IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

Sampling Methods

Numerous methods of sampling and analysis for fluorides have been developed and reported. The National Academy of Sciences [1] summarized much of the current data available on processing of biological samples. Pack and Hill [107] and others have reviewed sampling and analytical methods. [108-115] Tentative methods of analysis based on techniques available prior to 1970 have been published. [116]

In atmospheric sampling of fluorides, the usual sampling problems arise and are occasionally complicated by the presence of both gaseous and particulate forms. Sampling methods that separate gaseous from particulate fluoride rely on the reactivity of the gaseous forms with aluminum, alkali, or other materials. Habel [117] used a quartz filter device containing a membrane filter followed by a series of impingers to achieve a separation of the two fluoride components. Pack et al [118] used an assembly of 3 concentric aluminum tubes attached to an impinger to accomplish a sharp separation of gaseous and particulate compounds. A less distinct separation occurred when sodium bicarbonate-coated glass tubes were used in conjunction with an impinger. Mandl et al [119] found that when sodium bicarbonate-coated glass tubes were used, efficiency of gaseous uptake was affected by tube diameter. Mandl et al [119] also used a tape sampler which used 2 treated tapes, one to remove particulates and one to remove gaseous fluoride compounds.

Membrane filters were reported [118] to collect aerosols at average efficiencies greater than 98% of the amount absorbed in 2 impingers in

series while retaining less than 7% of gaseous fluoride. Mandl et al [119] reported that the pretreatment of filters with citric acid solution reduced the retention of gaseous fluoride. Other investigators reported that impregnation of the filters with potassium carbonate, [120] calcium oxide, [121] and sodium formate [122] allowed collection of the gaseous fluorides. Separation of gaseous and particulate fluorides was accomplished by Jahr [123] by the use of an untreated membrane prefilter, of 0.8-μm pore size, in conjunction with a sodium formate-treated 5-μm secondary filter. After sampling, the filter assembly was warmed to 75 C to allow diffusion of adsorbed HF from the first to the second filter. He determined the diffusion efficiency to be better than 99% after 20 hours of heating at 75 C. GH Farrah (written communication, September 1974) has submitted a method to the American Society for Testing and Materials (ASTM) Sub-Committee D 22.04 (tentative method, unpublished) using an untreated membrane filter backed by a carbonate/glycerol impregnated cellulose pad to effect particulate-gaseous separation. Collection efficiency, precision, and accuracy of the analytical method have not been submitted.

NIOSH compared two different sampling methods to collect airborne fluorides in potrooms and a cryolite recovery operation associated with operations in an aluminum reduction plant. [124] The first method consisted of a membrane filter for particulates, followed by a midget impinger filled with 0.1 N sodium hydroxide to absorb the gaseous fluorides. The second used a 0.8-μm pore size filter which was impregnated with sodium formate so that gaseous as well as particulate fluorides would be captured. Nine of 12 simultaneous, paired general area samples collected a higher total F (combined particulate and gaseous F) by the

sodium formate-impregnated membrane method than by the membrane filter-impinger method. The analytical method (ion-selective electrode) was the same for both sampling methods. Unfortunately, filter blank values were not included in the data.

Treated filters were used for rapid determination by Harrold and Hurlburt. [125] Luxon [126] used wool filters. The use of limed papers was investigated by Adams, [127,128] Robinson, [129] and Wilson et al. [130]

Farrah, [114] in discussing standard impingers, stated that although the standard impinger is easily cleaned, fairly rugged and compact and gives high collection efficiencies for gaseous and particulate fluorides, it has several operational drawbacks. Attention must be given to maintaining the liquid level within the impinger, and the liquid must be protected from freezing in cold weather. Glass fiber filter paper [131] proved to be a simple rugged system for efficient collection of both gaseous and particulate fluorides but suffered from high blank values.

For personnel monitoring of total fluorides, the sampling method of choice is the sodium formate-treated membrane filter [122-124] as outlined in Appendix I, because it permits the simultaneous collection of gaseous and particulate fluorides on a single filter, has a high collection efficiency, and the collection technique is relatively simple.

