphate plants; it is 30 to 40 tons per hour for run-of-pile, pulverized product manufactured in TVA cone - and setting belt-plants.

Equipment and annualized costs for fluoride scrubbing systems in triple superphosphate plants vary with the rate of exhausting gases from the process equipment and storage building areas.

The purchase, installed, and annualized costs of fluoride scrubbing systems for the ventilation air from run-of-pile triple superphosphate curing buildings will vary with the size and configuration of the building, building tightness, and building ventilation pattern. The annualized costs will also vary with curing-building utilization. Curing-building scrubbers are usually installed in parallel, with each scrubber ventilating the portion of the building in use. The utilization of curing-building scrubbers, therefore, will usually be less than 100 percent. At least one plant in Florida operates only one scrubber continuously on the triple superphosphate building.

Purchase, installed, and annualized costs of single-stage cyclonic-spray scrubbers are shown in terms of air-handling capacity in Figures 4-23 and 4-24. This scrubber system can be used for run-of-pile and granular triple superphosphate curing buildings where fluoride is liberated.

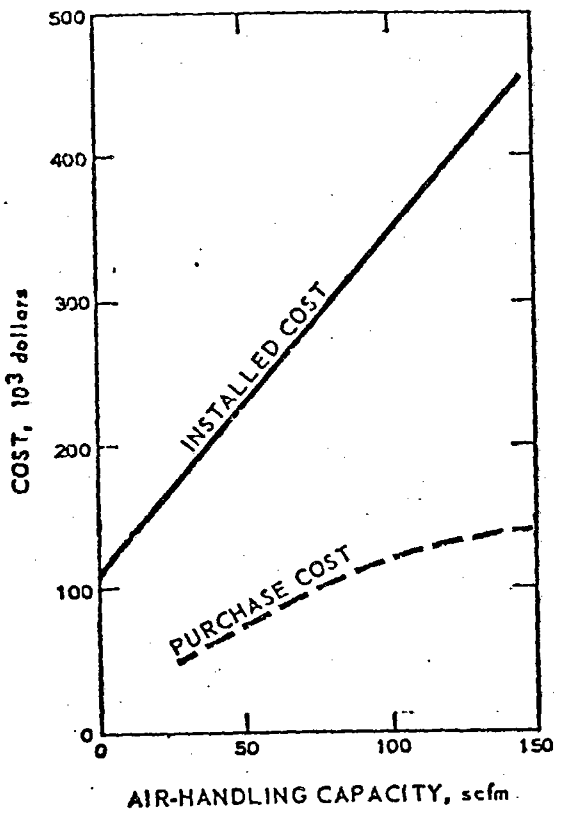

Figure 4-23. Single-stage cyclone-spray scrubbers used for run-of-pile,[13] triple superphosphate storage buildings (1969).[13]

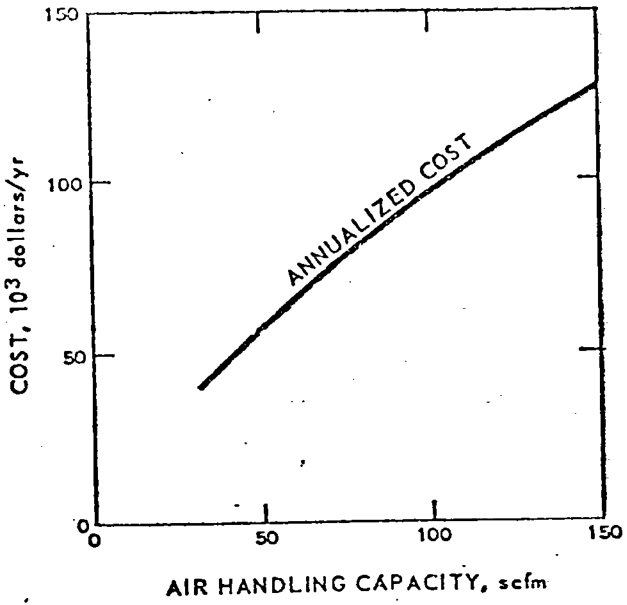

Figure 4-24. Single-stage cyclone-spray scrubbers used for run-of-pile,[13] triple superphosphate storage buildings (1969).[13]

Air volume and fluoride loadings from the curing building for a 31.5 ton per day (100% P_2O_5) triple superphosphate plant are indicated in Table 4-20.

Purchase, installed, and annualized costs for various fluoride scrubber systems installed in different triple superphosphate plants are shown in Table 4-21. Fluoride and dust concentrations in and total volumes of the fluoride-laden air evolved from each type plant can be obtained from Table 4-20.

4.6 DIAMMONIUM PHOSPHATE

4.6.1 Introduction

Ammonium phosphates have become the most popular form of phosphate fertilizers because of high plant nutrient content and low shipping cost per unit of P_2O_5. Production of diammonium phosphate in 1968 amounted to 1.8 million tons expressed as P_2O_5.[74] Fluorides are evolved from the phosphoric acid which is used to recover ammonia vented from the reactor.[87] Product dusts are generated in the dryer, cage mills, and screens, and are recovered in cyclones.

Table 4-21. PURCHASE, INSTALLED, AND ANNUALIZED COSTS OF FLUORIDE SCRUBBING SYSTEMS USED IN TRIPLE SUPERPHOSPHATE MANUFACTURE (1969)[85,105,106]

Process	Capacity	Scrubbing System	Efficiency	Purchase cost	Installed cost	Annualized cost
TVA cone and setting belt	32 tons/hr (100% P_2O_5)	Two-stage cyclonic-spray	99%	$ 79,000	$233,000	$ 62,700
		Two stage ejector-venturi	99%	70,000	207,000	65,700
Slurry process	18 tons/hr.	Two single-stage venturi-separator scrubbers to one cyclonic-spray tail-gas scrubber	99%	217,000	640,000	195,000
Multi-purpose	18 tons/hr.	Same as for slurry process, except two cyclonic-spray tail-gas scrubbers	99%	275,000	810,000	247,000

Effluents from the cyclones are scrubbed in impingement cyclonic, or venturi scrubbers. One installation recovers product dusts in a fabric filter.[88]

4.6.2 Process Description

All processes for the manufacture of fertilizer-grade diammonium phosphates (18-46-0) and (16-48-0) from wet-process phosphoric acid and ammonia are essentially the same in principle. Wet-process phosphoric acid of about 38 to 42 percent P_2O_5 equivalent is partially neutralized by anhydrous gaseous or liquid ammonia to a pH of about 5.6 using approximately 1.3 moles of ammonia per mole of phosphoric acid. The temperature is maintained at about 240° F by adjusting the acid dilution so that the water evaporation balances the heat of reaction.[90] Ammoniation is completed in an ammoniator-granulator (TVA process.)

In the TVA process, ammonia and the acid solution from the scrubber are fed into a single reactor, where approximately half of the water introduced in the process is evaporated (Figure 4-25). The slurry from the reactor and the dry, solid recycle diammonium phosphate consisting of fines, ground oversize, and some product size at a rate of between four to seven times the product rate are fed into

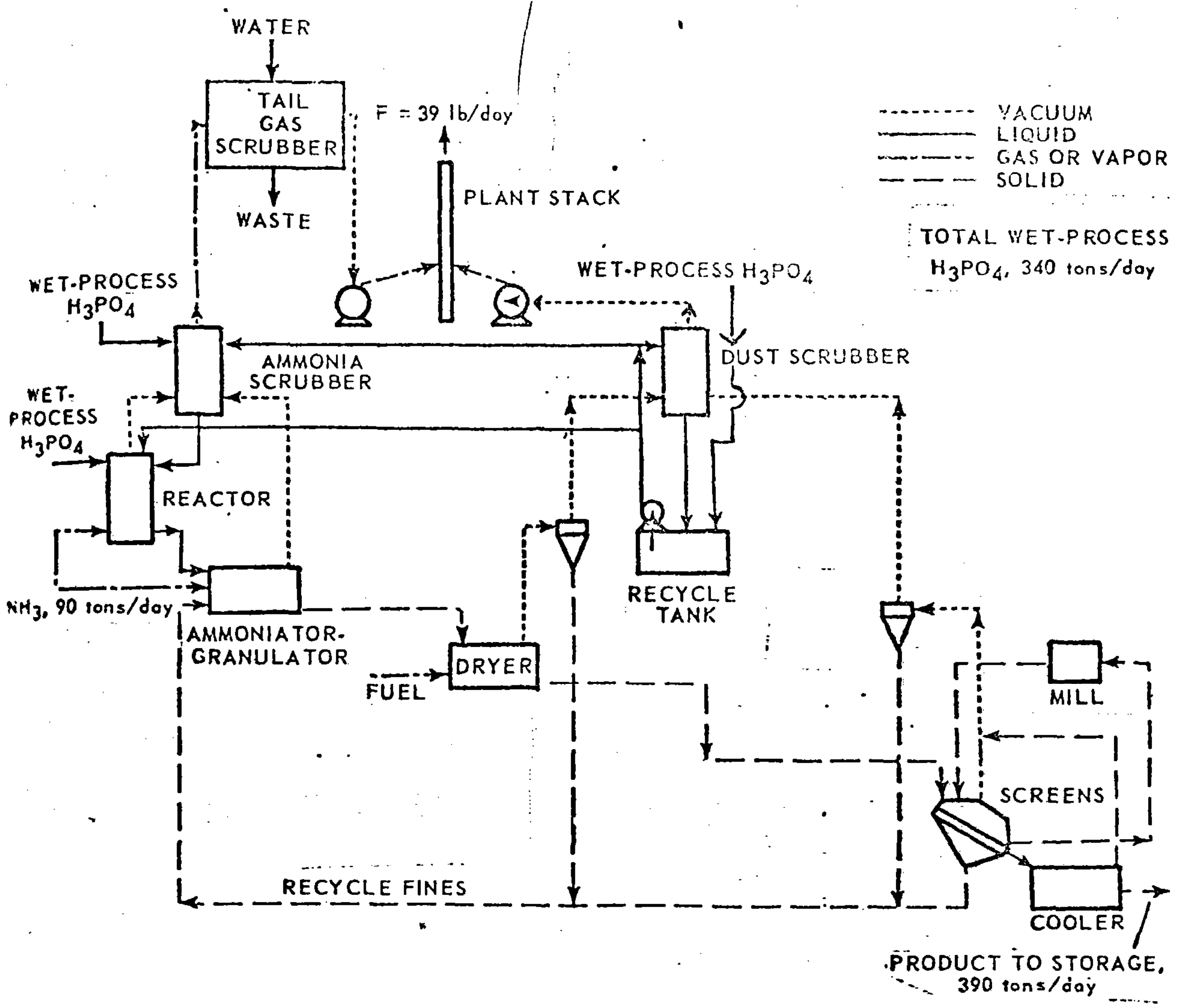

Figure 4-25. TVA process for diammonium phosphate production.[85]

a revolving ammoniator-granulator drum, where final ammoniation and granulation take place simultaneously and an additional 40 percent of the water is evaporated. The moist granules are dried, screened, cooled, and conveyed to bulk storage.

4.6.3 Fluoride Evolution and Control

The fluoride content (as F) of the wet-process phosphoric acid and the diammonium phosphate ranges from 1.8 to 2.0 and from 1.9 to 2.1 percent, respectively.[85] These analyses indicate that less fluoride is evolved in the production of diammonium phosphate than in the production of normal or triple superphosphate or wet-process phosphoric acid.

Diammonium phosphate plants generally have two different air pollution control systems: one to recover the ammonia and control any gaseous fluorides evolved from the reactor(s) and ammoniator-granulator (or blunger); another to control the dust from the dryer, cooler, and screen cyclones. The scrubber liquid for both control systems, which has a pH of about 2 and a fluoride content of about 8,000 ppm (by weight), is usually recycled from a storage or surge tank.[85]

The optimum conditions (pH 4.5 or lower at an absorption system temperature of above 160° F) for the recovery of ammonia also may cause fluoride to be stripped from the ammonia scrubber liquid. This may result in an evolution of 50 to 150 pounds of fluoride per day based on a 600 ton per day DAP plant.[98] These conditions require an efficient tail gas scrubber to reduce the emission to the atmosphere to an acceptable value.

The choice of a particular control device, for example, cyclonic-spray tower, venturi scrubber, impingement scrubber etc. - is usually made at the time of the original plant design. After a year or two of plant operation, modifications to the original equipment are sometimes made, such as the addition of sprays to ducts just upstream from the scrubber, replacement of small nozzles by larger (and fewer) spray nozzles in a tower to avoid plugging, etc.

The efficiency of a particular piece of control equipment depends upon such factors as: proper maintenance, the ratio of scrubber liquid to gas flow volume, characteristics of the scrubber liquid (pH, fluoride content, and temperature relative to incoming gas stream), and operation at optimum capacity.

4.6.4 Production

Fertilizer-grade diammonium phosphate is produced in most plants in this country at the rate of 30 to 35 tons per hour and these plants operate continuously except for routine maintainance. Most of these plants are located near wet-process phosphoric acid facilities, which in turn are usually located close to phosphate mines, as in Florida, North Carolina, Idaho, and California. A number of plants are also located on the Texas, Louisiana, and Mississippi gulf coast and in Illinois and Missouri, where the phosphate rock is shipped to these plants by barges on the Mississippi River.

In 1968, there were about 43 plants producing an estimated 1.8 million tons of diammonium phosphate expressed as P_2O_5.[102] The total consumption of diammonium phoshates in this country, including Puerto Rico, Hawaii, and Alaska, for the year 1968 was approximately 608,000 tons.[102] The excess of production over domestic consumption was exported to foreign countries.

4.6.5 Atmospheric Fluoride Emissions

The total estimated gaseous fluoride emissions in this country for the year 1968 was approximately 100 tons. This estimate is based on the annual production of 1.8 million tons of DAP (expressed as P_2O_5)[102], and on an average-sized plant that produces 600 tons of DAP per day and emits an average of 60 pounds of fluoride (expressed as F) daily.[85]

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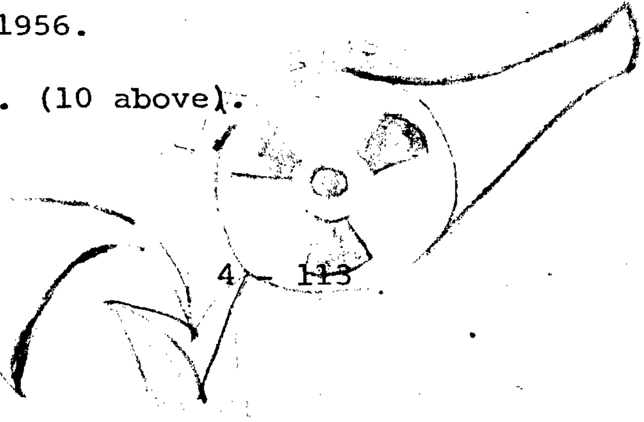

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5. MANUFACTURE OF PHOSPHORUS AND ITS COMPOUNDS

5.1 ELEMENTAL PHOSPHORUS

5.1.1 Introduction

Elemental phosphorus is produced by means of the electric furnace reduction of phosphate rock. Direct use of phosphorus for metal alloying, match production and pyrotechnics accounts for less than ten percent of the output. Most of the elemental phosphorus is burned to phosphorus pentoxide and absorbed in water to make high purity phosphoric acid which is in turn converted to phosphate derivatives for use in foods, detergents and so on. As much as 20 percent of this acid is reacted to make fertilizers.

Fluorides are evolved from the manufacturing process during preliminary heat treatment of the phosphate rock, during furnace reduction, and from the molten slag tapped from the furnace. The fluorides in the process effluent gases are removed by water scrubbing in equipment such as spray towers, venturi-type scrubbers, and cyclonic spray scrubbers.

The elemental phosphorus production capacity in the United States in 1968 was 658,000 tons with the actual production at 609,000 tons.[2] The annual evolution of fluoride was 37,300 tons with an estimated 5,500 tons of fluoride emitted to the atmosphere in 1968.[13]

5.1.2 Process Description

Elemental phosphorus is produced commercially by smelting a mixture of phosphate rock, silica, and a carbonaceous reducing agent (such as metallurgical coke) in electric furnaces. In preparing phosphate feed to prevent excessive dusting, at least part of the phosphate rock is treated before charging to the furnace. Phosphate fines are agglomerated[1] commercially by the following methods:

1. Pelletizing by tumbling or extrusion.
2. Nodulizing at high termperatures.
3. Sintering a mixture of phosphate fines and coke.
4. Briquetting with the addition of a suitable binder.

Fluorides are evolved during this preliminary treatment.

The feed materials are proportioned, mixed, and distributed uniformly within the furnace. Submerged electric arcs in the furnaces generate high temperatures, causing the reduction of the phosphate rock with the release of phosphorus, carbon monoxide, and lesser quantities of other gaseous reaction products, including fluorides. These gases emerge from the furnace and pass through electrostatic precipitators for the removal of dust. The cleaned furnace gases discharge into a condenser containing sprays of water maintained at a temperature somewhat above the melting point of phosphorus (111°F). Phosphorus is condensed from the gas stream and collects below a water layer in a sump. Fluorides are absorbed in the scrubbing water. The cooled gases, principally carbon monoxide, are eventually burned for the recovery of heat. The water used in the spray condenser is supplied from a recirculating system. The water contains dissolved phosphorus and fluorides, and it is continuously clarified to remove impurities.[12]

Calcium, silicon, and most of the other mineral constituents of the furnace charge form a molten slag which is tapped periodically. It is necessary to add some silica to most phosphate rocks to produce a slag of the desired fluidity. The iron compounds found in all phosphate rocks are reduced to elemental iron, which forms an alloy with phosphorus that collects in a separate layer below the slag and is also tapped from the furnace periodically.

A flow diagram of an idealized phosphorus furnace process is shown in Figure 5-1, based on full control of the feed preparation and furnace operations.[14] This does not represent current practice at all installations.

5.1.3 Fluoride Emissions

There are three main sources of fluoride evolution from the electric furnace process: (1) preliminary feed preparation of the phosphate rock; (2) evolution of gas from the furnace; and (3) evolution of gas from the molten slag tapped from the furnace.

5.1.3.1 Preliminary Feed Preparation - During the preliminary heat treatment for agglomeration of the phosphate fines, a mixture of hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4) is evolved together with products of combustion and dust. When nodulizing is used to achieve agglomeration, fluoride evolution can amount to as much as 45 percent of the input fluorine and the kiln gas contains as much as 2,900 ppm fluoride.[3] The trend has,

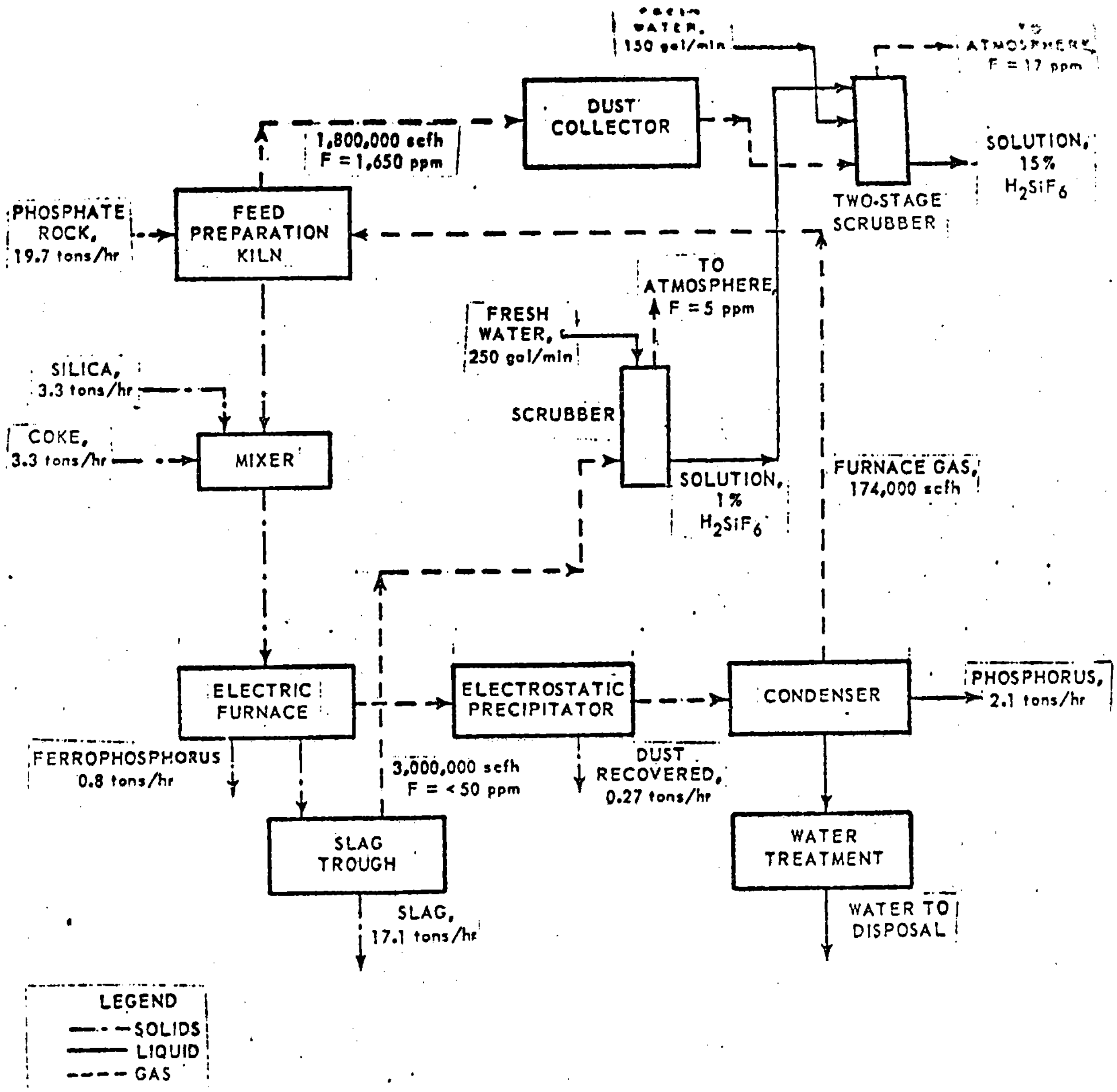

Figure 5-1. Block diagram for elemental phosphorus furnace, 25,000 kW.[14]

however, been away from the extreme temperature conditions involved in nodulizing and in general, fluoride evolution in rock pretreatment is not expected to exceed 20 percent of the input. In one modern installation in which phosphate material is agglomerated into flakes by compaction and is calcined at a maximum temperature of 2200°F, 10 to 20 percent of the input fluorine is evolved as a mixture of HF and SiF_4, at a gas loading of 1650 ppm fluorine.[3,4] This is equivalent to about 50 to 100 pounds of fluorine per ton of phosphorus produced.

