V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1945, Cook [228] compiled a list of standards and recommendations for maximum allowable concentrations of industrial atmospheric contaminants. The following 2 different maximum allowable concentrations were cited for fluoride dusts: 1 mg F/cu m, a nonofficial concentration in use as a guide by the Massachusetts Department of Labor and Industries Division of Occupational Hygiene, September 1945, and 2 mg F/cu m, an official concentration listed in Rules and Regulations for the Prevention and Control of Occupational Diseases by the Oregon State Board of Health, August 1945. No supporting documentation was given for these time-weighted averages for a 40-hour workweek.

The American Conference of Governmental Industrial Hygienists [229] in 1947 adopted a Maximum Allowable Concentration (MAC) for fluorides of 2.5 mg F/cu m. It was not stated if this MAC was intended as a ceiling value or as a time-weighted average. The April 1948 meeting of this same organization [230] adopted 2.5 mg F/cu m as a threshold limit value (TLV) which has remained unchanged since. This TLV for fluorides is a time-weighted average.

Data presented in the 1966 Documentation of the Threshold Limit Values for Substances in the Workroom Air [231] did not conclusively support this TLV. The report by Ronzani [232] related to the irritant effects produced when animals were exposed to 3 ppm hydrogen fluoride and was not concerned with human exposure to fluorides. The reports by Roholm, [18,233] Largent, [33] and notes taken by HE Stokinger (written communication, 1974) on Irwin's presentation at a 1954 symposium, were also considered when the ACGIH Documentation was published. Largent [33] concluded that fluorides might be stored in human tissues over periods of years when as little as 3 mg of NaF was ingested daily, but he had only indirect evidence based on 4 subjects. Data by Irwin as cited in the Documentation [231] supported the ACGIH TLV of 2.5 mg F/cu m. Irwin reported no significant bone changes in workers when fluoride air levels were below 4-5 ppm (3-4 mg F/cu m). Gaseous and particulate fluoride concentrations were approximately equal. Slight bone changes were recorded after 20 years among cryolite workers exposed at air levels of 5 ppm. According to Irwin (HE Stokinger, written communication, 1974) 29 of 265 workers excreting an average of 9.6 mg F/day in the urine showed a marked increase in density of the pelvic bone while only 2 of 402 employees excreting an average of 6.3 mg F/day in the urine showed marked increase in bone density. These notes did not further document the relationship between air concentrations and bone changes.

The 1971 Documentation [234] concluded that "the limit of 2.5 mg F/cu m is sufficiently low to prevent irritative effects and to protect against disabling bone changes." The Documentation reviewed studies concerning workroom air concentration and ingestion and excretion by Roholm, [18] Largent, [34] Williams, [209] Markuson, [227] Elkins, [235] Collings et al, [48] Irwin (unpublished work referred to above), Derryberry et al, [97] Agate et al, [26] Machle and Largent, [31] Largent, [33] Hodge, [236] Princi, [237] and Waldbott. [23]

In 1963, the Second International Symposium on Permissible Limits for Air of Workplaces, as reported by Truhaut, [238] adopted a MAC of 2.5 mg

F/cu m which was considered as a time-weighted average. No documentation was given to support the MAC.

The American Industrial Hygiene Association's Hygienic Guide on Fluoride-Bearing Dusts and Fumes (Inorganic), [211] published in 1965, recommended a MAC (8 hours) of 2.5 mg F/cu m. Data from the ACGIH Documentation of Threshold Limit Values were used as the basis for the value.

The United States of America Standards Institute [239] (now referred to as the American National Standards Institute) listed an acceptable 8-hour time-weighted average concentration for fluoride in dusts as 2.5 mg F/cu m (Z37.28-1966). This standard was supported by observations on animals exposed to HF and fluoride by Stokinger [240] and a review of Heyroth [241]; but it was pointed out that there was insufficient evidence and that further study was necessary.

