

FLUORIDE AS AIR POLLUTANT

by

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Fluoride, sulfur dioxide and ozone are recognized to be among the most serious air pollutants. Chlorine and ethylene follow next in importance (1).

Fluoride gases in the air exist principally as hydrogen fluoride (HF), silicon tetrafluoride (SiF_4) and their aqueous solutions. Fluoride compounds reach the air from two sources: 1. Volcanic action, 2. Man's industrial activities.

1. Volcanic Action

In Iceland records go back to 1100 A. D. of a disease among domestic animals, particularly among grazing sheep, which appeared after periodic eruptions of the volcano Hekla (2).

In June, 1912, the top of Mount Katmai in southwest Alaska was blown off by volcanic action. At about the same time a vast number of tiny volcanic vents or fumaroles appeared in the valley below. This area, 4 miles wide and 12 miles long, is appropriately known as the valley of "Ten Thousand Smokes". The fumarole vapors contain about 0.03% (300 ppm) fluorine. When discovered, this source was discharging an estimated 135,000 (3) to 200,000 (4) metric tons of HF into the atmosphere each year. Much of the F gas from ancient as well as more recent volcanic actions still circulates in the earth's atmosphere.

Forest fires also release F into the air, since all vegetation contains some fluoride.

2. The Man-Made Problem

Man is adding F in ever increasing quantities to the atmosphere. The two greatest acute air pollution episodes occurred in Belgium's Meuse Valley and in Donora, Pennsylvania.

The Meuse Valley Disaster: In early December 1930, fog and a thermal inversion with no movement of air, resulted in a disaster in the heavily industrialized Meuse Valley of Belgium.

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Several thousand people became ill. On the fourth and fifth days, 60 deaths occurred. VanLeeuwen (5), Holland's greatest authority on respiratory diseases, advanced the idea that gaseous fluorine emanating from certain factories caused the acute intoxication. Later (1937) Kaj Roholm (6) presented final and convincing evidence that this was correct.

The Donora Disaster: In 1948, Donora, Pennsylvania, experienced a disaster similar to the one in the Meuse Valley 18 years earlier. At the end of October, a fog bank on the tops of the valley walls surrounded the town for four days. This bank permitted little movement of air. There was an accumulation of gaseous waste products from several very large industrial plants, train engines and river boats. Operating in the valley were a zinc works, a steel mill with blast and open furnace, a wire mill and two nail galvanizing mills. All these plants emitted fluoride as well as other noxious gases.

Six thousand of the 13,000 residents became ill. Seventeen died on the fourth day, two more the next day and one eight days later. Philip Sadtler, a chemical engineer (7), was called by the Borough of Donora to investigate. There was evidence of acute F poisoning in persons who had been previously ill with chronic F poisoning. Blood concentrations of fluoride were 12 to 25 times normal. Dyspnea was noted in hundreds of cases.

Corn crops, known to be sensitive to fluorine, and other vegetation, were severely damaged. Inanimate materials, such as glass, had been attacked by acid gases. Many herbivorous animals showed the effects of chronic fluorine poisoning.

Two months after the disaster the Public Health Service undertook an investigation. They concluded that a mixture of gases was responsible but failed to pinpoint any single agent as the main cause.

Sources of Industrial Fluoride Air Pollution

In the utilization of coal as fuel, F gases are evolved. Coal contains between 40 to 295 ppm F (8), according to where it is mined. By 1966, the world output of coal had risen to 527 million tons. On the basis of an average of 120 ppm F, the burning of this coal would have released 63,000 tons of F into the air.

Bituminous coal consumption in the United States for 1963 was more than 400 million short tons (9). About half of this tonnage (209 million) was used by electric power utilities.