5.1.3.2 Electric Furnace - When phosphate rock, pretreated as described above, is charged to an electric furnace, about 10 percent of the remaining fluorine, or about 50 pounds of fluorine per ton of phosphorus, is volatilized and emerges with the furnace gas.[3] The dust carried out of the furnace with the gas also contains some fluorine compounds, most of which are removed in the gas cleaning unit and are usually returned to the process. When dust is recycled to the process, volatilization may amount to 60 pounds of fluoride per ton of phosphorus.[39]

5.1.3.3 Slag Tapping - Twenty percent of the input fluorine evolves during feed preparation and furnace operation, but the balance, or 80 percent, remains in the slag. The molten slag is tapped from the furnace at a temperature of 2600 to 2700°F and is either water-quenched or air-cooled. During the tapping operation, fumes are released from the slag. When the slag is water-quenched, about 0.7 pound of fluoride is released per ton of slag,[7,8] which is equivalent to six pounds of fluoride per ton of phosphorus. When the slag is air-cooled, however, the fluoride evolved is only a fraction of a pound per ton of phosphorus.

<u>5.1.3.4 Furnace Leaks</u> - Appreciable quantities of gas may leak from the seals around the electrodes and up through the chutes that feed the charge to the furnace. Such leakage constitutes a loss of phosphorus, which burns on contact with air, and also results in the release into the plant atmosphere of CO and fluorides. In some older plants, the atmosphere at the upper levels of the furnace buildings has at times been very noxious as a result of these leaks. The only reasonable solution to this problem is to prevent the leaks, and in modern plants this is done very effectively by the use of improved electrode seals[9] that reduce leakage to a negligible level.

5.1.3.5 Atmospheric Emissions - A substantial portion of the fluorides evolved during feed preparation have been emitted directly to the atmosphere. The fluorides evolved during furnace operation, however, are scrubbed out effectively in the spray condenser.

In one plant observed over a period of time, the atmospheric emissions of fluorides from the condenser averaged 0.002 pounds fluorine per 1000 standard cubic feet furnace gas with a maximum value of 0.007 pound of fluorine per 1000 standard cubic feet.[5] Average emissions from the condenser have been calculated to be equivalent to 0.17 pound of F per ton of phosphorus. These emissions are well below the limits established in one state.[6]

5.1.3.6 Summary of Emissions - For the overall phosphorus production process, the average evolution of fluorides has been estimated at 122.5 pounds of fluorine per ton of phosphorus with about 72 pounds evolved during feed preparation. Only minimal control has been exercised in the past over the fluorides evolved during feed preparation but the situation is changing and tighter controls are in effect today. An assumption of an average of 75 percent control over feed preparation and slag tapping appears reasonable for the situation as of 1968. On the basis of this control efficiency, an emission factor of 18 pounds fluorine per ton phosphorus has been calculated for the overall process.[13]

Table 5-1 shows the location and capacity of the plants producing elemental phosphorus in the United States. Also shown are the estimated annual fluorides evolved and emitted to the atmosphere based on the 1968 actual phosphorus production.

5.1.4 Control Techniques

The nature of the reduction operation in the electric furnace is such that evolved fluorides are automatically scrubbed by water during the condensation of phosphorus in the spray condenser. The fumes evolved during feed preparation are not as readily controlled. Substantial emphasis is currently placed on this area. Efficiencies as high as 96 to 99 percent have been accomplished by kiln gas scrubbers.[37]

Table 5-1 ELEMENTAL PHOSPHORUS PRODUCTION CAPACITY IN THE UNITED STATES: EVOLUTION AND ATMOSPHERIC EMISSION OF FLUORIDES, BASED ON 1968 PRODUCTION

Location	Number of furnaces	Nominal phosphorus capacity tons/yr
Pierce, Fla.	3	40,000
Nichols, Fla.	1	6,000
Tarpon Springs, Fla.	1	15,000
Charleston, S.C.	1	10,000
Niagara Falls, N.Y.	1	6,000
Columbia, Tenn.	3	68,500
Mt. Pleasant, Tenn.	1	20,000
Columbia, Tenn.	6	110,000
Mt. Pleasant, Tenn.	5	80,000
Muscle Shoals, Ala.	4	40,000
Pocatello, Idaho	4	142,500
Soda Springs, Idaho	3	90,000
Silver Bow, Mont.	2	30,000
	35	658,000

Annual production in 1968 - 609,000 tons P[2]

Estimated fluoride evolution in 1968 - 37,300 tons F[a]

Fluoride emission to atmosphere in 1968 - 5,480 tons F[b]

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[a] Calculation based on 3.0 percent F in phosphate rock and the evolution of 20.50 percent of F input.

[b] Calculation based on the emission of 18 lbs F per ton P.

5.1.4.1 Furnace Operation - The gases discharged from the furnace consist of carbon monoxide, hydrogen, and phosphorus vapor, plus suspended dust. The dust particles, most of which are smaller than two microns, are removed in the electrostatic precipitator. In order to minimize entrainment, the dust is wetted down (either within or outside the precipitator) and handled as a slurry. The furnace gases, after cleaning, are sprayed with water in the condenser. The cooling water stream absorbs the bulk of the fluorides evolved in the furnace operation as well as some phosphorus. The water, containing dissolved phosphorus and fluorides, is called "phossy" water and amounts to 1,300 gallons per ton of phosphorus. The water is clarified to remove phosphorus and is handled in a closed recirculating system. A certain portion of the water stream (about six percent) is replaced with fresh water to prevent the buildup of dissolved components. The clarified water contains fluorides maintained at 10 grams of F per liter by draw off.[12]

5.1.4.2 Feed Preparation and Slag Tapping - The gaseous fluorides evolved from feed preparation can be absorbed in equipment such as spray towers, wet-cyclonic scrubbers or venturi-type scrubbers. Collection efficiencies of

95-98 percent are readily obtainable in a single spray tower.[36] Efficiencies of about 99 percent can be obtained if a series of spray towers is used.[11] In general, the wet-cyclonic and venturi scrubbers are used because of economic considerations.

The fumes from the furnace tap-holes are collected by a water-cooled hood, scrubbed with water, and then exhausted by a fan through a high stack. The air-handling capacity of the fan is about 50,000 cubic feet per minute for collection of the slag fumes from one furnace.

5.1.5 Byproducts of Fluorine Recovery

Commercial fluorine compounds such as cryolite and aluminum fluorides can be recovered from phosphorus plant scrubber solutions. In the recovery process, waste gases are scrubbed with ammonia solution to form ammonium fluoride and ammonium fluosilicate. Then the scrubber solutions are ammoniated further to precipitate silicon and iron compounds, that are then removed by filtration. The subsequent steps used to recover specification-grade products from the purified solution depend upon phosphorus pentaoxide (P_2O_5) content.[33] Economical recovery of commercial fluorine compounds depends on three major variables: large plants produce more fluorine, phosphate rock high in fluorine content produces a concentrated scrubber gas, and high phosphate calcination temperatures drive off more of the fluorine in the phosphate. The fluorine available for product recovery may amount to 200 pounds of fluorine per ton of phosphorus.[33]

Costs for fluoride disposal are increasing because stringent pollution abatement standards are being put into effect. Double liming of wastewater is required at some places because the fluoride concentration of the wastewater must be reduced to low values. The increases in disposal costs also make valuable product recovery more attractive.[33]

5.1.6 Costs

Costs have been calculated for a fluoride emissions control system based on scrubbing the fumes from feed preparation and from tapping. The system for emission control during feed preparation consists of a dust collector and two cyclonic scrubbers in series. The fumes from slag tapping are collected in a hood, diluted with air, and the combined gases are then scrubbed with water in a single cyclone scrubber. The scrubbed gases are exhausted through a fan and discharged from a stack. Water is used as the absorbent and is recirculated through the scrubber system to produce 15 percent fluosilicic acid.

The cost for each system covers scrubbers, fans, pumps, tankage, ductwork and a 75 foot high stack. The annualized cost includes the cost of water and electric power consumption. The cost of water treatment for fluoride removal is not included. This addition will add about 40 percent to the purchase, installed and annualized costs.

The cost of the control system for a given plant is related directly to the gas flow rate through the scrubbers, which in turn, is a function of the plant capacity. Table 5-2 indicates the relationship between plant capacity (in terms of the annual tonnage of elemental phosphorus), furnace rating, and gas flow rate through the scrubbers.

Table 5-2 ELEMENTAL PHOSPHORUS CAPACITY, FURNACE RATING, AND GAS FLOW RATE THROUGH CONTROL SCRUBBERS

Phosphorus capacity tons/yr	Furnace rating, kw	Gas flow rates, scfm	
		Feed preparation	Slag tapping
17,000	25,000	30,000	50,000
31,000	45,000	54,000	58,000
43,500	64,000	77,000	65,000

The purchase, installed, and annualized costs of control systems versus plant capacity (in terms of furnace kilowatt rating) are shown in Figures 5-2, 5-3, and 5-4.

5.2 ANIMAL FEED SUPPLEMENTS

5.2.1 Introduction

The nutritional value of animal feeds has been increased through the addition of important elements such as phosphorus. Phosphorus is incorporated into feeds principally by the direct addition of phosphate rock that must be almost entirely free of fluorine. In the thermal defluorination of the Phosphate rock, carried

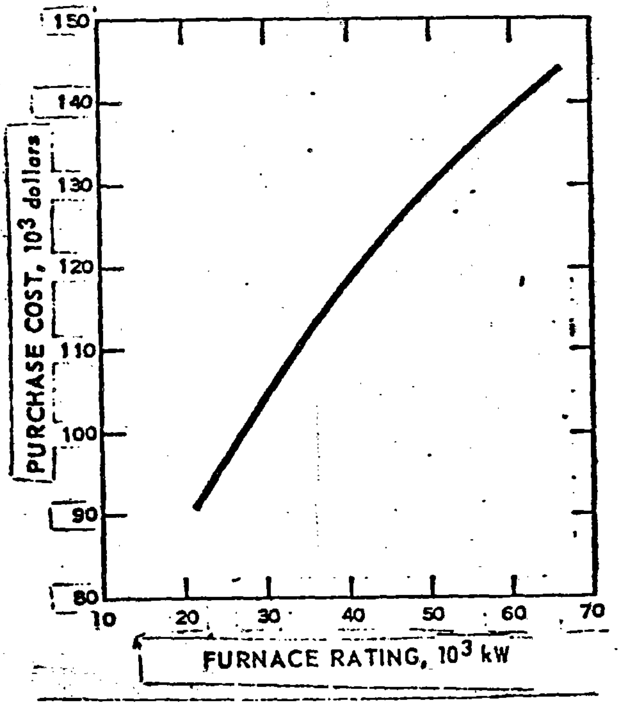

Figure 5-2. Elemental phosphorus plant; purchase cost of control systems versus furnace rating (1969).[13]

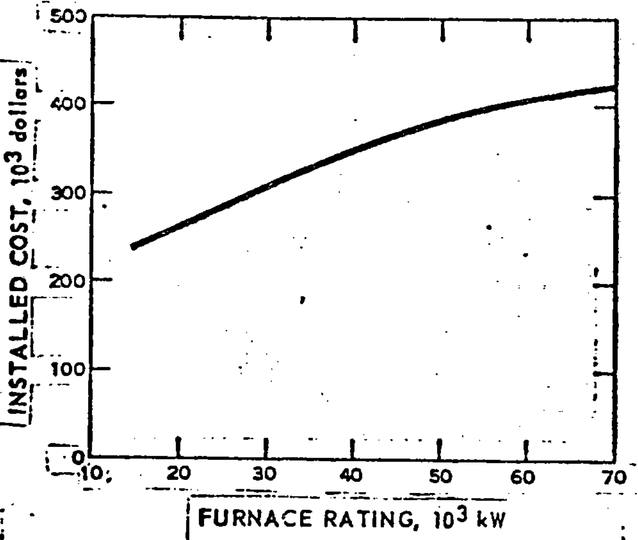

Figure 5-3. Elemental phosphorus plant; Installed cost of control systems versus furnace rating (1969).[13]

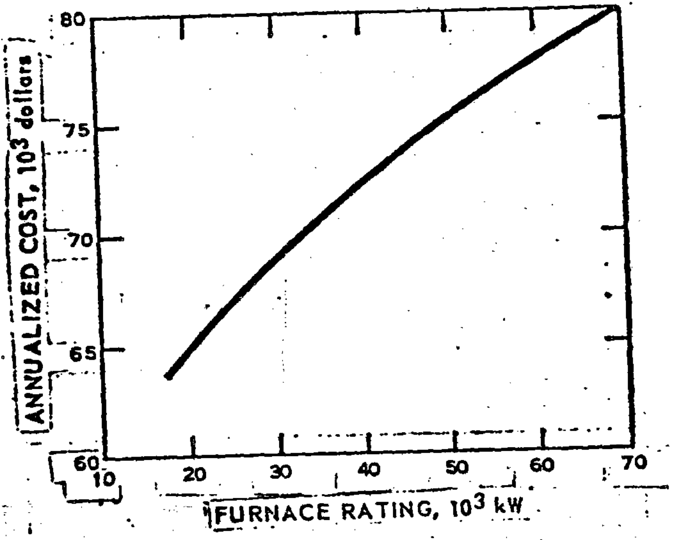

Figure 5-4. Elemental phosphorus plant; annualized cost of control systems versus furnace rating (1969).[13]

out in rotary kilns or fluid-bed reactors, over 90 percent of the fluorine present in the starting rock is evolved as fluorides.

The starting rock is basically fluorapatite, $Ca_{10} (PO_4)_6 F_2$. Although the composition varies, substitutions for calcium and phosphate sometimes occur. Carbonate substitution for phosphates and metal substitution for calcium tend to add more fluorine to the compound. The formula $[(Ca_{10-a-b} Na_a Mg_b)10(PO_4)_{6-x} (CO_3)_x Fy (F_z)]$ indicates the extra fluorine potential, (Fy).[38]

The evolved fluorides are scrubbed with water in equipment such as spray towers and multi-pass spray chambers in series with high energy scrubbers.

On the basis of an annual capacity of 194,000 tons of defluorinated phosphates (100 percent P_2O_5 basis) the indicated fluorine evolution is 21,632 tons per year, with 98 tons per year fluorine emitted to the atmosphere.[6,27]

5.2.2 Process Description

The most common process used in the manufacture of animal feed supplements involves the thermal defluorination of phosphate rock in rotary kilns or fluid-bed reactors. A shaft kiln has also been used,[17] but the operation has been abandoned. Phosphate rock is conditioned prior to thermal treatment by mixing it with phosphoric acid, or in some cases with other additives, and then granulating and drying the mix. The kiln, or reactor, product is screened, the coarse particles ground, and the fines bagged as product ready for consumption. The kiln gaseous effluent is directed to a dust collector and scrubber system for abatement of dusts and evolved fluorine. A block flow diagram for this process is shown in Figure 5-5.

5.2.3 Fluoride Emissions

The fluorine content present in all phosphate rock must be reduced to a low level to make it acceptable for animal feed. The allowable amount of fluorine varies with the animal and with the feed program, but typically, the fluorine content should not exceed one part per hundred parts of phosphorus.[15] Since a typical domestic rock will contain one part of fluorine to three to four parts of phosphorus,[26,27] about 95 percent of the fluorine must

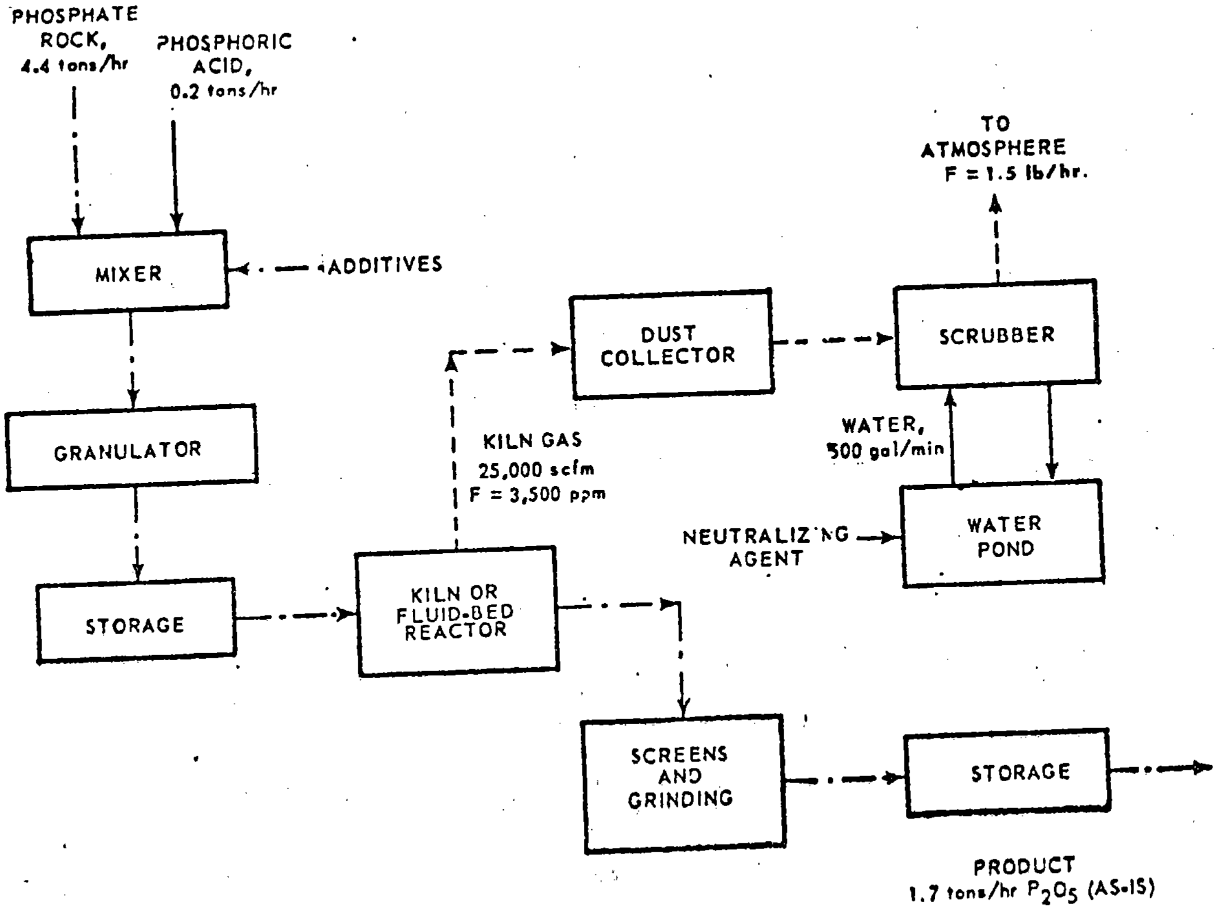

Figure 5-5. Block flow diagram for a phosphate rock defluorination plant.

be driven off to make the product acceptable. This is a greater proportion than is evolved in other phosphate processes and, as a result, the control of emissions in the defluorination process is particularly important.

Defluorination is accomplished by heating at temperatures of 2000 to 2500°F; however, heat alone will not induce complete defluorination since even at complete fusion, phosphate rock will retain significant amounts of fluorine unless some means, such as granulation in water, is employed to increase the surface of the reaction mix. The presence of water vapor in the kiln atmosphere will also aid in defluorination. Primarily, however, an acidic substance must be added to combine with the calcium present in the rock and release the fluorine. The most common additive is phosphoric acid, which not only converts all calcium to tricalcium phosphate but adds to the P_2O_5 content, and hence to the value of the product. In addition, soda ash is added. The addition of silica to yield calcium silicate has also been suggested, but it seems to be less effective than the addition of phosphoric acid.[16] Fluorine is released predominantly as HF since at the high temperatures used and in the presence of water vapor, most of the SiF_4 liberated reacts with water vapor to form HF and SiO_2.[3]

In contrast to fertilizer and elemental phosphorus processes in which emissions occur at several points, the defluorination process releases only negligible amounts of fumes at points other than the kiln itself. With proper design and maintenance of fume take-off systems, there is no difficulty in confining fluoride evolution to the ducts and the fume treating system. Because of the large amounts of fluoride involved, corrosion can be severe and very efficient fume treatment systems must be provided to reduce the discharge of atmospheric pollutants to an acceptable level.

In a particular plant treating a typical commercial phosphate rock (with a feed rate of 50 tons of rock per day), kiln gases were evolved at the rate of 13,700 scfm. The fluoride concentration in the kiln gases was measured at 3000 to 4400 ppm, equivalent to about 180 to 260 pounds of F evolved per ton of P_2O_5.[27] Measurements on the exit gases from the scrubber showed the emission of 1.5 pounds of F per ton of P_2O_5 at this particular plant.[27]

A removal efficiency in excess of 99 percent can be expected using multi-stage scrubbers. For such a system emissions of less than 1.0 pound of F per ton of P_2O_5 can be expected.[28,30]

5.2.3.1 Magnitude of Emissions

The average evolution of fluorides for this process has been estimated at 222.5 pounds of F per ton of P_2O_5.[29] Based on the measured emissions from a particular defluorination plant[27] the atmospheric emissions have been estimated at 1.5 pounds F per ton P_2O_5 for plants outside of Florida and 0.4 pounds F for Florida plants (the limit set by State regulations.[6])

Table 5-3 shows the locations and estimated capacities of various domestic plants that produce animal feed supplements from defluorinated phosphate rock. Also shown are the estimated fluoride evolution and emission to the atmosphere for the nation in 1968.