The Department of Environmental Resources in Pennsylvania [242] adopted the ACGIH TLV of 2.5 mg F/cu m and it also set a short-term limit for fluoride of 10 mg F/cu m for 30 minutes. In Pennsylvania's Short Term Limits for Exposure to Airborne Contaminants: A Documentation, [243] reports by the American Industrial Hygiene Association (Hygienic Guide Series--1956) and Heyroth [241] were considered.

According to a Czech source, [244] the Soviet Union, Poland, Hungary, Czechoslovakia, and East Germany recommended an 8-hour maximum allowable concentration for fluoride of 1.0 mg F/cu m, but West Germany recommended 2.5 mg F/cu m.

In the Soviet Union, Smelyanskiy and Ulanova [245] listed a mandatory maximum permissible concentration of 0.001 mg F/liter (1.0 mg F/cu m) in the workroom air which was established by the Main State Health Inspector of the USSR, January 10, 1959, No. 279-59. Maximum permissible concentrations were considered concentrations which could only be exceeded if workers were in an industrial area for an unspecified brief period.

The Czechoslovak Committee of MAC [244] suggested a mean MAC value of 1 mg F/cu m for all soluble fluorides. Total fluoride intake (inhalation plus food and water) were considered. The committee concluded that 8 hours of work with a mean concentration of 1 mg F/cu m would result in a daily urinary excretion of 5.5 mg F, taking into account 1 mg F/day of food and water intake. This level of urinary excretion was stated to be a "critical value," ie, F would be accumulated in the skeleton but without the appearance of osteosclerosis. A peak MAC of 2 mg F/cu m was also suggested. This peak could occur for a short time as long as the mean was not exceeded. These mean and peak values were based on studies by Roholm [18] and Largent. [33,34]

The present federal standard for fluoride is an 8-hour time-weighted average of 2.5 mg/cu m (29 CFR 1910.1000), published in the Federal Register 39:23541, June 27, 1974, as amended. The standard is based on the United States of America Standard Z37.28-1966. [239]

Basis for Recommended Environmental Standard and Biological Monitoring

(a) Occupational Environmental Standard

The occupational exposure limit is intended to prevent deleterious effects of skeletal fluorosis (osteosclerosis or increased bone density due to excessive absorption and retention of fluorides). Severe osteofluorosis was found by Moller and Gudjonsson [17] and Roholm [18] among cryolite workers who exhibited calcification of ligaments and pronounced bone density increases in the pelvis and spinal column. The most severe cases exhibited moderate-to-marked restriction of spinal motility. [18] Kaltreider et al [102] found skeletal fluorosis in 76 of 79 aluminum potroom workers who had worked at their jobs for more than 5 years. Twenty-six or 33% of the workers classified as having marked or advanced fluorosis showed restricted movements of the spine.

Three studies [18,93,94] reported pulmonary fibrotic changes on radiological examination. No attempt was made to correlate clinical symptoms with pulmonary function tests. Atmospheric F concentrations within the industries studied ranged from 15 to 20 mg/cu m, 2-3 mg/cu m, and 0.143-6.37 mg/cu m, respectively. The results of one study [18] indicated that pulmonary fibrosis caused by exposure to cryolite dust tended to diminish in workers who had been away from the factory for at least 3 years. Since the cryolite dust contained quartz (1-5%) as well as fluorides, the study did not conclude that the fluoride component of the cryolite was responsible for the fibrotic changes. X-ray findings reported in other epidemiological studies did not indicate the presence of pulmonary fibrosis. [38,95,96,102]

The increased incidence of bronchial asthma reported in 2 Norwegian aluminum factories by Evang [84] and Hjort [91] is not substantiated by other studies. Neither study was able to conclude that fluoride was the causal agent.

A study relevant to the development of an environmental standard is the one by Derryberry et al. [97] They provided comprehensive environmental and urinary fluoride excretion data on each worker included in the survey and demonstrated correlation with clinical and radiological findings. Environmental fluoride levels were evaluated from approximately 750 atmospheric samples over a period of approximately 25 years. An average daily fluoride exposure for each job was established and from these data a weighted atmospheric exposure was calculated for the period of employment of each worker. The range of individual average weighted exposure to F was 0.50-8.32 mg/cu m, with 1.78-7.73 mg/cu m being associated with a questionable or marginal increase in bone density. The difference in averages between the increased bone density group (average exposure 3.38 mg F/cu m) and the remainder of the exposed group (average exposure 2.62 mg F/cu m) is significant by both T test ($t = -2.75$, $p = 0.0045$) and rank test ($z = -2.2$, $p = 0.014$).