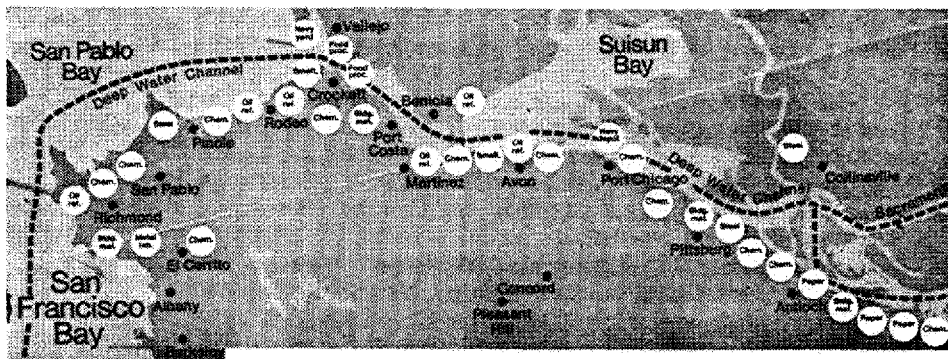
In New York City 11 power plants of Consolidated Edison Co. produce electricity and steam. Of the total fuel requirements for this company in 1966, about 43% was met by fuel oil, 36% by coal, 19% by natural gas and 2% by nuclear fuels (10). Because of the thick black smoke which emanates from the coal and oil burning plants, Consolidated Edison is now being required by the City of New York to utilize coal and oil with a lower sulfur content. A large precipitator which takes the particulate matter out of the residue from burning of coal and oil was installed in one of the plants at a cost of \$10 million. Yet much invisible fluoride gas is still being emitted from the coal burning power plants.

For the Los Angeles area, the Western Energy Supply and Transmission (WEST) Associates (11) are building two immense coal burning power stations. Each will put out three times the power of any local station. One is located near Davis Dam in California. The other, the Four Corners plant in the northwestern tip of New Mexico (12), will start supplying southern California by the middle of 1969. Controls against air and water pollution will be provided. However, it is not clear whether these controls will remove the F gases as well as SO_2 and other particulates.

Clay: Clay is used in manufacturing brick, tiles and ceramics. It contains several hundred ppm F. Much of the halogen is driven off into the air when these articles are fired. Coal used for fuel in this process contributes further to the total F emission. Damage to vegetation from fluoride emission from brickworks was first described in 1913 (13), fluorosis of farm animals from the same kind of industry by Blakemore in England, in 1948 (3).

Fig. 1

Services of Air Pollution in the San Francisco Area



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Six brick, tile and pottery factories are located in a relatively small area of southern Alameda County, California (14) (Fig. 1.) Commercial nurseries, apricot orchards and other vegetation have been adversely affected. In San Jose, in adjoining Santa Clara County, where three brick and tile plants are located, apricot leaves from trees contained 380 ppm F in 1961 (14) and 532 ppm in 1962 (15), the highest concentrations found in the six counties of the San Francisco Bay Area Air Pollution Control District.

Cryolite: Cryolite ($3\text{NaF}\cdot\text{AlF}_3$ or Na_3AlF_6) contains 54.3% fluorine (16). Its principal use is in the aluminum industry, as an electrolyte, for the reduction of aluminum oxide (Al_2O_3) to the free metal. For 100 years cryolite was mined at Ivigtut, Greenland. In 1963 mining was discontinued because of depletion of the deposit (17). However, stockpiled material at the mine site is sufficient to supply consumer needs for the next 15 to 25 years. In 1964, 18,531 short tons valued at \$727,675 were imported to the U.S.A. from Greenland by Pennsalt Chemicals Corporation of Natrona, Pennsylvania.

Natural cryolite is comparatively expensive. Hence, a synthetic cryolite industry has come into existence. Synthetic cryolite is made from hydrofluoric acid, which is produced from fluorspar (CaF_2).

In the production of aluminum, fluorides may pollute the inside of the plant and the surrounding atmosphere (16). Fluorosis of cattle due to F fumes from an aluminum factory in Switzerland was first reported during the period of 1911-18 (18), and in Norway (19) in 1934.

In the U.S.A. the aluminum industry has been involved in extensive litigation for damage to orchards, cattle and other livestock for many years. In 1955, for the first time, damage to human health was proved to the court in an Oregon cattle rancher, his wife and daughter (20). As much as 3,986 lbs. of F per day was emitted into the air from an aluminum factory, enough to etch the windows of the ranch. Air-cleaning equipment, installed at a cost of \$270,000 in 1946, had cut F emission from 7,000 lbs. to less than 4,000 lbs. per day. Additional controls installed in 1950 at a cost of \$2,100,000 cut the emissions to less than half a ton a day.

At The Dalles, Oregon, fluoride determinations were made on seven crops, June 30, 1958, within a one mile radius of the site where an aluminum factory was nearing completion. The average was 3 ppm. Three months after the start of operation of the plant, the same seven crops averaged 140 ppm F (21).