5.2.4 Control Techniques

Practically all the fluoride evolved from the thermal defluorination of phosphate rock is present in stack gases from the defluorination unit. A typical control method is the installation of a dust collector in series

Table 5-3 PLANT LOCATIONS, CAPACITIES, AND FLUORIDE EVOLUTION AND EMISSIONS TO THE ATMOSPHERE FOR PLANTS PRODUCING DEFLUORINATED PHOSPHATE ROCK ANIMAL FEED SUPPLEMENTS

Company[a]	Location	Estimated annual capacity[32]		
		Tons, as is	Tons P_2O_5	Tons P_2[f]
Borden	Plant City, Fla.	200,000	82,000	36,000
Occidental[31]	Houston, Texas	40,000	16,000	7,000
Occidental[31]	White Springs, Fla.	100,000	41,000	18,000
Olin	Pasadena, Texas	100,000	41,000	18,000
Rocky Mountain	Garrison, Mont.	35,000	14,000	6,000

Estimated annual evolution of F - 21,632 tons[b]
Estimated annual atmospheric emission of F - 98 tons[c]

[a] These figures do not include 500,000 tons per year Dical made by the reaction of phosphoric acid and limestone. The fluorine evolved from Dical is practically nil.

[b] Based on evolution of 222.5 per ton P_2O_5

[c] Based on emission of 0.4 lbs F for Florida plants and 1.5 lbs F for other plants for every ton P_2O_5

d. shut down 1969
e. start-up 1969
f. conversion factor .44 $16P_2$/lb P_2O_5

with wet-scrubbing equipment

Bases for the design of scrubbing facilities have been presented by many authorities.[18,19,20,21] Although they have the advantages of simplicity of construction and relative freedom from stoppages, simple spray towers do not have the necessary efficiency. A series of spray towers, or a multi-pass spray chamber[22] followed by a more efficient clean-up unit, is a possible answer to the scrubbing problems encountered by this industry. The clean-up unit could consist of a venturi scrubber, a floating-bed scrubber, or some other intensive contact device.[23,24]

A control system that has been successfully applied in the chlorine blowing operation in primary aluminum plants may also be effective for controlling effluents from thermal-defluorination feed plants. A two or three-stage floating bed scrubber is used to wet or humidify and coalesce the particles from chlorine blowing, and a venturi-type scrubber is then used to remove the coalesced particles. Neither a high energy scrubber or a floating-bed scrubber by itself can remove sub-micron particles from the chlorine blowing operation.

A commonly used control system is based on the so-called "hybrid" scrubber that consists of a horizontal chamber provided with several spray banks, followed by a packed section.[25] Practically all of the precipitated silica and any residual solids in the gas are removed in the spray section, where difficulties from these materials can be avoided. As much as 90 to 95 percent of the fluoride in the gas is absorbed in this section. The packed section, with its high absorption efficiency, then serves to reduce the fluoride content of the gas to the desired level.

Recirculating water is used to scrub the fluorides so that the scrubber exit liquor is a dilute solution of hydrofluoric and fluosilicic acids that is usually pumped to a pond. Water from the pond is neutralized with lime prior to its return to the scrubbers. Failure to neutralize the recycling water and reduce its fluoride content can result in stripping fluoride from recycle water and increasing the fluoride in the stack gases.

Tennessee Valley Authority developed a process for defluorinating rock phosphate as early as 1946. The process involves the injection of steam into a high temperature reactor charged with rock phosphate. The fluoride emission stack gas was passed into a tower packed with sized limestone lumps. A low grade calcium fluoride was obtained which could be used as a flux in metallurgical processes.[34]

In 1958, the Albany, Oregon station of the U.S. Bureau of Mines reported a similar study on Western phosphate. Fluorine recovery was directed to the production of synthetic cryolite or calcium fluoride. The process could also produce aluminum fluoride.[35]

5.2.5 Costs

The purchase, installed, and annualized costs of fluoride emission control systems are directly related to the plant size and type of scrubber system used. A typical hybrid scrubber system, previously described, has been used as a basis for the costs. The gas flow rate is 340,000 scf per ton P_2O_5 with a collection efficiency exceeding 99 percent for fluorides.[29]

For plant sizes ranging up to 80,000 tons per year (100 percent P_2O_5 basis), purchase and installed costs versus plant capacity are shown in Figure 5-6 and annualized cost versus plant capacity is shown in Figure 5-7. The cost of treating the recirculating pond water and the cost of liming are not included in the costs in the figures. This operation would add about 40 percent to the purchase, installed and annual costs.

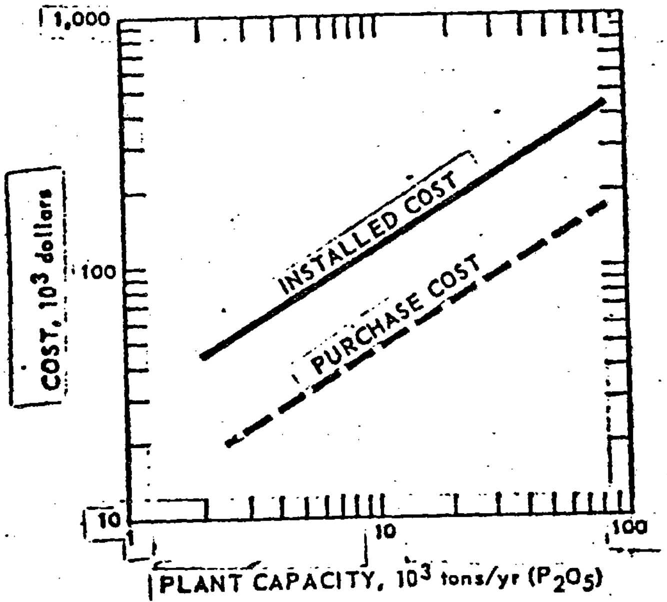

Figure 5-6. Purchase and installed costs of control systems versus plant capacity for phosphatic feed supplement plants (1969).[29]

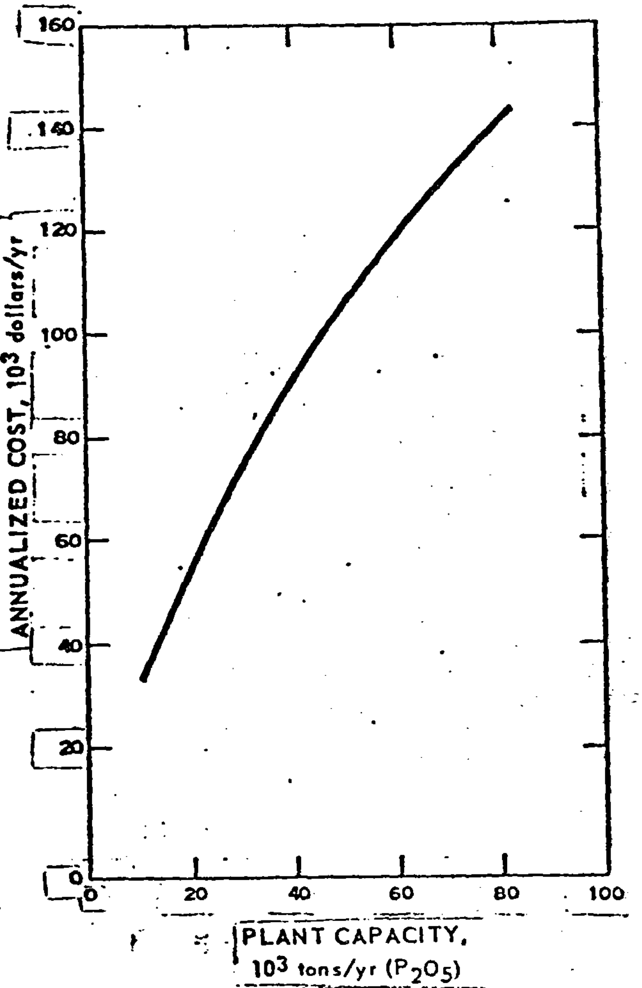

Figure 5-7. Annualized cost of control systems versus plant capacity for phosphate feed supplement plants (1969).[29]

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6. ALUMINUM MANUFACTURE

6.1 PRIMARY ALUMINUM

6.1.1 Introduction

The present day production of primary aluminum is based on the electrolytic decomposition of alumina (Al_2O_3) in reduction cells or "pots" (Hall-Heroult Process). The electrolyte consists of Al_2O_3 dissolved in molten cryolite (Na_3AlF_6). During the reduction process a significant amount of cryolite and fluoride salts volatilize from the cell bath, condense to form fume, and react with moisture to form gaseous hydrogen fluoride (HF). An induced gas stream entrains alumina and carbon particulates as it captures evolutions from the cell.

The cell gases are collected either at the point of evolution by separate hoods over or around the anodes of individual cells, or by ventilating the entire cell room and collecting the gases in building monitors. Sometimes both systems are used. In either case, the collected gases are treated to remove the major portion of the contained particulates and fumes, as well as gaseous HF.

Based on the actual 1968 production of 3,255,000 tons of primary aluminum,[3,26] the fluoride emissions (as fluorine) to the atmosphere have been estimated at 16,000 tons per year.[30]

This section discusses the nature of the fumes released in primary aluminum plants and will survey the various pollution control techniques employed.

6.1.2 Process Description

The production of primary aluminum is based on the electrolytic reduction of alumina at a temperature of approximately 1800 °F. The cell electrolyte consists of alumina dissolved in molten cryolite (Na_3AlF_6) and other fluoride salts. The cryolite bath has the unique quality of dissolving alumina at a reasonably low temperature, whereas alumina by itself has a melting point of 3700 °F.

The electrolytic cell is a carbon-lined, brick-insulated steel shell. The carbon serves as a cathode and is connected electrically to the outside by conductor bars embedded in the lining. The carbon anodes are inserted through a crust of alumina and frozen electrolyte over molten cryolite that floats above the liquid aluminum metal contained in the cell. The carbon anodes combine with oxygen liberated by the electrolytic dissociation of alumina to form gaseous by-products such as carbon monoxide and carbon dioxide.

The electrolytic cell is a carbon crucible, usually heat-insulated on the outside by a brick lining and an iron shell. The crucible acts as a cathode and is electrically connected to the outside by a set of iron bars. The carbon anodes are inserted through an alumina layer floating on top of molten cryolite that rests on liquid aluminum metal contained in the carbon crucible. The carbon anodes combine with oxygen liberated by electrolytic dissociation from alumina to form gaseous by-products as carbon monoxide and carbon dioxide.

There are two types of aluminum reduction cells, differing in the type and method of replacement of the anode carbon. In the prebaked anode system, the prefabricated carbon blocks used in each cell are raised or lowered separately or collectively to maintain their proper distance from the molten cathode layer and are replaced individually as they are consumed. In the plants using this system, separate facilities are required for fabricating and baking the anodes. The continuous anode, or Soderberg system, is based on the periodic replenishment of the anode materials during operation. The additions, in the form of a paste, are introduced into a rectangular compartment suspended over the pot and are baked by the heat of the pot as it moves downward in the compartment. The paste is fully baked when it reaches the molten electrolyte. There are two methods of introducing current to the anodes. The Horizontal Spike Soderberg (HSS) cell utilizes a series of horizontal spikes attached to flexible current carriers. The Vertical Spike Soderberg (VSS) cell utilizes a suspended vertical spike with a rigid connection.

6.1.3 Source and Nature of Emissions

6.1.3.1 Reduction Cells - The gases evolved from the reduction cells consist predominantly of carbon dioxide and carbon monoxide formed by the reaction of the carbon anodes with the oxygen released by the electrolytic dissociation of alumina.

Other gases are emitted in relatively small amounts during normal cell operation. These include sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), silicon tetrafluoride (SiF_4), hydrogen fluoride (HF), and water vapor. Hydrogen sulfide, COS, CS_2, and SiF_4 usually exist only within the cell and break down into simpler forms before they are emitted to the atmosphere. Hydrocarbons, such as pitch, volatilize from Soderberg anodes as they are baked in the cell, forming part of the cell gas effluent. A small amount of inert fluorocarbons, principally as CF_4, form during the anode-effect period that occurs if the Al_2O_3 concentration in the bath drops below two percent and the voltage rises.[5] Emissions from a cell may increase as much as tenfold during the anode effect;[5] such a cell is known as a "wild cell".

Most of the airborne particulates in the cell effluent consist of alumina and carbon from the dusting of these cell materials. Other components identified in the particulate matter include cryolite (Na_3AlF_6), aluminum fluoride (AlF_3), calcium fluoride (CaF_2), chiolite ($Na_5Al_3F_{14}$), and iron oxide (Fe_2O_3).[8,31,33,34]

Nature of Fluoride Emissions - Fluoride compounds are present in both the gaseous and particulate phases. An estimated 50 percent of the evolved fluorides are present as HF gas, which is highly water-soluble. The fluoride particulates are submicron in size, ranging from approximately 0.05 to 0.75 microns, with the majority, by count, being smaller than 0.25 microns.[6] Reaction of moisture with aluminum fluoride-containing compounds in the bath appears to be responsible for a substantial part of the HF found in reduction cell fumes.[31] At the bath temperature (970 °C or 1780 °F), the vapor pressure of cryolite is 2.1 mm Hg.[34] Generation of hydrogen fluoride must occur before the vapors are quenched by contact with cool air inasmuch as the equilibrium for hydrolysis of fluoroaluminates is favorable only near pot temperatures.[33]

Factors affecting fluoride evolution have been studied using a 10,000 ampere cell.[5] Variations in fluoride evolution during cell operation appear to be related to cell temperature and alumina concentration in the electrolyte. Generally, the fluoride evolution rate is accelerated by increased temperature, decreased NaF/AlF_3 weight ratio, and decreased alumina concentration. Only about 5 percent of the water introduced into the bath with the alumina is reacted to form hydrogen fluoride.[35]

Cell Emissions - The effluents from cells using Soderberg anodes usually contains somewhat more fluorides than those using prebake anodes (See Section 6.1.5).[2,14,28] Soderberg cells are usually larger than prebake cells of the same amperage rating because Soderberg cells are made to work on both sides of the cell whereas most prebake cells are worked in the center. The work area of a Soderberg cell is more than twice as large as that of a prebake cell with the same rated production. Since volatilization of fluorides at cell temperatures is related to exposed surface area, more fluorine is evolved from the Soderberg cell than from the prebake cell when operating parameters are similar. Moreover, Soderberg anodes produce more hydrocarbon fumes in the cell room than prebake cells produce.

The modern vertical spike Soderberg cell collects the gases, tars, and dusts from the cell in a more concentrated form than other types of cells, which makes fluoride removal from cell effluents somewhat less difficult. Collection is accomplished by minimizing the flow of dilution air into the collection hood by the use of a tight skirt around the hood. The geometry of a VSS cell, makes installation of an efficient hood difficult and reduces the efficiency of cell effluent collection. Hence the overall efficiency for collecting and removing fluoride emission from VSS cells is often lower than that for prebaked cells. A typical gas flow in a VSS installation of

0.6 million standard cubic feet (SCF) per ton of aluminum is substantially less than the volumes handled by other cells.[6] The uncollected fluorides from VSS cells enter the potroom environment, however, and often atmospheric emissions from the cell room are greater than those from the control equipment for the cells unless scrubbers are installed on the cell room roof monitors.

The hydrocarbon content of the raw gas from a modern VSS cell is reduced by burning the tar components and carbon monoxide present with a pilot burner located in the collection duct. The burner is usually employed only to ignite the mixture because the raw gas has sufficient intrinsic value to maintain combustion. Analyses of samples taken from the gas collection channel surrounding VSS anodes before and after the burner, showed the following:[6]

1. Before the burner, the gases contained approximately three percent hydrocarbons by volume, principally methane, ethane, and butanes. Altogether, 11 different hydrocarbons were identified.

2. In the combustion gases after the burner, the hydrocarbon compounds amounted to less than 0.1 percent by volume.

3. Fluoride evolution increased sharply during the anode effect that occurs when the Al_2O_3 content of the electrolyte drops below two percent.

Analyses[6] of precipitator dust from a typical Soderberg cell room showed that: (1) the water-soluble portion of the dust was mainly hydrated aluminum fluoride and cryolite; (2) the insoluble portion contained some cryolite and calcium fluoride; (3) the dust contained a substantial quantity of alumina, which is lost during the charge of the pots; and (4) no organic fluorine compounds, such as monofluorobenzene and monofluoracetic acid, could be detected. It was concluded: (1) that there was no evidence of an emission of organic fluorine compounds either in the form of gases or condensates; and, (2) that if they occurred at all, they would be present in only negligible quantities.

The composition of the burned gases from VSS pots can vary considerably because of variations in raw materials, operating conditions of the cells, and the design and operation of the gas burners. The following data have been suggested as mean values for the composition of the gases delivered to the gas washers: hydrogen fluoride (HF), 700 parts per million (ppm) by volume; sulfur dioxide, 200 ppm by volume; dust, 0.27 grains per standard cubic foot (scf); and tar, 0.02 to 0.06 grains per scf.[6]

6.1.3.2 Peripheral Operations - Peripheral operations must also be taken into account in considering the overall air pollution problems of aluminum plants. Emissions from the anode or paste preparation plants consist of hydrocarbons, carbon particles, and fluorides from the baking of recycled spent anodes that contain a small amount of cryolite. In the anode rodding rooms, fluorides may also be released during the melting of the cast iron recovered from spent anodes. Purification of aluminum by chlorine fluxing in the cast house is a source of chloride emissions (Section 6.2, Aluminum Foundries).

6.1.4 Control Techniques

There are three major approaches to air pollution control in aluminum reduction plants. One method is based on the collection and treatment of total cell-room gases; the second is based on the collection of the cell gases at the point of evolution, followed by treatment of this much smaller volume of gas; and the third combines both methods and has been used in Europe to achieve better than 95 percent control of all fluoride emissions.[37,42] Table 6-1 shows data for the various systems.

6.1.4.1 Cell Room Ventilation - One ventilation design for plants using prebaked anodes permits the unhindered release of the cell gases into the ambient air of the cell room. The ambient air enters through louvers on the sides of the cell room near ground level, sweeps across the cells, and exits through scrubbers.

The scrubbers are reinforced plastic spray chambers with propeller-type fans. A water solution of soda ash is used for scrubbing by recirculation of the liquid through the spray chamber nozzles. The liquid circulation rate is about ten gallons per 1000 cubic feet of air flow.[2,41]

The efficiencies of these types of scrubbing systems are shown in Table 6-2.

TABLE 6-2 FLUORIDE REMOVAL EFFICIENCIES FOR CELL ROOM VENTILATION SYSTEMS

Location	Removal efficiencies, Percent		
	SO_2	HF	Particulate
United States,[2,41]	70	90	85
Switzerland[30]	-	95	53
Sweden[30]	79	95	72
France[30]	-	90	-
Germany	-	90	-

TABLE 6-1

COLLECTION SYSTEMS FOR EMISSIONS FROM PRIMARY ALUMINUM PLANTS

		EFFLUENT					EMISSIONS							
							DUST				GAS			
Type	Collection System	Air vol. M^3/lb	Dust g/m^3	Dust lb/10^3lbAl	HF g/m^3	HF lb/10^3lbAl	g/m^3	lb/10^3lbAl	Collector	Efficiency %	g/m^3	lb/10^3lb	Scrubber	Efficiency %
HSS[22]	Cell	2-3 $(10)^5$	0.08 0.12	10.8	.04	4.3	.02 04	3.2	Cycl.	70	.005 .01	0.8	W.S. Series	81.25
	Room	$2(10)^6$	.015	12.9	.002	15.3	0.15	12.9	None	0	.002	15.3	None	0
VSS[22]	Cell	$1-5(10)^4$	1-5	38.8	.5-2.5	19.4	0.1	1.3	ESP	96.7	.005 .002	.16	W.S. Series	99.2
	Room	$3.5(10)^6$	.015	22.6	.001 .002	2.3	0.15	22.6	None	0	.0015	2.3	None	0
Alusuisse[39] V.SS.	Cell	-												
	Room	$8.47(10)^6$	.004	9.7	.002	12.1	.002	4.8	W.S.	50	.00025	0.6	W.S. Series	93
Montecatini[28] V.SS.	Cell	$3.5(10)^4$	.5	7.9	.005	5.2	.0055	.086	ESP	98.9	.002	.03	Cl.Series	99.4
	Room	$3(10)^6$	.0036	4.8	.330	2.8	.0018	2.4	W.S.	50	.0006	0.8	W.S.Series	71
Pechiney[37] Pre-Bake	Cell	-												
	Room	$8.2(10)^2$		30		13.0		4.5	W.S.	65		1.3	W.S.Series	90
Alusuisse[38] Pre-Bake	Cell	-												
	Room	$15(10)^6$	.0036	8.6	.0044	10.6	.0017	4.1	Spray	52	.00023	0.55	Spray	95
Rheinfelden[13] V.SS.	Cell										.002			
	Room										.0025			
Pechiney[36] V.SS.	Cell	$5.4(10)^4$	1.33	20.5	.73	11.2	.09	1.4	ESP	93	.01	.17	Spray	98.5
	Room	$6.5(10)^6$	.0083	15.4	.0025	4.6	.0027	5.1		67	.00051	0.94		79

6.1.4.2 Individual Cell Ventilation Systems - The other method of ventilation control employed is local exhaust ventilation by installation of a series of exhaust hoods to enclose the active areas of the cells.[6] Each individual pot hood is connected to a central exhaust header by means of convenient branch ducts. The cells are maintained under slight negative pressure by the exhaust fans. For prebaked or HSS pots, the volume of air drawn through each pot hood ranges from 1,000 to 5,000 cubic feet per minute.[6,18,22]

For VSS cells the volume of exhaust gases from each pot varies from 250 to 400 cubic feet per minute.[14,22] For hooded cells operating at 130,000 amperes, a typical air flow of 2,600 scfm per cell is equivalent to 3,730,000 scf per ton of aluminum. The required air flow for high (95 percent) capture of cell emission depends on the design of the cell hood. The hood should fit tightly around the cell with a minimum leakage when the portable cell panels of the hood are in proper position.

In order to recover the particulate matter and limit the release of air polluting gases, the waste gas is cleaned by single treating units or combinations consisting of a dry-type dust separator and a wet scrubber powered by an induced-draft fan.

In primary separation, particulates, principally alumina, are removed by dry-type, dynamic-precipitator centrifugal collectors, multiple-tube cyclones, or electrostatic precipitators.

