

VI. WORK PRACTICES

Safety precautions for handling anhydrous hydrogen fluoride (HF) are the subject of a considerable body of literature. [1,2,4,12,187-197] Less has been written on the handling of aqueous solutions of hydrogen fluoride (HF acid), particularly in low concentrations, although the problems and health effects from use of the two forms are essentially similar. [1,2,189,190,198,199] A major portion of the literature deals with work practices for the safe handling of HF in the alkylation process in petroleum refining and detergent manufacturing. [12,187,188,191,193,195] In general, stress is placed on proper plant design as the fundamental preventive measure, followed by precautionary use of respiratory, eye, and skin protection which vary in complexity depending on the degree of potential exposure. Other work practices receiving emphasis in the alkylation process are training and drills; distinctive identification of HF areas, tools, and plant equipment used for HF work; neutralization and inspection of all protective equipment, tools, and plant equipment before handling by unprotected personnel; neutralization of waste prior to disposal; and precautions necessary for the prevention of fire and explosion due to hydrogen generated by contact of metals with hydrogen fluoride. While these work practices have been described in connection with alkylation processes, they appear to be readily adaptable to other similar processes using HF.

Reports of work practices written specifically for the prevention of low-level exposures are limited. Handling of hydrogen fluoride in enclosed systems was recommended. [200] Recommendations have also been made for the

control of hydrogen fluoride exposures by using ventilation devices such as laboratory hoods, [1] using open construction practices, [187,196] using compressed air or portable air movers, [191] including natural or forced draft ventilation for work areas in plant design, [2] and using ventilation for hydrogen fluoride storage areas. [190] Ventilation systems should be designed and constructed to be corrosion-resistant and safeguards should be provided to prevent condensate from dripping onto workers. [2,190] Discharges from ventilating systems should not be located near fresh air intakes, equipment subject to corrosion by HF, or building exits or entrances. [2,190] In general, where equipment or processes containing hydrogen fluoride cannot be completely enclosed, good engineering practices should be used to control continuous low-level exposures and to minimize excursions. Good ventilation practices are recommended in the current edition [201] of Industrial Ventilation--A Manual of Recommended Practice published by the American Conference of Governmental Industrial Hygienists.

(a) Skin and Eye Protection

The severity of skin burns caused by contact with hydrogen fluoride has been extensively described. [1,22,24,25,32,188,194] Documentation of serious eye injuries due to exposure to hydrogen fluoride has been sparse [28,26,27] although it has been frequently stated without further elaboration [1,2,4,187,189,190,202] that hydrogen fluoride is a severe eye hazard. Mayer and Guelich [32] stated that burns from weak HF acid (1-20%) were not noticeable for several hours. No supporting data were given for this statement, but Largent [26] reported experiments which indicated that airborne HF concentrations averaging 2.59-4.74 ppm caused noticeable skin and eye irritation. On the basis of good practice, appropriate skin and

eye protective devices should therefore be worn when airborne concentrations of HF are likely to exceed the recommended workplace environmental limit, or when direct contact with HF or HF acid may occur.

What constitutes appropriate skin and eye protection is a subject of some complexity, depending on the particular process or operation involved, and the degree of potential hazard. Literature dealing with the use of HF in alkylation processes [187,188,191,193,195,203] listed 3-4 classes of protective clothing required for various process operations. References [1,2,4,46,189,194,196] dealing with less specific potential exposures to hydrogen fluoride were correspondingly less specific in their recommendations for protective clothing, but stressed the importance of complete skin coverage when working with or around hydrogen fluoride. Table VI-1 is a guide for selection of proper protective clothing. Considerable emphasis was placed in the development of this guide on the potential for skin burns caused by pinholes in impervious gloves, and it is of utmost importance to inspect gloves and other protective clothing prior to issue. [1,192,194,196,197] Care must be taken in removing protective clothing and equipment after use where hydrogen fluoride is present. The possibility of self-contamination if the clothing and equipment are removed in the wrong order and without thorough washing cannot be ignored. A written procedure for such removal must be prepared and enforced after proper employee instruction in its provisions. [189,190] After removal, protective clothing and equipment must be neutralized, washed, sanitized, and inspected prior to storage and reissue. Those handling the clothing and equipment prior to neutralization must themselves be protected. [1,188,189,191-196] In some cases, it may be appropriate for

identification purposes to use distinctive coloring for protective clothing worn in the presence of hydrogen fluoride. [187] Protective clothing made of porous materials, eg, cotton, must not be used [32] since it can become saturated with hydrogen fluoride with subsequent revaporization, thus causing an inhalation hazard to the wearer. Protective clothing must be made of neoprene, plasticized polyvinyl chloride or of an equally impervious material. [2]

Wherever skin and eye contact with hydrogen fluoride may occur, it is essential that adequate sources of water for washing are available.