Analytical Methods

Water soluble forms of fluorides can often be analyzed directly but unless determined otherwise, it should be assumed that the samples contain refractory forms of fluoride.

Various techniques for the isolation of fluoride from the sample have been developed. Tentative isolation methods including distillation, diffusion and ion exchange have been published. [116] Fluorides collected in bubblers and impingers can be concentrated by anion exchange resin in the hydroxyl form [132,133] or in the acetate form. Talvitie and Brewer [134] used cation exchange resin as a bacteriostatic agent to preserve urine and then passed the urine through an anion exchange resin. Bowley [135] used ion exchange coupled with colorimetry and titration. One of the oldest techniques for the separation of fluoride has been the steam distillation method devised by Willard and Winter. [136] Many modifications of the distillation method have been published. [137,138] Singer and Armstrong [139] introduced a diffusion method in which the sample is sealed in a multichamber cell with acid and a collecting base. Modifications with a variety of cells have applied the technique to urine. [140-144] The isolation method offering the greatest advantage is the diffusion method since large eluent volumes, constant operator attention, extensive glassware, and resin beds are not necessary for good analytical results.

Many manual and semiautomated methods for analysis of fluoride are available. The choice of a method depends on the type of sampling, separation, sensitivity, and accuracy required. Titrimetric methods were among the first to be used effectively for air samples. Willard and Winter

[136] titrated with a standard solution that complexed fluoride. Armstrong

modified this approach. [145] A frequently used complexing agent is

thorium with alizarin red as the endpoint dye. Many modifications have

been made with various dyes and complexing agents. [146,147] Talvitie and

Brewer [134] used a cation exchange resin to form hydrofluoric acid which

was titrated with base. A detailed review of most of the methods known

through 1950 is contained in reviews by McKenna. [108,109,110]

Trace amounts of fluoride ion may be estimated directly in body

fluids or water by measuring their inhibitory effect on the enzymatic

hydrolysis of ethyl butyrate. [148] Colorimetric methods outnumber all

other methods of fluoride analysis, although they were not used

successfully until 1943. [149] Thorium with an alizarin sulfonate lake was

decolorized by the fluoride. [150,151] Another colorimetric method

involved the use of zirconium-alizarin sulfonate. [152] A bleaching

system by Megregian [153] used zirconium-eriochrome cyanine-R complex.

According to Rausa and Trivello, [154] Belcher in 1959 introduced alizarin

complexone which forms a red chelate with cerium(III) and forms a blue,

stable complex in the presence of fluoride ion. Another colored complex of

lanthanum(III)-alizarin complexone is also used. [137,155-157] The

lanthanum methods are less sensitive but have a greater range and fewer

interferences. Other dyes which have been suggested are thorium-chrome

azurol-S, [158] and aluminum-dyes. [159]

The Megregian zirconium-eriochrome cyanine-R method was applied by

many laboratories [116,160-163] because it is almost as sensitive and

develops much faster than the zirconium-alizarin system. [152,164] The

zirconium-xylenol orange method forms a positive color which has greater

sensitivity. [165,166] In 1958, Bellack and Schouboe [167] introduced trisodium 4,5-dihydroxy 3-(p-sulfophenylazo) 2,7-naphthalenedisulfonate (SPADNS) as a dye for use with zirconium. It proved more stable and reacted more rapidly with a broader absorption spectrum which made it easy to use with simple filter photometers. This system can be substituted in many procedures based on the zirconium-alizarin system. [8,22] Other metal-dye complex systems have been used although not widely applied. [168,169] Noteworthy among them is the fluorescence-quenching technique using magnesium 8-hydroxyquinoline. [170]

The most commonly used and adaptable colorimetric methods are zirconium-alizarin, zirconium-SPADNS, the zirconium-eriochrome cyanine-R, and the lanthanum-alizarin or cerium-alizarin complexone systems. With minor differences in sensitivity and interferences, they are almost all interchangeable. Chemical interferences, eg, chloride can cause erroneous results in these types of methods.