The subsequent removal of fluorides from the main gas stream by wet scrubbing involves the absorption of highly soluble HF and the partial collection of fine particulate particles. To accomplish this, the exhaust from the primary separators is discharged directly to scrubbers employing packed trays and water sprays or sieve towers for the impingement collection of gaseous impurities. The open-type scrubber, commonly referred to in the industry as the "rain barrel", is normally constructed of redwood. To capture some of the dust particles and to remove the fluorine compounds by scrubbing, suitable spray headers are mounted within the interior. Redwood scrubbing towers are of low pressure drop (usually less than two inches water) and are 12 to 15 feet in diameter, and 40 to 60 feet high. Approximately six gallons of water are used for each 1000 cubic feet of gas.[6,10]

A successful control system used in VSS plants is shown in Figure 6-1. The control plant uses high efficiency cyclones, an electrostatic precipitator and two scrubbers in series.[14,15,22] The cell effluents are fed to a burner, where they are mixed with secondary air and burned. Here, the residual tar content is reduced sufficiently to eliminate fouling of downstream equipment. Particulates are removed in the high efficiency cyclones and the electrostatic precipitator. Gas velocity in the electrostatic precipitator is three feet per second and the total effective area of the collecting electrodes is approximately 300 square feet per 1,000 scfm gas flow to give about 98 percent efficiency.[16,29,43]

About 61 pounds of particulates are collected per ton of aluminum, produced in Soderberg cells,[22] compared to about 51 pounds of particulate collected per ton of aluminum produced in prebaked cells.[2,41]

The waste gases, largely free of dust, leaving the electrostatic precipitator are now sufficiently cool to pass to scrubbers made of polyvinyl chloride. These are equipped with spray nozzles directed toward the center. Each scrubber has a settling tank with a recirculation pump. When the solution in the first scrubber has reached

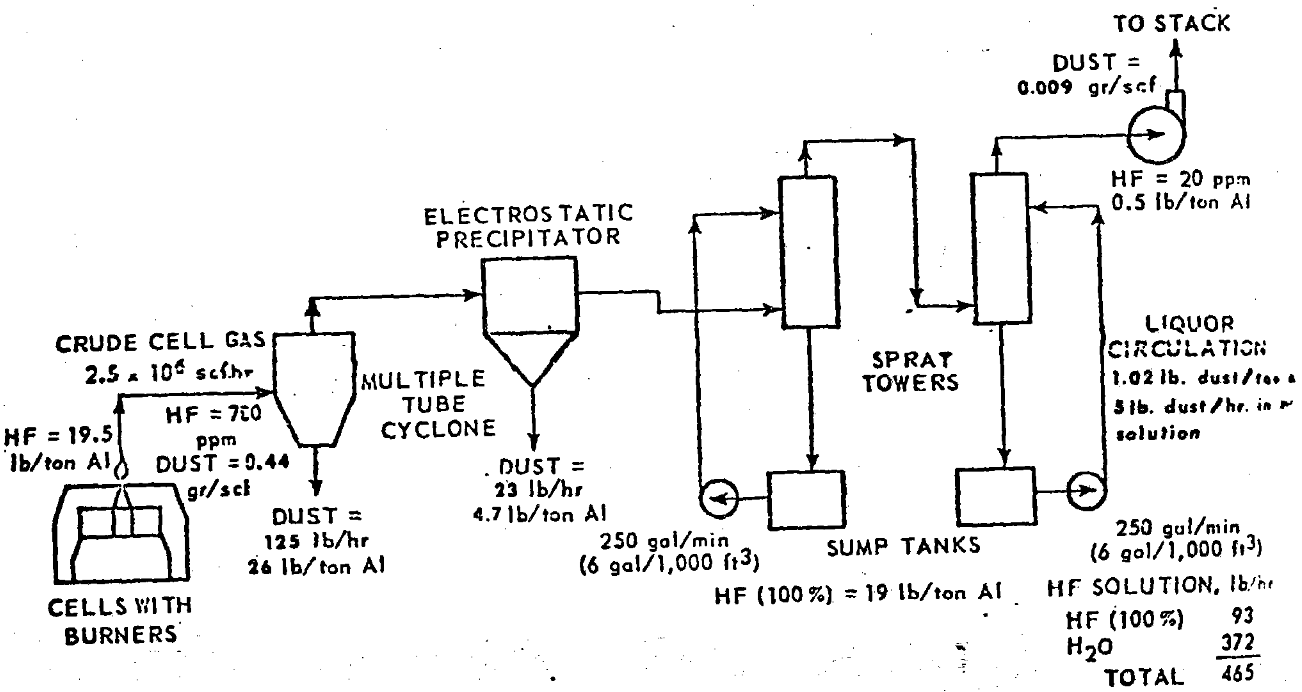

Figure 6-1. Typical control system for VSS Soderberg cells in c room with annual capacity of 43,000 tons aluminum.[14,15,22]

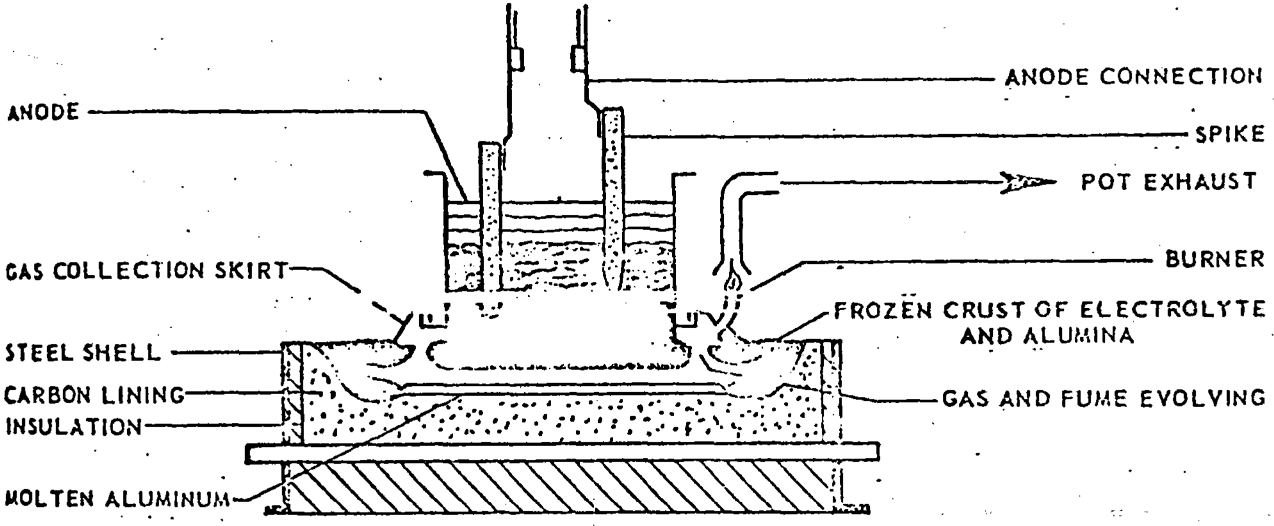

Figure 6-1a. Vertical-spike Soderberg cell.[14,15,22]

a content of about five percent HF it is drawn off and replaced by the solution of the second scrubber. The latter will then be run with fresh water. The use of this selective absorption system, based on pure water rather than on alkaline solutions for absorption, results in pure recovered HF solutions free of dust and SO_2 and thus suitable for synthetic cryolite manufacture.

This scrubbing plant, which has a low pressure drop and requires very little supervision, reports 99.6 to 99.9 percent efficiency for HF.[12,28] The gas at the final stage contains less than 20 ppm HF.

6.1.4.3 Alternate Cleaning Techniques - Sieve-Plate Tower

A compact sieve-plate gas absorber column, which self-cleans during continuous operation, was being used in 1963 in a VSS plant in Norway for the absorption of HF.[13] Fresh water is used as scrubbing fluid.

A full-scale tower is 4.5 feet in diameter and has three sieve plates. It operates with a gas flow of approximately 210,000 scfh, with a pressure drop of four to five inches of water per plate. Typically, the HF concentration in the inlet gas is 700 ppm, with a particulate loading range of 0.3 to 1.0 grains per scf.

ations of this tower have shown that with the production of a scrubbing solution containing about one gram of HF per liter, the absorption efficiency exceeded 97 percent for HF and was less than one percent for SO_2, making the solution suitable for synthetic cryolite production. In addition, about 80 percent of the fluorine content of the solid particles in the gas was washed out, as was about 70 percent of the total dust.[13]

Floating-Bed Wet Scrubbers - The design of Soderberg cells using horizontal spike anodes is such that large amounts of diluent air are required for good gas collection at the cell. The amount of dilution prevents economical combustion of the tars and hence the treating equipment is subject to fouling. Consequently, the choice of a control system for HSS is rather limited.

A floating-bed type of scrubber, reportedly self-cleaning, that overcomes the tar fouling problem has been reported to remove 95 percent of gaseous fluoride and sometimes up to 99 percent of total solids.[6]

Wet Scrubbing Systems - All wet scrubbing systems have the inherent disadvantage of converting an air pollution problem into a water pollution problem. In most areas the resulting liquid wastes cannot be discharged to a stream or delivered to a municipal sewage system. Treatment is required to remove the settleable solids, to control the pH to stated limits and to reduce the dissolved fluorides to low values.

Dry Collection Systems - A dry system for treating the effluent from prebaked anode cells uses fabric filters precoated with activated alumina or another adsorptive or reacting material. The cell effluent, mixed with some excess air introduced by infiltration, is collected under a cell hood and is drawn by an exhauster fan through the dust collectors. As the gas stream is filtered through the layer of filter-aid and cloth, the gaseous fluorides are adsorbed by or reacted with the filter-aid and the particulates are simultaneously trapped. It has been reported that up to 98 percent of the particulates and 96 percent of the gaseous fluorides are collected with this system.[18,30] A large amount of filter-aid is required for the reaction. If activated alumina is used i can be recycled to the electrolytic cells.

A still higher recovery of both gaseous and partic late fluoride has recently been reported.[30,33] This system has a total collection efficiency in excess of 9 percent. It is accomplished by passing the gases, collected from hooded pots, through a thin fluidized bed of metal grade alumina. Fabric filters above the fluidized bed prevent the escape of fugitive dust. The gaseous hydrogen fluoride is chemisorbed on the alumina in a monomolecular film which transforms to aluminum fluoride upon heating, as when the reacted material is subsequently recycled to the electrolytic cell. Additional hydrogen fluoride can be physically adsorbed on the alumina but it is subsequently released to the collection system when that material is exposed to the heat of the cell. For this reason, the rate of flow of alumina through the fluidized bed is controlled to limit the reaction to chemisorption.

The technique of placing a heavy bed of alumina on the cell crust on prebaked anode cells has long been practiced by industry.[6] Some contaminants are collected by adsorption or by filtering. Since the electrolyte forms a hard crust, the gas vents are usually small and the rate of gas evolution through them is so great that no significant collection of re-usable fluorides is accomplished.[30]

Comparison of Control Systems - Using typical performance characteristics, cell-room ventilation is compared with two individual cell ventilation systems in Table 6-3.[1,16]

The data indicate that atmospheric emissions of fluorides and particulates are lower for a control system based on cell ducting than for a system based on the ventilation of the entire cell room. Dry control systems that use alumina to capture the particulates and to chemisorb the gaseous fluoride offer the most efficient control at the lowest overall cost.[30]

Some minor losses occur when it is necessary to replace a prebaked anode. Losses can occur if the cell hooding has not been effectively done or if the hooding and the duct systems are not properly and carefully maintained. Good operating practice and continuing preventative maintenance can keep these losses less than 5 percent. In geographic areas where effective hooding of cells is not practiced and pressure exists from the enforcement of local and State air pollution control regulations, dual control systems for the abatement of fluoride have been installed.[40] These systems cleanse the effluents from the roof monitor of the cell room as well as cleansing the gases collected from the cells.

TREATMENT OF [illegible]
ON PLANT CAPACITY OF 100,000 TONS PER YEAR
ALUMINUM[2,18,22,27,30]

	System A(prebaked)	System B(prebaked)	System C(prebaked)
Collection system	Cell-room ventilation collection in building monitors	Individual cell local ducting	Individual cell local ducting
Treatment system	Wet scrubbing in spray towers	Mechanical separation followed by wet scrubbing	Dry cleaning using activated alumina
Gaseous effluent flow rate			
Overall plant scfm	7,700,000	280,000-1,400,000	280,000-1,400,000
Per cell, scfm	27,000	1,000-5,000	2,000-5,000
Per ton Aluminum, scf	40,000,000 to 60,000,000	1,500,000-7,300,000	1,500,000-7,300,000
Raw gas before treatment			
particulates, gr/scf	0.01	0.02-0.08	0.02-0.08
lb/hr	660	94-470	94-470
Fluorine as HF, ppm	10	30-200	30-200
Fluorine as HF, lb/hr	230	60-300	60-300
Atmospheric emissions			
Particulates, lb/hr	119	14-70	2-9
Fluorine as HF, lb/hr	23	6-30	4-12
Collection efficiencies,%	100	85-90	93-96
Removal efficiencies,%			
Particulates,%	82	85	99
HF,%	90	90	97
Installed cost of systems, 10^6 dollars	6.2	2.5-6.0	3.0-3.8
Annualized costs, 10^6 dollars	2.0	0.75-1.8	0.28-0.89

6.1.4.4 Control Techniques for Peripheral Operations

Effective removal of pollutants from the furnaces used for preparing the prebaked anodes is usually accomplished by maintaining maximum combustion efficiencies in these furnaces and by scrubbing the waste gases in venturi-type scrubbers to remove residual tars, soot, and particulates. The treated waste gases from these furnaces are exhausted through stacks.[6]

Emissions from anode and cathode fabrication plants contain sulfur dioxide, hydrocarbons, and tars; these are sometimes fed to primary combustion chambers of the curing ovens used for baking anodes. Scrubbers with alkaline solutions are used at the outlet of the combustion unit to remove about 70 percent of the sulfur dioxide.[2,41] Dust from other aluminum plant areas are controlled by various types of cyclones, bag filters, electrostatic precipitators, and various other filters.

Chlorine emissions can occur from casting furnaces when chlorine is used to flux the molten aluminum to remove gases, oxides, and other impurities. Furnace design and use of mixtures of nitrogen and chlorine have reduced the chlorine emissions.[10] High-energy scrubbers and/or floating-bed wet scrubbers have been used to abate these emissions.[17] For a more detailed discussion see Section 6.2.1.

Dust Loadings - The dust emitted to the atmosphere is a function of the dust concentration in the inlet air and the collection efficiency of the dust separators. Figures 6-2, 6-3, and 6-4 show, for cell-room ventilation and two types of cell emission collection systems, the relations between atmospheric dust emissions and the inlet dust concentrations over a range of collection efficiencies.

Emission collection systems differ characteristically from each other with regard to inlet dust concentration and volume of airhandled. Cell-room ventilation requires the largest volume of air (40 to 60 x 10^6 scf per ton of aluminum) with a relatively low dust concentration of 0.01 grain per scf. The dust content in the more concentrated effluent from VSS pots is typically about 1.0 grain per scf or higher.[15,22]

The control techniques discussed heretofore are based primarily on an engineering approach to abate pollution.

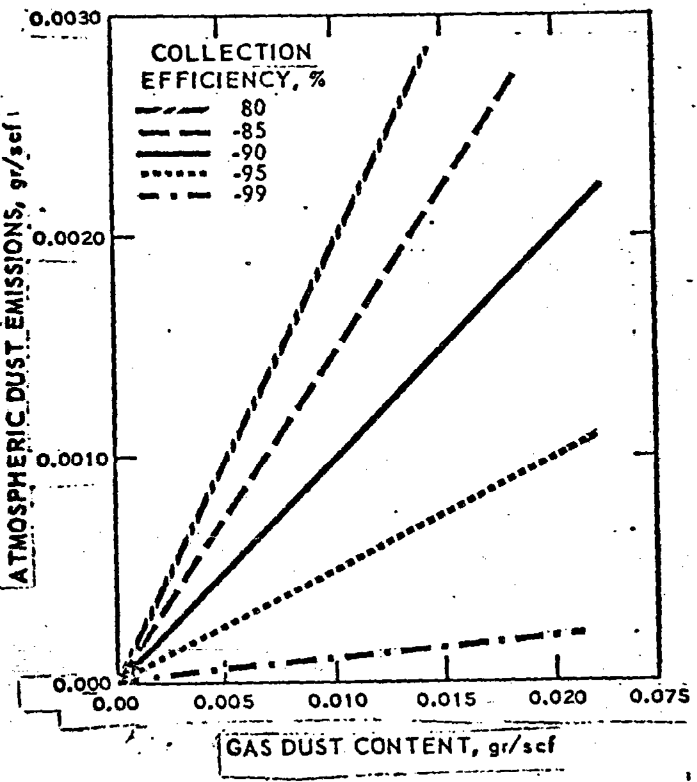

Figure 6-2. Relationship between atmospheric dust emissions and dust content of raw cell-room gas at various collection efficiencies of a cell-room ventilation system.[15,22]

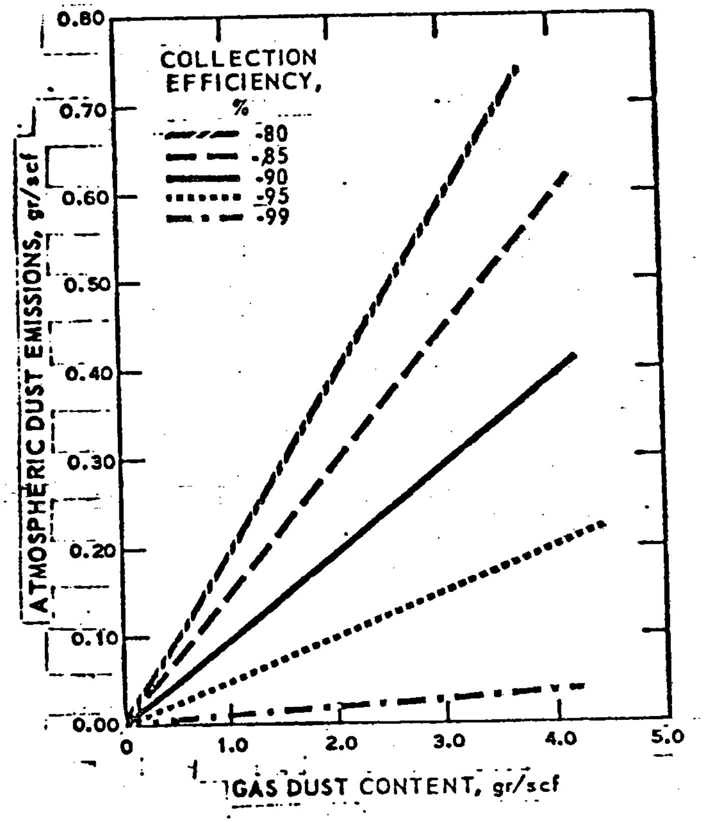

Figure 6-3. Relationship between atmospheric dust emissions and dust content of raw cell gas at various collection efficiencies of hooded VSS Soderberg cell system.15,23

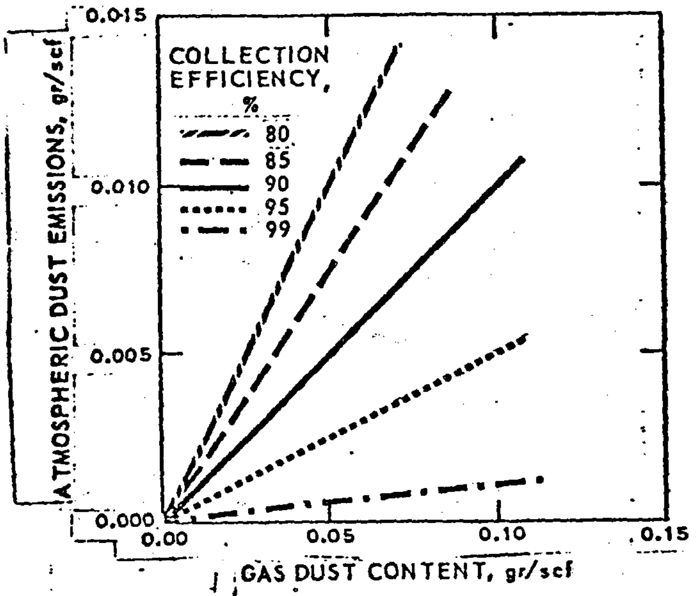

Figure 6-4. Relationship between atmospheric dust emissions and dust content of raw cell gas at various collection efficiencies of hooded HSS Soderberg cell system.[15,22] (System is also applicable for hooded prebake anode cells.)

Buffer Land Zone - The use of extensive peripheral land around a primary aluminum plant serves principally as a permanent monitoring area for both vegetation and ambient air. The monitoring is done to measure specifically the fluoride pickup in vegetation which, in turn, indicates the effectiveness of the air pollution control equipment.[30] Moreover, the area tends to collect some of the principal emission from the plant and may reduce fluoride impact on nearby commercial agriculture. This practice should not be construed to be an acceptable air pollution control technique but rather a method for monitoring fluoride emissions from a primary aluminum plant.

6.1.5 Magnitude of Emissions

The actual 1968 primary aluminum capacity and estimated fluoride emissions for all domestic plants are summarized by region in Table 6-4. Calculations based on information from the literature show that the uncontrolled fluoride emissions range from 40 to 65 pounds total fluorine per ton of aluminum for prebaked anode plants and for Soderberg plants.[11,12,14,15,16,27,28,30]

Collection and removal efficiencies must be considered when the total efficiency of a control system is estimated.

TABLE 6-4 ESTIMATED FLUORIDE EMISSIONS FROM U.S. ALUMINUM PRODUCTION, 1968 BASIS

Location	Primary Al production capacity,[3,26] short tons	F emissions before control,[a] tons[30]	Atmospheric F emissions, after control,[b] tons[30]
Pacific Northwest	1,155,000	35,000	5,600
Gulf Coast	820,000	25,000	4,000
TVA Region	530,000	16,000	2,600
Ohio Valley - New York State	750,000	24,000	3,800
Total	3,255,000	100,000	16,000

[a] Uncontrolled fluoride emissions (gaseous plus particulate) range from 40 to 65 pounds per ton of aluminum.[11,12,14,15,30]

[b] Atmospheric emission estimates were based on estimates of total plant efficiencies ranging from 73 to 86 percent for wet scrubbing systems and 90 to 95 percent for dry cleaning systems[11,12,14,15,18,30]; the overall efficiency of all plants was estimated at 84 percent.

total efficiencies ranging from 73 to 86 percent were estimated for control systems using primary dust collectors followed by wet scrubbing. Total efficiencies of dry control systems were estimated at 90 to 95 percent.