TABLE VI-1

PROTECTIVE CLOTHING SELECTION GUIDE

Examples of Type of Operation	Protective Clothing and Equipment
Receiving and neutralizing protective clothing, safety equipment, tools Laboratory operations with aqueous hydrogen fluoride in a ventilated hood, eg, pouring, heating, observing reactions Photoetching	Chemical goggles, face shield, impervious gloves, impervious apron, shoe covers or overshoes
Electroplating operations using hydrogen fluoride solutions	Same as above, except impervious boots instead of overshoes
In association with hydrogen fluoride systems or equipment, routine operating work or maintenance of nonacid equipment, reading instruments, operating valves in closed systems, re-assembly of thoroughly cleaned acid equipment Inspections of hydrogen fluoride hazard areas by supervisors or visitors Entering low concentrations of acid vapor	Impervious head and neck covering (hood) or chemical goggles and face shields, impervious gloves, impervious overshoes or boots

TABLE VI-1 (CONTINUED)

PROTECTIVE CLOTHING SELECTION GUIDE

Examples of Type of Operation	Protective Clothing and Equipment
<p>Nonroutine operations associated with hydrogen fluoride systems or equipment, repair operations not involving the opening of acid-bearing equipment, washing down, start-up or shut-down of plant sections, assembling of acid equipment not thoroughly neutralized, greasing valves</p> <p>Mixing or adding hydrofluoric acid to electroplating solutions</p>	<p>Impervious head and neck covering (hood), or chemical goggles and face shield, impervious gloves, impervious jacket and trousers, boots</p>
<p>Sampling hydrogen fluoride, opening HF acid equipment, dismantling valves and pumps contaminated with hydrogen fluoride, breaking unions, opening meters, connecting or disconnecting tank cars or cylinders, venting hydrogen fluoride containers</p>	<p>Impervious head and neck covering (hood), impervious jacket and trousers, impervious gloves, boots, plus air-supplied respirator as specified in Table I-1</p>
<p>Entering vessels, repairing hydrogen fluoride leaks, emergency operations, clean-up of spills, entering high concentrations of acid vapor or sprays of acid</p>	<p>(1) Impervious gloves; impervious boots, continuous-flow air-supplied impervious suit with body harness and safety line, if required, and auxiliary self-contained air supply</p> <p>(2) Impervious full-body suit and self-contained positive-pressure full-facepiece breathing apparatus, as specified in Table I-1</p>

[1,2,4,32,188-194] The most important first-aid measure for skin or eye contact with hydrogen fluoride is immediate flushing with water, which must be continued until medical assistance is obtained. Eyewash fountains and safety showers with quick-acting valves must be located at strategic points near hydrogen fluoride work areas. When washing eyes after contact with HF, it may be necessary to hold the eyelids open to ensure complete

washing. Safety showers should be equipped with automatic alarms to indicate use and summon aid. [12,188,194] The use of warm water for washing contaminated skin has been suggested to prevent shock, [12,187,191] while cold or iced water has been suggested to alleviate pain. [1,2, 4,193] In any case, hydrogen fluoride must be flushed from the skin without the delay caused by searching for water of a particular temperature. Immediate flushing is important to prevent deep penetration of hydrogen fluoride under the skin.

Eye protection must consist of chemical-type goggles with hooded ventilation openings in addition to face shields if eyes and face are not protected by respiratory protection. Since contact lenses prevent effective eye irrigation, they must not be worn in the vicinity of hydrogen fluoride.

(b) Respiratory Protection

Canisters used with respirators have limitations:

- (1) They do not protect in atmospheres deficient in oxygen.
- (2) The capacity of the canister to absorb hydrogen fluoride is limited by factors of concentration of hydrogen fluoride, breathing rate of the wearer, temperature, and humidity. [204] 30 CFR 11 lists maximum use concentrations in percent by volume for various types of gas masks:

Acid-gas front- or back-mounted gas mask: 2% (20,000 ppm)

Acid-gas chin-style gas mask: 0.5% (5000 ppm)

Acid-gas escape mask: 0.1% (1000 ppm)

- (3) Canisters have limited shelf life. Canisters must be replaced after each use and at the expiration of the shelf life recommended by the manufacturer.