While the work of Derryberry et al [97] is of value in developing an environmental standard, inherent weaknesses found within the study limit the extent to which the findings of the authors can be directly applied to the determination of an environmental limit. The test population utilized in the study was very small. This placed limitations on the statistical significance of the findings. In the study, 17 out of 74 workers exposed to various concentrations of F were diagnosed as showing bone density changes of minimal or questionable degree. The authors stated that these diagnoses were made by a radiologist who had prior knowledge that the tested individuals had potential fluoride exposures and who did not feel that the radiographs showed sufficient increase in bone density to be recognized as such in routine radiological practice.

The Derryberry et al [97] study is of value, however, in that it is a comprehensive study and it does indicate that a threshold for minimal increases in bone density exists. Considering all aspects of the study, this threshold is best represented by the average exposure of 3.38 mg F/cu m.

It is virtually impossible to correlate medical findings with exposure levels from other available studies. [26,93,102] These studies include the following shortcomings: exposure levels were taken only at the time of the study and may not represent long-term exposure; insufficient individual or group data were given to correlate exposure with medical findings; and workers were often selected for the study. Tourangeau [93] observed 2 cases of generalized and 3 cases of localized osteosclerosis (degree not given) in a selected group of 10 out of 104 aluminum potroom workers. Unfortunately, the fluoride exposure of this selected group was not provided. Kaltreider et al [102] found 76 cases of osteosclerosis in a group of 79 aluminum foundry workers with a weighted average 8-hour atmospheric exposure of 2.4-6.0 mg F/cu m. Of the affected 76 cases, 46 had slight osteosclerosis, 4 moderate osteosclerosis, and 26 marked osteosclerosis with restrictive motion of the spine. Unfortunately, exposure levels were measured only at the time of the study. Agate and co-workers [26] found abnormal X-ray appearances not considered to be necessarily synonymous with skeletal fluorosis in 48 of 189 furnace room workers selected for study. These abnormal findings ranged from skeletal fluorosis to minor bone irregularities. A breakdown in the subject selection method employed in the study forced the authors to resort to conducting clinical examinations on volunteers from the study population. Exposure levels were given as between 0.14 and 3.43 mg F/cu m within the furnace areas.

Support of the present environmental limit by the 1971 Documentation [231] and the United States of America Standards Institute (now referred to as ANSI) [236] as well as the evidence provided by Derryberry et al [97] indicate that a time weighted average exposure limit of 2.5 mg F/cu m will prevent the occurrence of deleterious health effects resulting from F deposition.

It is recognized that many workers handle small amounts of fluoride or work in situations where, regardless of the amount used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with many of the provisions of this recommended standard, which has been prepared primarily to protect worker health under more hazardous circumstances. Concern for worker health requires that protective measures be instituted below the enforceable limit to ensure that exposures stay below that limit. For these reasons, "exposure to fluoride" has been defined as exposure above half the environmental limit, thereby delineating those work situations which do not require the expenditure of health resources, of environmental and medical monitoring, and associated recordkeeping. Half the environmental limit has been chosen on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas in which a hazard may exist. However, because of nonrespiratory hazards such as those resulting from skin irritation or eye contact, it is recommended that appropriate work practices and protective measures be required regardless of the air concentration.

(b) Biological Monitoring

Since the recovery of fluorides from physiological fluids can be related to environmental exposures and/or osteofluorosis, a valuable means of monitoring employee health is provided. Many authors [28,31,32,246,247] have demonstrated that under exposure conditions leading to F retention in bone, urinary F excretion reflects the amount of fluorides absorbed. Largent and Machle [31] demonstrated in their balance studies that a straight-line correlation existed not only between absorption and urinary excretion but also between absorption and retention of fluorides. Separate studies [38,46,48,49] demonstrated rapid absorption and urinary excretion of fluorides when respirable inorganic fluoride dust or fumes were inhaled.

