ENVIRONMENT, HEALTH AND SAFETY DEPARTMENT
University of Wisconsin-Madison

Safe Handling of Hydrogen Fluoride and Hydrofluoric Acid

Hydrogen Fluoride (HF) is a commonly used substance on campus, but a very dangerous one. As an anhydrous material, it is a colorless gas or fuming liquid. Anhydrous HF has a boiling point of 19.5°C or 67°F. Because its boiling point is just below room temperature and because it reacts rapidly with water it is typically stored and sold in stainless steel compressed gas cylinders. It is more often used as an aqueous solution (hydrofluoric acid). Concentrated hydrofluoric acid solutions (typically sold as 48% to 52% by weight, though industrially grade is as high as 70%) is an extremely potent, dangerous and corrosive substance, capable of dissolving many materials, including oxides. However, even at lower concentrations HF is highly dangerous and great care must be taken to prevent exposure. It is used on campus for a variety of important applications, including; the etching of glass and semiconductors, the acid digestion of minerals and soils, and the removal of oxide coatings from stainless steel ("pickling"). Additionally, dilute hydrofluoric acid is often found in common rust removers.

This guidance document will help you understand its properties, the health hazards it poses, and how to work safely with this acid.

Health Hazards

Hazard Statement

Fatal if inhaled. Fatal when in contact with skin. Fatal if swallowed. Causes severe skin burns and eye damage.

It is important when working with HF to understand the health hazards posed by this substance. It is both *highly corrosive* and *highly toxic*. Below is a brief summary of these hazards.

Inhalation Hazards: Inhalation of HF gas can cause severe burns of the lung tissue leading to fluid buildup, pneumonia and possible death. The inhalation hazards are not limited to working with the anhydrous HF gas since inhaling vapors of aqueous hydrofluoric acid can lead to the same result. HF fumes have a pungent, irritating, penetrating odor and can be smelled at 0.04 ppm (a relatively safe level) though you should not rely on odor to determine safe concentrations since the odor threshold will vary widely with individuals. The Threshold Limit Value (the concentration to which most workers can be exposed on a daily basis for a working lifetime without adverse effect) is 3 ppm while 30 ppm is considered immediately dangerous to life and health.

Skin Exposure: Skin exposure can lead to serious burns, tissue destruction and death (necrosis), and systemic toxicity. Pain associated with hydrofluoric acid exposure is usually described as deep, burning, or throbbing and is often disproportionate to apparent skin involvement. Chemical burns from HF are typically very painful and slow to heal. Burns to the fingers and nail beds may leave the overlying nails intact, and pain may be severe with little surface abnormality. Burns with areas larger than 25 square inches (160 cm^2) have the potential to cause serious systemic toxicity.

HF's Unique Properties

While hydrofluoric acid is highly corrosive, it is also a fairly weak acid (i.e. it does not greatly dissociate into H+ and F- in solution). Therefore, unlike strong acids, such and nitric or hydrochloric acid, it can penetrated deeply into tissue before finally dissociating. At this point the free hydrogen ion can cause chemical burns while the fluoride ions can locally form insoluble salts with calcium and magnesium ions or (more dangerously) systemically bind the free calcium and magnesium in the blood (fluoride poisoning) resulting in death due to cardiac arrhythmias.

Grade 3 Hydrofluoric (HF) acid burns of the fingertips. Image reprinted with permission from eMedicine.com, 2011. Available at: http://emedicine.medscape.com/article/773304-overview

While exposures to HF concentrations 14.5% or greater lead to burns that are felt immediately and tissue destruction is rapidly apparent, the effects of lower concentrations can be latent for as long as 24 hours after exposure. In some instances with exposures to dilute solutions there can be minimal or no obvious surface injury. Latent symptoms can seriously delay proper treatment. By the time symptoms are noticed the damage has spread internally. [The 14.5% concentration is a guideline only as different sources give various concentrations which will cause immediate injury. It is also important to note that buffered HF solutions are commonly used and that these solutions can pose similar hazards.

Eye Exposure: Exposure of the eyes to HF may result in blindness or permanent eye damage.

Ingestion of HF: Ingestion of hydrofluoric acid has rarely been reported, though this likely leads esophageal burns and to systemic toxicity and cardiac arrhythmias (similar to skin exposure).