Polarographic and other electrochemical methods have been developed for fluoride, but have received little attention in the published literature. [171]

A recently developed gas chromatographic detection method for fluoride [68,172-176] may be useful for analyzing gaseous fluorides in the presence of particulate fluorides. X-ray diffraction was applied to fluoride analysis by Lennox and Leroux. [177] Neutron activation analysis was applied by Spoonemore [178] and atomic absorption, [179] nondispersive infrared analysis, [180] photonuclear activation, [178] pyrohydrolysis, [181] and particulate identification have been used for analyzing fluoride. Mass spectrometric methods [182] have not been widely used.

A number of fully and semiautomatic sampling instruments have been devised for the measurement of fluoride levels in air and urine. [95,137,138,142,163,170,183-191]

The development of the fluoride ion-selective electrode provided a rapid, direct method of analysis. [192] The electrode employs a crystal that develops a potential dependent only on fluoride ion activity which is measured in reference to a calomel electrode by an expanded-scale pH meter. Both potentiometric and direct measurements were developed. [193-196] Methods have been published for analysis of fluoride in air and stack samples, [122] blood, plasma, urine, bones, teeth, and other materials. [95,183,191,197-202] The fluoride ion-selective electrode has made measurement of urinary fluoride concentrations easy, rapid, and routine. [197,198,203] It offers the most rapid, simple, and specific method for measuring fluorides in urine when used between pH values of 4.5-8. Sun [198] compared results of ion-selective electrode urinalysis obtained by direct measurement, microdiffusion-colorimetric, and microdiffusion-electrode methods. No significant difference was found in 45 samples analyzed by ion-selective electrode, either directly or after microdiffusion. A comparison has been made between SPADNS and electrode methods for stack emission samples. [204] In some cases interfering substances such as aluminum made prior preparation or separation of the sample necessary before the final analysis with the electrode, but interference effects were generally found far less often with electrode analysis than with chemical analyses when a TISAB solution containing CDTA is used. [192] The great working range of concentration makes the method very useful (0.03 μg/ml to 20 mg/ml) with sufficient accuracy ($\pm$1%) for

most determinations. [122,172,183,193-196,199,200,205,206] Further studies are indicated for ionic fluorides in biological fluids. [207] The American Society for Testing and Materials [208] outlined 2 methods for water analysis (SPADNS photometric and ion-selective probe) which are commonly applied with minor modifications to collected air samples of soluble fluorides and to urine samples. Incomplete solubility or complexing of the fluoride are conditions which require prior processing of the sample.

The method of choice for fluoride analysis in air or urine samples is determination by ion-selective electrode as outlined in Appendix II. The relative adaptability, ease of analysis, reproducibility, and linearity of response over an analytical range of nearly 100,000 provide a sound basis for the choice of method. If test conditions indicate an isolation step is necessary because of the possible presence of complexing ions, eg, aluminum, iron, and silicon, diffusion should first be used for separation and concentration.

Environmental Levels and Engineering Controls

A number of studies have been conducted to determine the workroom levels of fluorides in various industrial operations. Engineering controls were often mentioned, but few details of control installations were reported, and in most cases effectiveness of control methods was not determined by actual measurement. Generally, these studies tended to indicate that fluoride levels in industry were not grossly excessive, suggesting that effective control is readily obtainable by standard methods. The following studies, categorized by type of industrial

operation, have been selected as examples.

(a)   Foundry Operations

In 1942, Williams [209] reported concentrations of various airborne materials generated during the casting of magnesium metal. Fluorides were used as oxidation inhibitors and fluxes. Fluorides used as inhibitors were not identified except as soluble fluoride salts. Fluxes were generally composed of ammonium acid fluoride, ammonium fluoborate, or ammonium fluosilicate. Cores were sprayed with aqueous 20% solutions of fluorides, also not identified. Furnaces were reportedly ventilated. Major fluoride exposures occurred during addition of fluoride inhibitors to molten magnesium and during the shakeout of finished castings. Samples indicated that HF was present in the workroom air in insignificant amounts compared to particulate fluorides. Results of sample analyses are shown in Table IV-1.