Fluorspar: Fluorspar (CaF_2) mining started in England about 1775 and in the U.S.A. after 1820 (22). Calcium fluoride (the purified

form) contains 51.1% calcium and 48.9% fluorine (16). Although the United States has been the world's largest fluorspar producer, domestic consumption far exceeds the output: over half the supply is imported (17), 80% of which comes from Mexico.

From 1930 to 1964, the world output of fluorspar rose from about 250,000 tons per year to 2,770,000 tons. 80% of this output was used in the metal industry (6). It takes about 6.5 lbs. of fluorspar to produce a ton of steel.

Hydrogen Fluoride: In spite of the enormous increase in the need of fluorspar for production of steel, its consumption now takes second place to that of hydrofluoric acid. One of the largest uses of hydrofluoric acid is in the production of synthetic cryolite for the aluminum industry (4).

Since 1942 anhydrous hydrogen fluoride has been employed as a catalyst in the production of high octane gasoline, replacing sulfuric acid for that purpose in about half the refineries. One refinery in California required 500 to 750 tons of hydrogen fluoride each year (23). According to the Shell Petroleum Handbook, "Commercial operations are complicated by the poisonous nature of the catalyst and its solubility in the hydrocarbons being processed". Both the air around refineries and the resulting gasoline are thus contaminated with fluoride. A year after the process was first used in Los Angeles, people began to complain of the eye-irritating effects of the smog. F causes conjunctival irritation.

Hydrogen fluoride is also used in making fluorocarbons, aerosols, plastics and refrigerants. Furthermore, it is employed in the field of atomic energy, to produce uranium tetrafluoride from uranium oxide. The tetrafluoride is then used to produce uranium hexafluoride, that most volatile compound utilized in the separation of uranium isotopes by thermal diffusion (22).

Pure liquid fluorine, derived from hydrofluoric acid, is being developed as a rocket fuel. A fluorine-hydrogen rocket generating 40,000 lbs. thrust was successfully fired in 1964 (24).

In the Santa Cruz Mountains of California (25), Lockheed Missiles Space Co. is developing rocket fuels, chiefly liquid hydrogen and liquid fluorine. They are known as "cryogenics" because they must be kept "super cold" all the way to the moon.

In the manufacture of liquid fluorine, in its testing and utilization, large amounts of fluorine are released into the atmosphere.

Phosphate Rock: Fluorides make up between 3 and 5% of phosphate rock. The United States has an enormous reserve of phosphate

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rock. Its fluorine content is estimated to be equivalent to 900 million tons of fluorspar (22).

Seventy-five per cent of the marketable phosphate rock in the United States is produced in Florida's Polk and Hillsborough Counties. In this area 13 companies operate 17 plants (26) which produce phosphate fertilizer, phosphoric acid, and elemental phosphorus. In every step of the processing, F is released. The daily emission amounts to 17 tons (27). About 30% of the F is evolved; the rest remains in the phosphate fertilizers. In 1952, production of phosphates in the U.S.A. reached 12 million tons; in 1961, 17.5 million tons containing about 525,000 tons of fluoride (28).

The gases evolved in phosphate production are HF and SiF_4 . In the above-named area shrubbery and citrus trees have been damaged for fifty miles in one direction and sixty miles in another. Some 25,000 acres of citrus have been destroyed (27).

Fluoride gas enters the green leaves of all growing things. In forage grass it may build up to concentrations as high as 1000 ppm. Concentrations in excess of 30 ppm are toxic to cattle. Polk County cattle have suffered from fluorosis. Respiratory ailments are common among the inhabitants of that area. Gaseous silicon tetrafluoride is decomposed in moist air passages to hydrogen fluoride and fluosilic acid (H_2SiF_6) (29). The latter then gives off silica which is deposited in the lungs.

The first law suits for damage by the superphosphate industry to vegetation and herbivorous animals started in 1891 (6). In the U.S.A. litigation in Florida and Tennessee has involved millions of dollars.

