

EMERGENCY RESPONSE GUIDELINES FOR ANHYDROUS HYDROGEN FLUORIDE (HF)

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1.0 Introduction

1.1 Legal Notice

The *Emergency Response Guidelines for Anhydrous Hydrogen Fluoride* (Guidelines) were prepared by the American Chemistry Council's (ACC) Hydrogen Fluoride Panel (Panel). This document is intended to provide general information to persons addressing an emergency response in the course of handling and transporting anhydrous hydrogen fluoride (AHF). It is not intended to serve as a substitute for in-depth training or specific requirements, nor is it designed or intended to define or create legal rights or obligations. It is not intended to be a "how-to" manual, nor is it a prescriptive guide. All persons involved in handling and transporting AHF have an independent obligation to ascertain that their actions are in compliance with current federal, state and local laws and regulations and should consult with legal counsel concerning such matters. The *Guidelines* are necessarily general in nature and individual companies may vary their approach with respect to particular practices based on specific factual circumstance, the practicality and effectiveness of particular actions, and economic and technological feasibility. Any mention of specific products in these *Guidelines* are for illustration purposes only, and are not intended as a recommendation or endorsement of such products.

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1.2 To the Reader

As members and affiliated companies of the American Chemistry Council, the Hydrogen Fluoride Panel supports efforts to improve the industry's responsible management of chemicals. To assist in this effort, The Panel supported the creation and publication of these *Guidelines*. The Panel is composed of the following companies:

Arkema Inc.	Honeywell
Daikin America, Inc.	Mexichem SA de CV
DuPont	Solvay Fluorides, LLC

1.3 **Purpose and Use of** *Guidelines*

These *Guidelines* have been developed for use by producers and industrial users of AHF, chemical companies and independent or contractor emergency response personnel, ACC's CHEMTREC[®], Local Emergency Planning Committees (LEPCs), and transporters of AHF and their emergency response personnel.

The purpose of this product stewardship document is to provide the reader with a better understanding of the properties of AHF and to serve as a resource in the development of producers' and users' design, operation, maintenance, training and emergency response practices. References to applicable regulations and industry practices are made in the text, tables, figures, and appendices, as appropriate. Contact an AHF supplier for further information as necessary.

This edition of the Guidelines, issued in 2007, is the first edition. It is available through an AHF supplier in hard copy and on the internet at <u>www.americanchemistry.com/hydrogenfluoride</u>. It may also be available through an AHF supplier on its individual company website. This document may be updated. Readers should also stay abreast of new developments and information about AHF, including but not limited to physical properties, handling technology, medical treatment and regulatory requirements that occur after the date of publication of this document.

Contact an AHF supplier or visit <u>www.americanchemistry.com/hydrogenfluoride</u> to obtain the most current version of these *Guidelines,* for questions, or to get more information about any information presented in this document. The Hydrogen Fluoride Panel encourages comments on the content of this document and a more in-depth dialogue concerning the issues presented.

2.0 Chemical Identification, Production, and Use

2.1 Chemical Identification

Hydrogen fluoride (HF)¹ is a colorless gas at temperatures above about 67°F (19.5°C), and a clear, colorless, corrosive, fuming liquid at lower temperatures. It has an extremely acrid odor. Released AHF will quickly volatilize in air at room temperature, forming dense white vapor clouds.²

HF readily dissolves in water to form colorless hydrofluoric acid solutions; dilute solutions are visibly indistinguishable from water. It is highly soluble in alcohol and many organic compounds.

Undiluted, or pure, HF is often referred to as anhydrous³ hydrogen fluoride or AHF, while solutions of HF in water are generally referred to as hydrofluoric acid or by the percentage of HF in the solution, such as "70% HF" or "49% HF." 70% and 49% HF are the most commonly available commercial concentrations in North America. See Appendix A for more information on the physical properties and characteristics of AHF, 70% HF, and 49% HF.



Source: WebElements http://www.webelements.com

HF is highly reactive with many substances. It is highly corrosive, and contact between HF and metals, glass, concrete, strong bases, sodium hydroxide, potassium hydroxide, ceramics, leather, natural rubber, and other materials may result in violent reactions. Due to these properties, it is usually shipped in steel cylinders as a compressed gas. If stored, it is stored in corrosion-resistant containers. It should also be noted that the corrosive action of HF on metals can result in the formation of hydrogen gas.

Substance	Hydrogen Fluoride
Chemical Abstract Service Registry Number (CASRN)	7664-39-3
Group	Inorganic Corrosive
Synonyms	anhydrous hydrofluoric acid aqueous hydrogen fluoride antisal 2B hydrofluoride hydrofluoric acid fluorhydric acid fluorohydric acid fluoric acid fluoride HF HF-A AHF
RTECS	MW7875000
UN#	1052 (anhydrous); 1790 (solution)
DOT ID (Guide #)	1052 (125) (anhydrous) 1790 (157) (solution)

¹ The chemical structure of hydrogen fluoride is H-F, molecular weight 20.01. HF may exist in complexes or polymers, such as H_6F_6 , due to hydrogen binding.

² The NIOSH Pocket Guide to chemical hazards describes HF as a colorless gas or fuming liquid below 67°F. <u>http://www.cdc.gov/niosh/npg/npgd0334.html</u>. (Note that solutions containing HF will also fume in air, with fuming reported for HF concentrations of at least 48%).

³ "Anhydrous" means "without water."

2.2 Production of HF

In industrial settings, HF is generally derived from the reaction of concentrated sulphuric acid (H_2SO_4) on fluorspar (CaF_2) . The process generally used is to react 93 to 99 percent sulfuric acid and pulverized acid grade fluorspar (calcium fluoride). The reaction occurs in a heated rotary kiln at a controlled temperature for approximately 30 to 60 minutes. The reaction products are hydrogen fluoride gas and calcium sulfate.

Once it is produced, AHF can be shipped by a variety of methods. As noted above, due to the reactivity of the material, it is generally shipped in a steel container or vessel. In North America, approximately 85 to 90 percent of AHF is shipped in rail cars, with the remainder shipped in tank trucks (cargo tanks), portable tanks, and cylinders. The majority of AHF produced in the United States originates from two Gulf Coast area facilities. Significant quantities are also imported into the United States from Mexico and Canada. Over 70 user facilities located throughout the United States receive shipments of bulk AHF. Smaller quantities are also widely used throughout the country.

2.3 Uses for HF

HF is a valuable commercial chemical with many important uses. Among its many uses, it is a raw material for refrigerants, herbicides, pharmaceuticals, high-octane gasoline, aluminum, plastics, electrical components, and fluorescent light bulbs. It is also used for etching glass and metal. In low concentrations (e.g., 2.5 to 12 percent), it is present in a variety of over-the-counter products available to consumers. See Appendix B for examples of specific product applications for HF.

3.0 Environmental Fate and Effects

HF is very reactive in the environment and quickly forms salts. Plants and some wildlife are susceptible to HF exposure. Very low HF vapor concentrations (0.1 to 0.5 ppm) can injure or kill vegetation. Birds are very susceptible due to their high respiratory rates. Fish can be affected with very low fluoride concentration in water. When HF is released into the atmosphere, it will react and dissociate on contact with soils, water, structures and all living matter.

4.0 Health Factors, Industrial Hygiene, and First Aid

4.1 Health Factors

This section provides a brief overview of information pertaining to potential acute (short term) health hazards associated with exposure to HF. A comprehensive discussion of health effects information pertaining to HF is beyond the scope of these *Guidelines*. For more information, contact a supplier of HF. Additional information, including first aid information, also may be found in the supplier's Material Safety Data Sheet (MSDS).

4.1.1 General Health Information

Hydrogen Fluoride is extremely hazardous in both liquid and vapor states. It can cause severe injury to any tissue with which it comes in contact (chemical burn). Exposure by contact with skin, or by inhalation or ingestion, can lead to severe toxic systemic effects (Acute Fluoride Intoxication) and potentially death. Death can occur from severe electrolytic imbalance (hypocalcemia and hypomagnesaemia) that leads to cardiac arrhythmia (fibrillation), which, in turn, can lead to cardiorespiratory arrest and multiple organ failure (kidney and liver).

HF is easily absorbed by tissue, penetrating and then rapidly dissociating into Hydrogen and Fluoride. HF is highly corrosive and will destroy tissue on contact, but the fluoride ion will also migrate through, and continue to damage, tissue. The disassociated fluoride ion will continue reacting to create fluorinated salts, which can cause serious toxic systemic effects. Washing the exposed tissue with water does not neutralize or stop the reaction, which limits the benefits of water washing (decontamination). HF-specific first aid treatments bind the fluoride to calcium, and rapidly starting such treatments is critical to stopping further tissue damage.

The local (harm to the part of the body a substance comes into contact with) and systemic (harm that changes the function of other organs) toxic effects that can occur following exposure to HF can vary widely depending on the amount of fluoride absorbed by the body. Effects may range from mild and reversible, such as mild irritation of the skin, eyes and respiratory tract, to serious and potentially life-threatening.

Hyperkalemia (excessive concentration of potassium in the exposed area) is often cited as the cause of intense pain.

4.1.2 Acute Inhalation Exposure

Inhalation of HF results in a burning, prickling feeling in the nose and throat accompanied by coughing and pain under the sternum. Nausea, vomiting, diarrhea and gum ulceration have also been reported effects. Exposure to low concentrations of HF can result in irritation of nasal passages, dryness, bleeding from the nose, and sinus disorders. Continued exposure to low concentrations can result in an ulcerated and perforated nasal septum. Inhalation exposure to low concentrations of vapor may initially cause no signs or symptoms; however, if not treated, respiratory distress may occur. Exposure to high concentrations of HF can result in laryngitis, bronchitis, burning of lung tissue, and pulmonary edema (fluid accumulation in the lungs). These symptoms may have a delayed onset of 12 to 24 hours following exposure.

4.1.3 Skin Contact

Skin contact with hydrogen fluoride may cause severe burns that develop after several hours and form skin ulcers. Exposure to aqueous HF solutions (1% to 70% in water) may produce delayed burns which become apparent one to eight hours following exposure. Following exposure to solutions with HF concentrations below 20%, burns may not be immediately painful or visible, but may be displayed 24 hours or more after exposure. Exposure to high concentration HF solutions, to AHF, or to vapor with a high concentration of HF will result in immediate, visible and painful injury to the exposed tissues. Exposure to low concentration solutions (e.g., below 20-30%) may result in burns that are not noticeable for several hours.

4.1.2 Eye Contact

Eye contact with HF results in a feeling of burning, redness, and secretion. Even a splash of a dilute HF solution can quickly result in conjunctivitis, keratitis, or more serious destruction of eye tissue.

For more general information about potential health effects of hydrogen fluoride, consult resources such as the U.S. Center for Disease Control's Fact Sheet about Hydrogen Fluoride;⁴ ATSDR's Toxicity Profile on Fluorides,⁵ European Union HF Risk Assessment,⁶ and Australian National Occupational

⁴ <u>http://www.bt.cdc.gov/agent/hydrofluoricacid/facts/asp</u>

⁵ATSDR's ToxFAQ[™] for Fluorine, Hydrogen Fluoride, and Fluorides (September 2003), <u>http://www.atsdr.cdc.gov/tfacts11.html</u>

⁶ Hydrogen Fluoride Risk Assessment (EU) (December 2, 1999), <u>http://ecb.jrc.it/</u>

Health and Safety Commission's Guide to Hydrogen Fluoride.⁷

4.1.3 Chronic Hazard

Skin ulcers, bone and tooth damage, and irritation of the nose, throat, and lung tissue have been reported from chronic (long term) exposures to HF.