If the odor of hydrogen fluoride becomes noticeable while wearing a gas mask, the hydrogen fluoride concentration is too high for safety, the mask is not properly fitted, or the canister is not effective. If the odor is noticeable, the area should be left without delay. Canister masks are not suitable [2,204] for use in emergencies because the concentration of hydrogen fluoride may be unknown, or an oxygen deficiency may exist. Because of the severe effects of hydrogen fluoride on skin, only full-face respiratory protection may be worn.

(c) Fire and Explosion

Hydrogen fluoride is nonflammable and will not promote ignition in contact with organic material. [2] In contact with metals, however, hydrogen fluoride can generate hydrogen which can be an explosion and fire hazard. [2,189,190,198,205,206] Metal containers of hydrogen fluoride must be vented regularly to prevent accumulation of hydrogen. [189,190] Sources of ignition must not be present during, such venting and ventilation must be provided for removal of any hydrogen released. [2,189,190] Repairs to hydrogen fluoride systems involving cutting or welding must be preceded by purging with inert gas or dry air, keeping the systems hydrogen-free during the repair process. [2,189]

Metal containers which have contained hydrogen fluoride must never be washed out with water, since this destroys the passivation (a nonreactive coating caused by reaction of the HF and container) and allows hydrogen to be formed. [189,190,2,187,194] Sparkproof tools must be used in opening tank cars and metal containers to prevent ignition of hydrogen. [2]

Ziehlke et al [207] reported on the explosive rupture of an HF cylinder due to prolonged storage and consequent corrosion and leakage.

They reported that the date of the last test of the cylinder was October 1955, and the explosion occurred in June 1969. Recommended preventive measures [207] included limiting reserves of hydrogen fluoride to required amounts, periodic examination for leakage and deterioration, observance of the 5-year retest limitations (49 CFR 173.34, 49 CFR 173.264), venting for reduction of hydrogen pressure, and use of inert gases instead of air for pressure transfer of HF from containers. A 4-month limitation on storage of cylinders has been recommended. [189]

(d) Leaks and Spills

Leaks and spills of hydrogen fluoride present a serious problem because of hazards to personnel, corrosion of materials, and difficulty of safe disposal. Detection of leaks is reasonably simple as HF fumes visibly in moist air, [4,187,188,191] and fuming is also readily detectable above HF acid of greater concentration than 48%. [2] Small leaks can be detected by holding an open bottle of concentrated aqueous ammonia near the suspected site of the leak [4] and observing the white fume formed if hydrogen fluoride or other acid gases are present. The strongly irritating and pungent odor [2,187,188,191] of hydrogen fluoride may be indicative of leaks. Early warning of leaks has been facilitated by painting flanged connections in hydrogen fluoride piping with a special acid-indicating paint which changes color in contact with the acid. [195,203] Regular inspection was recommended for early leak detection. [188,194,203] Use of length-of-stain detector tubes near locations of possible leaks for leak detection has been recommended. [188] Where water is used for cooling, for example in heat exchangers, leaks of hydrogen fluoride may be detected by the measurement of the conductivity or pH of the cooling water. [191,195]

When leaks or spills are detected, immediate control is imperative, followed by safe disposal of the hydrogen fluoride. Workmen repairing leaks or cleaning up spills should work on the windward side, if possible, or air-movers may be used to blow the acid gases away from the workmen. [2,191] Complete protective clothing is required for those controlling leaks and spills. [188,190,191,193] Areas in which significant quantities of hydrogen fluoride are located should be surrounded by raised curbs to confine spills [187,188,191,195] and to delineate the hazardous area. Curbs may be emphasized by painting them a distinctive color. [12,187,188,191,193] Floors of hydrogen fluoride areas should be constructed of concrete, or the areas should be covered with a neutralizing material, such as a layer of oyster shell or limestone. [12] Floors should slope to drains leading to neutralizing pits. [187,191,195] Lime or limestone may be used to neutralize waste hydrogen fluoride in these pits, [187,191,195] or soda ash may be used. [2] However, the latter produces sodium fluoride, which is toxic to warm-blooded animals, [2] and may cause a foaming reaction that may be undesirable. Accordingly, such neutralizing pits must be isolated and secured against entry by animals or unauthorized personnel. Pit alkalinity should be checked daily [187] to ensure sufficient neutralizing power for emergencies. Spills should be neutralized, then washed into drains, [2,194] or washed into the pits and then neutralized. [2,4,191] Pools of runoff from washdown of spills should be guarded until neutralized. [198,205,206] Small spills of hydrogen fluoride can be greatly diluted and flushed into sewers with large quantities of water. [2]

Leaking cylinders should be removed to the outdoors or to isolated well-ventilated areas. The cylinder contents should be transferred to a more suitable container or disposed of by routing to a neutralizing or reaction vessel, when the process system is so designed, or in any other safe manner. [2,4]