Williams [209] stated that concentrations exceeding 10 mg F/cu m caused nasal irritation but that filter respirators appeared to provide adequate protection. He also stated that provision of exhaust ventilation for furnace and shakeout operations would keep fluorides within "reasonable

TABLE IV-1

CONCENTRATIONS OF FLUORIDE GENERATED
DURING THE CASTING OF MAGNESIUM METAL

Operation	Range (mg F/cu m)	Average (mg F/cu m)
Shakeout	0.94-18.0	8.77
Molding	0.44-10.6	1.88
Melting	0.74-1.76	1.26
Core spraying	0.58-0.94	0.7

From Williams [209]

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limits" throughout the foundry. He recommended that core spraying operations be conducted in booths, apparently meaning ventilated booths.

In 1943, Largent and Ferneau [37] studied the urinary excretion of fluorides by workers in 3 magnesium foundries. Only 3 air samples for total fluorides were taken, an insufficient number to provide conclusive indications of the severity of exposure. The foundry from which the largest number of samples were collected was recently constructed, was clean, and was provided with extensive ventilation for core making, core spraying, melting, and shakeout operations. The cooling sheds were also reported as being well ventilated. Highest exposures, as indicated by urinalysis, were found in the core spraying and pouring areas, although extensive ventilation was present in both locations. Core spraying took place in ventilated booths and, in addition, the workers were provided with respirators. Largent and Ferneau [37] conjectured that laxity in wearing the respirators was responsible for the elevated urinary fluoride levels.

Methods for the collection of fluoride fumes in air were studied in 1945 by Williams and Silverman. [210] To confirm their laboratory results, they sampled the air of a magnesium foundry. Parallel samples were taken using electrostatic precipitators and Whatman filter papers. Fluoride concentrations were found ranging from 0.079 to 1.13 mg F/cu m. Unfortunately, no details of sampling locations or engineering controls were given.

Stimulated by the work of Largent and Ferneau, [37] Bowler et al [94] in 1947 made a similar study of an English foundry engaged in the casting of magnesium alloys. They did not attempt to determine gaseous fluorides. Fluoride concentrations ranged from 0.143 to 6.37 mg F/cu m. No mention

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was made of controls except the statement that the "baleout" type of furnace was partially enclosed. Whether or not this enclosure was effective could not be determined by the sampling and analytical results, since sample locations were identified only as "near furnaces."

(b)   Electric Arc Welding, Brazing, and Soldering

Low hydrogen coated welding electrodes use fluorides, generally calcium fluoride, as a coating component. Fluxes used in silver brazing and aluminum soldering contain fluorides. [211,212] A number of studies have been made of the fluoride hazard of these operations. In 1941, Tebbens and Drinker [213] studied the fumes and gaseous products of welding with coated electrodes and the engineering factors required for control. Laboratory tests indicated that from 1 to 5 mg F/cu m were produced by welding with a single rod in a volume of 1,000 cu ft without exhaust ventilation. Gaseous fluorides were not found in significant amounts. Based on further tests to determine ventilation requirements, they recommended 250 cubic feet per minute per welder for control by general dilution ventilation when using fluoride-coated rods in spaces of 2000 cu ft or less, and 150-200 cu ft/minute for control by local exhaust ventilation with the intake positioned a few inches from the arc.

Studying welding fumes in steel fabrication, Drinker and Nelson [214] in 1944 observed that hydrogen fluoride was not present in fumes from fluoride-coated rods. They recommended local exhaust ventilation for control with a minimum air flow of 200 cu ft per minute per welder.