Total atmospheric emissions are estimated at 16,000 tons of fluoride, particulate and gaseous in 1968. The total fluorides evolved from plants before control equipment are estimated at 100,000 tons in 1968.

6.1.6 Cost of Fluoride Emission Control Systems

As discussed previously, fluoride emission control systems in the primary aluminum industry are generally of two configurations: (1) overall cell-room ventilation, and/or (2) treatment of effluents collected by individual cell hoods connected by a duct network. Costs of equipment (shown as purchase and installed costs) and annualized costs have been developed on an individual basis for each type of control.

Figures 6-5, 6-6, and 6-7 show the purchase, installed, and annualized costs for a system based on forced ventilation of the cell-room. Costs are indicated for plant sizes (expressed as annual production capacities of primary aluminum) ranging up to 180,000 tons. Costs for hooded

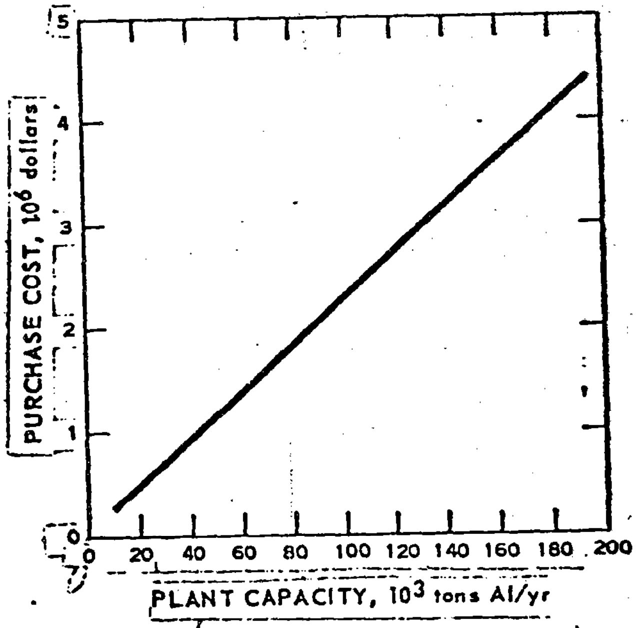

Figure 6-5. Purchase cost of cell-room ventilation system versus plant capacity (1969).[2,9,19] (Air flow through cell-room is of the magnitude of 40 to 60 million scf per ton of aluminum.)

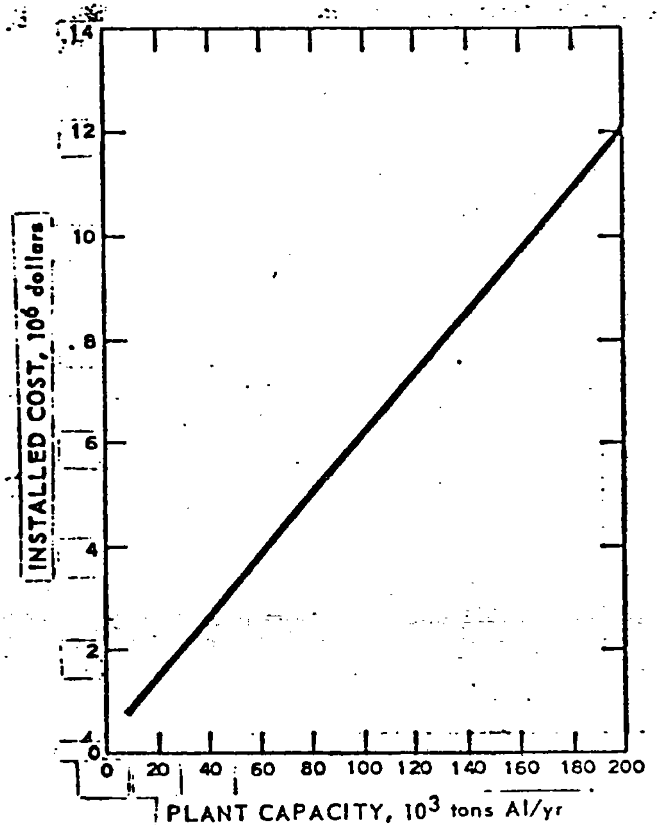

Figure 6-6. Installed cost of cell-room ventilation system versus plant capacity (1969).[2,9,19] (Air flow through cell-room is of the magnitude of 40 to 60 million scf per ton of aluminum.)

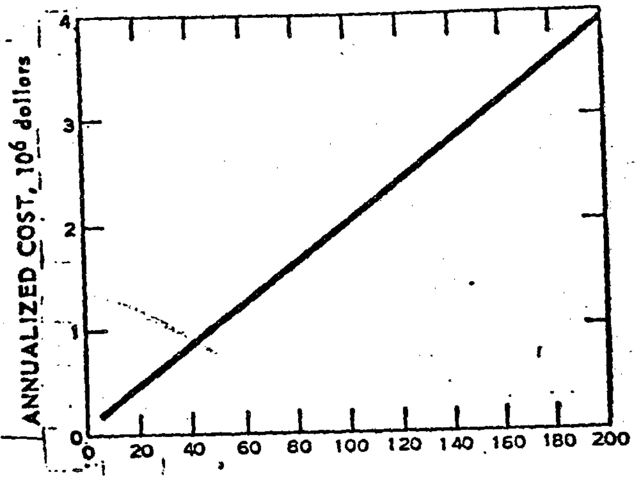

Figure 6-7. Annualized cost of cell-room ventilation system versus plant capacity (1969).[2,9,19] (Air flow through cell-room is of the magnitude of 40 to 60 million scf per ton of aluminum.

cell collection systems are shown in Figures 6-8, 6-9 6-10. See Sections 6.1.3.1 and 6.1.4.4 for discussion of exhaust requirements for the various types of aluminum cells.

Although an aluminum plant may be designed on the basis of one or the other type of control system, certain plants utilize both types of controls at the same time. For these plants, the costs shown for each system would be additive. As a case in point, Figures 6-11 6-12 and 6-13 show the combined equipment and annualized costs for a VSS Soderberg plant using both a hooded cell collection system and cell-room ventilation.

Basis for Costs - The purchase cost represents the cost of buying the major pieces of equipment, such as scrubbers, ducts, burners for VSS cells, fans, etc. The installed cost is defined in Section 2.

The annualized cost includes depreciation calculated on a straight-line basis using ten years as the useful life of the equipment.

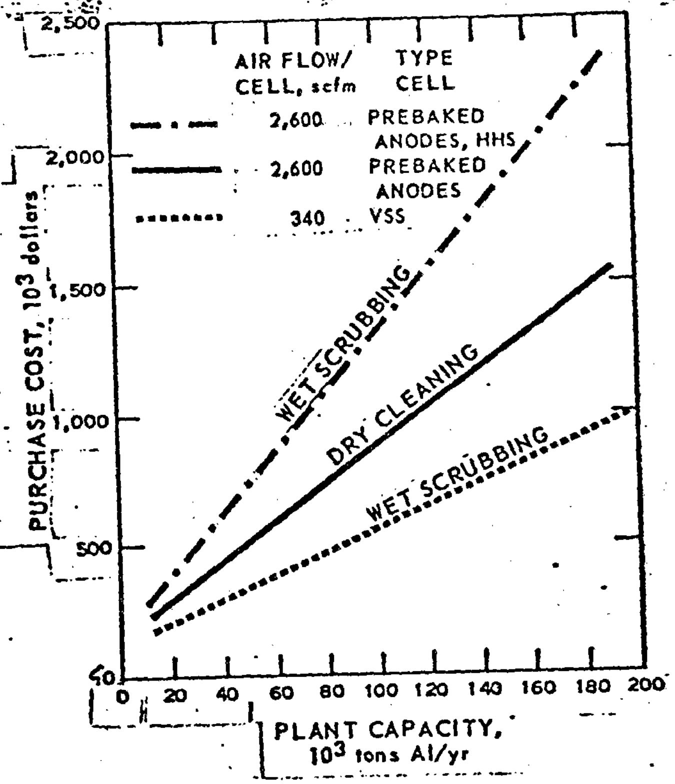

Figure 6-8. Purchase cost of cell emissions collection systems versus plant capacity (1969).[9,12,13,14,18,19]

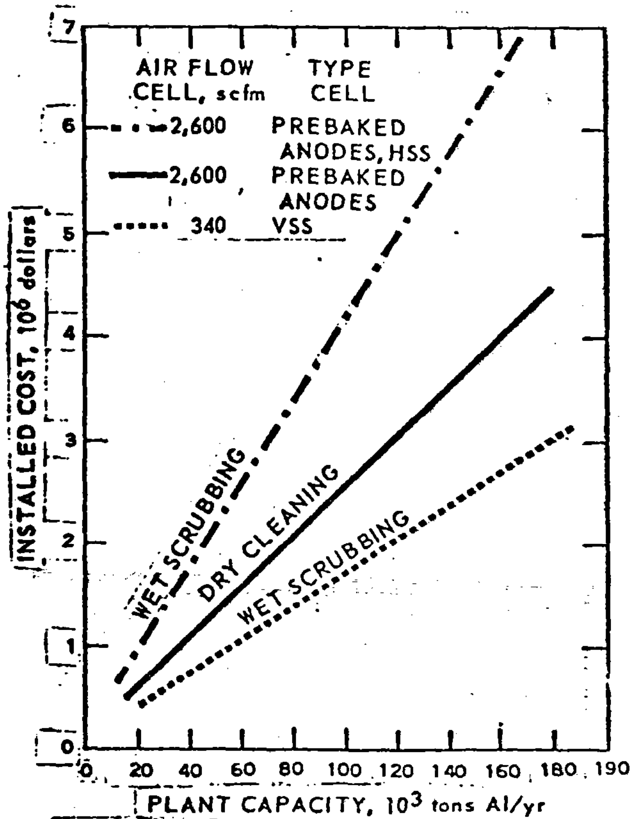

Figure 6-9. Installed cost of cell emissions collection systems versus plant capacity (1969).[9,12,13,14,18,19].

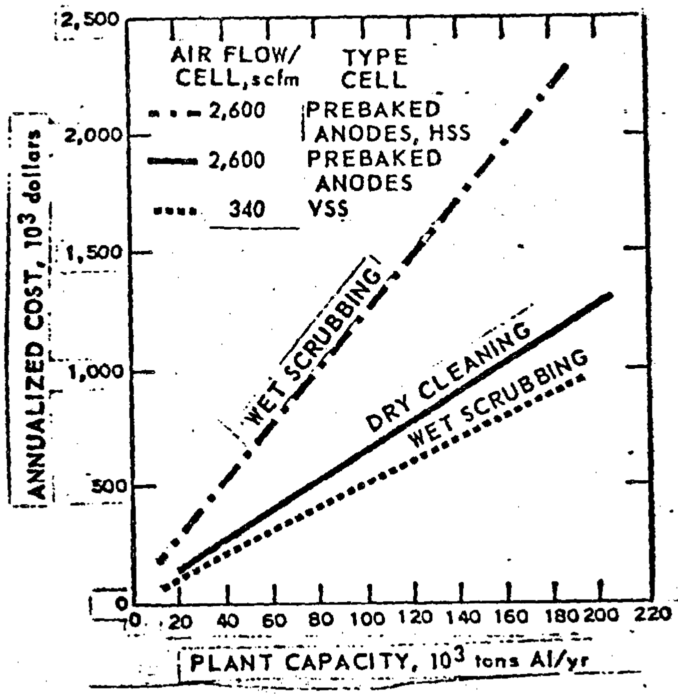

Figure 6-10. Annualized cost of cell emissions collection systems versus plant capacity (1969).[9,12,13,14,18,19]

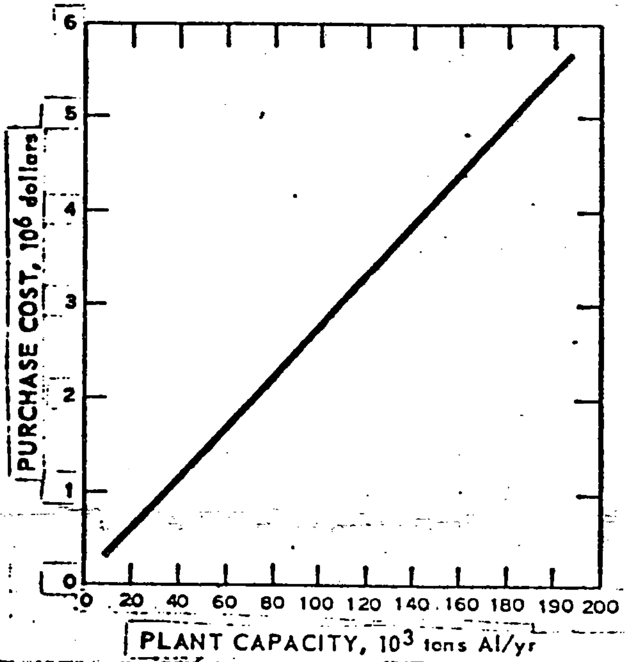

Figure 6-11. Purchase cost of emission control equipment for VSS Soderberg cells versus plant capacity (1969).[12,13,14,16,18,19] (Cell fume collection system plus cell-room ventilation used.)

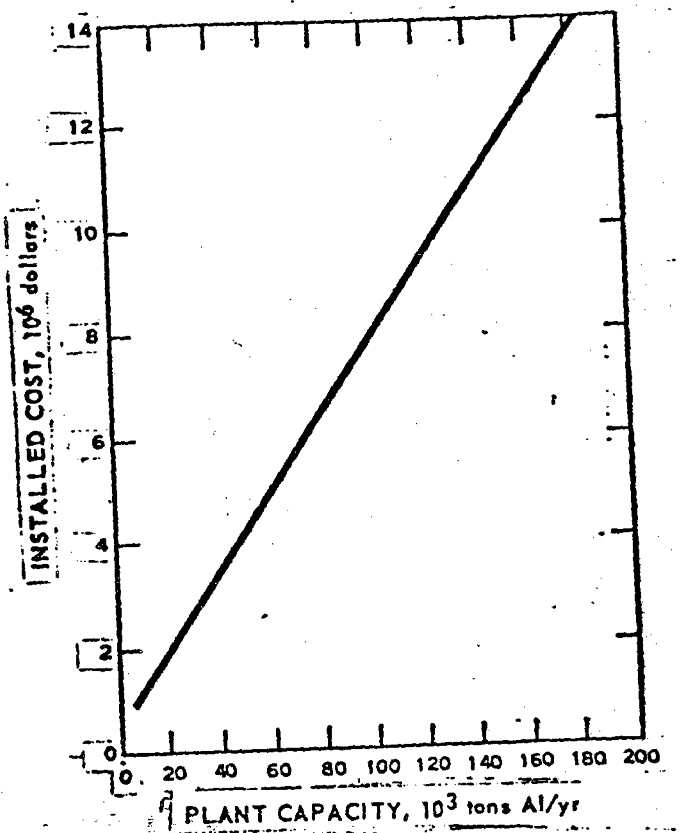

Figure 6-12. Installed cost of emission control equipment for VSS Soderberg cells versus plant capacity (1969).[12,13,14,16,18,19] (Cell fume collection system plus cell-room ventilation used).

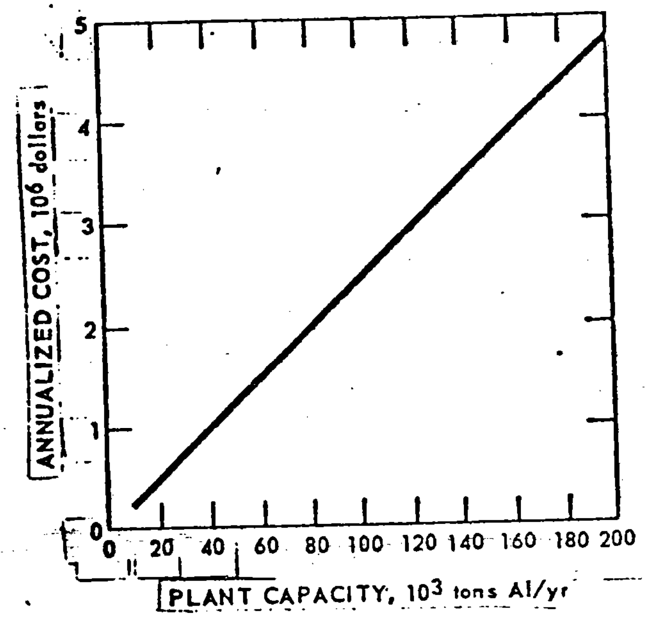

Figure 6-13. Annualized cost of emission control equipment for VSS Soderberg cells versus plant capacity (1969).[12,13,14,16,18,19] (Cell fume collection system plus cell-room ventilation used).

6.2 ALUMINUM FOUNDRIES

6.2.1 Introduction

Primary aluminum is normally cast into pigs, furnaced, alloyed, and cast into ingot; or, in some instances, delivered in the molten state for subsequent furnacing, alloying, and casting into semi-finished shapes. Pigs are subsequently remelted and the resulting molten metal is alloyed before casting into ingots or into semi-finished shapes.

Seconday smelters consumed 1,000,000 tons of scrap in 1968 to produce aluminum alloy pig to specification for the casting industry.[25] Aluminum castings account for nearly one-fifth of all aluminum shipments. In 1967, 2,800 foundries shipped over 750,000 tons.[24] Die castings amounted to 57 percent of the total shipped and were produced by 10 to 15 percent of the foundries.

The alloying of molten metal, and the secondary refining and alloying operations require the use of fluxes for (1) removing dissolved gasses, (2) removing and/or controlling undesired metal constituents, and (3) the breaking and floating of suspensions of metallic oxides in the melt.

Usually the fluxes employed are gaseous, with chlorine and nitrogen the principal gases employed. A small quantity of solid flux is used, most of which is in the form of metallic chlorides. A very small quantity of these fluxes contain fluorides.

6.2.2 Source and Nature of Emissions

Flux materials employed in the remelting of aluminum are a source of the airborne contaminants from this operation. In addition, dirt, oil, grease and other contaminants present in scrap aluminum can cause large quantities of smoke and fumes to appear in atmospheric emissions.

Fluxes - A discussion of the various types of fluxes used in melting aluminum is available.[21] Cover fluxes, such as sodium chloride and calcium fluoride, protect the metal from contact with air and thus prevent oxidation. Solvent fluxes, such as aluminum chloride, vaporize at the melting temperature and, by boiling, cause the oxides and dirt to rise to the top of the molten metal where they can be skimmed off. Aluminum fluoride and chlorine are fluxes used to reduce the magnesium content in aluminum alloys.

Emissions from aluminum fluxing are primarily gaseous chlorine and hydrogen chloride and, sometimes, small quantities of gaseous hydrogen fluoride. Solid particulate emissions consist largely of metallic chlorides and metallic oxides with occasionally small quantities of metallic fluorides.

Particle Size of Fumes - One study found that the major constituent in the fume from salt-cryolite fluxing in a furnace was sodium chloride plus smaller quantities of aluminum and magnesium compounds. It was indicated that the particles of fume were all smaller than two microns, most of them being 0.1 micron.[21]

During chlorination, an acidic fume is emitted from the furnace and contains mostly submicron particles of aluminum chloride and aluminum oxide, 100 percent of the particles being smaller than two microns and 90 to 95 percent smaller than one micron.

A review of the literature on aluminum melting indicates that the major area of concern has been the atmospheric emissions of aluminum oxide, aluminum chloride, chlorine, and hydrogen chloride, so that the attention paid to fluoride emissions from this operation is relatively small. It has been estimated, however, that the emissions from an open-hearth furnace processing aluminum alloys contain gaseous fluorine in concentrations ranging from 0.005 to 0.012 grains per standard cubic foot. Fluorine in particulates ranges from 0.11 to 0.80 grains per scf during melting of aluminum.[23]

6.2.3 Control Techniques

Abatement of smoky emissions from the melting furnace is accomplished by:[21]

1. Removing oil, grease and moisture from scrap in a drying operation before charging furnace.
2. Charging dried scrap to a separate charging chamber in the furnace.
3. Providing an adequate hood for capturing all effluents from the charging chamber.
4. Passing these effluents through properly designed afterburners before emitting them to the atmosphere.

Two systems for the abatement of emissions from the chlorination have been described. The first requires the design of the melting furnace to have a separate fluxing compartment.[21] Fumes from it are collected and directed through packed-bed scrubbers that use a ten percent caustic solution. After scrubbing, the effluents are passed through a fabric filter, precoated with alumina, before being discharged to the atmosphere. Experience has shown that the scrubber effluents must be heated above the dewpoint to prevent blinding of the fabric.

The second system uses a separate fluxing compartment in the melting furnace and passes fluxing effluents through a floating-bed scrubber and/or a high-efficiency scrubber with a pressure drop of 30 or more inches.[12] A significant reduction in the quantity of fumes in fluxing effluents has been reported from the use of a mixture of chlorine and dry nitrogen.[10] Chlorine fluxing is done until nearly all magnesium is removed; then nitrogen is used to remove the remaining occluded gases and other impurities.

The above techniques, used to control atmospheric emissions of aluminum oxide, aluminum chloride, chlorine, and hydrogen chloride, will also control fluoride emissions. No published information was found concerning the importance of fluoride emissions from aluminum melting. The quantity of fluoride, either gaseous or particulate, is either insignicant or unknown.