Exposure Limits for HF			
OSHA (PEL)	3 ppm, 8 hr TWA		
ACGIH (TLV) 2 ppm (1.7 mg/m ³), Ceiling			
ACGIH (TLV) 0.5 ppm (0.4 mg/m ³), 8 hr TWA			

The U.S. Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit (PEL) of 3 ppm, 8-hour, time-weighted average for HF.⁸ The threshold limit value (TLV[®]) established by the American Conference of Governmental Industrial Hygienists (ACGIH[®]) for HF is 2 ppm (Ceiling), 0.5 ppm 8 hr TWA . The TLV refers to the airborne concentration and represents the condition under which ACGIH believes that nearly all workers may be repeatedly exposed, day after day, without adverse health effects. The value is a time-weighted average (TWA) concentration for an 8-hour workday and 40-hour work week. It only serves as a guide in the control of health hazards, and not as a fine line to distinguish between safe and dangerous concentrations. It should be noted that where the TLV is lower than the PEL, OSHA has taken the position in the past that it will embrace the more restrictive limit and use it in conjunction with the general duty clause in its enforcement role. TLVs, RELs, and PELs are subject to change by their associated peer review groups. As with other references in these *Guidelines*, users must check the current reference for up-to-date information.

EPA has issued Acute Exposure Guideline Levels, or AEGLs, for HF. AEGLs describe the risk to humans (general public) resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals. The National Advisory Committee for AEGLs develops these guidelines to help both national and local authorities, as well as private companies, deal with emergencies involving spills, or other catastrophic exposures. Acute exposures are defined as single, non-repetitive exposures (emergency exposure periods) for not more than eight hours.

• AEGL 3 is the airborne concentration (expressed as ppm and mg/m³) of a substance at or above which it is predicted that the general population, including "susceptible" but excluding "hyper susceptible" individuals, could experience life-threatening effects or death.

• AEGL 2 is the airborne concentration (expressed as ppm and mg/m³) of a substance at or above which it is predicted that the general population, including "susceptible" but excluding "hyper susceptible" individuals, could experience irreversible or other serious, long-lasting effects or impaired ability to escape.

• AEGL 1 is the airborne concentration (expressed as ppm and mg/m³) of a substance at or above which it is predicted that the general population, including "susceptible" but excluding "hyper susceptible" individuals, could experience notable discomfort. Airborne concentrations below AEGL 1 represent exposure levels that could produce mild odor, taste or other sensory irritations.

⁷ National Health and Safety Commission (AU), *Hydrogen Fluoride*, (December, 1989). <u>www.nohsc.gov.au/PDF/Standards/HydrogenFlouride.pdf</u>

⁸ The National Institute for Occupational Safety and Health (NIOSH) has also established a recommended exposure limit (REL) for HF of 3 ppm (2.5 mg/m³) TWA, 6 ppm (5 mg/m³) 15 minute ceiling. The REL is a recommended exposure level averaged over a ten hour workday.

ACUTE EXPOSURE GUIDELINE LEVELS (AEGLs) for HF Issued by EPA National Advisory Committee						
Classification 10-Minute 30-Minute 60-Minute 4-Hour 8-Hour						
AEGL-1 (Nondisabling)	1 ppm (0.8 mg/m ³)	1 ppm (0.8 mg/m ³)				
AEGL-2 (Disabling)	95 ppm (78 mg/m ³)	34 ppm (28 mg/m ³)	24 ppm (20 mg/m ³)	12 ppm (9.8 mg/m ³)	12 ppm (9.8 mg/m ³)	
AEGL-3 (Lethal) 170 ppm (139 mg/m³) 62 ppm (51 mg/m³) 44 ppm (36 mg/m³) 22 ppm (18 mg/m³) 22 ppm (18 mg/m³)						

The American Industrial Hygiene Association (AIHA) publishes Emergency Response Planning Guidelines (ERPGs). These guidelines set one-hour exposure limits for effects on the general public for use in emergency response situations. ERPG-1 is the allowable concentration for mild transient effects or objectionable odor (discomfort). ERPG-2 is the concentration for serious health effects or impaired ability to take protective action (disability). ERPG-3 is the allowable concentration for life-threatening effects (death).

EMERGENCY RESPONSE PLANNING GUIDELINES (ERPGs) for HF Issued by the American Industrial Hygiene Association			
ERPG 1 (60 min)	2 ppm	ERPG 1 (10 min)	2 ppm
ERPG 2 (60 min)	20 ppm	ERPG 2 (10 min)	50 ppm
ERPG 3 (60 min)	50 ppm	ERPG 3 (10 min)	170 ppm

The National Institute for Occupational Safety and Health (NIOSH) has set an IDLH (immediately dangerous to life or health) level for HF of 30 ppm. The current NIOSH definition for an immediately dangerous to life or health condition is a situation "that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment." NIOSH's intention in setting an IDLH is to "ensure that the worker can escape from a given contaminated environment in the event of failure of the respiratory protection equipment." NIOSH's respirator decision logic uses IDLH criteria to aid in the selection of respirators for emergency and certain other situations.

4.3 **HF Exposure Management**

There are many excellent resources available for developing a plan to treat HF exposures. For example, ATSDR's Medical Management Guidelines for Hydrogen Fluoride can be a useful guidance tool,⁹ and the Australian National Occupational Health and Safety Commission has also published a useful resource tool. The HF manufacturer's Material Safety Data Sheet (MSDS) will also include specific first aid instructions; first aid instructions on an MSDS accompanying HF should be followed.

Development of a first aid plan should be done in consultation with appropriately trained medical personnel. To facilitate proper and timely first aid treatment, it can be useful to arrange in advance and have available medical receiving facilities and names of physicians (backup as well as primary) trained in HF emergency treatment. A medical contact list for HF producers is provided in Appendix H.

Excerpts from one available reference source, ATSDR's Medical Management Guidelines for Hydrogen Fluoride, are reproduced in Appendix I to assist users of these Guidelines in the development of their own first aid procedures. ATSDR's Guidelines are one of many available sources of first aid information related to HF. It is noted that specific first aid procedures may vary based on fact-specific circumstances, recommendations of trained medical personnel, and other factors.

Another useful component of a first aid program can be to develop exposure route flowcharts. Several examples are reproduced in Appendix J.

Personal decontamination procedures used by some HF manufacturers are included in Appendix K.

5.0 **Personal Protective Equipment**

Personal protective equipment (PPE) serves to complement but not substitute for engineering controls including safe working conditions, adequate process control, ventilation and proper conduct by employees working with HF. The appropriate selection and use of personal protective equipment will normally consider the total and fact-specific situation in addition to the toxic properties of compounds to which a worker may be exposed. These situations may involve the presence of other materials that can magnify potential concerns associated with HF. Therefore, the information presented in this section with regard to PPE selection is to be considered as a potential reference point for general guidance. Users need to select appropriate personal protective equipment based on their specific needs and circumstances. Other chemicals or factors may require the use of additional protection. Except in extreme emergencies, no one should be given personal protective equipment without suitable training.

Location, care and selection of appropriate PPE are dictated by the proposed use of the equipment. Companies have assigned personnel, facilities and programs for suitable care, decontamination and repair of all equipment. These programs include a process to check with the PPE manufacturer regarding the suitability of the PPE and materials of construction for a particular use; in addition, they check the specific use instructions and restrictions of the PPE manufacturer. Companies provide training so that employees using PPE in HF service are extensively experienced in the use of the relevant PPE prior to its use in HF service. Consult the manufacturer's product use recommendations where provided.

⁹ <u>http://www.atsdr.cdc.gov/MHMI/mmg11.html</u>

5.1 Protective Clothing

HF is highly corrosive and reactive, and rapidly penetrates tissue with which it comes into contact. Workers in contact with HF should be aware of the permeation, penetration, and degradation characteristics of HF on PPE and take appropriate precautions. In particular, workers should be aware of the limits of PPE in HF service; for example, such PPE may not be designed to come into contact with liquid streams of HF.

For HF, NIOSH's recommendation for skin protection is to prevent skin contact, and the recommended protective clothing barriers are Tychem[™] (8 hour) and Teflon[™] (4 hour).¹⁰ The Quick Selection Guide to Chemical Protective Clothing also provides that the following PPE designations would be appropriate where contact with HF is anticipated:

• Level A (fully encapsulating suit - highest level of respiratory, skin and eye protection).

The Level A suit is ordinarily used in most emergency response situations. Level A protection, when used in compliance with the manufacturer's instructions and recommendations, should provide adequate gaseous HF resistance (adequate penetration and permeation times).

The definitions of the four levels of PPE may be found in the Hazardous Waste Operations and Emergency Response (HAZWOPER) regulations, 49 CFR §1910.120, Appendix B. More information is available in the Hydrogen Fluoride Industry Practices Institute's (HFIPI) "Personal Protective Equipment Guideline For Anhydrous Hydrogen Fluoride," most recent edition.

5.2 Respiratory Protection

The Occupational Safety and Health Administration (OSHA) has provided requirements for respiratory protective equipment. (See Title 29 CFR 1910.134 as amended). Such equipment is carefully maintained, inspected, cleaned and disinfected at regular intervals and before use by another person. Consult a reliable safety equipment dealer for details on the proper use of approved equipment.

In its Pocket Guide to Chemical Hazards, NIOSH makes respirator recommendations for HF:11

5.3 Decontamination

Decontamination of PPE following a response is an important part of any Emergency Response Plan (ERP). For more detailed discussion, see Section 10.5, Decontamination of PPE.

¹⁰ See Recommendations for Chemical Protective Clothing, a Companion to the NIOSH Pocket Guide to Chemical Hazards (Table H) (recommendations based on *Quick Selection Guide to Chemical Protective Clothing, Third Edition*, by Krister Forsberg and S.Z. Mansdorf (1997)), <u>http://www.cdc.gov/niosh/ncpc/hcpc.html</u> (NOTE: the Fourth Edition of the Quick Selection Guide was published in 2003; the most recent Edition should always be consulted by the user).

¹¹ <u>http://www.cdc.gov/niosh/npg/npgd0334.html</u>

6.0 Emergency Response

Every emergency situation will be different. It is not the intention of these *Guidelines* to address every potential emergency situation; it is intended to help producers, users, and others as a resource in the development of their own emergency procedures for responding to an HF incident.

Emergency responders must be properly trained and equipped in accordance with OSHA standards on emergency response and emergency fire protection (29 CFR 1910.38, 1910.120 and Subpart L). The first priority in responding to an emergency situation is the safety of the emergency responders, employees, and people in the surrounding community. The second priority is to determine the incident's impact on the surrounding environment, and to set a strategy to stabilize the situation and minimize the impact. The third priority is the conservation or protection of equipment and property.

6.1 Specific Emergency Response Considerations

6.1.1 Establishing Response Perimeter

Establishing an emergency response perimeter is a common feature of an emergency response plan. The DOT North American Emergency Response Guidebook provides the following guidance for incident isolation:

Response Code 125	Initial Isolation All Around	Then Protect Persons Downwind During:	
Spill Size	Meters (feet)	Day Kilometers (miles)	Night Kilometers (miles)
Small Spill	30 m (100 ft)	0.1 km (0.1 mi)	0.5 km (0.3 mi)
Large Spill	210 m (700ft)	1.9 km (1.2 mi)	4.3 km (2.7 mi)

6.1.2 Monitoring Wind Direction

Noting wind direction and speed and existing weather conditions informs the emergency response. After noting wind and weather conditions and whether fumes are visible from the HF, place the hot zone perimeter at an appropriate distance away from visible fumes.

HF vapor is heavier than air. However, the initial release may result in an exothermic reaction causing the vapor cloud to temporarily rise.

6.1.3 Exposure Limits

Some known HF exposure limits are displayed in Section 4.2.

6.1.4 Air Monitoring Equipment for HF

Flame ionization detectors (FID) and photo-ionization detectors (PID) are not appropriate airborne monitors because HF is not flammable and detecting its ionization potential is beyond current technology.