Some of the phosphate companies have installed very efficient air pollution control devices. However, storage sheds, conveyor belts and other parts of the operation still emit F directly to the atmosphere (26). The fluoride which is recovered by these devices has reacted with the silica to form fluosilicic acid or its salts. Although a process is known for converting these salts to synthetic cryolite, the process is too expensive to compete with the hydrofluoric acid process. The presence of silica in the molecule is the problem (4, 16, 22, 28). About the only commercial use for fluosilicic acid and sodium silicofluoride is the sale to municipalities to add to their water supplies for fluoridation. What is not sold to cities must be neutralized and discarded. It is being diluted with water and metered into water courses. Sodium silicofluoride is the form most used for water fluoridation, the primary reason being its low cost. Three percent of the fluoride (15,000 tons) in the phosphate rock mined in one year would fluoridate all the water supplies in the U.S.A. (28) for a year.

Disposal of Waste Fluoride

More than fifty different industries emit F into the atmosphere. Devices to reduce the quantities of such emissions increase the amounts of F that must be disposed of by other means. Wet collectors add to the total quantity of liquid F waste which must be discharged into water courses.

A new triple superphosphate fertilizer plant at Brewster, Florida, employs a battery of neoprene rubber-lined scrubbers for control of F and SO₂ emissions (30). The liquid from the scrubber is treated by chemical and physical means to reduce the F concentration to below 5 ppm before it is discharged into the Alafia River. This conforms to the stream pollution control requirements of the state (31).

At the Lewis Flight Propulsion Laboratories, Cleveland, Ohio, hydrogen fluoride is removed from the exhaust of engines under test by means of small scrubbers. Fluoride in the exhaust of the scrubber is thus reduced to less than 100 ppm. The scrubbing liquid is then diluted and metered slowly into a sewer. In the sewer the F concentration is limited to 1 ppm.

The Atomic Energy Commission plant at Fernald, Ohio, produces uranium and thorium metal. The Miami River on which this plant is located provides a means for disposal of liquid wastes. Their biggest single problem is fluorides. Hydrogen fluoride and metal fluoride by-products are generated. Solids from off-gases containing hydrogen fluorides, removed from scrubber systems by filtration, are stored in a pit on a site prepared to prevent ground water contamination. Neutralized soluble fluorides are discharged into the river with other treated wastes. The discharges are regulated so that a permissible average level in the river below of 1.2 ppm is not exceeded. An average of 15,000 lbs. of F per month has been discharged into the stream (30). The Miami River flows into the Ohio just below Cincinnati, and people downstream from Fernald use this water.

At San Jose, California, where General Electric Co. has installed equipment for processing uranium isotopes from uranium hexafluoride, waste water containing fluorides is discharged into the sewer.

During World War II, the Columbia Geneva Division of the U.S. Steel Corporation at Provo, Utah, increased steel production enormously. The plant polluted the air with F so that crops and livestock suffered visibly. Some \$4.5 million were paid out in settlements in and out of court. The company then spent \$9 million on air cleaning equipment. It installed electrostatic precipitators which recaptured about 90% of the fluoride (30). With no large body of water nearby, conventional scrubbing methods could not be used. Discharge of such

large quantities of wash-water as would have been required, might have created a stream pollution hazard more serious than the air pollution problem. The method chosen was that of converting the gaseous fluoride to solids by reaction with fine particles of calcium and subsequently collecting them with cyclones and electrostatic precipitators. The waste material thus collected is hauled to a protected location at a clay pit, where it is covered over with other solid mill wastes and permanently confined. Forty tons of lime dust a day are required.

By multiplying the number of industrial plants using our sewers, lakes, rivers and streams for discharge of their fluoride wastes by \$9 million, one can estimate the cost of stopping pollution of the air, countryside and waterways at billions of dollars.