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7. STEEL MANUFACTURE

The raw materials for iron-making -iron-ore, coal, and limestone - are only rarely associated with fluoride-bearing materials. In the few instances reported, fluoride, occurring with iron ore, appeared in the blast furnace slag or was emitted during sintering to agglomerate fines.[1,2,3]

In the manufacture of steel, however, the use of fluorspar flux for controlling the fluidity of slag results in the evolution of fluorides, probably as HF, SiF_4, SF_6 and particulates.[14]

7.1 IRON ORE EMISSIONS

Data on the fluoride content of iron ore consumed domestically are unavailable in the general literature since only one instance of fluoride pollution related to this source has been reported. Some British ores have been examined and found to contain as much as 0.12 percent fluorine. This will normally be captured by the blast furnace slag, with the fluorine content of the slag reaching 6 percent.[3]

In the one instance of fluoride pollution reported in the United States, a local ore containing probably 0.03 percent fluorine caused fluoride emissions during the sintering of ore fines to reach a concentration of 150 ppm in the off-gas. Control of emissions was achieved by two methods:

1. Hydrated lime (minus 325 mesh) was injected into the sinter plant off-gas to absorb the fluoride, and dust was partially removed in a cyclone. A second injection of limestone (minus 200 mesh) was made, followed by dust separation by means of an electrostatic precipitator, effecting a 96 percent removal of the fluoride.[1,2]

2. Limestone was added to the sinter mix in amounts up to 6 percent to remove nearly half the fluorides previously emitted. To effect heat recovery as well as to limit fluoride emissions, 40 percent of the sinter plant off-gas is re-circulated. Final cleaning is accomplished by injecting limestone and by separating dust in cyclones, followed by an electrostatic precipitator. Efficiency reported is 96 percent.[1,2]

This system reportedly costing $9 million, removes 1.5 tons of fluorine per day from the sinter plant and 2.5 tons per day from the open hearth shop.

7.2 STEEL MANUFACTURE

Fluorspar is used in the manufacture of steel as a fluxing agent to reduce the slag melting point and to increase slag fluidity. The meager data[4] in the literature suggest that the fluorides evolved from the slag react with the fume in the off-gas and are separated in the dust collectors. Although it is true that certain dust collecting systems remove fluorides, emissions can and do occur under some circumstances. The enormity of the dust control burden has obscured the problem of the presence of fluorides and the mechanisms by which they are removed from steel-making off-gases.

7.2.1 Fluorspar Consumption in Steel Making

Table 7 - 1 lists by type of furnace, the steel production and attendant consumption of fluorspar for 1968.[10,11]

Table 7 - 1 CONSUMPTION OF FLUORSPAR IN STEEL MAKING IN 1968

Furnace	Steel production,[10] tons	Fluorspar used,[11] tons	Fluorspar Consumption, lb/ton steel
Open hearth	65,836,000	108,690	3.30
Basic oxygen	48,812,000	307,125	12.58
Electric	16,814,000	68,997	8.34

The amount of fluorspar used will vary widely from the listed average according to the raw materials used and the steel-making practice at the particular steel works and may also show a marked variation from heat to heat. Open hearth use may range from 0 to 10 pounds per ton with a 4-pound overall average.[5] Fluorspar use in the BOF (basic oxygen furnace) varies from 6 to 28 pounds per ton, averaging about 12 pounds. This usage rate is particularly significant since the BOF steel production rate now outpaces the open hearth.[6]

7.2.2 Magnitude of Fluorspar Breakdown

Conditions required for the breakdown of fluorides have been studied.[7] Pure calcium fluoride begins to decompose at about 2200°F. The retention of fluoride is necessary for the control of slag fluidity; at steel-making temperatures (2400 to 3000°F), a partial breakdown of fluorides is inevitable. The extent of breakdown depends upon the slag temperature, the concentration of fluorides in the slag and the length of time the slag is held at temperature.

Specific data on the evolution of fluorides from steel-making slags is not available in the literature; however, an estimate can be made from published data.[1] In this

Table 7.2 SUMMARY OF FLUORIDE EVOLUTION AND EMISSION - 1968

Type Furnace	Steel Production tons[10]	Fluorspar used lb/ton steel[11]	Fluoride evolution lb/ton steel		Fluoride emission tons/year		
			Gaseous	Particulate	Gaseous	Particulate	Total
Open hearth	65,800,000	3.30	0.12	0.47	3,800	13,000	16,800
Basic oxygen	48,800,000	12.58	0.44	1.77	6,400	2,000	8,400
Electric	16,800,000	8.34	0.40	1.58	3,300	11,600	14,900
				Totals	13,500	26,600	40,100

Notes:

1. Assume 15 percent of open hearth have dust removal systems[12].
2. Assume 40.9 percent of BOF capacity is equipped with high energy venturi scrubbers and 59.1 percent with electrostatic precipitators[13].
3. Assume 13 percent of electric furnace installations have bag filters[9].

instance, total fluorides (calculated as fluorine) of 2.5 tons per day were collected from the operation of an open-hearth shop with ten 250-ton furnaces. For a nonoxygen practice, an average heat time of ten hours can be assumed and, with a fluorspar usage of four pounds per ton, spar consumption would be 30,000 pounds per day. Fluorine equivalent in a 72 percent of CaF_2 metallurgical-grade spar would be 10,500 pounds. The fluoride breakdown represented by 2.5 tons per day of collected fluoride amounts, therefore, to about 50 percent.

Total fluoride evolution is summarized along with emissions in Table 7 - 2.[10,11]

7.2.3 Emission Control Techniques

The removal of fluorides from steel furnace off-gases depends upon absorption on lime particulates, followed by separation of the particulates, or upon absorption by water. Control equipment specific for fluorides is not installed in today's practice, but is considered in selecting either a dry or wet dust separation system. Wet systems tend to provide better removal of fluorides.

7.2.3.1 Basic Oxygen Furnace - All BOF furnaces in the United States are equipped with high-efficiency electrostatic precipitators or venturi scrubbers. No published data are available for fluoride emissions from these dust control systems. A fluoride elimination of 97.5 percent is estimated for the wet-scrubbing systems.[8] Probably less than 1 percent of the fluoride is eliminated in dry, electrostatic systems.

7.2.3.2 Open Hearth Furnaces - Although dust control equipment has been added to some existing open hearth shops, the growing obsolescence of the open hearth and the economics of steel-making have reduced, until recently, the tendency to invest in control equipment. However, recent changes in scrap pricing and the high capital investment for new BOF furnaces have revived open hearth technology with accompanying installations of emission control equipment. Fluoride elimination is expected to be 97.5 percent effective with wet-scrubbing system.[8]

7.2.3.3 Electric Furnaces - About 13 percent of the electric furnaces located in steel mills in the United States are equipped with dust separation equipment.[9] The majority of these are bag filters with dust removal efficiencies reachin

3 percent. The waste gas is cooled by water sprays and/or air dilution before reaching filters. Data are unavailable for the fluoride elimination efficiency of this system.

The fluoride content of off-gases from a 90-ton German furnace has been measured.[4] These data indicate that 85 percent of the fluoride is present as particulate matter. Fluoride elimination efficiencies following cleaning of the water-cooled gas in a bag filter are reported to be 90 percent for particulate fluorides and 65 percent for gaseous fluorides.

7.2.3.4 Waste Gas Cleaning System - Dust collection is a necessity on any new steel-making facility. Major new steel-making installations will most likely be BOF. The most effective system appears to be one using a high energy, wet scrubber to remove particulates and 97 to 98 percent of the fluorides.

7.2.4 Estimate of Fluoride Evolution and Emission

Table 7-2 summarizes a calculated estimate of fluoride evolution and emission from steel-making processes. In making this estimate, it was assumed that 1) 50 percent of the fluoride contained in the spar is retained by the slag and 50 percent is evolved, 2) of the fluoride evolved, 20 percent is gaseous and 80 percent is particulate, 3) high energy venturi scrubbers remove 99 percent of gaseous and 95 percent of particulate fluorides, 4) electrostatic precipitators remove 95 percent of particulate and no gaseous fluorides, and 5) bag collectors remove 99 percent of the particulate and no gaseous fluoride.

7.3 FOUNDRIES

7.3.1 Iron Foundries

Metallurgical-grade fluorspar consumed in 1968 as a flux in iron foundries amounted to 33,154 tons. The fluorine content of spar used as flux will remain in the slag, except for some particulates from the feed which may be entrained in the off-gas.

7.3.2 Non Ferrous Foundries

Approximately 14,200 tons of metallurgical-grade fluorspar and 6,300 tons of acid grade were consumed in 1968 in nonferrous foundries. An estimated 4,000 tons of fluoride was emitted to the atmosphere, based on an assumed evolution of 50 percent of the fluoride and with no control of emission.

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8. THE CERAMIC INDUSTRY

The ceramic industry, in contemporary terms, covers those manufactures in which earthy mixtures are transformed into useful articles through the application of heat. Common brick and construction products such as tile and clay pipe are derived from clay and shale. Other ceramics include glass, frits, enamels and new products based on mineral oxides.

8.1 BRICK AND TILE

8.1.1 Introduction

In general, the production of brick and other clay-derived products is based on firing the shaped clay in kilns at high temperature to develop a rigid form for the product. Clays usually contain 0.02 to 0.3 percent fluorine by weight. During kiln firing, a substantial portion of bound fluorine is evolved as a mixture of gaseous fluorides (HF and SiF_4) plus entrained particulates.

Descriptions of control techniques for kiln firing have not been found in the literature. No kilns are controlled at present. Present annual fluoride emissions to the atmosphere are estimated as 18,500 tons fluorine.

8.1.2 Process Description

The heavy clay industry includes producers of building brick, fire brick, wall and floor tile, ceramic pipe, and related products. The production of this ware involves the plasticizing of the clay, or a mixture including clay, by the addition of water so that it may be shaped or formed by some means into the desired object. After being shaped, the object is dried to increase its strength so that it may be handled, and it is then fired at elevated temperatures (frequently in the range of 2000°F) until there has been some vitrification or fusion of the components to develop a glassy bond that makes the shape permanent.

The heavy clay industry originally used batch kilns for heat treatment of the ware. The release of pollutants from such kilns is sporadic and proper control is complicated. Kiln design has evolved, however, through semi-continuous kilns to continuous kilns. The bulk of the output of the industry now comes from continuous tunnel kilns, and control techniques should be devised primarily for this type. German observers [1,2] have reported, furthermore, that forestry and agricultural damage from fluoride emissions occurs more often from continuous tunnel kilns than from semi-continuous kilns.

A typical tunnel kiln consists of three sections: a preheating section, a firing section, and a cooling section. Formed ware is stacked on cars that are pushed into the preheating section and move slowly through the length of the kiln. Fuel is burned only in the central firing section. Heat economy is effected by preheating the combustion air as it is drawn through the cooling section in contact with the fired ware, and by utilizing the heat in the combustion gases to preheat and dry the ware as it moves toward the firing section.

8.1.3 Fluoride Emissions

The fluorides that evolve from brickyards have their origin in the clays that are usually obtained locally. Samples of clay used for brick-making in England were found to contain 450 to 550 ppm of fluorine on a dry basis.[3,4] It may be assumed that a representative average fluorine content in clay is of the same order of magnitude as the fluorine in the earth's crust, or 0.065 percent.[14]

The evolution of fluorides during brick-making is apparently a function of the firing temperature. It has been reported that 30 percent of the bound fluorine is evolved from the kiln.[4] Studies in Germany indicate still higher quantities of fluoride evolution, about 95 percent of the input fluorine.[2,5]

The concentration of fluorides in the stack gases has been reported as high as 740 ppm F.[4] Tests on the stack gases from German brickyards, however, indicate much lower concentrations (less than 1 ppm F).[5]

On the basis of the release of 95 percent of the input fluorine from a typical tunnel kiln, the evolution of fluorides is expected to average 1.23 pounds fluorine per ton of clay.

8.1.3.1 Magnitude of Fluoride Emissions - Table 8-1 shows the geographical distribution of clay production and the estimated fluoride evolution in each region of the U.S. The base year is 1968. It is assumed that the evolved fluorides are currently emitted to the atmosphere.

Table 8-1. ESTIMATED EVOLUTION OF FLUORIDE FROM HEAVY CLAY AND SHALE;[6] GIVEN BY REGION FOR 1968.

	Clay Consumption[a] 10^3 tons/yr.	Fluoride Evolution[b] tons/yr.
New England	400	250
Middle Atlantic	3,600	2,210
South Atlantic	5,800	3,570
East North Central	6,550	4,030
West North Central	1,800	1,110
East South Central	3,900	2,400
West South Central	5,550	3,410
Mountain	500	310
Pacific	1,900	1,170
Total	30,000	18,500

[a] Clay and shale used for making only brick, tile, refractories, and heavy clay construction products.

[b] Evolved fluorides currently emitted to atmosphere
Conversion Factor: 1.23 $\frac{\text{lbs F}}{\text{ton clay}}$

8.1.4 Control Techniques

Apparently, the emissions from brick yards are uncontrolled and pollution abatement systems are still to be developed on a firm basis. The emissions of fluorides can be reduced by operation at minimum kiln temperatures (below 2000°F) and through the choice of clays with low fluoride content.

8.2 GLASS AND FRIT

8.2.1 Introduction

Glass products involve the high temperature conversion of inorganic raw materials into homogeneous melts which are fabricated into useful articles. The common soda-lime glass is based on sand, limestone and soda ash.

Frit is produced byquenching a melt of various minerals which yields a mass of friable particles. Ceramic coatings are essentially water suspensions of ground frit and clay. Fluorine compounds are added as fluxes in the formulation of glass and frit and for increased opacity and other desirable properties.

8.2.3 Fluoride Emissions

Fluorine compounds are frequently added in the formulation of glasses and frits. The most common source of fluorine is calcium fluoride (fluorite or fluorspar), although cryolite (Na_3AlF_6) is sometimes used, as is also synthetic sodium fluosilicate. These compounds are used as fluxes or to impart such properties as brilliance or opacity to the products.[8,9]

Release of fluorides from frit and enamel when cryolites or sodium fluosilicate is used as a flux is greater than the fluoride released when the flux is fluorspar.[4] Moreover, fluorspar is the cheapest flux and thus is the one most commonly used.

The melting temperatures in the glass tanks usually range between 2600°F and 2900°F. Those temperatures are high enough to volatilize partially any fluorides present in the melt. In frit preparation, the temperatures are lower, but when frit is prepared in rotary furnaces, the mechanical action favors the entrainment of volatile products by the flue gas. In glazing and enameling, the temperatures are usually lower but a tremendous surface exposure enhances the release of any volatile compound generated.

Only a fraction of the fluoride in these materials is emitted in processing. During production, the loss of fluoride from a glass batch amounts to about 20 percent of the fluorine introduced.[10] Fluorine compounds react with the other glass constituents to produce volatile silicon, aluminum, and sodium fluorides. The losses of these compounds from a glaze are rather unpredictable, being easily affected by small differences of batch composition, firing schedule, and kiln atmosphere, so that the final product is not uniform.[11]

The emission of fine particulates from the melting furnaces is a major air pollution problem in the glass industry. Fabric filters are usually necessary for trapping the fine particulates. One sample of trapped dust showed a fluoride content as high as 8.6 percent by weight.[7] Gaseous fluorides (as HF) which pass through the fabric filter can be removed by scrubbing with water.

When frit is melted, significant quantities of dust and fume are evolved and fluorides have been shown to be present in the stack gases from a rotary frit smelter (largely particulate) in concentrations ranging from 0.035 to 0.20 grains per scf.[7]

Fabric filters or venturi water scrubbers are usually employed as control equipment for frit smelters. The collection efficiency of venturi scrubbers has been shown to range from 31 to 68 percent for particulate matter and 50 to 93 percent for fluorides when they were used to control the fluoride content of fumes evolved from frit smelters.[7]

The fluorides emitted to the atmosphere by the glass industry can be expected to vary quantitatively with the fluoride compounds used in the formulation of the glass and frit products. Fluorspar is the most common fluorine-based additive, and the magnitude of fluoride emissions can be estimated on the basis of fluorspar consumption by the glass industry, for which figures are readily available.

8.2.3.1 Magnitude of Emissions , - Table 8-2 shows the annual consumption of fluorspar by the glass industry in the United States. The equivalent fluoride input comes to 15,200 tons of fluorine per year. Assuming 20 percent of the input fluoride is evolved, the annual evolution comes to 3,040 tons of fluoride. Assuming an average control efficiency for the nation of 10 percent,[15] 2,740 tons of fluoride would be emitted to the atmosphere annually.

Table 8-2. CONSUMPTION OF FLUORSPAR[a] IN GLASS AND FRIT MANUFACTURE,[12] TONS/YR.

Fluorspar in Glass Industry	24,184
Fluorspar in Enamel Industry	4,757
Combined	28,941
Fluorine Equivalent	15,200

[a] Fluorspar contains 97 percent CaF_2.

8.2.4 Control Techniques

Wet centrifugal scrubbers and fabric filters are used to trap the fine particulates from glass melting furnaces. Fabric filters operate at a collection efficiency of over 99 percent, which is much higher than the efficiency obtainable by low pressure, wet centrifugal scrubbers. The furnace gases must be cooled by air dilution or heat exchange before they pass through into the fabric filters.[7] A combination of fabric filters and wet scrubbers may be necessary for complete control of mixtures of gaseous and particulate fluorides.

Fabric filters and venturi water scrubbers are two types of control equipment used for frit smelters. The fabric filters operate at higher efficiencies than the venturi water scrubbers, although the latter are satisfactory if a pressure drop of at least 20 to 25 inches is maintained across the venturi throat with a throat velocity between 15,000 and 20,000 feet per minute. Water usage amounts to 6 gallons per 1,000 cubic feet of gas.[7]

8.2.5 Costs

Costs have been calculated for a fluoride emission control system based on a water jet-activated, single-stage venturi scrubber operating at a pressure drop of at least 20 inches water across the venturi constriction. The scrubber is connected by ductwork to a regenerative furnace melting a typical glass formulation that includes fluorides. The gaseous effluent from the scrubber is exhausted by a fan.

Figure 8-1 shows the purchase and installed costs of control systems versus glass furnace capacity. Figure 8-2 shows the annualized costs versus furnace capacity.

8.3 FIBERGLASS MANUFACTURE

8.3.1 Introduction

Many siliceous mixtures can be made in fibrous form by blowing or drawing a molten mixture of rock, slag, or mineral oxides, causing it to solidify as fine strands. This is the manner in which wool-like fibers used for thermal insulation and absorption are produced. Fibrous glass is used for textile applications and electrical insulation.

The melting of glass constituents in a cupola or reverberatory furnace is a source of evolution of particulate matter and condensed fumes. A portion of any bound fluorine in the starting materials is evolved as gaseous fluorides.

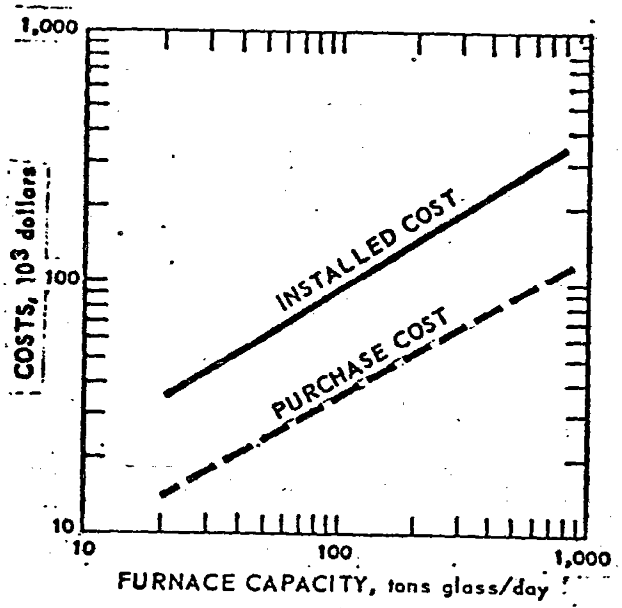

Figure 8-1. Installed and purchase costs of control systems for glass and frit furnaces (1969).[15]

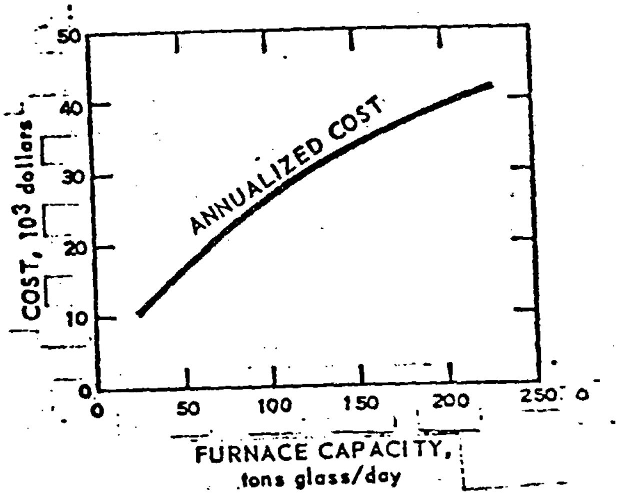

Figure 8-2. Annualized cost of control systems for glass and frit furnaces (1969).[15]

Local exhaust systems employing fabric filters are used to control the emissions from mineral wool furnaces.[13]

8.3.2 Emissions

The material or mixture to be converted into fiber products is melted in a cupola or reverberatory furnace. The stack gases from the furnace carry condensed fumes that have volatilized from the furnace. The gas carries about 20 pounds of fumes per ton of product from a cupola or about 5 pounds from a reverberatory furnace.[13] The minerals used in the charge may contain fluoride, or fluoride compounds may be added in making up the charge. In either case, fluoride compounds are found in the gas. Another source of fume discharge to the atmosphere is the blowchamber. The air stream which serves to form the fibrous product carries out with it fumes, oil vapors, aerosols, and wool fibers. This stream may carry 50 pounds of particulate matter per ton of product, of which 90 percent consists of glass wool fibers.[13]

8.3.3 Control Techniques

Since the emissions from rock wool furnaces and from blowchambers consist predominantly of particulate matter, as either condensed fumes or entrained fibers, efficient control requires the use of fabric filters.[13]

The gas must be cooled to 275° F or lower before going to the baghouse. Most of the fluoride compounds are condensed on cooling and are collected in the baghouse.

It is sometimes more practical to reduce or eliminate the fluoride used in the charge rather than incur the expense of providing additional pollution control equipment. Since phosphorus furnace slag always contains fluoride, the avoidance of the use of this slag will reduce or eliminate fluoride emissions from a slag wool furnace.