The following types of air monitoring detectors have been successfully used to detect HF: **Detector Tubes Detector Tubes**

Advantages	Disadvantages	Advantages	Disadvantages
 Portable No batteries or power source required 	 One time use detector tubes Not continuous, gives only a "snapshot in time" Large number of detector tubes may be needed Tubes have limited shelf life Qualitative mesaurements based on color change in tubes Correction factor required for temperture and humidity Glass tubes are potential puncture hazard ("sharps") Potential false positive readings due to other chemical interactions 	 Portable Continuous Data logging capabilities Direct reading instrument (quantitative measure) 	 HF exposure higher than range will require recalibration Power source (battery/electric) required 1-5 minute response lag time Limited range (based on sensor) Maintenance requirements Potential false positive readings due to other chemical interactions

6.1.5 Mitigation of HF with Water Spray

AHF fumes appear as a white fog and can significantly impede visibility. HF fumes are very watersoluble. Water sprays may reduce acid and vapor. A spray volume adequate to manage fumes is used in mitigation; spray volume from 500 to 1,000 gallons per minute (gpm) per nozzle is generally used. The number of nozzles used is dependent on leak size and the amount of visible fumes. HF removal efficiencies of 90+% have been demonstrated with water to HF ratios of 40 to 1. High velocity water spray may create its own draft, inducing additional air movement.

CAUTION: Water runoff will contain weak acid solutions.

Insufficient water on liquid spills is likely to cause increased vapors and extreme heat; copious water amounts are recommended. Liquid HF that has been diluted to below 40% is less likely to emit significant vapors.

Supplying water in the form of a spray or fog (rather than a stream) on the fume cloud or down wind of the source can help reduce acid and vapor. As noted above, the water supply will create runoff containing weak acid solutions, so it is important to contain or appropriately manage the runoff. Proper waste disposal concerns and environmental impacts should be considered.

CAUTION: Spraying mitigation water onto the damaged container or directly onto the container should be avoided where possible because this can accelerate corrosion and make the leak larger.

6.1.6 Neutralization

HF solutions can be neutralized with alkaline materials. Runoff containing HF can be neutralized with alkaline materials such as lime, soda ash, bicarbonate of soda, sodium hydroxide or potassium hydroxide. Alkaline chemical neutralization may result in significant heat or gas generation and will result in inorganic salt formation. Some inorganic salts may be environmental toxins. Use of calcium-based compounds yields salt neutralization products with less environmental impact.

HF contaminated soil can be neutralized using lime slurry or ground limestone slurry. Contaminated soil must be removed and disposed of in compliance with applicable state and federal environmental regulatory requirements, such as appropriately labeled containers and disposal in approved facilities (e.g., RCRA TSD facility).

CAUTION: Most neutralizing agents have high heats of dilution/reaction; use appropriately diluted neutralizing agents.

See the next page for a chart illustrating typical alkaline materials used for neutralization of HF.

6.1.7 Run-off Control

Run-off is generally isolated away from the mitigation area so it can be treated. Clay, other nonsand containing soils, or some absorbent socks can be used to control run-off. Quantities of run-off can be substantial, because mitigation can generate run-off at a rate of 500 to 1,000 gallons per minute. Where possible, avoid isolating run-off where metal is exposed, because aqueous hydrogen fluoride reacts with metal and forms hydrogen gas, which can be explosive. In addition, HF contact with metal creates a scale of iron fluoride, and this scale produces HF again when exposed to water.

6.2 **Reporting Requirements**

6.2.1 Federal and State Requirements

Report releases as required by federal, state and local authorities. Federal law requires prompt notification to National Response Center (800-424-8802) for reportable quantity (RQ) releases. The RQ for AHF is 100 pounds, measured as 100% HF. Consult state and local officials for other reporting requirements.

6.2.2 CHEMTREC® and HF Mutual Aid Network

CHEMTREC[®] is an American Chemistry Council public service that provides 24-hour services to callers needing information and assistance for emergencies involving chemicals and hazardous materials. CHEMTREC's service is also used by thousands of companies that ship hazardous materials to help meet the DOT regulations requiring a 24-hour emergency telephone number. **CHEMTREC: (800) 424-9300 or (703) 527-3887 (collect).**

The member companies of the American Chemistry Council have entered into a Mutual Aid Agreement for HF. To activate the network, call CHEMTREC.

Procedures for activating the Hydrogen Fluoride Mutual Aid Network are on page 14. An example flowchart for emergency response is on page 15.

TYPICAL ALKALINE MATERIALS (BASES) FOR NEUTRALIZATION OF HF					
Alkaline Material	Common Name(s)	Form(s) Available	Hazards / Reaction	Lb 100% Baseper Lb 100% HF	Salt Properties
Calcium Carbonate (CaCO ₃)	Limestone	Pebbles	-Slow Reaction -Slow Evolution of Carbon Dioxide Gas (CO ₂) -Pebble Surface Can Become Passivated	2.50 lb / lb HF	Calcium Fluoride (CaF ₂) Non-hazardous Sol. In Water = 0.004%
Calcium Hydroxide [Ca(OH)2]	Hydrated Lime	Dry Powder Slurry in Water	-High Heat of Neutralization -Slippery When Wet	1.85 lb / lb HF	Calcium Fluoride (CaF ₂) Non-hazardous Sol. In Water = 0.004%
Calcium Oxide (CaO)	Quicklime	Dry Powder	-DOT Class 8 (Corrosive) -Very High Heat of Hydration and Neutralization	1.40 lb / lb HF	Calcium Fluoride (CaF ₂) Non-hazardous Sol. In Water = 0.004%
Potassium Hydroxide (KOH)	Caustic, Potash	85% Solid Beads or Flake <45% Solution	-DOT Class 8 (Corrosive) -Very High Heat of Dilution and Neutralization -Poison	2.80 lb / lb HF	Potassium Fluoride (KF) DOT Class 6 (Poison) Sol. in Water >40%
Sodium Bicarbonate (NaHCO ₃)	Bicarb, Baking Soda	Dry Powder	-Rapid Evolution of Carbon Dioxide Gas (CO ₂) -Poison	4.20 lb / lb HF	Sodium Fluoride (NaF) DOT Class 6 (Poison) Sol. in Water = 4.0'
Sodium Carbonate (Na₂CO₃)	Soda Ash	Dry Powder	-Rapid Evolution of Carbon Dioxide Gas (CO ₂) -Poison	2.65 lb / lb HF	Sodium Fluoride (NaF) DOT Class 6 (Poison) Sol. in Water = 4.0%
Sodium Hydroxide (NaOH)	Caustic Soda	100% Solid Beads or Flake <50% Solution	-DOT Class 8 (Corrosive) -Very High Heat of Dilution and Neutralization -Poison	2.00 lb / lb HF	Sodium Fluoride (NaF) DOT Class 6 (Poison) Sol. in Water = 4.0%

Notes:

- 1. Any alkaline material may be used for HF neutralization. The chart above lists those most commonly used to mitigate spills. Others, such as Ammonium Hydroxide (NH₄OH), may be used but may have features that make their use less desirable (e.g., odor).
- 2. Commonly used neutralizing materials are listed alphabetically (Column 1). Selection of the appropriate alkaline material is a function of many factors, including:
 - Availability and Ease of Acquisition
 - Physical Form and Ease of Handling
 - Disposal of the Neutral Salt or Salt Solution (Column 6)

Also note that calcium based materials yield non-hazardous but very insoluble Calcium Fluoride. Materials yielding salts that may be classified as poison, but with high water solubility, may be preferable for scrubbing applications.

- 3. The amount of alkaline material required for neutralization (Column 5) is based on pounds of equivalent 100% Alkali per pound of 100% HF. The factor will have to be adjusted based on the Alkaline form used (Column 3).
- 4. Use care to control the chemical reactions. For example, to better control the Heat of Neutralization, dilute the HF Spill and Neutralizing Alkaline Solution as much as is practical, considering the need to contain and control all effluents.
- 5. When using carbonates (e.g., Soda Ash), the rate of Carbon Dioxide gas evolution is generally controlled from upwind of the containment area.

CHEMTREC[®] Procedures for Activating Hydrogen Fluoride Mutual Aid Network

If the Shipper is Known - CHEMTREC will:

- Call Shipper.
- Service details of emergency, location, contact names, other relevant information.
- Provide Shipper with company name, phone number(s) and location of the nearest Response Team.
- Advise the Shipper that CHEMTREC is available for additional assistance if required.

If the Shipper is Unknown - CHEMTREC will:

- Solution Call the nearest Member Responder.
- Advise the Contact that the Shipper is unknown, provide details of the emergency and request assistance.
- If the Shipper is subsequently established, CHEMTREC will contact Shipper, provide details of emergency and actions taken, including company name and phone numbers of the Response Team called by CHEMTREC.

HF Mutual Aid Network Understandings and Practices

- Shipper has primary responsibility for incident response.
- Member's Responder(s) is expected to provide assistance until the Shipper assumes responsibility.
- However, the Mutual Aid Network Agreement does not require a Member's Responder to stay at the HF Distribution Incident scene any longer than 24 hours. Assistance is designed to protect "life and the environment" and reduce any public inconvenience.
- A shipper may find it timely to fly to an incident if other Member Responder(s) are over 200 miles from an incident. Emergency response teams, equipment, procedures and decisions must be established in advance of an incident. These *Guidelines* may assist in establishing such protocols.
- The HF Mutual Aid Network encourages periodic and systematic review and practice of plant emergency response procedures.



7.0 Damage Assessment

7.1 Introduction

This section is intended to assist first responders with the evaluation of the extent of AHF railcar or tank truck damage. (See also Appendices C-F, Descriptions of HF Containers, for typical descriptions and orientations.) Assessment of equipment damage helps inform the decision whether to proceed with immediate AHF transloading or to move (e.g., dragging, lifting with a crane) the damaged railcar or tank truck a short distance in order to place it in an upright position or otherwise position it in a manner suitable to support more detailed damage assessment. This section does not address every possible scenario of damage to a railcar or tank truck. Transloading AHF is inherently dangerous and should only be performed by properly trained, equipped and protected personnel. Although any damage assessment should be conducted only by personnel with appropriate training and experience, for significant incidents, an on-site damage assessment conducted by highly trained personnel is often made before moving the railcar or tank truck from the incident scene.

This section addresses damage assessment of AHF transportation equipment, specifically:

- AHF railcars (per AAR Terminology); made from A-516 grade 70 carbon steel, post weld heat treated, with head shields;
- AHF tank trailers; made from 316 stainless steel with relief valve settings at 190 psig; and
- AHF tank trailers; made from A-516 grade 70 carbon steel and relief valve settings at 120 psig.

The damage assessment will be dependent on the fact-specific circumstances of the incident. Some first responders may find it helpful to think of the damage assessment in two phases: primary assessment and secondary assessment, and this section is structured accordingly. Some damage assessments may have one phase; others two or three, depending on the complexity of the incident, the urgency of the response needed, and other factors.

7.2 Primary Assessment

A primary assessment is generally conducted from a safe upwind vantage point. Consider making the following observations or collecting the following information to help inform the primary assessment (the following table provides general considerations for transportation equipment based on the primary assessment):

- Equipment for fumes or leakage at manway, nozzles, valves, relief devices, tanks, heads
- Tanks and heads for punctured or damaged areas
- Pressure tank for cracking at welds, scores, gouges, dents, rail and wheel burns, and stub sill underframe attachments
- Tank position (on end, on side, upside-down, upright)
- Whether the tank is or was exposed to fire or heat
- Whether any hazardous situations or products are present that could threaten emergency response personnel
- Other relevant information, as appropriate for the site-specific circumstances

General Considerations for All Railcars and Trailers Based on Primary Assessment			
Condition	Action to Consider	Notes	
Leaking AHF from fittings, valves, relief devices	Tighten fasteners, install capping kit	Avoid water on AHF leaks (corrosive)	
Leaking AHF (that cannot be stopped by tightening, or capping)	Transload in place; Do Not Move	Avoid water on AHF leaks (corrosive)	
Pressure within 15% of relief device setting	Transload in place; Do Not Move	If exposed to fire or heat, spray water to cool tank	

7.3 Secondary Assessment

As conditions permit safe access, and with the use of appropriate personal protective equipment, consider collecting and recording the following additional data:

- Railcar/trailer placard information year built, identification number
- For tank truck, determine material of construction
- Ambient temperature and pressure tank temperature
- Pressure in the tank
- Quantity of AHF in tank
- Full or half head shields on railcars
- Other relevant information, as appropriate for the site-specific circumstances

Some examples of the type of information that may be inspected, measured, and recorded in the secondary assessment are as follows:

- AHF leakage look carefully for leaks at relief devices, valves, flanged/gasket joints, welds, scores, gouges, wheel burns, rail burns, dents, and stub sill and other tank attachments;
- Crack length and direction look for cracking associated with welds, scores, gouges, dents, wheel burns, stub sill and other tank attachment welds, and fasteners in flanged joints. *PARTICU-LARLY NOTE* any cracking at welds in conjunction with scores, gouges, wheel burns, rail burns, and dents. Large open cracks may be found visually; however, small tight cracks may require dye penetrant examination. Cracks in the pressure tank or welds directly on the tank are critical. Cracks in pads or attachments are often non-critical and may not require a response (acceptable) unless they have the potential to extend into the pressure tank;
- Length, maximum depth and direction of scoring, gouging, wheel burns, rail burns, cold worked areas, and dents — PARTICULARLY NOTE the condition at welds and weld heat affected zones the metal depth removed by crossing scores, gouges or wheel burns;
- Minimum radius-of-curvature and depth of dents, rail burns and cold worked areas;
- Accessibility to internal dip pipe, dip pipe position and condition versus transloading requirements; condition of railcar/trailer regarding pressurization to 50 psig for transloading.