In 1953, Ferry [215] measured the fluoride concentrations to which a welder might be exposed under varying conditions. He first determined the concentrations of fluoride in various locations with respect to the

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welder's helmet, finding the lowest concentrations at the rear of and inside the helmet, and the highest concentrations outside the helmet at the front and sides. Concentrations inside the helmet ranged from 0.7 to 2.8 mg F/cu m. The range of concentrations outside the helmet was 0.35-30.0 mg F/cu m. He further confirmed that gaseous fluorides were not present in determinable amounts. Field samples were taken to determine welders' exposures without local exhaust ventilation and to determine general air concentrations in work areas. While the 6 areas investigated varied in type of work and size, general ventilation was reportedly good or fair in all. Breathing zone samples were collected under the welders' helmets, while general air samples were collected in the room air away from the direct path of welding fumes. Results of analyses were reported only in ranges vs number of samples in each area. Breathing zone concentrations ranged from undetectable to 10.0 mg F/cu m. Of 63 samples, 40 were below 1.5 mg/cu m, while 33 were below 1.0 mg F/cu m. General air samples ranged from undetectable to 0.64 mg F/cu m. Work habits of welders were considered to be the most significant cause of variation in results. Ferry [215] concluded that the number of variables was too great to permit accurate exposure evaluation by air sampling and recommended monitoring by urinalysis.

In 1966, Smith [216] studied the total welding fume and fluoride exposure of welders using low hydrogen electrodes under a variety of conditions in the fabrication of pressure vessels and submarines. The environments studied were classified as "confined" (totally enclosed volume of less than 2000 cu ft), "enclosed" (compartments with at least one side open and a volume generally greater than 2000 cu ft), and "open" (open air

or large workshop). Total fume samples collected on cellulose filter papers in these 3 degrees of confinement indicated wide variations in concentrations, ranging from 0.4 to 112.0 mg/cu m.

The effects of using local exhaust ventilation were demonstrated [216] by the results shown in Table IV-2. While the median concentrations indicate some control of total fumes by use of ventilation, the ranges indicate that, in some instances, exposures were higher with ventilation than without. Smith stated [216] that locating exhaust ducting too far from the fume source reduced effectiveness. Presumably this was the reason for the discrepant results listed in the table. Three hundred and two welding fume samples taken in 6 different industrial situations contained median fluoride concentrations ranging from 0.55 to 2.93 mg /cu m. Seventy-eight percent of the samples contained less than 2.5 mg F/cu m and 7% contained more than 5 mg F/cu m. Samples taken in "confined" areas generally showed higher concentrations of fluorides than did samples taken in areas classified as "enclosed" or "open." Fluoride concentrations greater than 2.5 mg/cu m were found in all confined and enclosed welding locations. Thirty-seven percent of the samples taken in confined environments showed concentrations of fluoride exceeding this value. Smith [216] calculated that the weighted exposures for an 8-hour day in the areas studied ranged from 0.17 to 0.88 mg F/cu m. He stressed the importance of adequate ventilation for control.

In 1969, Krechniak [50] studied the fluoride hazard of automatic submerged arc welding in a shipyard production hall where 30-50 welding stands were in operation. Air samples were obtained from the welder's breathing area. Particulate sampling for fluorides was carried out using

TABLE IV-2

FLUORIDE FUME EXPOSURE OF WELDERS
USING LOW HYDROGEN ELECTRODES

Environmental Condition	Number of Samples	Total Fume Concentration (mg total fume/cu m)		
		Maximum	Minimum	Median
Confined,				
Without exhaust	66	112.0	1.0	21.0
With exhaust	40	41.9	6.3	17.6
Enclosed,				
Without exhaust	76	57.6	0.7	10.2
With exhaust	25	77.8	1.4	5.6

From Smith [216]

filter paper. In order to determine volatile F compounds, air was "blown" into polyethylene bottles containing dilute sodium hydroxide. Analysis showed an average concentration of gaseous fluoride compounds of 1.4 mg HF/cu m and 0.32 mg particulate F/cu m at the welder's stand. Pantucek [217] did not find gaseous fluorides in fumes from basic coated electrodes; however, the sampling and analytical methods were not specified.

In investigating exposures to cadmium and oxides of nitrogen, Mangold and Beckett [51] determined fluoride exposures due to silver brazing with fluoride flux. Air samples taken in a large open shop showed fluoride concentrations ranging from 0.02 to 0.16 mg/cu m with a mean of 0.12 mg/cu m. Samples taken aboard ship under more confined conditions showed that fluorides ranged from 0.28 to 0.80 mg/cu m with a mean concentration of 0.51 mg/cu m. The investigators did not feel that fluorides presented a hazard in this type of operation. No local exhaust ventilation was used.