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9. OTHER FLUORIDE SOURCES

9.1 MANUFACTURE OF FLUORINE COMPOUNDS

9.1.1 Introduction

Nearly all commercial and industrial fluorine compounds are prepared from hydrogen fluoride, which is manufactured by reacting sulfuric acid with fluorspar. In 1968, fluorspar consumption for this purpose amounted to 659,524 tons.[1] Hydrogen fluoride production for the same year was 302,000 tons.[18] Table 9-1 shows the production of hydrogen fluoride and its distribution among the consuming industries.

9-1 HYDROGEN FLUORIDE PRODUCTION AND UTILIZATION[2]

	1957	1961	1963	1968
Production, T/Y	140,500	190,300	188,400	302,000[18]
Utilization, %				
Fluorinated organics	28	40	40	40
Aluminum	40	33	35	40
Atomic energy	12	12	10	20*
Petroleum	4	4	5	-
Stainless steel	5	3	3	-
Other	11	8	7	-

*Total for Atomic energy, Petroleum, Stainless steel and other uses.

Until the mid 1930's, total fluorspar consumption amounted to less than 150,000 tons annually, of which less than ten percent were used to produce hydrogen fluoride. Predominant uses were for glass etching and polishing, foundry scale removal, and minor production of metal fluorides. Between 1935 and 1941, fluorspar consumption increased to slightly more than 300,000 tons per year, with 16 percent used to produce hydrogen fluoride, which in turn was converted to synthetic cryolite and fluorspar for the aluminum industry.

In 1942, fluorspar consumption spurted to 360,000 tons, with 26 percent used for hydrogen fluoride. This spurt resulted from two wartime developments: (1) use of hydrogen fluoride alkylation catalysts for aviation gasoline, and (2) use of fluorocarbons (Freon refrigerants) for aerosol propellants used in dispensing insecticides for mosquito control.[3] The latter use doubled the rate of growth of the fluorocarbon industry. The fluorocarbon industry consumes over 40% of the HF produced, and is growing at an annual rate of about 6%. Table 9-2 shows the consumption of fluorocarbons according to end use.

TABLE 9-2 CONSUMPTION OF FLUOROCARBONS[a], [19]

	1965		1970[b]	
Use	Million lbs	% of total	Million lbs	% of total
Aerosols	215	46.2	150	27.1
Refrigerants	135	29.0	175	31.5
Plastics	50	10.8	90	16.2
Solvents	25	5.4	75	13.5
Blowing agents	20	4.3	45	8.1
Exports	10	2.1	5	0.9
Miscellaneous	10	2.2	15	2.7
Total	465	100.0	555	100.0

[a] Source: Oil, Paint, and Drug Reporter, 1966.

[b] Predicted consumption.

9.1.2 Manufacture of Hydrogen Fluoride

Fluoride emissions from hydrogen fluoride production operations only occur from spills or from leaks. Precautions begin with tank car unloading vapor control. All storage areas are diked to contain liquids in case of leakage. All pumps are of packless design to prevent leakage. All instruments in the hydrogen fluoride system are sealed to prevent loss of material. Any agitator shaft should be equipped with a double rotary seal purged with hydrocarbon liquid. The fluoride scrubber should be designed for 99.9% recovery of normal amounts of hydrogen fluoride that might be in the noncondensables.[24] Any vented streams are scrubbed with water to eliminate fluorides and recover product.

Figure 9-1 is a schematic flow diagram for the manufacture of hydrogen fluoride. Ground fluorspar and 96 to 98 percent sulfuric acid are charged to an externally fired rotary kiln. A typical acid-grade fluorspar specification is as follows: CaF_2, 97.5 to 98%; SiO_2, maximum of 1.0%; S, maximum of 0.05%; H_2O, maximum of 0.1%; and $CaCO_3$, principal remainder. Calcium sulfate residue is discharged through an air lock and discarded. Acid may be neutralized by mixing the residue with powdered limestone or slacked lime.[4] The product hydrogen fluoride is scrubbed with sulfuric acid, and then distilled to 99.98 percent purity. Carbon dioxide and sulfur dioxide generated from impurities in the feed are vented to the atmosphere after being scrubbed with water to

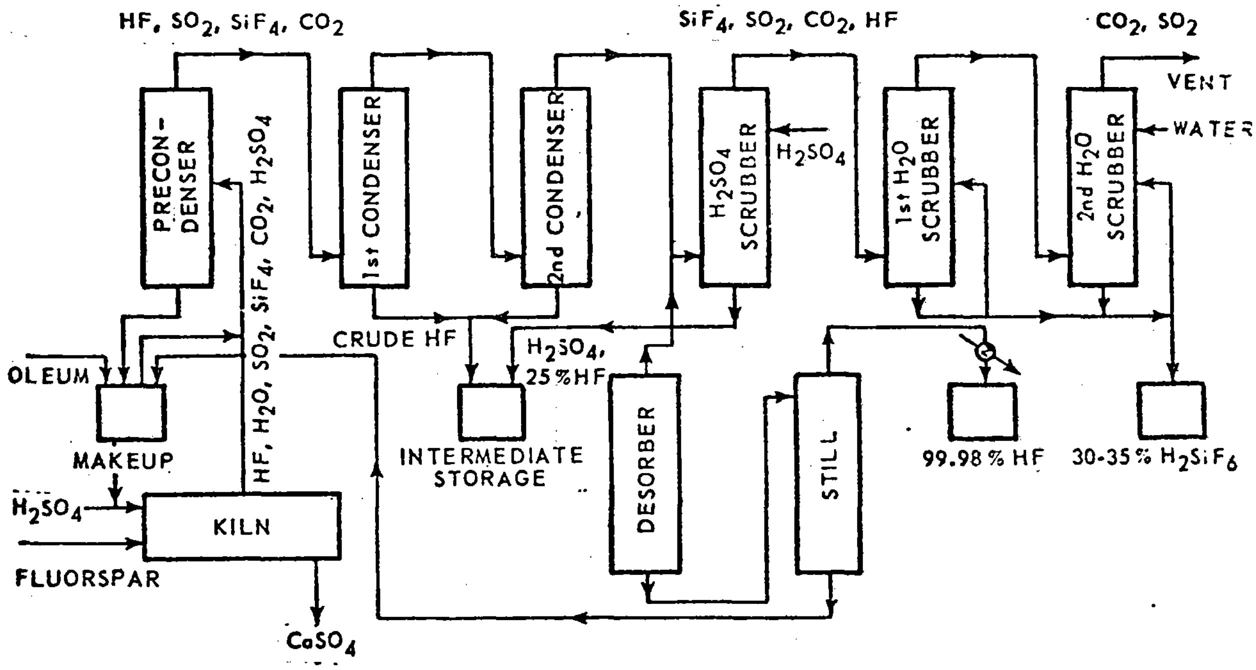

Figure 9-1. Schematic flow diagram for the manufacture of hydrogen fluoride.

remove any hydrogen fluoride and silicon tetrafluoride present.

Acid vapors from storage tanks and process vents may be removed by use of an ejector. The ejector can handle large quantities of water, and also act as an exhauster. This allows for virtual elimination of the small acid content of the waste gases.[23] Of course, water pollution standards must be met in disposal of the water stream.

9.1.3 Manufacture of Fluorine

Fluorine is produced by the electrolysis of a solution of anhydrous potassium bifluoride containing free hydrogen fluoride. Impurities which are removed from the fluorine in sodium fluoride towers are purged from the towers with air and neutralized with sodium carbonate. Since fluorine is a powerful oxidizing agent as well as a highly toxic element, fluorine systems must be maintained well to avoid any leaks or accidental spills.

Figure 9-2 is a flowsheet illustrating the production and liquefaction of elemental fluorine. Gaseous hydrogen fluoride is introduced through a feed pipe below the surface of the electrolyte, which is maintained at about 204 °F. Electrolytic cells operate at 4000 to 6000 amperes at 8 to 12 volts. The fluorine gas produced contains hydrogen fluoride as its major impurity. This is removed in sodium fluoride towers and the fluorine is liquefied by cooling with liquid nitrogen.

Hydrogen fluoride is swept from the sodium fluoride with air. Any fluorine is burned with propane and the hydrogen fluoride is scrubbed out with sodium carbonate.

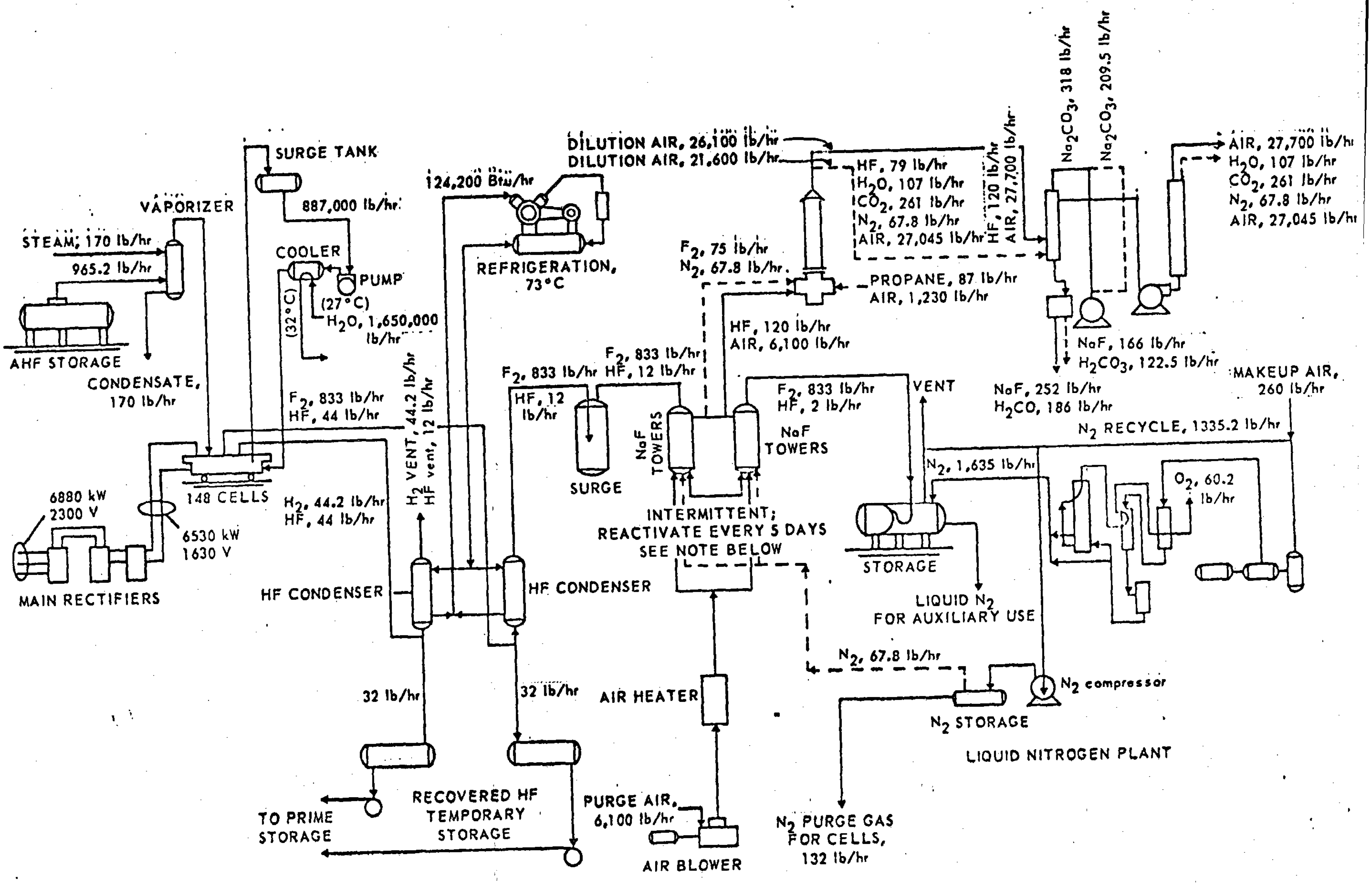

Figure 9-2. Material flowsheet of elemental fluorine production and liquefaction plant, 10 ton/day capacity. (Step 1. Purging residual F_2 at rates indicated. All but a trace of residual F_2 will be removed in 15 min. N_2 purge is maintained for 1 hr to remove last traces. Step 2. HF removal at rates indicated. All but a trace of HF will be removed in 10 hr. Air purge is maintained for 10 hr.)

9.1.4 Manufacture of Fluorocarbons

These compounds are used in a wide variety of compression systems in domestic and commercial refrigerators. They are non-flammable and relatively non-toxic. Raw materials used in their production, however, are highly toxic and production equipment must be well-maintained to avoid leaks or spills. Any vented off-gases are scrubbed with water to eliminate fluoride emissions.

Fluorinated derivatives of methane are designated commercially by a two-digit numerical code in which the first digit is the number of hydrogen atoms present in the compound, plus one, and the second is the number of fluorine atoms in the compound.

Thus, CF_2Cl_2 is designated commercially as "Freon 12," "Genetron 12," etc.; CHF_2Cl becomes "Freon 22," "Genetron 22," etc.; $CFCl_3$ is designated as "Freon 11," "Genetron 11," etc.; and CH_2F_2 is "Freon 32," "Genetron 32," etc.

Production of these materials is illustrated by a description of the manufacture of dichlorodifluoromethane (CF_2Cl_2), which is designated as "Freon 12," "Genetron 12," etc. Figure 9-3 is a flowsheet showing the process for the

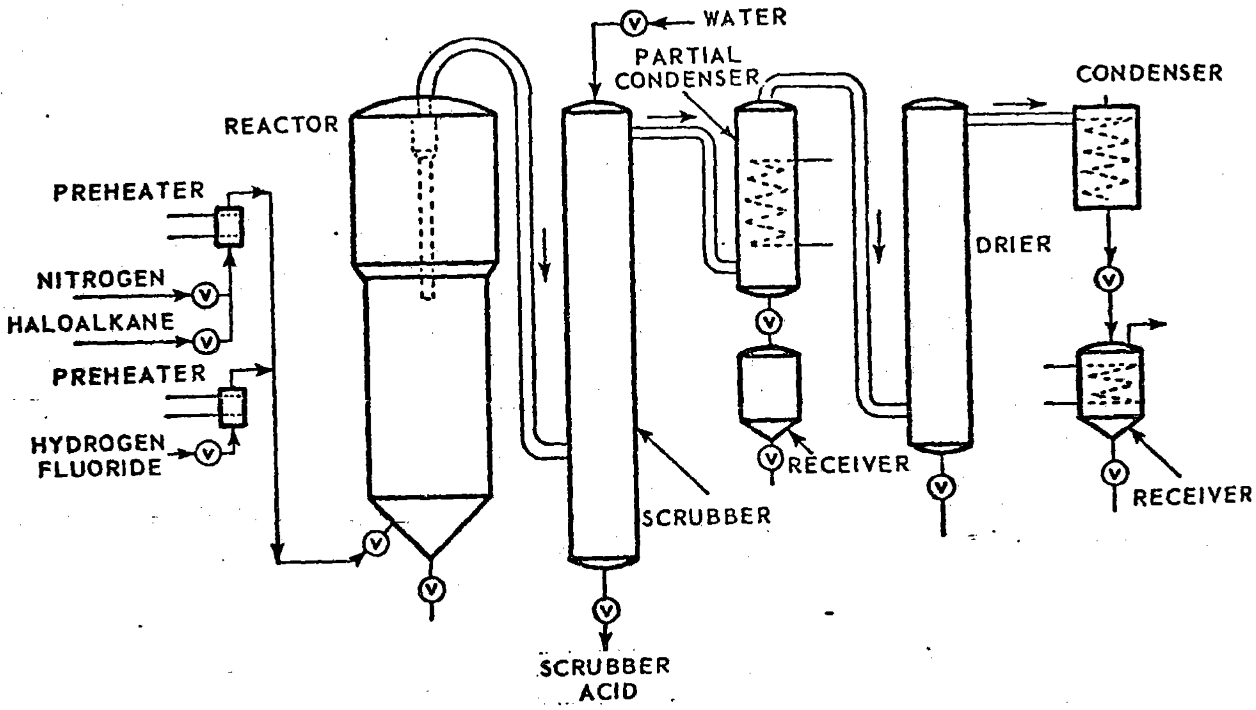

Figure 9-3. Flow diagram for dichlorodifluoromethane manufacture from tetrachloromethane[5] (Source: U. S. Patent 2,744,147).

manufacture of this compound from tetrachloromethane.[5] Tetrachloromethane and hydrogen fluoride are reacted in the vapor phase at 302 °F to 932 °F over a fluidized catalyst. The reaction products are scrubbed with water to remove hydrogen chloride and any residual hydrogen fluoride. The product is then dried and condensed. Dichlorodifluoromethane represents more than half of the entire output of the organic fluorine industry. It is used extensively as a propellant for pressurized spray products.

Tetrafluoromethane (CF_4) is used as a refrigerant, an aerosol propellant, and as a dielectric. It is also used as a raw material for the manufacture of tetrafluoroethylene. Tetrafluoromethane is manufactured by reacting dichlorodifluoro methane with hydrogen fluoride at elevated temperatures using an appropriate catalyst such as antimony trifluoride. Another process for its manufacture combines dichlorodifluoromethane or trichlorofluoromethane and fluorine in a flame process, as shown in Figure 9-4.[5] The reaction products are passed through a rock salt tower to remove fluorine and/or chlorine fluorides, are scrubbed with caustic soda, and are then condensed in cold traps. The

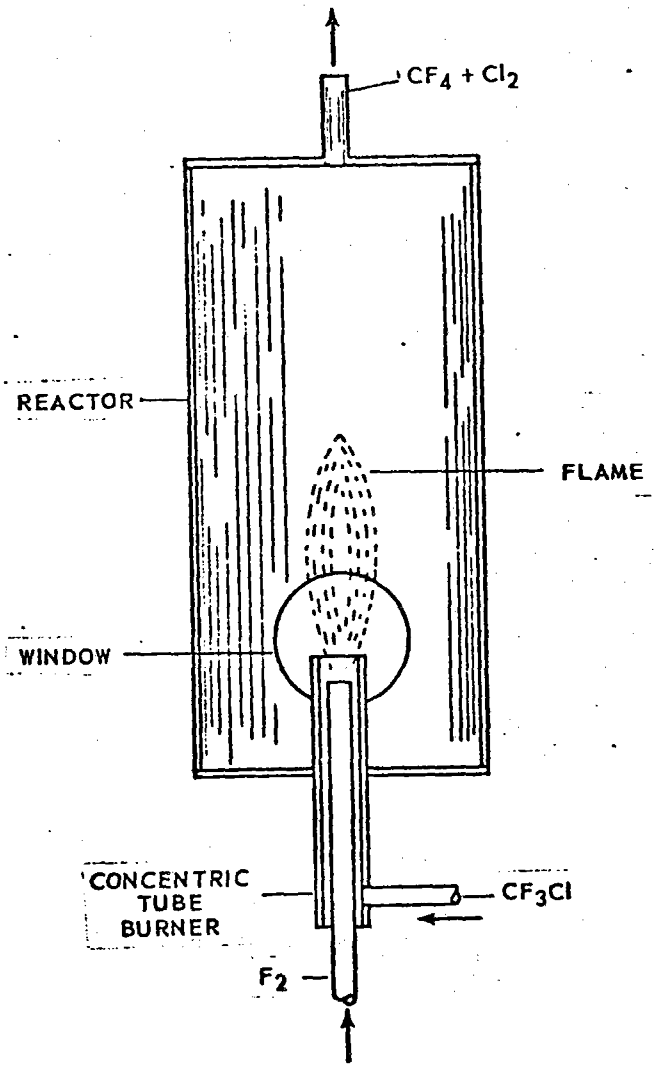

Figure 9-4. Reactor for tetrafluoromethane manufacture by flame process (Source: U.S. Patent 2,895,999).

condensed product is distilled to give tetrafluoromethane. All fluorides are eliminated from vent gases through scrubbing as described.

Tetrafluoromethane may also be manufactured from carbon and fluorine produced electrolytically in a molten electrolyte. Figure 9-5 shows such a cell. This process yields a substantially pure gas containing 95 to 99 percent tetrafluoromethane.

9.2 SEPARATION OF URANIUM ISOTOPES

Uranium hexafluoride, the most volatile compound of uranium, has found extensive application in the separation of uranium isotopes by thermal diffusion. It is manufactured by the reaction of elemental fluorine with uranium tetrafluoride made from uranium dioxide by reaction at 1022 °F with hydrogen fluoride. All materials involved in the preparation of the hexafluoride, as well as hexafluoride itself, are highly reactive and toxic. Extreme precautions are taken to completely contain these materials and avoid any emissions.