Typical Railcar (and some Trailers) Valve Arrangement in Dome



Collecting information from the first and secondary assessments, as well as any other relevant information, helps responders evaluate whether the damaged railcar or tank truck can be moved from the incident site. Railcars or tank trucks with significant damage that threaten the integrity of the equipment are generally not moved, but transloaded in place.

The following considerations may be useful in assisting the evaluation:

- A crack, gouge, wheel burn, or dent at near a weld tend to suggest more significant structural damage than similar damage to the base metal
- The larger or deeper the crack, gouge, wheel burn, or dent, the more suggestive of significant damage
- The closer the crack, gouge, wheel burn, or dent to a weld, the more suggestive of significant damage
- In winter temperatures where the railcar or tank truck shell temperature has dropped, the lower temperature may affect equipment and materials.

8.0 Leaks

This section focuses on mitigation of leaking AHF containers. Depending on the fact-specific circumstances of an incident, emergency response personnel may address other concerns in advance of dealing with leaks.

8.1 Type of HF Leak (Vapor or Liquid)

AHF liquid can vaporize, with a total vapor volume 285 times greater than the liquid (this means that one cubic foot of liquid AHF will make more than 285 cubic feet of HF vapor). Positioning a container so that the leak is in the vapor space, if possible, will help minimize the leak.

Liquid HF trapped in a vessel liquid full can fail catastrophically as it is warmed up due to thermal expansion. This also applies to plug and ball valves.

CAUTION: Because AHF liquid can vaporize, avoid trapping liquid AHF in lines between closed valves or in the cavity of plug and ball valves.

8.2 Leak Locations

8.2.1 Equipment Leaks

Most leaks occur in fittings. Fitting leaks tend to be small and can occur for a variety of reasons. Often, tightening the valve or fitting stops the release. Some locations for these leaks are:

- Flanges
- Pressure Plates
- Relief Valves
- Process Valves
- Plugs
- Stems of Packed Valves

8.2.2 Equipment Breaches

These leaks are typically caused by impact or improper repairs. The leaks can be any size. They usually are:

- Punctures found at the impact site
- Cracks found along body plates and welding seams

8.2 Compatible Equipment and Materials

There are a number of materials that have been successfully used in HF service to address HF leaks. The materials here are some of those that have been successfully used for gaskets and patching leaks.

8.3.1 Materials Demonstrated to Be Suitable for Use (Compatible) to Address HF leaks

- Polypropylene good for all HF concentrations
- Polytetrafluoroethylene (PTFE); Teflon®
- EPDM
- Hypalon[®]
- Viton[®]
- Steel
- A516-70 Carbon Steel for HF concentrations of 70% or greater
- Butyl Rubber (n-Butyl Rubber or Chlorobutyl Rubber)

8.3.2 Materials Not Suitable for Use (Reactive) to Address HF Leaks

- Strong bases or alkaline materials
- Fiberglass
- Glass or ceramics
- Asbestos
- Sand
- Glass lined equipment
- Glass filled PTFE (for all HF concentrations)
- Steel for concentrations of less than 70% HF
- Nylon
- Wood

8.3 Techniques/Equipment Used to Address Leaks

The chart below illustrates some methods and practices to address leaks that have been effective in industry experiences. Other techniques and equipment may be appropriate given particular circumstances.

Methods/Tools to	Type of Leaks	Special Conditions of Use
Address Leaks		
Metal Crimping Capping Kits	Works on stainless steel tubing Relief valves on railcars and some tank trucks Process valves on railcars and some tank trucks 	Capping Kit must be specifically made for HF service (check with kit manufacturer and/or instructions) Contact railcar or tank truck owner, or HF
		producers, for experience regarding selection of appropriate capping kit
Plugs	- Small leaks in pipe - Small leaks in vessels	Plug material should be HF compatible, or use a compatible gasket material for the contact surface between the HF and the plug
Pneumatic Bags	 Irregular sized leaks 	Surface contacting HF must be HF-
and Strap	- Leaks with uneven surfaces	compatible. Metal strapping or steel chains should be used; many plastic strapping materials can degrade when in HF contact
Stainless Steel Self Tapping Screws	Very small puncture holes	A hole may be required to install a tap screw (especially in rail cars)
		CAUTION: use care if the leak was not caused by impact. A condition called hydrogen blistering could have occurred in the vessel, which could result in a bigger hole when a tap screw is used.
Pipe Clamps and	- Piping leaks	Clamps that cover lines or flanges must be
Flange Clamps/ Covers (intended for high	- Fitting leaks	intended for high pressure leak service. The clamp gasketing material must be compatible with HF and, when sealed, provides for pressure service.
pressure service leaks)		
Blind Flanges	Can be installed temporarily for leaky valves	Can be installed for short-term transport or as an unloading seal
		CAUTION: AHF liquid should not be blocked in a non-vented, non-pressure vessel because of the expansion potential
Pressure Plate Attached by Welded Bolt or Stud	 Small vessel leaks Vessel leaks with close to flat surfaces 	After bolt or stud welding is completed, use an HF- compatible gasketing material to seal pressure plate onto damaged vessel.
Hot or Cold Tapping	Small flowing leaks that need to be diverted before sealing	A stub is installed which diverts flow from leak tapping before it is sealed. See Section 9.3, Hot/Cold Taps, for more detail.

9.0 Emergency Transloading

9.1 Introduction

Emergency on-site transloading is an option on those occasions when the damaged container cannot be safely moved to a manufacturing or user facility experienced with handling bulk AHF, or when the damaged container has not been immediately managed at the incident site. When possible, all containers being used to receive the material from a damaged transport container may be placed on portable scales to indicate material transfer.

In most cases, the liquid transfer hose will be connected to the damaged tank at the lowest point connection. If the damaged vessel is on its side, the vent line may best facilitate gravity transfer.

This section presents a series of illustrations of typical transloading practices. Company practices may vary, and responses to any particular incident may vary based on specific facts and circumstances.

9.2 Using Existing Valves and Fittings on Non-leaking Containers

9.2.1 Differential Pressure Transfer

To conduct a differential pressure transfer, connect the liquid hose from the damaged vessel liquid valve discharge to the receiving container liquid inlet. The liquid transfer line will have a block and bleed valve assembly for pressuring the line. Install the block and bleed valve assembly as close as is practical to the damaged container. Leak check the connections with nitrogen or air prior to HF introduction.

Run a vent line from the receiving container vapor vent to a neutralization container. (See discussion of neutralization facilities below at Section 9.4, Venting/Field Scrubbing).

The receiving vessel is maintained at a slight positive pressure to minimize HF vaporization by controlling the vapor line bleed valve. Appropriately pressure the damaged container with nitrogen or dry air (10-15 pounds maximum is generally used).

Open the vapor line from the receiving container to a neutralization system. Open the damaged container liquid transfer line isolation valve to the receiving container's isolation valve. The transfer operation will take considerable time due to the damaged vessel's low pressure and the neutralization system capacity. The liquid transfer hose will sag, immediately indicating the transfer is flowing.

When the transfer operation is concluded, the liquid hose will jump, and the nitrogen or dry air can be heard blowing through the hose. Close the damaged container's liquid line transfer valve, purge the line to the receiving vessel, and close the receiving vessel's liquid transfer valve. Vent the receiving container to atmospheric pressure through the neutralization system.

9.2.2 Gravity Transfer

Gravity transfer requires the receiving container to be located below the damaged container. Either the damaged container can be elevated or the receiving container can be placed below it, terrain permitting. The receiving container is vented to the damaged container or to a scrubbing system to prevent pressure buildup.

Gravity transfer will be slower than differential pressure transfer due to HF flashing. Inducing a small amount of pressure in the damaged container may be necessary to initiate liquid transfer.

9.2.3 Pump Transfer

Pump transfer of AHF liquid is a practice used in stationary plant environments, and it is technically feasible to use field transfers using this technique.

CAUTION: Although technically feasible, there is currently little to no industry experience with this technique. This technique should only be attempted by personnel with appropriate expertise and in consultation with HF experts.

If this option is under consideration, consult with appropriate technical experts, such as the pump manufacturer, with HF transfers.

9.2.4 Non-sealable Breached Container

This type of leaking container presents a technically challenging transfer. The HF will generally flash off (volatilize) and interrupt transfer. However, the HF flashing will then cause the remaining material to liquefy and pool in the damaged container. This breached container is emptied and decontaminated prior to removal. Generally, a breached container that cannot be sealed is not moved.

Gravity transfer can be used where the terrain is conducive to gravity flow. If the terrain is not suitable for gravity transfer, excavation may allow a receiving container to be placed below the breached container. The breached container requires a dip tube submerged into the liquid. Initiating flow is particularly challenging, as the material will prefer to flash when it enters the pipe and transfer hose.

9.3 Hot/Cold Taps

CAUTION: Although technically feasible, there is little to no industry experience with this technique. This technique should only be attempted by personnel with appropriate expertise and in consultation with HF experts.

A sealed container with unusable unloading connections may be given a "Hot Tap." A hot tap is created by welding a nipple onto the damaged container at the vessel low point. Additionally, any pressure that may build due to the welding heat must be controlled. With this technique, after installation of the welded nipple, a special apparatus would be mounted on the nipple that would seal the connection, provide a drain/transfer hose connection with an isolation valve, and allow drilling through the container wall. Once the container is punctured with the drill, the drill is extracted into a containment cavity. The drill bit has a packing gland to prevent/minimize any leakage during drilling and extraction. A flex hose is connected on the apparatus that would connect to the receiving container for gravity transfer.

A "Cold Tap" apparatus is similar to the "Hot Tap" equipment noted above. The primary difference is the method of attaching to the damaged container. Some bases of the cold tap apparatus are magnetic, with chain/belt reinforcement to assist in holding the apparatus onto a carbon steel (C/S) container. The drilling function and hose connection/isolation valves are the same as the hot tap apparatus.

9.4 Venting/Field Scrubbing

Receiving containers or vessels are vented to prevent pressure build up. Acidic HF vapors are contained by a neutralizing scrubber. The simplest system to accomplish this consists of a flex hose or piping attached through a check valve to the vent of the receiving vessel and discharging sub-surface into a container filled with a suitable alkaline material. See chart "Typical Alkaline Materials (Bases) for Neutralization of HF" in Section 6.3.6, Neutralization, for scrubbing media options.

The transfer/vent hose or pipe may be of copper, stainless, carbon steel or any other HF compatible material. See Section 8.3, Compatible Equipment and Materials, for further discussion.

To minimize the likelihood of pluggage and precipitation in the scrubber vessel, an alkaline material that will yield a soluble salt product (e.g., Caustic Soda or Caustic Potash) should be considered. Note: The spent scrubber salt solution may need further treatment to remove dissolved fluoride prior to ultimate disposal.