(e) Materials of Construction

The corrosion of metals by hydrogen fluoride varies with the concentration of HF. Accordingly, materials suitable for anhydrous HF containers, for example, may not be suitable for HF acid. Fehr [192,194] reported that the corrosive characteristics of hydrofluoric acid changed as the concentration increased from 65 to 80%; below 65% it had a low corrosion rate on lead, while above 65% it rapidly attacked lead. Below 60% it has a high corrosion rate on steel, while, above 80%, practically no action occurred on steel. Fehr [192,194] also stated that rubber, Neoprene, and many plastics showed excellent resistance to weak hydrofluoric acid, but were increasingly attacked at concentrations above 60% and 80% in aqueous solutions. He reported satisfactory use of steel for handling anhydrous hydrogen fluoride. Materials containing silica, eg, cast iron, glass, and asbestos, were unsatisfactory. In 1950, Whitaker [208] reported on materials used in plants manufacturing hydrogen fluoride. He substantiated the satisfactory performance of mild steel for storage tanks and cylinders for HF. Experiments with HF acid showed that 60% acid caused excessive pressure in drums, due to hydrogen formation, even though the drums had been passivated. When the acid concentration was increased to 65%, no pressure was produced in passivated or in new, unpassivated drums. Further experiments showed [208] that there was a breakpoint near

64% below which steel was undesirable as a container for HF acid. The Manufacturing Chemists' Association [2] stated that 70% HF acid exerts an effect on steel adequate to passivate containers for packaging and transportation purposes.

Containers for HF and HF acid are specified in 49 CFR 173.264. In general, HF acid of less than 70% concentration may be packed and shipped in rubber, wax, polyethylene or other HF-acid-resistant material in wooden or fiberboard boxes, or unlined steel tank motor vehicles; HF acid of between 60-80% strength can be shipped in unlined metal barrels, drums, or tanks, provided they have been properly passivated; HF acid of less than 65% strength can be shipped in rubber drums; HF acid of less than 62% strength can be shipped in lined metal barrels or drums (lining not specified, but must pass prescribed tests); HF acid of less than 40% strength can be shipped in rubber-lined tank cars; while anhydrous hydrogen fluoride may be shipped in steel cylinders, tank cars, tank motor vehicles, or portable tanks. A comprehensive list of materials of construction for hydrofluoric acid was listed by the Manufacturing Chemists' Association, [2] while steel is generally used for handling and storing anhydrous hydrogen fluoride. [2]

Porous materials, such as concrete, wood, pipe insulation, or plaster, absorb hydrogen fluoride and present a hazard until thoroughly neutralized or disposed of in a safe manner. [2,189,194] Cotton clothing readily absorbs hydrogen fluoride. [32] It can become saturated after long exposure, becoming a source of HF which may be an inhalation hazard to the wearer. Accordingly, cotton clothing should not be worn around HF processes.

(f) Storage

Hydrogen fluoride containers stored for extended periods of time may develop cracks; corrosion may occur due to loss of passivation. Hydrogen generated because of loss of passivation can produce excessive pressure and rupturing of the weakened container. [207] The National Safety Council [189] recommends a 4-month maximum storage time for HF cylinders, while the Manufacturing Chemists' Association [2] recommends a maximum storage time of 90 days for unlined steel drums of HF acid. Accordingly, users of hydrogen fluoride must ensure that stocks on hand are limited to amounts required for current use, and that containers are used on a first-in, first-out (FIFO) basis.

Vents for HF storage tanks must be connected to an acid-absorption system so that HF cannot escape, causing a hazard. Such vents must never be connected directly to a container of liquid because of the danger of suck-back, with possible violent results. [2,187]

Drums or other containers of HF must be stored with the closures up to facilitate venting and prevent discharge of liquid during venting operations. [189] Hydrogen fluoride must be stored in cool, well-ventilated areas, out of the direct rays of the sun and away from other sources of heat. [1,2,4,189,190,199] Personal protective equipment must be worn when venting HF containers. [2] Venting should be performed on receipt and at weekly intervals, [2,190] using sparkproof tools.

Under no circumstances must hydrogen fluoride ever be stored or placed in containers having siliceous material as a component. Meyer [199] reported accidents due to perforation of polyester-bonded glass-fiber tanks containing solutions of hydrogen fluoride. Mayer and Guelich [32]

described the deaths of two workmen who were splashed with hydrofluoric acid from a 5-pint glass bottle which had inadvertently been filled with 70% hydrofluoric acid. The gases generated by the reaction of hydrogen fluoride with the glass caused sufficient pressure to rupture the bottle.