(1) Postshift Urinary F Biological Level

Collings et al [46,48] and Largent [28] demonstrated a rapid rise in urinary fluoride output within 2 hours of exposure which remained at high levels for 2-4 hours after cessation of exposure. Thus, end-of-shift urine samples, as recommended by NIOSH, will reflect exposure conditions occurring during the working day. This is especially desirable since it supplies data relevant to employees' working practices and engineering control measures.

Although numerous studies have demonstrated [61,62,70-72,96,97] that slightly increased bone density is not synonymous with disability or a reduced functional capability, the urinary excretion limits should be established below that point at which skeletal fluorosis begins to occur rather than at that point where the first signs of disability or functional impairment are approached.

The study by Derryberry et al [97] provides long-term individual worker postshift urinary excretion data which can be compared to reported cases of suspected increased bone density. In this study, average postshift urinary fluoride levels for the examined group of workers were determined from 2,850 urine samples, averaging 38 specimens per man. Reference to Table III-12 demonstrates that as the average urinary fluoride level excretion increased the percentage of suspected osteosclerosis increased gradually until the excretion range of 8-8.9 mg F/liter was reached, at which point 3 of 5 members of the group in that range revealed an increase in bone density.

A definite though asymptomatic increase in bone density was found by Kaltreider et al [102] in 76 of 79 aluminum potroom workers. The results of spot urine samples collected during the shift at unspecified times were given only as the averages for the 3 occupational groups of pot tender, tapper-carbon changer, and craneman and revealed urinary F concentrations of 8.7, 9.8, and 9.6 mg/liter, respectively (no correction for specific gravity). In a second study [102] in which the fluoride exposure was reported to be "quite modest" in comparison with exposures of the earlier study, there were no cases of increased bone density among 231 potroom workers excreting an average postshift urinary F concentration of 3.0 mg/liter corrected to 1.024 specific gravity.

The above results [97,102] indicate that an average of postshift urinary F concentrations less than 8.0 mg/liter will lead to few cases of definite osteofluorosis. It is concluded that a postshift biological level of 7.0 mg/liter calculated as an average will provide an acceptable margin of safety.

(2) Preshift Urinary F Biological Level

Upon cessation of F exposure, the initial rapid rise of urinary F concentration is followed by a return to stable and relatively low levels of F excretion within 24 hours. [28,36,46] Urinary F concentrations approached preshift values within 1-6 days. [27,28,36,38,46,48] These studies reveal that the time required for the preshift sample to stablilize is quantitatively related to the urinary F concentration in the postshift sample, and that urinary F analyses conducted preshift after a period of 1 day or more without exposure will provide a stable baseline value indicative of a worker's residual F retention (body burden).

The relationship of the concentration of fluoride in the preshift urine sample to the onset of osteofluorosis has not been precisely demonstrated, but a limited number of industrial exposure studies [101,102, H R Henderson, written communication, September 1974] as well as one nonindustrial exposure study enable some inferences to be drawn regarding the relationship of osteofluorosis to the preshift urine sample.

Preshift urinary F excretions were analyzed in 25 chemical workers exposed to HF or particulate fluorides in concentrations ranging from 0.077 to 10.0 ppm as HF and 0.1-0.49 mg/cu m as particulate F. [101] Preshift specimens, which were collected after the workmen had been away from the plant on their days off, ranged from 0.33 to 4.48 mg F/liter. Corresponding levels for a control group of 10 office workers were 0.5-1.88 mg F/liter.

Additional data on environmental and urinary F levels of the same plant population were made available by the company (H R Henderson, written communication, September, 1974). Over a 10-year period periodic urinary F levels of 13 HF workers revealed the average preshift levels for the workmen ranged from 2.0 to 5.7 mg/liter. One of 4 workers with high preshift urinary F concentrations who had negative X-rays for osteosclerosis when examined 2 years earlier demonstrated minimal osteosclerosis upon a follow-up examination. His average preshift urinary F level was 5.3 mg/liter, ranging from 2.6 to 16.3 mg F/liter.