The efficiency of the scrubber can be increased by use of a diffusion sparger on the sub surface line discharge. The line and sparger are carefully secured in the scrubber container.

The scrubber container capacity and the strength of the alkaline scrubbing medium will influence the rate at which the transfer can proceed. The transfer rate is adjusted to accommodate the scrubber capability. If plastic or plastic lined vessels are used (e.g., polyethylene or polypropylene), the transfer rate is controlled so as to not overheat the scrubber, which may cause the container walls to distend. A cold water curtain on the external surface of the scrubber may control the heat evolution.

The scrubber media is generally monitored for pH. A pH of 7 or less, stable for a reasonable period (generally at least 15 minutes), indicates the alkaline scrubbing medium has been expended. If the medium is expended, cease the transfer, remove the scrubber salt solution for ultimate proper disposal, and replenish the scrubber with fresh alkaline solution before continuing.

A successful field transfer of a full truck load of AHF was accomplished using a portable 4000 gal. high-density polyethylene tank filled with water and the pH maintained at 10 with soda ash. A stainless steel hose with a stainless steel check valve installed was connected to the vapor space of the receiving trailer and used as a sparger in the scrubber tank. The volume of water was sufficient to serve as a heat sink for the heat of neutralization for the entire transfer. No foaming or off gassing was experienced.

10.0 Decontamination of Transfer Equipment

10.1 Purging/Evacuating to Non-Fuming Condition

After a damaged container is emptied, water flooding is often used to complete damaged container purging, and continues until the container is completely clean. Ice and slaked lime may be used with water to reduce the extreme heat of reaction and possible HF and water vaporization. Refer to chart "Typical Alkaline Materials (Bases) for Neutralization of HF" in Section 6.3.6, Neutralization, for heat of reaction/dilution information. The effluent pH is checked until neutral and stable for an appropriate period, generally at least 15 minutes, because the pH may drift downward.

10.2 Flushing with Neutralizing Solutions

Large amounts of water are generally used to flush an empty container. Alternatively, use ice followed by slaked lime or ground limestone. Formation of insoluble CaF_2 , while non-hazardous, may render the container unusable.

Water is likely to cause increased vapors and extreme heat. Hydrogen gas, which may be explosive, could also be generated.

HF-contaminated soil can be neutralized using milk of lime slurry or ground limestone slurry. Dispose of soil in accordance with applicable local, state, and federal requirements. To minimize the possibility of reactions, transportation containers for HF-contaminated soil are non-metallic or lined with an acid-resistant material.

Any remaining acid can be neutralized with slaked lime, to a neutral pH. The neutralized solution pH may change and must be monitored until stable.

10.3 Sealing Equipment for Transportation

Tools are decontaminated before leaving the incident site. Due to HF reactivity, it may be necessary to dispose of the tools following decontamination. Checking equipment for a neutral pH is a valuable step in verifying that the equipment has been properly decontaminated.

After decontamination, the container can be sealed and water filled (with proper venting). Remaining trace AHF will be readily absorbed into the water, which supports the safe transport of the container. Empty metal containers holding residual HF and water traces may result in hydrogen gas formation, which could be explosive, so it is important that they are properly vented.

10.4 Transporting Cleaning Effluents

Dispose of cleaning effluents in accordance with applicable local, state, and federal requirements. Dilute acid solutions may be transported in lined containers; neutralized solutions may be shipped in plastic containers. It may be appropriate for dilute acid solutions to be discharged into aqueous waste systems through slaked lime or ground limestone. The resultant calcium fluoride CaF₂ is non-hazard-ous.

10.5 Decontamination of PPE

Protection of emergency response personnel from inadvertent exposure to HF requires thorough decontamination of PPE prior to removal of contaminated or even potentially contaminated PPE. Decontamination of PPE following a response is an important part of any Emergency Response Plan (ERP). A typical decontamination procedure prior to removal of PPE used in an HF response might include:

- 1. rinse with water
- 2. rinse with dilute neutralizing agent, such as Baking Soda (sodium bicarbonate, (NaHCO₃))
- 3. rinse with water

PPE should be cleaned and inspected in accordance with the manufacturer's guidelines. If PPE cannot be thoroughly decontaminated (due, for example, to an unknown amount of permeation), dispose of the PPE properly.

APPENDIX A - Physical Properties and Characteristics of AHF, 70% HF, and 49% HF

Concentration	ANHYDROUS HF (AHF)	70% HF	49% HF
General Description	 A clear, colorless, corrosive fuming liquid with an extremely acrid odor. Forms dense white vapor clouds if released. 	- A fuming, corrosive liquid acid.	- A corrosive, liquid acid.
	 Both liquid and vapor can cause severe burns. Exposure requires specialized medical treatment. 	 Both liquid and vapor can cause severe burns. Exposure requires specialized medical treatment. 	 Both liquid and vapor can cause severe burns. Exposure requires specialized medical treatment.
Appearance	Colorless liquid, fumes in air	Colorless liquid, fumes in air	Colorless liquid
Physical State (at 70ºF)	Liquid	Liquid	Liquid
Molecular Weight	20.01	20.01 (HF)	20.01 (HF)
Chemical Formula	HF	70% HF in H ₂ O by weight	49% HF in H₂O by weight
Odor	Sharp Pungent Odor	Sharp Pungent Odor	Sharp Pungent Odor
Specific Gravity	Water=1.0) 0.97 @ 70°F (21.1°C)	Water=1.0) 1.225 @ 70°F (21.1°C)	Water=1.0) 1.175 @ 60°F (15.5°C)
Solubility in Water	100% by weight	100% by weight	100% by weight
рН	Not Applicable	Not Applicable	3.4pH
Boiling Point	67.2°F (19.54°C)	151°F (66°C)	224°F (106°C)
Melting Point	-118°F (-84°C)	-95.8°F (-71°C)	-34°F (-37°C)
Vapor Pressure	776 mmHg at 70°F (21°C)	110 mmHg at 70°F (21°C)	27 mmHg at 70°F (21°C)
Vapor Density (Air=1.0)	2.21 at 70°F, 1.76 at 80°F	2.21 at 70°F, 1.76 at 80°F	2.21 at 70°F, 1.76 at 80°F
Evaporation Rate	Not Applicable	Not Applicable	Not Applicable
% Volatiles	100%	100%	100%
Ionization Potential	15.98 eV	15.98 eV	15.98 eV
Flash Point	Not Flammable	Not Flammable	Not Flammable

NOTE: This Appendix presents data for anhydrous, 70% and 49% hydrofluoric acid because these are the most commonly available concentrations. Note, however, that HF solutions may be available in lower percentages. The user should be aware that even lower concentrations may be extremely hazardous, and should consult the manufacturer's MSDS for specific safety information.

APPENDIX B - Examples of Specific HF Product Applications

Catalyst

• Petroleum alkylation units to produce high octane gasoline blending stock

Fluorochemicals

- Refrigeration process cooling, food preservation, industrial-home-auto air conditioning and refrigeration
- Electronics cleaning and etching for silicon based semi-conductor devices
- Pharmaceutical intermediates and anesthetics
- Agrochemical intermediates
- Metered dose inhalers
- Fire extinguishing agents
- Foam blowing agents polyurethane and polystyrene insulation for domestic appliances, construction, food processing and packaging

Metal Processing

- Aluminum manufacture
- Metal extraction tantalum, beryllium, titanium, niobium
- Metal processing surface treatment of stainless steel, titanium and high-strength aerospace alloys chemical milling
- Nuclear reactor fuel production for electric power generation and military applications

<u>Fluoropolymers and fluoroelastomers</u> (these are chemically resistant across a broad temperature range)

- Aerospace and military wire cable insulation, seals, hoses, space apparel
- Automotive seals, fuel/brake hoses, control cables
- Chemicals lined pipes/valves/pumps, gaskets/seals, tank linings, wire insulation
- Semiconductors high-purity handling equipment, silicon wafer carriers, garments
- Power Generation acid resistant filter bags, radiation resistant wire insulation
- Telecommunications LAN Cable, wiring, fiber optic cladding and cable
- Consumer non-stick cookware, waterproof/breathable clothing, appliance wiring
- Protective clothing fire fighting and hazardous response

APPENDIX C - Description of AHF Tank Car



Image courtesy of Honeywell International

AHF is typically shipped 80-90 net tons, 23,000 U.S. gallon shell full, non-insulated tank cars designed according to the Association of American Railroads (AAR) "Manual of Standards and Recommended Practices, Specifications for Tank Cars." The Hydrogen Fluoride Industry Practices Institute (HFIPI) recommends that new railcar construction for AHF service conform to DOT classification 112S500W. AHF tank cars are painted white and have a "safety orange" center band.

Special conditions noted here are contained in the DOT exemption for AHF rail cars, DOT-SP 11759. Full head shields are mandatory for new construction [49 CFR 173.31(e)(2)]. The minimum pressure rating is 300 psig, for tank car transport of "Poison Inhalation Hazard" materials such as AHF [49 CFR 172.102 Special Provision B71 and 173.319(c)(3)]. Some manufacturers also ship AHF in DOT 112S400W and 112S340W tank cars with half head shields, which may continue to be used for the car's service life.

Current regulations mandate jackets and/or insulation for tank cars transporting AHF. Due to the special need for external inspection access, both US DOT and Transport Canada have granted AHF service exemptions to this requirement.

Bottom outlets are prohibited [49 CFR 179.100-14(a)]. All access valves are located within a cylindrical protective housing mounted on a top center cover plate [49 CFR 179.100-12]. A hinged cover is provided with provision for a cable seal at the front and a back secure latch [HFIPI Tank Car Unloading Guideline for AHF, latest edition].

Two (2) primary liquid valves connected to dip piping are mounted on the longitudinal axis. Two (2) primary vapor valves in contact with the vapor space are mounted on the horizontal axis. A pressure relief valve is mounted in the protective housing center.

For further information on the valve types used for AHF Tank Cars, refer to the latest edition of the HFIPI's "New Tank Car Guideline for Anhydrous Hydrogen Fluoride" (www.hfipi.org).

APPENDIX D- Description of AHF Tank Trailer



DOT 412 (current design criteria)



MC 312 design (construction pre-1996)

Images courtesy of Honeywell International

Trailers in AHF (UN 1052) service are typically 5,300 gallon capacity, single compartment, noninsulated, non-coiled, non baffled and designed according to DOT-412 specifications or, for units constructed prior to September 1995, MC-312 specifications. Payload is usually 36,000 to 40,000 lbs. Tank and piping construction material is A516 Grade 70 carbon steel or 316L stainless steel. Alloy 20 is also used for piping, but not for the tank. Bottom outlets are not authorized for HF service. Acid is unloaded by applying regulated nitrogen pressure to the vapor space and discharging product through a standpipe terminating at an external valve. All root valves are contained in a single protective dome at the top, trailer rear. Tanks typically contain product and vapor at ambient temperatures.

Differences between MC-312 and DOT-412 are significant and are addressed separately.

<u>MC-312</u>

Root valves for liquid loading, liquid discharge or nitrogen pressurization may be either manual ¼ turn valves or rising stem internal or external valves that may be remotely operable. They are contained in a protective housing at the trailer rear. If the nitrogen pressurizing and liquid discharge valves are manual, remotely actuated, air operated emergency shutdown valves are also provided. Manual root valves require climbing on the cargo tanks' top. Remotely operable valves are typically air-to-operate open, spring-to-close and operable from several locations at grade around the trailer. Pressure relief valves are also mounted within the rear dome. All product and pressure relief valves may be capped using either a Chlorine Institute "C" Kit or devices designed for AHF service and provided by the shipper.

APPENDIX D- Description of AHF Tank Trailer (Continued)

DOT-412

All root valves (internal or external) in product contact must be remotely operable and are typically contained in a protective housing at the trailer top rear. Enhanced relieving capacity must be designed into DOT-412 pressure relief devices and the devices must be mounted in the longitudinal and lateral center of the vapor space. All valves and pressure relief devices are capable of being capped using either a Chlorine Institute "C" Kit or devices designed for AHF service and provided by the shipper.