Bibliography

1. Panel discussion, American Association for Advancement of Science January 1967, Washington, D.C.
2. Roholm, Kaj: Fluorine Intoxication. Arnold Busck, Copenhagen, 1937.
3. Blakemore, F., Bosworth, T.J. and Green, H.H.: Industrial Fluorosis of Farm Animals in England, Attributable to the Manufacture of Bricks, the Calcining of Ironstone, and to Enamelling Processes. Jour. Comp. Path. Therapeut. 58:267-291, 1948.
4. Finger, G.C.: Fluorine Resources and Fluorine Utilization, a Chapter in "Advances in Fluorine Chemistry", Stacey, Tatlow and Sharp, Vol. 2 (1961) Butterworth & Co., Ltd., London.
5. Van Leeuwen, W. Storm,: Die Nebelkatastrophe im Industriegebiet südlich von Lüttich. Münch. med. Wchnschr.78:49, 1931.
6. Roholm, Kaj: The Fog Disaster in the Meuse Valley, 1930: A Fluorine Intoxication. Jour. Ind. Hyg. and Toxicology 10:126-137, 1937.
7. Chemical and Engineering News 26:3692, 1948.
8. Churchill, H. V., Rowley, R.J. and Martin, L.N.: Analyt. Chem. 20:69, 1948.
9. Smith, W.S. and Gruber, C.W.: Atmospheric Emissions from Coal Combustion - An Inventory Guide. U.S. Dept. of H. E. W., PHS, April, 1966.
10. Business Briefs, Journ. Air Pollution Control Assn. 17:190, March 1967.
11. Southwest to See New Type Smoke. Washington Post, June 30, 1966.
12. Electricity from Coal for Southern California by 1969. NEWS, Air Pollution Control Association, West Coast Section, July 1968.
13. Wislicenus, H.: Bericht über die zur Beseitigung von Ziergeleir-auschäden, etc. Jahrb. Berg-u. Hüttenwesen Sachsen, 1913.
14. James, H., Wohlers, H.C. and Linsky, B.: Survey of Fluoride Sources in the Bay Area Air Pollution Control District. Information Bulletin 1-62, March 9, 1962. Bay Area Air Pollution Control Distr. 1480 Mission St., San Francisco, California 94103.
15. James, Howard A.: Survey of Fluoride Sources in the Bay Area Air

- Pollution Control District. Oct. 26, 1962. (Address as in No. 14).
16. Davenport, S.J. and Morgis, G.G.: Review of Literature on Health Hazards of Fluorine and Its Compounds in the Mining and Allied Industries. Bureau of Mines Information Circular 7687, U.S. Dept. of the Interior, June 1954.
 17. Peterson, E.C.: Fluorspar and Cryolite. Preprint from Bureau of Mines Minerals Yearbook, 1964 (Address as in No. 16).
 18. Christiani, H. and Gautier, H.: Le fluor au point de vue de l'hygiene industrielle. Action du fluor sur les animaux. Ann. d'hyg. 3:210, 1925.
 19. Slagsvold, L.: Fluorforgiftung (with German and English summaries) Norsk Veterinaer Tidsskr., 46:2, 1934.
 20. Martin et al. versus Reynolds Metals Co. in U.S. District Court, Portland, Oregon, August 25 1955.
 21. Compton, O.C. et al.: Comparison of Fluorine Levels in Crops Before and After Aluminum Factory Operation in The Dalles Area. Misc. Paper 95, Aug. 1960. Oregon State College of Agri. Station.
 22. Ambrose, Paul M.: Fluorine, a chapter from Mineral Facts and Problems, 1965. Bureau of Mines, preprint from Bulletin 630, U.S. Dept. of Int. (Supt. Documents, U.S. Gov. Printing Office, Washington, D.C., 20302.
 23. Callahan, J.R.: Fluorine Industry. Chem & Met. Eng. 52:94-99, March, 1945.
 24. A Fluorine-Hydrogen Rocket Generating 40,000 Pounds of Thrust. Chem. and Eng. News 42:39, April 6, 1964.
 25. Lindsey, Bob: Gettin' Chilly in Mountains. San Jose Mercury, Oct. 16, 1965.
 26. Huffstutler, K.K. and Starnes, W.E.: Sources and Quantities of Fluorides Evolved from the Manufacture of Fertilizer and Related Products. Jour. Air Pollution Control Assn. 16:682-684, 1966.
 27. Lewis, Howard R.: With Every Breath You Take. Crown Pub. 1965.
 28. Maier, Franz J.: Water Fluoridation Practices. McGraw-Hill, 1962.
 29. Saunders, B.C.: The Physiological Action of Organic Compounds Containing Fluorine, chapter in Advances in Fluorine Chemistry Vol. 11, Stacey, Tatlow & Sharpe, Butterworth & Co. Ltd. London, 1961.
 30. Gartrell, F.E.: Water Pollution Potential of Air Pollution Control Devices, chapter in Air Pollution, Vol. 2, first edition, edited by Arthur C. Stern. Academic Press, New York, 1962.
 31. Stokinger, H.E. and Woodward, R.L.: Toxicological Methods for Establishing Drinking Water Standards. Jour. AWWA 50:515-519, April, 1958.