Fluidized bed recovery of fluorine in the manufacture of UF_6 is a method of controlling fluorine emissions. The

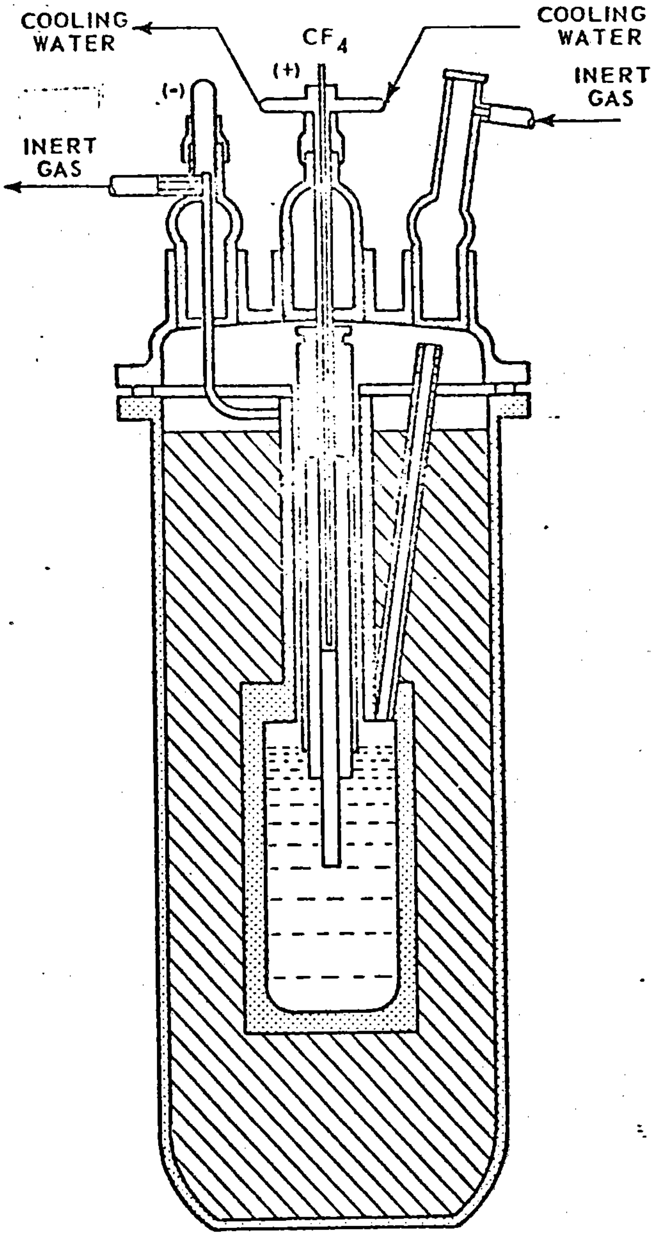

Figure 9-5. Electrolytic cell for tetrachloromethane manufacture from carbon and fluorine[5] (Source: U.S. Patent 2,990,347).

idized bed fluorine cleanup reactor has proven to be a ghly efficient process for the recovery of dilute fluorine the waste gas of the hexafluoride process. Figure 9-6 llustrates a prototype fluidized bed cleanup reactor. UF_4 s added to the fluid bed reactor in large excess. The olids phase and gas phase are intermixed and together behave like a boiling fluid. Fluorine recovery efficiencies have averaged greater than 95 percent and the reactor on stream efficiencies has averaged approximately 90 percent.[20]

In the manufacture of high purity metallic uranium from the hexafluoride and in the fabrication of nuclear fuel elements, hydrogen fluoride is generated. The off-gases containing hydrogen fluoride are scrubbed with potassium hydroxide and calcium hydroxide. The potassium fluoride recovered is sold and the calcium fluoride is discharged to pits in the ground. Neutralized scrubber liquids containing soluble fluorides are discharged into a river in a controlled fashion to limit the fluoride content of the stream to 0.8 ppm.[6]

9.3 COMBUSTION OF COAL

Various coals from mines around the world have been analyzed and found to contain from 0.001 to as high as 0.048

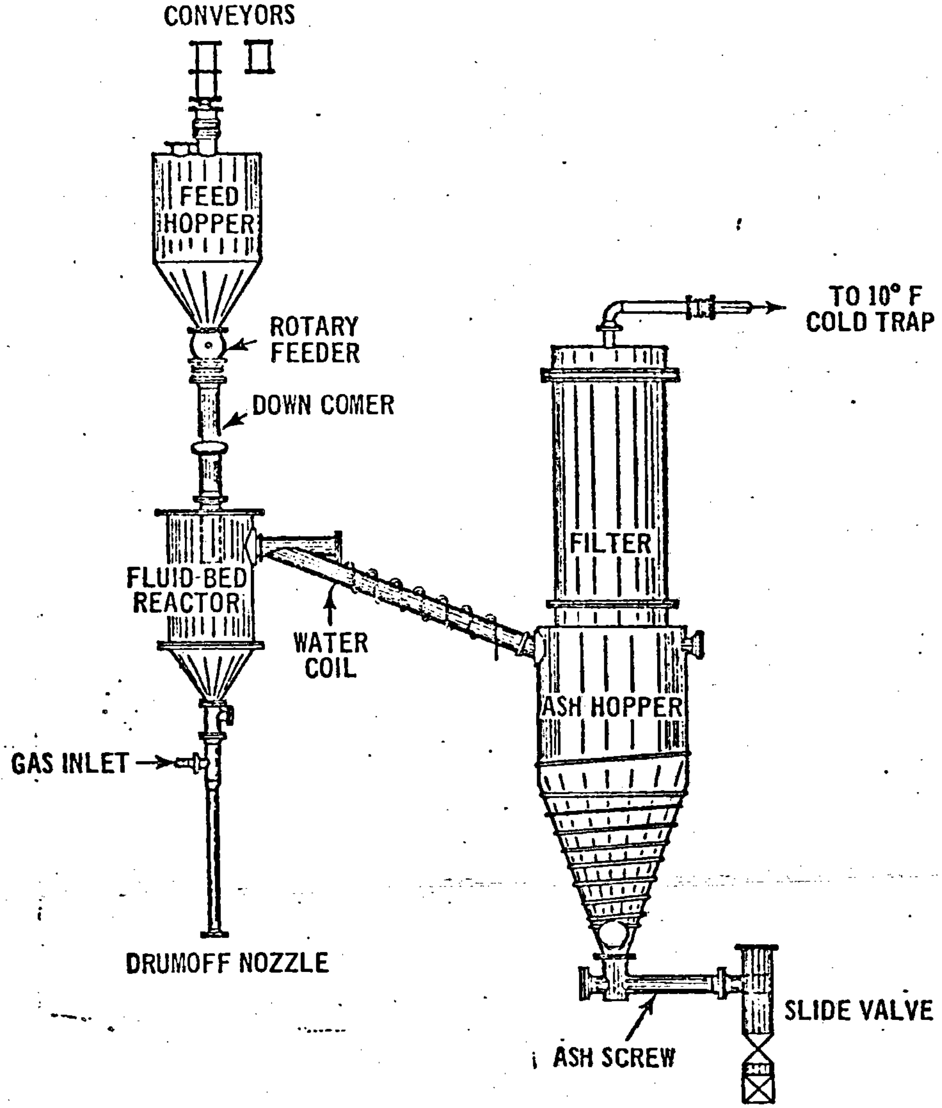

Figure 9-6. Prototype fluidized bed cleanup reactor.

cent fluorine, usually as fluorapatite or, occasionally, calcium fluoride.[7]

Samples from 83 coal mines in the United States were alyzed for fluorine and found to contain from 0.001 to .019 percent, with an average of 0.008 percent.[8] During ombustion, about one-half of the fluorides included in the oal may be expected to evolve to the atmosphere.[21] Approximately 90 percent of this emission was particulate and 10 percent gaseous. It was found that independently of the fluoride content in coal, the concentration of fluoride in the dust largely depended upon the composition of the ash. The emitted quantity of fluoride is thus correspondingly low in strongly basic ashes, and in those containing aluminum oxide.[22] The gaseous effluent was mainly hydrogen fluoride and silicon tetrafluoride.

The total coal consumption in 1968 amounted to 498.8 million tons.[9] Coal consumption in coke and gas plants was 96.525 million tons; the balance, approximately 402.3 million tons, was burned to produce steam and energy. The emission of fluorides from the combustion of this coal was calculated to be 16,000 tons.

For an individual 500-megawatt generating station, coal consumption would be 1.5 million tons per year and the total fluorides emitted would be 60 tons per year. Fluoride concentration in the stack gases, assuming theoretical combustion air, would be 5 parts per million. Fluorides are removed by Sulfur Oxides scrubbers. Fabric filters remove particulates which contain fluorides. No control of emissions designed specifically for fluorides is practiced.

9.4 PORTLAND CEMENT MANUFACTURE

Portland cement is manufactured by heating a properly proportioned mixture of minerals consisting of lime, silica, alumina and iron oxide to temperatures of 2600 - 2900 °F. Clays containing mica-like minerals such as muscovite and illite may have fluorine in amounts of 0.02 to 0.30 percent.[10] The fluorine content of limestone is usually low, amounting to only 0.006 to 0.06 percent, and is present as apatite and fluorite.[10] At firing temperatures the fluorine can be expected to volatilize as hydrogen fluoride and as silicon tetrafluoride. Since the cement kiln contains an overwhelming concentration of lime, all volatilized fluoride reacts with the lime to form calcium fluoride. From 80 to 98 percent of this calcium fluoride appears in the kiln product, depending upon the efficiency of dust collection. Since more stringent dust controls are being applied to the cement manufacturing process, no separate requirement for fluoride control is indicated.

9.5 ROCKET ENGINE TESTS WITH FLUORINE-CONTAINING PROPELLANTS

The National Aeronautics and Space Administration (NASA) requires contractors making rocket test firings using fluorine-containing oxidizers to provide exhaust gas scrubbers to neutralize the toxic products of combustion. When short duration tests (two to four seconds) are made, scrubbers are not necessary, since the quantity of toxic products is small. NASA also requires that contractors maintain liaison with local pollution authorities and abide by local control regulations.[11]

Published handbooks on the use of fluorine-containing propellants in rocket systems include much of the information that has been generated on air pollution control techniques.[12,13]

9.6 FUSED SALT ELECTROLYSIS OF MANGANESE

9.6.1 Introduction

Although essentially all of the ferromanganese consumed in the United States is made by the reduction of manganese ore in blast furnaces or submerged arc furnaces, a fused salt electrolysis process for making manganese has been patented and is in commercial use. Some fluorides are evolved from the molten calcium fluoride electrolyte. These are collected by the use of exhaust fans to ventilate the cell room and are cleaned in a venturi scrubber. All soluble fluorides are removed in the scrubber and all but a trace of gaseous and particulate fluorides are removed. Total emissions of fluoride are estimated to be about eight tons per year.

9.6.2 Process Description[14]

The electrochemistry of the process is somewhat similar to that of the Hall Process of reducing aluminum. Moreover, both in the Hall Process and in this process the basic purpose of the fused electrolyte is to supply an electrically conductive solvent for the oxide of the product metal. The chemistry within the fused electrolyte, however, is different. The solubility of the MnO in the fused electrolyte of this process is largely the result of compound formation between the MnO and the acid oxides present in the fused electrolyte. None of the Mn is in direct combination with fluorine. Compound formation of MnO with the acid oxides is an essential feature of the process since it sufficiently inactivates the MnO to prevent it from directly reacting with the carbon. If this were not the case, objectionable quantities of high carbon metal would occur in the product. The acid oxides are equally important in facilitating the rapid and positive solution of MnO. Metal is withdrawn periodically from the cell as a liquid at a temperature slightly higher than its melting point of 2300 °F.

9.6.3 Source and Nature of Emissions

The gases evolved from the electrolysis cells are largely carbon monoxide formed at the carbon anode by the electrolysis reaction. The rate of gas evolution is sufficient to entrain some particulate calcium fluoride in the feed material. Although calcium fluoride melts at about 2500 °F and does not have a significant vapor pressure below about 3632 °F, other oxides, required for proper operation of the process, are present which react with the calcium fluoride in the electrolyte and volatilize as AlF_3, SiF_4, BF_3 and NaF. These fluorides condense to form fumes and hydrolyze in contact with atmospheric moisture to form gaseous HF and H_2SiF_6.[15]

9.6.4 Control Technique and Magnitude of Emission

Exhaust fans provide general cell room ventilation and draw outside air across the cells to dilute the carbon monoxide and the contained fluorides.[16]

The exhaust gases containing 60 ppm by volume total fluoride are delivered by venturi scrubbers which reduce the fluoride to five ppm, mostly insoluble CaF_2 particulates. The total annual emissions havebeen estimated to be eight tons per year.

9.6.5 Cost of Fluoride Emissions Control System

Although the cell room ventilation system in this plant is typical of that used in aluminum reduction cell rooms, the gas scrubbing equipment chosen was the high efficiency venturi scrubber. The cost of installing and operating such a system is directly related to the exhaust gas volume to be treated and can be estimated from available correlations.[17] The described control system is estimated to have an installation cost of about \$65,000 and an annualized operating cost of about \$30,000.[17]

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10. EMISSION FACTORS

On the basis of information available in the literature pertaining to fluoride emissions from various industrial sources, estimates have been made of the evolution of fluorides from industrial processes and of the controlled or uncontrolled emissions of fluorides to the atmosphere. Table 10-1 is a compilation of evolution and emission factors for each industrial source. The factors are the ratios of fluoride emission, in terms of combined fluorine, to units of production or units of material feed.

The emissions consist of gaseous fluorides, principally HF and SiF_4, and particulate fluorides.

TABLE 10-1. FACTORS FOR FLUORIDES EVOLUTION AND EMISSION TO ATMOSPHERE

Section	Industry	Factor basis	Evolution factor	Atmospheric emission factor
4.3	Wet-process phosphoric acid			
	Digestion	Lb F/ton acid (P_2O_5)	$14.5^{1,2,3}$	0.10^{14}
	Evaporation	" " " "	120.0^{23}	$—^{23}$
	Gypsum ponds	" " " "	$1.12^{5,6}$	$1.12^{5,6}$
4.4	Super phosphoric acid	" " " "		
	Vacuum evaporation	" " " "	22.0^{7}	$—^{8,9}$
	Submerged combustion	" " " "	13.0^{7}	$0.03^{8,9}$
4.2	Normal superphosphate	Lb F/ton P_2O_5	73.0^{10}	13.4^{14}
4.5	Triple superphosphate	" " "	48.0^{11}	0.48^{14}
4.6	Diammonium phosphate	" " "	2.9^{14}	0.10^{14}
5.1	Elemental phosphorus	Lb F/ton P	$122.5^{12,13}$	18.0^{14}
5.2	Animal food supplements	Lb F/ton P_2O_5	222.5^{15}	$0.4\text{-}1.5^{16,17}$
6.1	Primary aluminum	Lb F/ton Al	$40\text{-}65^{19}$	$3\text{-}80^{19}$
6.2	Aluminum foundries	" " "	negligible	—
7.0	Steel manufacture			
	Open hearth	Lb F/ton steel	0.12^{14}	0.47^{14}
	Basic oxygen furnace	" " "	0.44^{14}	1.77^{14}
	Electric furnace	" " "	0.40^{14}	1.58^{14}
	Ceramics			
8.1	Brick and tile	Lb F/ton clay	$1.23^{20,21}$	$1.23^{20,21}$
8.2	Glass and frit	Lb F/ton fluorspar feed	$210.^{22}$	$189.^{14}$

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11. RESEARCH

11.1 Current Research

The necessity for preventing damage to vegetation and grazing animals caused by the toxic effects of fluoride air pollutants has led to the development of a variety of methods for removing fluorides from plant effluents. Selection of control equipment of varying degrees of sophistication depends upon the nature of the source of emission, the extent of removal dictated by State and local statutes, and the plant economics. Well-recognized principles are employed in new plant designs to minimize the volume of effluents to be treated and to minimize the investment and operating costs of the control equipment.

Since the state-of-the-art with respect to fluoride control is well advanced, recent research has been directed toward: (1) recovery of marketable fluorine compounds as by-products of phosphate rock processing, and (2) recovery and reuse of fluorides released from aluminum reduction cells.

Although a large proportion of the fluoride evolved from phosphate rock during the manufacture of wet process phosphoric acid finds its way to the gypsum and cooling water ponds, data on the amount and the manner of fluoride release from these ponds are meager and controversial. Some university and industry studies are underway on this subject.

11.1.1 Fluoride By-Product Recovery from Phosphate Rock Processing

Table 3-1 (see Section 3) shows that nearly 400,000 tons per year of fluoride must be removed from plant effluents during the processing of phosphate rock. Probably 300,000 tons is recoverable from wet-process phosphoric acid plants, or an amount greater than the total consumption of fluorine for all domestic needs. Presently, except for fluosilicic acid and its sodium salt, all domestic consumption is satisfied by hydrogen fluoride (HF) derived from fluorspar. Of the fluorspar used, about 75 percent is imported, of which 70 percent comes from Mexico.[1]

In order to produce fluoride competitive with HF derived from imported fluorspar, industries must first separate by-product fluoride, which is evolved from phosphate rock processes chiefly as silicon tetrafluoride (SiF_4), from its contained silicon. A number of processes have been patented for accomplishing this separation. Dehydration of the hydrofluoric acid product is an added burden for competing in those markets requiring the anhydrous acid. As the demand for fluorine grows and as prices of fluorspar-derived HF escalate, the recovery of by-product fluoride from phosphate rock processes warrants considerations that make recovery economically attractive.

Fluosilicic Acid - Fluosilicic acid (H_2SiF_6) is recovered most readily from the evaporators in wet-process plants. Marketed as the acid or as the sodium salt for fluoridation of water supplies, it commands an estimated market of 20,000 tons per year. About one-half dozen plants have been installed for recovery of the acid, with a total annual capacity of about 45,000 tons as H_2SiF_6 or 35,000 tons as F.[2]

One plant has been built in England for producing about 15,000 tons of potassium fluosilicate annually for use in special fluxes and in white vitreous enamels.[3]

A pilot plant has been built in Florida for precipitating sodium fluosilicate directly from wet-process phosphoric acid before the acid is concentrated.[3] This salt is used in the manufacture of vitreous enamels and opalescent glass, as a coagulent for latex, as an insecticide, and for water fluoridation.

Cryolite (Na_3AlF_6) - One plant has been built in Florida which separates silica from fluosilicic acid by precipitation with sodium carbonate. The resultant sodium fluoride is reacted with sodium aluminate to produce synthetic cryolite.[4]

Other processes under development separate silica from sodium fluosilicate by reaction with ammonia. The ammonium fluoride formed is reacted with sodium aluminate to produce cryolite and the by-product silica is sold for use as a filler in rubber.[3,5]

Aluminum Fluoride - An Austrian plant has been constructed that reacts fluosilicic acid with aluminum hydroxide to precipitate silica. The precipitate is recovered by centrifugation. The aluminum fluoride in solution is precipitated as a hydrate and then calcined to remove water of crystallization.[6]

One plant under construction in Florida will produce aluminum fluoride from fluosilicic acid.[7]

Hydrofluoric Acid - A process for the recovery of hydrofluoric acid from waste fluosilicic acid has been investigated.[8] The fluosilicic acid is precipitated with lime and then hydrolyzed with steam at 1800°F.

11.1.2 Fluorine Recovery from Phosphorus Plants

Fluoride compounds volatilize when phosphate rock is processed to make elemental phosphorus. TVA has investigated methods for recovering commercial fluoride compounds from phosphorus manufacturing.[17]

Waste gases from phosphorus processing must be scrubbed to prevent air pollution and scrubbing liquids need to be handled properly to prevent water pollution problems. Judicial selection of scrubbing techniques and of subsequent processing for aqueous wastes, allow the recovery of commercial products as cryolite and aluminum fluoride. The fluoride for product recovery is reported to be as much as 200 pounds per ton of phosphorus.

Economic recovery of commercial fluoride has several prerequisites: phosphate rock with a minimum of 2.5 percent of fluoride, sufficient plant capacity to give an adequate source of fluoride and proper processing conditions to allow maximum recover of available fluorides.

11.1.3 Recovery and Re-Use of Fluorides from Aluminum Reduction Cells

In the production of primary aluminum, 47 pounds of cryolite and 58 pounds of aluminum fluoride are consumed per ton of virgin metal.[9] This is equivalent to 65 pounds of fluoride per ton, or a 1968 consumption of 107,000 tons for the production of 3.3 million tons of aluminum.

The hydrogen fluoride released from the aluminum reduction cells can be absorbed in caustic solution, combined with leachings from spent cell linings, and recovered as sodium fluoride. Perhaps 40,000 to 45,000 tons of fluoride can be recovered and re-used. Whether or not recovery is economically attractive depends upon the market supply and demand for fluorspar and hydrogen fluoride.

One plant absorbs the hydrogen fluoride evolved in a recirculating solution of sodium carbonate maintained at a pH of 8.5. After the fluoride concentration builds to 1000 ppm by weight, a portion of the scrubber liquor is continuously withdrawn. This portion is reacted with sodium aluminate to precipitate cryolite which is filtered and calcined before being returned to the reduction cells.

A new process utilizes a fluidized bed of activated alumina to chemisorb the hydrogen fluoride evolved from aluminum reduction cells. The product is calcined to convert the chemisorbed fluoride to aluminum fluoride and cryolite, and is returned to the reduction cells.[10]

11.1.4 Fluoride Release from Gypsum Ponds

As much as 75 percent of the fluoride contained in phosphate rock may find its way to the gypsum and cooling water ponds during manufacture of wet process phosphoric acid. This fluoride escapes as a vapor, is precipitated as it percolates into the soil, and is also discharged in the water overflow from the ponds. The mechanisms operative during vapor release and during soil percolation are subject to considerable controversy. Some study is being conducted using operating models and data are being accumulated from producing plants.[11,12]

11.2 Proposed Research

11.2.1 Brick and Tile

Abatement of fluoride emission from the production of brick and other clay products fired in kiln at high temperatures has not been achieved in the United States. No published literature was found that deals with existing or experimental control equipment for fluoride emissions from brick and tile kilns. Consequently, experimental research is needed to identify the scope of the problem and to develop satisfactory control equipment.

11.2.2 Source Testing

More applied research is needed to develop standard methods of obtaining representative samples of fluoride emissions. NAPCA presently favors traverse sampling of ducts containing fluoride effluents. The number of traverse sampling points is related to the distance between sampling ports and obstructions or bends in the duct, and/or shape of the duct.[13] Ideally, the sample port should be 8 to 10 diameters downstream and 2 diameters upstream from any obstructions or bends in the duct. A heated (230°F) probe draws an isokinetic sample from the duct and discharges it to a heated cyclone and then to a heated filter. These devices remove the particulate fluorides but not the condensable fluorides.[14] The filter discharges into a series of four Greenberg-Smith impingers that are in an ice bath. The first two impingers contain distilled water to collect gaseous and condensable fluorides. The third impinger is dry to catch any entrainment. The fourth impinger contains a dessicant (silica gel) to remove all water from gases before they enter a dry measuring meter and a vacuum pump that exhausts the sampling train.[13]

NAPCA plans to conduct a study of methods for source sampling of particulate and gaseous fluorides, and to publish a report of the study within the next 2 years.[14] A primary aluminum company is researching its method for sampling particulate and gaseous fluorides in order to develop an adequate and accurate procedure.[14]

The extent of present and proposed research on the development of an adequate and accurate method for source sampling of fluoride emissions, both particulate and gaseous, is indicative of the need for careful selection of method. Industries planning to abate fluoride emissions should investigate the methods used by State and local control agencies before selecting performance critera for control equipment. The fertilizer industry generally supports and uses the sampling techniques and methods of analyses developed by the Florida State Board of Analysis.[18,19,20] This method is less complex and perhaps not quite as accurate as the present NAPCA method but appears to be satisfactory in its present usage.

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