APPENDIX E - Description of Hydrofluoric Acid Solution (Aqueous HF) Cargo Tank



Image courtesy of Honeywell International

Cargo tanks in Aqueous HF (UN 1790) service are typically 4,500 gallon capacity, single compartment, non-insulated, non-coiled, non baffled and designed according to DOT-412 specifications or, for units constructed prior to September 1995, MC-312 specifications. Payload is usually 36,000 to 40,000 lbs. Acid strength encountered in commerce can be 25%, 38%, 49% or 70%. Construction material of the tank is carbon steel. Tanks are lined with chlorobutyl rubber or, for acid strength at or below 49%, may be lined with fluoropolymer (e.g. PTFE). All external piping is fluoropolymer or plastic lined. Bottom outlets are not authorized for HF service. Acid is unloaded by applying regulated air pressure to the vapor space and discharging product through a standpipe terminating at a valve at the trailer top rear. Pressurizing and loading valves and pressure relief devices are typically installed at the tank top center. All valves and tank openings are protected by a protective dome or tombstone type rollover protection. Tanks typically contain product and vapor at ambient temperatures.

Other differences between MC-312 and DOT-412 are significant and are addressed separately.

<u>MC-312</u>

Root valves for liquid loading, liquid discharge or air pressurization may be either manual ¼ turn valves or rising stem internal or external valves that may be remotely operable. If the liquid discharge valve is manual, a remotely actuated, air operated emergency shutdown valve is also provided. Remotely operable valves are typically air-to-operate open, spring-to-close and operable from several locations at grade around the trailer. Pressure relief valves may be mounted at the rear but are usually found in the tank center.

DOT-412

All root valves (internal or external) in contact with the product must be remotely operable. Enhanced relieving capacity must be designed into DOT-412 pressure relief devices and the devices must be mounted in the longitudinal and lateral center of the vapor space.

APPENDIX F - Description of ISO Containers

AHF ISO containers are carbon steel framed tanks. They normally come in two sizes. One is about 20 feet long (6,000-6,700 gal) and the other is about 30 feet long (8,900-10,000 gal). Both containers are 8 feet in width and can range in height from 8 to 8.5 feet. They are baffled and all fittings, manhole openings are welded on the container. All valves and fittings are in a locked or sealed housing to protect them against damage caused by overturning or impact and from unauthorized access. Typically the vapor valves are painted yellow and the liquid valves are painted red. The liquid valves are attached to a dip pipe that terminates in a sump. All outlet valves have an internal stop valve.

For aqueous hydrogen fluoride "IM101" DOT 51 intermodal containers are used. Their nominal size is 4,500 to 5,000 gallons. Carbon steel or stainless steel construction material is lined with either chlorobutyl or an appropriate fluoropolymer material.

APPENDIX G - References to Regulations and Other Guidance

American Conference of Governmental Industrial Hygienists:

• TLVs ® and BEIs ® Based on the Documentation of the Threshold Limit Value for Chemical Substances and Physical Agents & Biological Exposure Indices

Agency for Toxic Substances and Disease Registry (ATSDR):

- "Managing Hazardous Materials Incidents" series (http://www.atsdr.cdc.gov/mhmi.html) contains recommendations for on-scene (pre-hospital), and hospital medical management of patients exposed during a hazardous materials incident.
- Toxicological Profile for Fluorides

American Industrial Hygiene Association (AIHA):

• AIHA 2005: Environmental Response Planning Guidelines and Workplace Environmental Exposure Level Handbook

Australia:

 "Priority Existing Chemicals (PEC) Assessment Report No. 19," June 2001, National Industrial Chemicals Notification and Assessment Scheme (NICNAS) http://www.nicnas.gov.au/publications/CAR/PEC/PEC19/PEC19index.asp

CHEMTREC:

• "Users Guide for Emergency Responders," published by ACC (www.chemtrec.org)

Environmental Protection Agency (EPA):

• "Chemical Profile for Hydrogen Fluoride," published by Office of Solid Waste and Emergency Response

European Union:

 "Commission Recommendation 2004/394/EC of 29 April 2004" http://europa.eu.int/eur-lex/pri/en/oj/dat/2004/l_199/l_19920040607en00410068.pdf

National Fire Protection Association (NFPA):

• 472 "Professional Competence of Responders to Hazardous Materials Incidents"

National Institute of Occupational Safety and Health

• NIOSH Pocket Guide to Chemical Hazards (www.cdc.gov/niosh)

Occupational Safety and Health Administration:

• Permissible Exposure Limit

U.S. Department of Transportation:

- North American Emergency Response Guide (ERG), latest edition (<u>http://hazmat.dot.gov</u>)
- U.S. National Academy of Sciences:
 - "Acute Exposure Guideline Levels for Selected Airborne Chemicals, Volume 4," 2004. http:// www.nap.edu/books/0309091470/html/

United Nations:

- "Environmental Health Criteria #227, Fluorides," World Health Organization, 2002. http://www.who.int/ipcs/publications/ehc/en/ehc227.pdf
- UN1052 and UN1790 regulations for trailers in AHF and aqueous HF service

APPENDIX H - Emergency Medical Contacts

DUPONT

Raymond Strocko, MD	Phone:	302-774-8666
DuPont Medical Emergency number (24 hr):	Phone: (Outside US)	800-441-3637 302-774-1000
HONEYWELL		
Honeywell Medical Emergency number (24 hr):	Phone:	800-498-5701
MEXICHEM FLUOR (Mexico)		
Dr. Miguel Trevino	Phone:	(011) 52-868-811-1005
SOLVAY		
Dr. George Dirkers	Phone: Pager:	618-251-5202 618-338-0186
Pre-hospital Management

- Victims exposed only to hydrogen fluoride gas or vapors do not pose substantial risks of secondary contamination to rescuers. However, victims whose clothing or skin is contaminated with hydrogen fluoride liquid, solution, or condensed vapor can secondarily contaminate response personnel by direct contact or through off-gassing vapor.
- Hydrogen fluoride is irritating to the skin, eyes, and mucous membranes. It is a corrosive chemical that can cause immediate or delayed onset of deep, penetrating injury. Systemic effects can occur from all routes of exposure and include pulmonary edema, nausea, vomiting, gastric pain, and cardiac arrhythmia. Absorption of fluoride ions can cause hypocalcemia, hypomagnesemia, and hyperkalemia, which can result in cardiac arrest.
- Rapid decontamination is critical. Calcium-containing gels, solutions, and medications are used to neutralize the effects of hydrogen fluoride. Patients may require support of respiratory and cardiovascular functions.

Hot Zone

Rescuers should be trained and appropriately attired before entering the Hot Zone. If the proper equipment is not available, or if rescuers have not been trained to use it, assistance should be obtained from a local or regional HAZMAT team or other properly equipped response organization.

Rescuer Protection

Hydrogen fluoride is corrosive to the respiratory tract and skin and is a serious systemic poison.

Respiratory Protection: Positive-pressure, self-contained breathing apparatus (SCBA) is recommended in response situations that involve exposure to potentially unsafe levels of hydrogen fluoride.

Skin Protection: Chemical-protective clothing is recommended because skin exposure to either vapor or liquid may cause severe burns and systemic toxicity.

ABC Reminders

Quickly access for a patent airway, ensure adequate respiration and pulse. If trauma is suspected, maintain cervical immobilization manually and apply a cervical collar and a backboard when feasible.

Victim Removal

If victims can walk, lead them out of the Hot Zone to the Decontamination Zone. Victims who are unable to walk may be removed on backboards or gurneys; if these are not available, carefully carry or drag victims to safety.

Consider appropriate management of chemically contaminated children, such as measures to reduce separation anxiety if a child is separated from a parent or other adult.

Decontamination Zone

Victims exposed only to hydrogen fluoride gas or vapor who have no skin or eye irritation do not need decontamination. They may be transferred immediately to the Support Zone. Other patients will require decontamination as described below.

Rescuer Protection

If exposure levels are determined to be safe, decontamination may be conducted by personnel wearing a lower level of protection than that worn in the Hot Zone (described above).

ABC Reminders

Quickly access for a patent airway, ensure adequate respiration and pulse. Stabilize the cervical spine with a collar and a backboard if trauma is suspected. Administer supplemental oxygen as required. Assist ventilation with a bag-valve-mask device if necessary.

Basic Decontamination

Rapid decontamination is critical. Victims who are able may assist with their own decontamination. Quickly remove and double-bag contaminated clothing while flushing exposed skin and hair with plain water or saline for at least 30 minutes. Cover exposed skin with a calcium-containing slurry or gel (2.5 g calcium gluconate in 100 mL of water-soluble lubricant, such as K-Y Jelly, or 1 ampule of 10% calcium gluconate per ounce of K-Y Jelly).

Use caution to avoid hypothermia when decontaminating children or the elderly. Use blankets or warmers when appropriate.

Irrigate exposed or irritated eyes with plain water or saline for at least 20 minutes. Remove contact lenses if easily removable without additional trauma to the eye. Continue irrigation during other decontamination procedures. Use of ophthalmic anesthetic eyedrops will increase patient comfort and efficiency of irrigation.

In case of hydrofluoric acid ingestion, **do not induce emesis**. Do not administer activated charcoal. Victims who are conscious and able to swallow should be given 4 to 8 ounces of water or milk. If available, also give 2 to 4 ounces of an antacid containing magnesium (e.g., Maalox, milk of magnesia) or calcium (e.g., Tums).

Consider appropriate management of chemically contaminated children, such as measures to reduce separation anxiety if a child is separated from a parent or other adult. If possible, seek assistance from a child separation expert.

Transfer to Support Zone

As soon as basic decontamination is complete, move the victim to the Support Zone.

Support Zone

Be certain that victims have been decontaminated properly (see *Decontamination Zone* above). Victims who have undergone decontamination or have been exposed only to vapor generally pose no serious risks of secondary contamination. In such cases, Support Zone personnel require no specialized protective gear.

ABC Reminders

Quickly access for a patent airway. If trauma is suspected, maintain cervical immobilization manually and apply a cervical collar and a backboard when feasible. Ensure adequate respiration and pulse. Administer supplemental oxygen as required and establish intravenous access if necessary. Place on a cardiac monitor. Monitor ECG for prolonged Q-T interval or QRS duration.

Additional Decontamination

Continue flushing exposed skin for 15 minutes. **Do not inject or use calcium chloride** for treating skin burns. It will cause extreme pain and may further injure tissues.

Treat the burned areas with calcium gluconate gel (2.5 g in 100 mL water-soluble lubricant, such as K-Y Jelly, or 1 ampule of 10% calcium gluconate per ounce of K-Y Jelly). Initially, the health care provider should wear rubber or latex gloves to prevent secondary contamination. Continue this procedure until pain is relieved or more definitive care is rendered.

If the eyes are still irritated, continue irrigating with water or saline. Remove contact lenses if present and easily removable without additional trauma. Continue irrigating the eyes with saline during transport. Use of ophthalmic anesthetic eyedrops will increase patient comfort and efficiency of irrigation.

In cases of ingestion, **do not induce emesis**. Do not administer activated charcoal. Victims who are conscious and able to swallow should be given 4 to 8 ounces of water or milk. If available, also give 2 to 4 ounces of an antacid containing magnesium (e.g., Maalox, milk of magnesia) or calcium (e.g., Tums).

Advanced Treatment

In cases of respiratory compromise secure airway and respiration via endotracheal intubation. If not possible, perform cricothyroidotomy if equipped and trained to do so.

Treat patients who have bronchospasm with aerosolized bronchodilators. The use of bronchial sensitizing agents in situations of multiple chemical exposures may pose additional risks. Consider the health of the myocardium before choosing which type of bronchodilator should be administered. Cardiac sensitizing agents may be appropriate; however, the use of cardiac sensitizing agents after exposure to certain chemicals may pose enhanced risk of cardiac arrhythmias (especially in the elderly). Hydrogen cyanide poisoning is not known to pose additional risk during the use of bronchial or cardiac sensitizing agents.