Long-term Exposures: Long-term or chronic exposure to HF may result in fluorosis, a syndrome characterized by weight loss, bone embrittlement, anemia, and general ill health.

Best Practices for Safe Handling

Here are some key points to remember when handling HF:

- Avoid contact with all solutions. Wear proper PPE (see below).
- Be prepared for an emergency, whether it be a spill or exposure. Pre-planning is essential before beginning any HF work. Know where eyewash and safety showers are located as well as the first aid materials such as calcium gluconate (see below).
- Only use compatible plastic or teflon-coated labwares for HF solutions and do not store in glass bottles.
- Make sure you are trained on any procedure involving HF.

Read all the sections below carefully before beginning your work with HF.

Engineering Controls

Because of the dangers of inhalation of HF vapors special precautions must be used when working with HF. All operations with anhydrous HF should be performed in a properly function fume hood or gas

cabinet. HF solutions in concentrations greater than 5% must also be performed in a fume hood. However, since certain reactions can release HF vapors some operations involving concentrations less than 5% are should still be performed in a fume hood as well as all operations that are likely to form an aerosol. Simply heating solutions can cause HF to be released. **When in doubt use the fume hood**!

It is also important to note that HF, at high temperatures or concentrations, is well-known to etch glass and corrode metals. This can cause damage to glass sashes, which are expensive to replace, and other components. Special fume hoods, made with polypropylene and polycarbonate, have been designed to handle HF. These fumes hoods often have ducts that are coated in Teflon or constructed of materials campatible with HF. Contact EH&S (265-5000) or the Physical Plan fume hood group (3-3333) if you have questions.

Personal Protective Equipment

Proper choice of Personal Protective Equipment (PPE) is imperative. A risk assessment should be performed prior to beginning any operation involving HF to identify the appropriate PPE for the specific operations.

Eye Protection

Always use chemical splash goggles together with a face shield when handling concentrated HF. Safety glasses, even those with side shields, do not provide adequate eye protection. At any concentration chemical splash goggles should be the minimum eye protection because of the ability of HF to cause blindness.

Body Protection

Because of the hazards associated with skin exposure it is vital that PPE is worn to protect the entire body. Long sleeve shirts, pants, and closed-toe shoes must be worn when working with HF. A laboratory coat must also be worn. If working with concentrated HF an acid-resistant apron made out of natural rubber, neoprene, or viton should be worn.

Gloves

Glove selection is very important. Viton, nitrile, or butyl gloves are typically worn when working with HF. However it is always important to consult the manufacturer's glove selection guide when selecting a glove for HF. Always check for leaks prior to glove use. As an added precaution a second pair of nitrile exam gloves can be worn under the gloves for protection against leaks. If gloves become contaminated with HF, remove them immediately, thoroughly wash your hands, and check your hands for any sign of contamination.

Exposures

Exposure to HF solutions requires immediate action. Delays can lead to more extensive injury and, in serious cases, can cause death. Remember also that effects are delayed so even exposure incidents which are not painful require proper attention, including a medical evaluation. In all emergencies call 911.

Access to eye wash and safety showers is necessary for any work involving HF. Additionally, a first aid kit containing 2.5% calcium gluconate gel should be readily available. Calcium gluconate is topically applied to areas where skin has been exposed. This works by forming insoluble calcium fluoride, preventing the fluoride from combining with the body's calcium. Periodically check the calcium

gluconate to ensure that it has not expired. Calcium gluconate solutions are also commercially available for eye exposures.

Skin Exposure

Immediately wash all the affected areas of skin. Using the sink may be appropriate for exposures to the hands and forearms, but contamination of the head, legs or torso should be handled with a safety shower. When using a safety shower remove all affected clothing. Remember that your health is more important than your modesty! However, unlike dermal exposures to other mineral acids, washing with water is not sufficient. If calcium gluconate is available and the contaminated area is accessible then washing can be reduced from the typical 15 minutes to 5 minutes followed by immediate application of the gluconate gel. This will minimize the migration of the HF. Contaminated clothing should be carefully put in a bag and placed in a fume hood or other safe location to prevent inadvertent exposure to other individuals.

Eye Exposure

Immediately irrigate eyes at eyewash for at least 15 minutes with copious quantities of water keeping eyelids apart and away from eyeballs followed by a washing with a calcium gluconate solution. Do not apply calcium gluconate gel to eyes. Seek prompt medical attention.