No osteofluorosis was found in a group of 147 potroom workers excreting a preshift average of 1.4 mg F/liter of urine ranging from 0 to 11.9 mg F/liter. [102] Urine samples were collected after 48 hours off work and the values were corrected to a specific gravity of 1.024.

Stevenson and Watson [71] reviewed medical records of patients residing primarily in Texas and Oklahoma where water supplies contained up to 8 ppm of fluoride. A diagnosis of fluoride osteosclerosis was made in 23 patients living in communities whose water supplies contained 4-8 ppm of F. It was concluded that fluoride osteosclerosis did not develop in patients drinking water with an F content of less than 4 ppm.

The preceding data [102, 101, H R Henderson, written communication, September 1974] suggest that preshift urinary values up to 5.3 mg F/liter were not associated with osteofluorosis. While the findings of the nonindustrial exposure study [71] cannot be strictly applied to the determination of a preshift level, the results of the study indicate that a preshift level below 5.3 is needed. It is concluded that a preshift level of 4 mg/liter will provide adequate worker protection. The validity of the value, as a preshift level, should be tested and adjusted in the future as more information is gained.

(c) Urine Specific Gravity

Urinary fluoride values corrected to a standard specific gravity provide better correlation with F intake than uncorrected values, as demonstrated by Buchwald. [39] Elkins et al [40] concluded that the true mean value for the specific gravity of 35,506 samples analyzed in their lab was 1.022. They concluded that since the value most widely used for specific gravity correction in the United States is 1.024, it should continue as a standard reference to enable data comparisons among different investigators.

(d) Renal Disease

The importance of urinary excretion in minimizing fluoride retention in bone is illustrated by experience with patients with renal disease. Evidence of interference with normal clearance of fluorides and increased bone deposition caused by kidney dysfunction rather than induced by fluoride has been presented by several authors. [28,61,74,75] Emphasis should, therefore, be put on eliciting a history of renal disease and providing a means of disease detection during physical examinations.

(e) Radiological Examination

The onset of increased bone density is most apparent in the lumbar spine and pelvis. [97] Since changes in the osseous system may be the only evidence of increased absorption and retention of fluorides, a periodic X-ray of the pelvis may be valuable in cases where urinary F levels have been found to be high. It should be noted that the first changes produced by fluoride absorption and retention are difficult to recognize without prior knowledge that the individual had a fluoride exposure. Radiological examination of the pelvis can result in irradiation of the gonads and embryos. [248] This may lead to deviation from normal mutation rates and may produce developmental abnormalities in the human embryo. Due to the difficulty of ensuring adequate protection for female gonads and for embryos, it is recommended that radiological examination of the female pelvis not be conducted. Since male gonads can be protected adequately during pelvic X-ray, preplacement male pelvic exams should be considered to obtain baseline radiologic information.

VI. WORK PRACTICES

Prevention of occupational diseases from fluorides involves the prevention of inhalation or ingestion of fluorides. Inhalation of fluorides is best prevented by controlling fluorides at their sources of emission by means of enclosure of processes or by local exhaust ventilation. Ingestion of fluorides is prevented by means of good housekeeping and personal hygiene procedures. Properly designed and maintained ventilation systems will prevent dispersal of fluorides in the workroom atmosphere, not only preventing their inhalation, but preventing their accumulation on surfaces, thus minimizing maintenance problems and the chance for redispersal during cleanup with attendant inhalation and ingestion hazards. Good ventilation practices, such as those outlined in a current edition [249] of Industrial Ventilation--A Manual of Recommended Practice, published by the American Conference of Governmental Industrial Hygienists, should be followed. Where exhaust ventilation is used, an adequate source of make-up air should always be provided, with conditioning for temperature and humidity as required.

Mechanization and enclosure of processes offer additional methods of engineering control which may be effectively used under some circumstances.