Consider racemic epinephrine aerosol for children who develop stridor. Dose 0.25-0.75 mL of 2.25% racemic epinephrine solution in 2.5 cc water, repeat every 20 minutes as needed, cautioning for myocardial variability.

Patients who are comatose, hypotensive, or are having seizures or cardiac arrhythmias should be treated according to advanced life support (ALS) protocols.

Hypocalcemia (manifested by tetany and dysrhythmias) is probable after ingestion of even small amounts of hydrogen fluoride. With medical consultation, treat hypocalcemia with intravenous injections of a 10% solution of calcium gluconate.

For inhalation victims, 2.5% calcium gluconate (2.5 g of calcium gluconate in 100 mL of water or 25 mL of 10% calcium gluconate diluted to 100 mL with water) administered by nebulizer with oxygen has been recommended, but the success of this therapy has not been demonstrated.

Transport to Medical Facility

Only decontaminated patients or patients not requiring decontamination should be transported to a medical facility. "Body bags" are not recommended.

Report to the base station and the receiving medical facility the condition of the patient, treatment given, and estimated time of arrival at the medical facility.

If hydrofluoric acid has been ingested, prepare the ambulance in case the victim vomits toxic material. Have ready several towels and open plastic bags to quickly clean up and isolate vomitus.

Multi-Casualty Triage

Consult with the base station physician or regional poison control center for advice regarding triage of multiple victims.

Persons who have had only minor or brief exposure to hydrogen fluoride gas or vapor and are initially asymptomatic are not likely to develop complications. After their names, addresses, and telephone numbers are recorded, patients may be released from the scene with follow-up instructions (see *Patient Information Sheet* below).

Inhalation Exposure

Immediately transport to a medical facility those patients who have inhaled hydrogen fluoride and have upper respiratory irritation or other acute symptoms.

Skin/Eye Contact

All persons who have eye exposure or serious skin exposure (i.e., fingertip exposure or skin exposure greater than the total surface area of the palm) or any evidence of burns (e.g., erythema, pain, or blisters) should be transported to a hospital as soon as possible. Continue skin and eye irrigation or treatment during transport. Patients who have had even mild skin or eye contact with hydrogen fluoride should be brought to the attention of a physician as soon as possible because they may have delayed pain and systemic complications.

Ingestion Exposure

In cases of ingestion, patients should be transported to a hospital without delay. Watch patients carefully because systemic effects are likely to occur.

Emergency Department Management

Patients exposed only to hydrogen fluoride gas or vapor do not pose substantial risks of secondary contamination to personnel outside the Hot Zone. However, patients whose clothing or skin is contaminated with hydrogen fluoride liquid or solution can secondarily contaminate personnel by direct contact or through off-gassing vapor.

Hydrogen fluoride is a corrosive chemical that can cause deep, penetrating injury. Absorption of fluoride ions can result in hypocalcemia and cardiac arrest. Hypocalcemia should be considered a risk in all instances of inhalation or ingestion and whenever skin burns exceed 25 square inches (an area about the size of the palm).

Because of hydrogen fluoride's rapid skin penetration and the serious toxicity of the fluoride ion, rapid decontamination is critical. Calcium-containing gels, solutions, and medications can be used to neutralize the fluoride ion. The intense pain of hydrogen fluoride burns should not be suppressed with local anesthetics because the degree of pain is an indicator of treatment efficacy. Treatment may also include support of respiratory and cardiovascular functions.

Decontamination Area

Previously decontaminated patients and patients exposed only to hydrogen fluoride gas or vapor who have no skin or eye irritation may be transferred immediately to the Critical Care Area. Other patients will require decontamination as described below.

Because coming in contact with hydrogen fluoride-soaked clothing or skin can cause burns, ED personnel should don chemical resistant jumpsuits (e.g., of Tyvek or Saranex) or butyl rubber aprons, multiple layers of latex gloves, and eye protection.

Be aware that use of protective equipment by the provider may cause fear in children, resulting in decreased compliance with further management efforts.

Because of their relatively larger surface area:body weight ratio, children are more vulnerable to toxicants absorbed through the skin. Also, emergency room personnel should examine children's mouths because of the frequency of hand-to-mouth activity among children.

ABC Reminders

Evaluate and support airway, breathing, and circulation. In cases of respiratory compromise secure airway and respiration via endotracheal intubation. If not possible, surgically create an airway.

Treat patients who have bronchospasm with aerosolized bronchodilators. The use of bronchial sensitizing agents in situations of multiple chemical exposures may pose additional risks. Consider the health of the myocardium before choosing which type of bronchodilator should be administered. Cardiac sensitizing agents may be appropriate; however, the use of cardiac sensitizing agents after exposure to certain chemicals may pose enhanced risk of cardiac arrhythmias (especially in the elderly). Hydrogen cyanide poisoning is not known to pose additional risk during the use of bronchial or cardiac sensitizing agents.

Consider racemic epinephrine aerosol for children who develop stridor. Dose 0.25-0.75 mL of 2.25% racemic epinephrine solution in 2.5 cc water, repeat every 20 minutes as needed, cautioning for myocardial variability.

Patients who are comatose, hypotensive, or are having seizures or cardiac arrhythmias should be treated in the conventional manner.

Basic Decontamination

Rapid skin decontamination is critical. Patients who are able may assist with their own decontamination. If the patient's clothing is wet with hydrogen fluoride, remove and double-bag the clothing while flushing the skin with water (preferably under a shower). Flush exposed skin for at least 20 minutes. Use caution to avoid hypothermia when decontaminating children or the elderly. Use blankets or warmers when appropriate.

Flush exposed eyes with plain water or saline for at least 20 minutes. Remove contact lenses if present and easily removable without additional trauma to the eye. Continue irrigation while transporting the patient to the Critical Care Area. An ophthalmic anesthetic, such as 0.5% tetracaine, may be necessary to alleviate blepharospasm, and lid retractors may be required to allow adequate irrigation under the eyelids.

In cases of ingestion, **do not induce emesis.** Do not administer activated charcoal. If it has not been given previously and the patient is alert and able to swallow, administer 4 to 8 ounces of water. (More information is provided in *Ingestion Exposure* under *Critical Care Area* below.)

Critical Care Area

Be certain that appropriate decontamination has been carried out (see Decontamination Area above).

ABC Reminders

Evaluate and support airway, breathing, and circulation as in *ABC Reminders* above. Children may be more vulnerable to corrosive agents than adults because of the relatively smaller diameter of their airways. Establish intravenous access in seriously ill patients if this has not already been done.

Patients who are comatose, hypotensive, or are having seizures or cardiac arrhythmias should be treated in the conventional manner.

Monitor heart, renal, and liver functions. Hypocalcemia may cause prolonged Q-T interval and cardiac rhythm abnormalities.

Inhalation Exposure

Calcium gluconate (2.5 grams of calcium gluconate in 100 mL of water or 25 mL of 10% calcium gluconate diluted to 100 mL with water) may be administered with oxygen by nebulizer to victims who have severe respiratory distress.

Pulmonary edema or edema of the upper airway may occur. Observe the patient for at least 24 hours and monitor with repeated chest examinations, blood gas determinations, and other appropriate tests. Follow up as clinically indicated.

Skin Contact

A burn specialist or plastic surgeon should be consulted early in the treatment of fluoride burns.

Because of their relatively larger surface area:body weight ratio, children are more vulnerable to toxicants absorbed through the skin.

If blisters have formed, they should be opened and drained and debrided of necrotic tissue before treatment; early debridement may facilitate healing.

Do not inject calcium chloride to treat skin burns. It will cause extreme pain and may further injure tissues.

Treat the burned area with calcium gluconate gel (2.5 grams in 100 mL water-soluble lubricant, such as

K-Y Jelly) until the pain is relieved. If used as definitive treatment, the gel should be applied 4 to 6 times daily for 3 to 4 days. Initially, health care providers should wear rubber gloves to protect their fingers from secondary contamination. If some relief of pain is not obtained within 30 to 60 minutes, consider calcium gluconate injections.

Subungual (under the nail) burns often do not respond to immersion treatment. The treatments for hand burns require expert assistance; consult a poison center, medical toxicologist, or hand surgeon. Care must be used because multiple injections into the fingers can lead to pressure necrosis. It will be necessary to split or remove the nail.

Large burns or deeply penetrating burns (i.e., from delayed treatment or exposure to hydrogen fluoride concentrations greater than 50%) may require injections of sterile aqueous calcium gluconate into and around the burned area. The recommended dose is to inject up to 0.5 mL of 10% calcium gluconate solution per cm2 of affected skin surface using a small-gauge needle (#30). No local infiltration of anesthetic should be used, but in the case of severe burns, regional or general anesthesia may be considered. Injection may not be feasible in the case of burns to the fingers; in such cases, intraarterial infusion should be considered.

Intra-arterial calcium gluconate has been found to be effective for the treatment of burned digits and upper extremities. The radial artery has been preferentially used, with the brachial artery used if there is incomplete anastomotic flow between the radial and ulnar circulations. The initial dosage is 10 mL of 10% calcium gluconate diluted with 40 mL D5W given intra-arterially over 4 hours. If pain is unrelieved, 20% concentrations have been used. After the first dose, the infusion can be stopped, but the line should be maintained so that further doses can be infused if pain recurs. Once the patient has been pain-free for 4 hours, the catheter can be removed. Although anesthesia can be used, it is not recommended since it invalidates the pain relief which is a titration endpoint for effective treatment.

Eye Contact

Immediate consultation with an ophthalmologist is indicated.

Do not use oils, salves, or ointments for injured eyes. Do not use the gel form of calcium gluconate in eyes, as described for skin treatment.

Irrigate exposed eyes with 1 to 2 L of plain water or saline. Administering drops of a 1% aqueous solution of calcium gluconate (50 mL of 10% solution in 450 mL of sterile saline) has also been suggested as a possible therapy. After irrigation, the pH of the eye should be checked and a complete ophthalmic examination should be carried out.

A topical anesthetic can minimize the tendency for eyelid closure and facilitate irrigation. One or two drops of proparacaine or tetracaine will usually provide rapid-onset ocular anesthesia for 20 minutes to an hour. If exposure was minor, perform visual acuity testing. Examine the eyes for corneal damage and treat appropriately.

Ingestion Exposure

Do not give emetics and do not administer activated charcoal. If the patient is conscious and alert, and treatment has not been administered previously, immediately give 4 to 12 ounces of water to dilute the acid. Orally administer a one-time dose of several ounces of Mylanta, Maalox, or milk of magnesia; the magnesium in these products may act chemically to bind the fluoride in the stomach. Do not give sodium bicarbonate to neutralize acid because it can cause burns.

Consider endoscopy to evaluate the extent of gastrointestinal-tract injury. Extreme throat swelling may require endotracheal intubation or cricothyroidotomy. Gastric lavage is useful in certain circumstances to remove caustic (acidic) material and prepare for endoscopic examination. Consider gastric lavage with a small nasogastric tube if: (1) a large dose has been ingested; (2) the patient's condition is evaluated within 30 minutes; (3) the patient has oral lesions or persistent esophageal discomfort; and (4) the lavage can be administered within 1 hour of ingestion. Care must be taken when placing the gastric tube because blind gastric-tube placement may further injure the chemically damaged esophagus or stomach.

Because children do not ingest large amounts of corrosive materials, and because of the risk of perforation from NG intubation, lavage is discouraged in children unless performed under endoscopic guidance.

Toxic vomitus or gastric washings should be isolated (e.g., by attaching the lavage tube to isolated wall suction or another closed container).

Systemic Toxicity

Treat hypocalcemia using intravenous 10% calcium gluconate infusions with doses of 0.1 to 0.2 mL/ kg up to 10 mL. Infusions can be repeated until serum calcium, ECG, or symptoms improve. Calcium levels should be checked hourly. Treat hypomagnesemia with 2 to 4 mL of 50% of magnesium sulfate intravenously over 40 minutes.

Laboratory Tests

Routine laboratory studies for all exposed patients include CBC, glucose, and electrolyte determinations. Patients exposed to hydrogen fluoride should also have serum calcium, potassium, and magnesium levels monitored. Chest radiography and pulse oximetry (or ABG measurements) may be useful for patients exposed through inhalation.