In 1964, McCann [218] investigated the health hazard from flux used

in joining aluminum electric cables. The flux was believed to contain ammonium fluoborate, aminoethylethanolamine, and zinc oxide. The majority of the fluoride in the fume was particulate rather than gaseous matter. The cable joiners worked in relatively confined spaces such as tent-covered trenches, houses, substations, and manholes. Fumes were generated when the cable was brushed with flux and when hot solder was poured over each core end after fluxing. Sampling tests were performed in a simulated work situation. Ventilation was purposely made poor, and large amounts of flux were used. Breathing zone concentrations were found to range from 1.2 to 5.3 mg F/cu m. McCann [218] calculated peak concentrations of 5.0-34.6 mg F/cu m. While these levels were recognized as being high, it was stated that under the worst conditions jointers were exposed to such levels for only a few minutes a day. Recommended preventive measures included education of the jointers, minimal use of flux, good personal hygiene, use of barrier creams and gloves, and avoiding breathing the fumes. Filter respirators were recommended for confined spaces. Apparently, it was considered impractical to utilize local exhaust ventilation under the work circumstances. Time-weighted exposure data were not reported.

(c)   Aluminum Production

In 1946, Yaffe [219] reported an investigation of concentrations of fluorides in aluminum plants. Samples were collected to determine airborne concentrations of gaseous and particulate fluorides in locations which would be representative of exposures of potmen, tappers, and carbon crews. Exposures of crane operators were not reported. Total fluoride in the air ranged from 0.18 to 5.84 mg F/cu m, of which about 50% was gaseous (primarily HF). Average time-weighted exposures were calculated by Yaffe

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[219] who found no significant differences in the exposures of the various occupational categories. Time-weighted average (TWA) exposures ranged from 0.8 to 1.0 mg F/cu m. Engineering controls were not reported.

In 1949, Agate et al [26] reported investigations of fluoride exposures in an aluminum plant. Gaseous and particulate fluorides were determined separately. In addition, particle size determinations were performed on particulate fluorides. Three furnace rooms were included in the investigation. Furnace room "A" was described as having ventilation provided only by convection currents and natural ventilation through doors and windows. Furnaces in furnace room "B" were enclosed and provided with an exhaust system, while furnace room "C" was described only as clean, cool, and visually clear of fumes. Total fluoride ranged from 0.37 to 3.43 mg/cu m in furnace room "A" with gaseous fluorides (primarily HF) ranging from 44 to 74% of the total. Furnace room "B" samples contained total fluorides ranging from 0.41 to 2.72 mg/cu m, with 39-65% gaseous. Furnace room "C" airborne fluorides ranged from 0.14 to 0.60 mg/cu m with gaseous fluorides comprising 15-62% of the total. Background air samples taken throughout the factory showed concentrations of total fluorides ranging from 0.015 to 0.141 mg /cu m. Particle size distributions were essentially the same for all furnace rooms, 100% of the particles being below 60 μm in size, with only 6-12% by weight being below 10 μm.

Breysse [220] studied exposures of aluminum potliner removers in 1959. Samples taken inside pots while removing liners ranged from 0.6 to 2.35 mg F/cu m. Airborne concentrations varied directly with the method of pretreatment, specifically with the amount of water used. A method using "wagon drills" to break up potliners was to be instituted which would

preclude the necessity for entry of personnel into the pots to break up the liners. It was felt that this would reduce exposures considerably. Dust control measures were recommended, but they were not described.

A succinct discussion of the 3 major aluminum production methods and the problems encountered in use of ventilation for control of cell effluent was presented by Hickey [221] in 1968, who stated that the prebake, horizontal stud, and vertical stud Soderberg processes could all be equipped with ventilated enclosures on the cells. However, effectiveness of this ventilation depended on strict maintenance procedures, careful initial design, and maintaining enclosure integrity (doors and shields closed) as much as possible. Hickey [221] stated that the control of cell effluent from the prebake process involved the fewest problems. Few hydrocarbons were emitted and particulate matter was easily collected in multiple cyclones or fabric filters. Particle size of particulate fluorides was reported to range from 0.05 to 0.8 μm. He added that good door and shield maintenance and rigid operational practices could hold effluent from the building itself (and presumably this involves air within the building to which workers may be exposed) to 5-10% of total cell effluent.