(g) Training and Drills

Federal Occupational Safety and Health Standards, 29 CFR 1910.134, require training in the use of respiratory protection. Other references [2,12,189,190,193,195] stress the importance of training and drills for emergency situations. Accordingly, a requirement for training and drills is recommended. Trusty [12] recommended that those physicians who are unfamiliar with the medical management of hydrogen fluoride emergencies and likely to be called upon for HF emergency work be instructed in the proper procedures. He stressed the importance of properly advising the physician of the nature of the emergency so that proper treatment could be instituted.

(h) General Handling Precautions

Tools and equipment which have been used on hydrogen fluoride systems, or have been in contact with hydrogen fluoride, must be washed thoroughly and neutralized before being handled by unprotected personnel. [2,187,188,190,191,194] Such tools and equipment must be identified as potentially hazardous by being marked or painted a distinctive color. [194] Entry into areas restricted because of the presence of hydrogen fluoride must be controlled by a permit system. Permits must be issued by a responsible person, designated by management, who must also be responsible for determining the type of protective clothing required for entry. [12,188,191,193,195]

(i) Labeling

Trevethick [1] stated that solutions of HF acid at concentrations of 40% or above emit extremely irritating and toxic "fumes." The Manufacturing Chemists' Association [2] stated that solutions of HF acid above 48% HF emit "fumes." It appears, therefore, that solutions of HF of these concentrations or above would present an immediate inhalation hazard when handled or used. Dilute solutions in contact with the skin may have a delayed effect, while solutions of higher concentrations will have an immediate effect, as discussed above. Therefore, a separation of aqueous hydrogen fluoride solutions at the 40% concentration has been made for the purpose of ensuring proper precautionary labeling.

VII. COMPATIBILITY WITH EMISSION STANDARDS

There is presently no federal ambient air standard for hydrogen fluoride. A number of states have promulgated standards [209-213] for control of emission of fluorides. For example, Wyoming has adopted a fluoride regulation which states [209] that fluorides measured as HF in the ambient air shall not exceed 0.80 $\mu\text{g}/\text{cu m}$ or 1.0 ppb (part per billion) as a 24-hour average. Pennsylvania's standard [210] sets the limit for fluorides (total soluble as HF) as 5 $\mu\text{g}/\text{cu m}$ averaged over 24 hours. Montana's limit is 1 ppb (0.8 $\mu\text{g}/\text{cu m}$) as HF. [211] Washington [212] and New York [213] set two standards, one for forage and one for ambient air. In Washington, concentration of F in forage by dry weight (calculated as F ion) is not to exceed 40 ppm 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 ambient air, calculated as HF, are not to exceed 3.7 $\mu\text{g}/\text{cu m}$, averaged over 12 hours, 2.9 $\mu\text{g}/\text{cu m}$ for 24 hours, 1.7 $\mu\text{g}/\text{cu m}$ averaged over 7 days, 0.84 $\mu\text{g}/\text{cu m}$ averaged over 30 days, and 0.5 $\mu\text{g}/\text{cu m}$ averaged over the period March 1 through October 31 of any year. In New York, concentration of F in forage by dry weight (as F ion) is not to exceed 40 ppm averaged over a growing season not to exceed 6 months, 60 ppm averaged over 60 days, and 80 ppm averaged over any 30-day period. Gaseous fluorides, calculated as F ion, are not to exceed a 12-hour average of 4.5 ppb (3.7 $\mu\text{g}/\text{cu m}$), 3.5 ppb (2.85 $\mu\text{g}/\text{cu m}$) per 24-hours, 2.0 ppb (1.65 $\mu\text{g}/\text{cu m}$) averaged over 1 week and 1.0 ppb (0.8 $\mu\text{g}/\text{cu m}$) averaged over 1 month. The American Industrial Hygiene Association [214] recommended a Community Air Quality Guide for HF of 4.5 ppb (0.0036 $\text{mg}/\text{cu m}$) for 12

hours, 3.5 ppb (0.0028 mg/cu m) for 24 hours, 2.0 ppb (0.0016 mg/cu m) for 1 week, and 1.0 ppb (0.0008 mg/cu m) for 1 month.

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.

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 specified various concentrations of fluoride in effluent ranging from 0.05 kg/1000 kg of product/day to 2.0 kg/1000 kg of product/day, depending on the process and the technology used. These limits were apparently not based on biologic effects, but on the best practicable, or best available, technology.

Since these limits are not based on human health effects, they are not directly comparable with the recommended standard of Chapter I.