Disposition and Follow-up

Patients in whom treatment fails to diminish pain and those who have respiratory distress, ingestion exposure, fingertip or eye burns, or substantial skin burns should be admitted to an intensive care unit and watched carefully for 24 hours. (Substantial skin burns are those covering an area greater than the palm of a hand, and causing skin change, or producing pain within 1 hour of exposure.) ECG monitoring may help determine treatment need and effectiveness.

Patient Release

Patients who have eye exposure who have no signs of irritation after treatment do not require hospitalization.

Patients in the ED who have burns covering less than an area equivalent to the palm of the hand and who have normal serum calcium levels who have responded to treatment can be discharged for outpatient follow-up after remaining stable for at least 6 hours. They should be advised to seek medical care promptly if pain recurs (see the *Hydrogen Fluoride-Patient Information* Sheet).

Follow-up

Obtain the name of the patient's primary care physician so that the hospital can send a copy of the ED visit to the patient's doctor.

Survivors of a serious exposure should be evaluated for damage to the lungs and heart. Patients who have serious systemic hydrogen fluoride poisoning may be at risk for respiratory sequelae and should be monitored for several weeks to months. Healing of skin burns may be prolonged and eye exposure can lead to permanent damage. Ingestion may produce progressive damage to the stomach and esophagus for weeks after exposure and may result in persistent narrowing of the esophagus.

Patients who have corneal injuries should be reexamined within 24 hours.

--End of Exerpt from ATSDR's Medical Management Guidelines for Hydrogen Fluoride--

GENERAL PROCEDURE TO BE FOLLOWED





APPENDIX 1

- A. <u>SLOW INFUSTION OF INTRA-ARTERIAL CALCIUM GLUCONATE</u> MAINLY USED FOR LIMB AND FACIAL EXPOSURES. INSTAL INTRA-ARTERIAL CATHETER AND CONNECT TUBING TO AN INFUSER THAT WILL SLOWLY INJECT CALCIUM GLUCONATE 2.5% INTO THE EXPOSED AREA.
- B. <u>BIER BLOCK</u> THE TECHNIQUE CONSISTS OF SIMULTANEOUSLY USING A PROXIMAL TOURNIQUET AND THE INTRA- VENOUS ADMINISTRATION OF CALCIUM GLUCONATE IN THE EXPOSED LIMB TO ELEVATE THE CALCIUM LEVELS LOCALLY.
- C. <u>CALCIUM ACETATE TREATMENT</u> USED IN THE SAME WAY AS CALCIUM GLUCONATE. CONCENTRATED ADMINISTRATION ROUTE AND DURATION OF TREATMENT IS DONE THE SAME WAY. TOXICOLOGY FOR CALCIUM ACETATE IS NOT WELL DOCUMENTED.



APPENDIX 2

OTHER EYE TREATMENTS FOR HF EXPOSURES.

- A. SUBCONJUNTIVAL INJECTION OF A 1% CALCIUM GLUCONATE HAS BEEN SUCCESS FULLY USED.
- B. SURGICAL REMOVAL OF EYES WHEN CONTAMINATED TISSUE AND RETINAL DEATH HAVE OCCURRED. THIS DRASTIC PROCEDURE IS DONE TO AVOID CONTAMINATION OF NEIGHBORING ANATOMICAL STRUCTURES.





APPENDIX K - Personnel Decontamination Procedures

CAUTION: Personnel responding to an HF exposure must wear appropriate Personal Protective Equipment to prevent secondary exposure. Wear surgical gloves, as a minimum, to protect against a secondary HF burn. Nitrile, PVC or neoprene gloves provide a higher degree of protection than latex gloves and should be used if available.

Eliminating HF contact quickly will minimize fluoride absorption.

Skin:

- Proceed to the nearest water source and begin flushing affected area with copious quantities of water.
- Under the water flow remove all clothing, jewelry and shoes.
- When using chemical goggles or a full face respirator, face the water flow, close eyes, remove the equipment and let the water flow away from the eyes.
- Flush with water for five minutes.
- Immediately administer first aid and promptly seek medical attention.

Eyes:

- Proceed to the nearest water source.
- Under low pressure, clean water flow, open and close eyes continuously.
- Flush with water for five minutes.
- Immediately administer first aid and promptly seek medical attention.

Respiratory Tract or Gastrointestinal Tract cannot be decontaminated. Immediately administer first aid and promptly seek medical attention.

First Aid Procedures

CAUTION: Significant Exposures to the skin, via inhalation or ingestion will lead to systemic toxic effects such as hypocalcemia and/or Acute Fluoride intoxication due to fluoride ion absorption. Please refer to the next section's Medical Treatment decision tree procedures for various exposure routes.

NOTE: Personnel who respond to an HF exposure incident must wear appropriate Personal Protective Equipment to prevent secondary exposure.

After thorough water decontamination and for inhalation or ingestion, where skin and possibly eyes need to be decontaminated, follow the First Aid procedures listed below. Ensure that the person to be treated is in a clean and safe environment.

Skin:

- Relief of pain symptoms indicate whether treatment is effective. Therefore, local anesthetics should not be used for skin exposure.
- Massage calcium gluconate gel (2.5% calcium gluconate in water soluble gel) for 20 to 30 minutes or until medical assistance is rendered.
- Alternatively, immerse or compress affected area with approximately 0.13% iced Zepharin (benzalkonium chloride) solution.
- Calcium gluconate gel may be topically used for any body part, except eyes.

APPENDIX K - Personnel Decontamination Procedures (Continued)

Eyes:

- One to two drops of ophthalmic anesthetic should be administered to each eye to alleviate irritation and facilitate irrigation.
- Irrigate each eye with 500 to 1,000 cc of calcium gluconate 1% solution (in normal saline), or until specialized medical assistance is obtained.

Inhalation:

- Trained medical response personnel should initiate oxygen administration at a flow of 10 to 12 lts/min.
- Continuously nebulize a 2.5% solutions of calcium gluconate (in normal saline) for a minimum of 15 to 20 min.
- If person is in respiratory arrest, do not administer direct mouth-to-mouth resuscitation. Use indirect methods such as Microshield® or Ambu Bag®, or equivalent.
- Continue until further medical assistance is rendered.

Ingestion:

- Do not induce vomiting.
- If conscious, orally give large amounts of calcium or magnesium-based antacids, calcium solutions, milk or milk by-products or water.
- Do not administer oral treatment to an unconscious person.
- Seek medical attention immediately.

APPENDIX L - Definitions and Acronyms

- AAR: Association of American Railroads
- ACGIH: American Conference of Governmental Industrial Hygienists
- AEGL: Acute Exposure Guideline Level
- AIHA: American Industrial Hygiene Association
- AHF: Anhydrous Hydrogen Fluoride
- ACC: American Chemistry Council
- APF: Assigned Protection Factor
- ATSDR: Agency for Toxic Substances and Disease Registry

Chemical Company: Legal entity that manufactures, transports, or uses HF products, including AHF and HF acid by rail, water or truck in the United States, Canada, or Mexico.

CFR: Code of Federal Regulations

CHEMTREC® (Chemical Transportation Emergency Center): 24-hour, 365-days per year chemical transportation emergency center operated by the American Chemistry Council.

- DOT: U.S. Department of Transportation
- EPA: U.S. Environmental Protection Agency
- ERP: Emergency Response Plan
- ERPG: Emergency Response Planning Guideline
- FID: Flame ionization detector
- GPM: Gallons per minute
- HAZWOPER: Hazardous Waste Operations and Emergency Response
- HF: Hydrogen Fluoride (used for both anhydrous and aqueous HF)

HFIPI: Hydrogen Fluoride Industry Practices Institute

HF Mutual Aid Network: Network of Member Responders, coordinated by the American Chemistry Council through its Chemical Transportation Emergency Center (CHEMTREC[®]), providing emergency response to Hydrogen Fluoride Distribution Incidents (HFDI).

APPENDIX L - Definitions and Acronyms (Continued)

HF Mutual Aid Network Agreement: The Hydrogen Fluoride Mutual Aid Network Policy Statement and Agreement establishing the HF Mutual Aid Network, and the HF Mutual Aid Network Operations Framework, both of which are mutually incorporated by reference.

HF Mutual Aid Network Contact: Telephone number designated by each Member for emergency calls from the HF Mutual Aid Network 24 hours per day, every day of the year.

HF Mutual Aid Network Management: Task group composed of a single representative from each HF Mutual Aid Network Chemical Company Member.

Hydrogen Fluoride Distribution Incident (HFDI): A term used in the HF Mutual Aid Agreement to describe a distribution incident involving HF, AHF or HF Acid solutions that in the Shipper's, Transporter's or local authority's judgment may require a Member Responder's presence to provide Technical Advice and Assistance. In such case, the incident: (i) presents a significant injury possibility for persons at or in the vicinity thereof; or (ii) presents a significant serious environmental damage possibility; or (iii) is capable of causing such injury or damage if response is mishandled. An HFDI response conditions will exist if the person(s) notifying CHEMTREC? of the incident reports any of the following: (i) the incident involves a derailment, over-the-road accident, or marine accident which resulted in visible structural HF container damage; (ii) the incident involves a derailment, over-the-road accident, or marine accident in which the HF container has overturned regardless of whether structural damage is visibly apparent; (iii) any incident resulting in a fire in close proximity to the HF container; or (iv) any incident involving an HF release or a potential release, determined according to this Framework as established by the HF Mutual Aid Network Management. CHEMTREC (with Responder's advice when necessary and/or available) may determine whether a HFDI exists based upon initial reports. The Responder at the scene will determine when the HFDI has ended, subject to the Shipper's discretion.

- ISO: International Standards Organization
- LEPC: Local Emergency Planning Committee

Member: Chemical Company who executes the HF Mutual Aid Network Agreement and agrees to make their Responders available to the HF Mutual Aid Network.

Member's Responder: Any duly designated response personnel employed by, or any for-hire company, contractor, or independent contractor retained by a Member, who functions as an HFDI Responder.

MSDS:	Material Safety Data Sheet
NFPA:	National Fire Protection Association
OSHA:	Occupational Safety and Health Administration
PEL:	Permissible Exposure Limit

APPENDIX L - Definitions and Acronyms (Continued)

PID: Photo-Ionization Detector

PIH: Poison Inhalation Hazard

PPE: Personal Protection Equipment

Promptly: In response context, means responding to or being at the scene of a HFDI as soon as reasonably possible, considering the incident seriousness, the potential public exposure, potential environmental harm, the Responder proximity and the geographic, weather, travel, and other relevant conditions.

PSIG: Pounds per square inch (gauge)

- PTFE: Polytetrafluoroethylene
- RCRA: Resource Conservation and Recovery Act

RQ: Reportable Quantity

Responder: An individual, qualified as set forth in this Framework, and designated by a Member.

Response Levels: Degree of technical advice and assistance that Members agree to provide during an HFDI.

Shipper: Name appearing on the product shipping papers involved in a HFDI including Shipper's associations, brokers, forwarders, consolidators, and other intermediaries, or notwithstanding the above.

Technical Advice and Assistance: Information and assistance (including hands-on assistance, if appropriate) which may be given by a Responder, and which may include identifying the HF hazards,, and determining measures, if any, to be taken, including communications, precautions, evacuation if necessary, and chemical handling and containment.

Transporter: Entity responsible for the physical conveyance of the HF, AHF, or HFA from one location to another. The Transporter may, or may not, be a Member.

TSD: Treatment Storage and Disposal

American Chemistry Council Hydrogen Fluoride Panel Members

Arkema Incorporated http://www.arkema.com/sites/group/en/home.page

> Daikin America Incorporated http://www.daikin.cc

DuPont http://www2.dupont.com/DuPont_Home/en_US/index.html

Honeywell http://www.honeywell.com/sites/sm/chemicals/hfacid

Mexichem Fluor http://www.mexichem.com/web_mexichem/index.php

Solvay Fluorides, Incorporated http://www.solvay-fluorides.com/