In 1970, Hiszek et al [222] studied health hazards of fluorides in aluminum plants. Working conditions were briefly mentioned in minimal detail. Every electrolytic cell was equipped with "fume-absorbing" or burning devices which disposed of most of the effluent gases. Based on 88 measurements with air cleaning devices in full operation, the average fluoride content of the plant air was 1.1 mg/cu m.

In a health survey of aluminum workers, Kaltreider et al [102] in 1972 reported workroom air levels of 2.4-6.0 mg F/cu m in a prebake type aluminum plant in which the cells were not hooded. Thirty-six to 50% of the fluorides sampled were gaseous (primarily HF).

(d)   Phosphate Fertilizer Production

Although the production of phosphate fertilizer is one of the major sources of airborne fluorides, few studies have been made detailing worker exposure. In 1961, Rye [38] reported clinical observations of phosphate workers. He reported that the dried phosphate rock contained an average of 3.5-4.2% fluoride. The study covered 3 operations: the production of phosphate rock, phosphoric acid, and triple superphosphate (TSP). The production of phosphate rock involved drying, screening, and grinding operations productive of dust, 10% of which was below 10 μm in size. Controls for this process were not reported, nor were airborne fluoride concentrations. However, analysis of urine for fluoride and the physical examination of workers did not reveal evidence of excessive fluoride exposure. Treatment of the phosphate rock with sulfuric acid to produce phosphoric acid generated gaseous fluorides. Engineering controls were present but were not described. Airborne concentrations of fluoride, calculated as HF, were below 3 ppm. The production of TSP produced both gaseous and particulate airborne fluorides in the proportion of 60% particulate to 40% gaseous. Exhaust ventilation was installed on the mixing cone and setting belt, but further details were not given. Total fluoride concentration in the air of the storage building, where the major exposure occurred, was given as 2-4 ppm as HF (approximately 1.5-3.1 mg F/cu m). Rye stated that a major portion of the particulate matter was

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below 1 μm in size. Respirators were required to be worn, and administrative controls in the form of duty rotation were used to reduce exposure in the storage building.

In 1962, Derryberry et al [97] reported results of a study of worker health in a phosphate fertilizer plant. Operations involved handling and calcining of phosphate rock, production of elemental phosphorus, conversion of phosphorus to phosphoric acid, acidulation of pulverized phosphate rock with phosphoric acid, production of calcium metaphosphate, and storage, aging, bagging, and shipping of finished products. Gaseous and particulate fluorides were produced throughout these processes. Most of the dusts and gases were reportedly removed by scrubbers and local exhaust systems, but details were not given. Time-weighted exposures ranged from 0.50 to 8.32 mg F/cu m with an average of 2.81 mg F/cu m. Unfortunately, this range was not broken down to indicate exposures at each of the various industrial operations, nor was the distribution of total F in terms of gaseous and particulate components reported.

Kuznetsova [223] in 1969 reported air-sampling results in a phosphate plant. Near the conveyor, the mean particulate F content of the air was 1.3 mg F/cu m and 0.27 mg F/cu m at the processing equipment platforms. In the crushing department, equipment operators were exposed to 1.3 mg F/cu m. Similar exposures occurred near the drying drums. In the double superphosphate department, the highest concentration, 2.8 mg F/cu m, was found in the work area of the equipment operators. The powdering and drying process produced 3.1 mg F/cu m of air. Existence of control measures was not reported.