Many of the industrial processes emitting fluorides produce simultaneous exposure to gaseous as well as particulate fluorides. If respiratory protection is required, it must be of the type to provide protection against both. In 1971, the AIHA and ACGIH Joint Committee on Respirators [250] published a list of sorbents for contaminants listed in the ACGIH 1970 TLV table. For fluoride exposure, a combination of a toxic dust or fume filter and a soda-lime activated carbon cartridge was recommended. Manufacturers' equivalents of this combination should be provided when cartridge or canister respiratory protection is used.

Soluble and acidic fluorides can cause skin, eye, and respiratory irritation. [212,251] Adequate protective clothing and eye and face protection must be utilized when exposure to these compounds occurs. Eyewash fountains and showers should be available for immediate care. Eyes affected by fluorides should be immediately flushed with copious amounts of water, forcibly holding open the lids, if necessary.

Fluorides which form acidic solutions when mixed with water should be stored away from water. [212] Many fluorides produce hydrogen fluoride in contact with acids. Hydrogen fluoride is extremely corrosive and hazardous. Unwarranted contact of fluorides with acids should be avoided.

Fluorides are not fire or explosion hazards. However, acidic solutions of fluorides may generate hydrogen in contact with metals. Water may be used on fires involving fluorides.

Labeling of fluoride fluxes and use of ventilation for welding with fluoride coated rods are required by 29 CFR 1910.252. Close observance of the specified distances between ventilation intakes and source of welding or brazing fumes is important for effective control.

Workers should exercise care in handling of bags and barrels of fluorides to prevent container rupture and spillage. [252] Spills are preferably cleaned up with an industrial vacuum cleaner, but wet methods may be of value in instances where such procedures will not increase exposure or pollute sewers and drains above environmental limits.

Good personal hygiene involves washing thoroughly before eating or drinking, and after handling fluorides. [211,212,252] Contaminated impervious protective clothing should be washed off before removal. Food or beverages should not be consumed in work areas. [253]

A number of states have promulgated standards for fluoride content of community air and vegetation. (See Chapter VII.) It is therefore imperative that any discharge of fluorides to the environment comply with all applicable regulations. This may require air cleaning devices on the discharge ducts of ventilation systems used for control of fluorides in workroom atmospheres, and close control of effluents discharged to streams, onto the ground, or to sewers and drains.

VII. COMPATIBILITY WITH EMISSION STANDARDS

There is no federal community air standard for fluorides. A number of states have promulgated standards for control of emission of fluorides. These standards were not established on the basis of protection of human health but on the basis of damage to livestock and vegetation. The levels established are well below those found to adversely affect human health. For example, Wyoming has adopted a fluoride regulation and standard which states [254] that fluorides measured as HF shall not exceed 0.80 μg/cu m or 1.0 ppb (part per billion) as a 24-hour average. Pennsylvania's standard [255] sets the limit for water soluble fluorides as 5 μg HF/cu m averaged over 24 hours. Montana's standard is 1 ppb as HF, and New York's is 3 ppb averaged over a 24-hour period. [256] Washington [257] has established 2 standards, one for forage and one for community air. Fluoride concentration of forage by dry weight is not to exceed 40 ppm F averaged over 12 consecutive months, 60 ppm averaged over 2 months, and 80 ppm more than once in any 2 consecutive months. Gaseous fluorides in community air are not to exceed an average of 3.7 μg HF/cu m for 12 hours, 2.9 μg/cu m for 24 hours, 1.7 μg/cu m over 7 days, 0.84 μg/cu m over 30 days, and 0.5 μg/cu m over the period March 1 through October 31 of any year.

Standards for fluorides in effluent from aluminum smelting operations have been proposed by the Environmental Protection Agency in the Federal Register 38(230):33170-83, dated 30 November 1973. The proposed 40 CFR 421 specifies various concentrations of fluoride in effluent ranging from 0.05 kg/1,000 kg of product a day to 2.0 kg/1,000 kg of product a day, depending on the process and the technology used. These standards apparently are not based on any human health effects, but on the best practicable or best available technology. For this reason they are not directly comparable with the recommended environmental limit of Chapter I.