(e)   Water Supply Fluoridation

In 1950, Zufelt [224] reported exposures in a water fluoridation facility. The charging hopper was equipped with exhaust ventilation. The feed machine had been made as dusttight as possible. Operators were fitted with rubber gloves and dust respirators for use when filling the hopper. Atmospheric fluoride concentrations ranged from 0.025 to 0.134 mg/cu m, calculated as HF (approximately 0.024-0.127 mg F/cu m) in the general atmosphere of the operating area before and after hopper filling operations. A sample taken in the breathing zone of an operator who was filling the hopper with sodium fluoride showed 8.89 mg /cu m as HF (about 8.46 mg F/cu m). This operation was completed in 5 minutes, and never occurred more than once a day. Details of the ventilation system were not reported.

(f)   Mining and Cryolite Manufacture

Roholm [18] in his classic monograph discussed the processing of cryolite ore mined in Greenland. Operations included crushing and grinding, drying, conveying, and packing. Dust from rooms in which the various processes took place was exhaust ventilated through filters. The collected dust was used in manufacturing. Attempts had been made to enclose and ventilate machines and drying stoves, but details were not given. Masks were supplied to workers. Total dust content of the air ranged from 22 to 994 mg/cu m. Since this dust was about 97% cryolite these figures correspond to approximately 12-536 mg/cu m as fluoride.

Fluorspar mining was the subject of a study by de Villiers et al [225] reported in 1971. Sixty-seven samples at 27 locations underground showed a mean of 0.44 mg F/cu m, while 7 samples taken above ground showed

a mean of 0.17 mg F/cu m. Control measures, if any, were not reported.

(g)   Pottery Manufacture

During a health survey of the pottery industry, Luxon [226] determined the nature and amount of fluoride compounds emitted during the firing of pottery. Etching of window panes had indicated the presence of such compounds. He found that the compounds were particulate and were probably composed of ammonium fluosilicates. Breathing level workroom air samples showed concentrations up to 3.5 mg F/cu m. Exhaust ventilation fitted to the entrances of the kilns was found to afford effective control, but specifications of the exhaust system were not reported.

(h)   Steel Manufacture

Although steel manufacturing uses the largest quantity of fluorspar as a metallurgical fluxing agent, [12,15] only a limited number of studies have been made of fluoride exposures resulting from this process. Markuson, [227] in 1947, reported on the use of sodium fluoride in the manufacture of rimmed steel. Fluoride fumes were generated when 4-ounce paper bags of sodium fluoride were added to the mold while molten steel was being poured. Samples were taken for total fluoride, including both gaseous and particulate fluorides. Samples of crane cab air showed 3.02 mg F/cu m. The highest concentration found on the pouring platform was 1.3 mg F/cu m. On a time-weighted average basis, exposures were 0.85 mg F/cu m and 0.365 mg F/cu m for an 8-hour day, respectively. Crane cabs were later equipped with filtered ventilation, but the author doubted their efficacy because of the extensive and frequent maintenance required. Local exhaust ventilation was recommended, but details were not given.

In 1948, the US Public Health Service [95] conducted a survey of potential health hazards associated with use of sodium fluoride at 4 steel plants. Differential sampling indicated the absence of gaseous fluorides, while X-ray analysis showed that fluoride fumes were composed of the parent material, sodium fluoride. Ventilation existed only as natural ventilation modified by convection currents from the heat sources in the plants, all of which had monitor roofs. Crane operator exposures ranged from 1.0 to 51.2 mg NaF/cu m (about 0.45-23.1 mg F/cu m) while pouring platform exposures ranged from 0.2 to 21.9 mg NaF/cu m (about 0.09-9.9 mg F/cu m) with a median of 1.6 mg NaF/cu m (about 0.72 mg F/cu m). Exposures were calculated from the median values of the daily samples and from an estimate of the average hours per day spent in each exposure area. Time-weighted exposures ranged from 0.4 mg NaF/cu m (about 0.18 mg F/cu m) for ladlemen, pourers, and platform men, to 2.2 mg NaF/cu m (about 1.0 mg F/cu m) for ladle cranemen. Despite the lack of engineering controls, extensive physical examinations failed to disclose evidence of physiological damage by the sodium fluoride. Therefore, no controls were recommended except positive pressure ventilation for crane cabs, with filtering of intake air.