Inhalation

Move the exposed person to fresh air. In all cases of overexposure through inhalation seek prompt medical attention.

Ingestion (Swallowing)

If HF has been swallowed do not induce vomiting. Drink large amounts of water to dilute the acid. If available several glasses of milk or several ounces of milk of magnesia can be given. Antacids such as Tums or Rolaids may also be given. In all cases of ingestion seek prompt medical attention. Do not give any fluids to an unconscious victim.

Spill Clean-up and Decontamination

All spills of HF solution presents a hazard – even within a fume hood – and precautions must be taken including use of appropriate PPE. Small spills can usually be cleaned, with proper precautions, by the user. When using HF solutions spill kits should be readily available. Sodium carbonate (soda, ash), sodium bicarbonate, lime, or a spill absorbent material (specified for use with HF by the manufacturer) should be used for cleaning spills. **Spill kits that contain kitty litter or sand should not be used because HF reacts with silica to produce silicon tetrafluoride, a toxic gas.**

For large spills, especially those involving concentrated HF, the lab should be cleared, the door closed and a sign should be posted to prevent entry of others. Contact EH&S (265-5000) during working hours and 911 after hours. If the spill resulted in a personal exposure perform the decontamination procedures described above.

Training

Before working with hydrofluoric acid, workers should be trained in:

• The properties and hazards associated with HF;

• General handling and storage techniques as well as the specific procedures involving HF (as outlined in SOPs);

• The appropriate personal protective equipment requirements;

• First aid procedures (including use of calcium gluconate gel) and emergency response;

• Spill control procedures.

Storing HF

Cylinders of anhydrous HF are typically low pressure (5-15 psi). However, at least one documented spontaneous rupture is known to have occurred. This was probably the result of moisture entering the container ultimately causing a high-pressure buildup of hydrogen gas. ***Do not store for more than 2 years***. If the regulator on a cylinder shows signs of an increase in pressure this could be an indication of hydrogen gas formation.

Store all solutions of HF in properly labeled, chemically compatible containers, e.g., polyethylene, polypropylene, or Teflon, and store separately from metals, concrete, glass, strong bases, sodium hydroxide, potassium hydroxide, and ceramics. ***Never store in metal or glass container (or other silicon containing bottle).*** Periodically check the condition of the container since plastic containers can get brittle over time. Also remember to store in a secondary container, such as a tray.

Hydrofluoric acid must be stored in a well-ventilated cabinet, separate from incompatible chemicals like bases, metals and organic compounds.

Disposal

Cylinders of anhydrous HF should be returned to the vendor. If you have old cylinders that you cannot send back then contact EH&S for assistance. Solutions of hydrofluoric acid can be neutralized and disposed of down a laboratory drain. Instructions for this can be found in the "Laboratory Safety Guide". However, due to the health hazards of this chemical extreme care must be taken when performing this task and it is not recommended that this be performed with large quantities and/or high concentrations. Also, chemical suppliers will sell HF mixtures with various non-aqueous solvents such as HF-pyridine or HF-alcohol mixtures***. It is not appropriate to neutralize these mixtures.*** EH&S will gladly pick up any HF solutions during its weekly rounds. Submit a request for a pickup online. Make sure you complete the Surplus Chemical Form and leave with the chemicals to be picked up. As with all materials for pick-up, clearly label the container.

References and Resources

The following references and links provide additional information on the hazards associated with HF and safe work practices:

Centers for Disease Control and Prevention (CDC) Fact Sheet:
http://www.bt.cdc.gov/agent/hydrofluoricacid/basics/facts.asp
Agency for Toxic Substances and Disease Registry (ATSDR) Medical Management Guidelines:
http://www.atsdr.cdc.gov/mhmi/mmg11.pdf
eMedicine information on hydrofluoric acid burn:
http://emedicine.medscape.com/article/773304-overview

Occupational Health & Safety Administration (OSHA) information on hydrogen fluoride:
https://www.osha.gov/dts/chemicalsampling/data/CH_246500.html
From the Journal of Chemical Health and Safety – "The agonizing effects of hydrofluoric acid exposure: A case study", Vol.15, Issue 1, 2008.
http://www.sciencedirect.com/science/article/pii/S1871553207000461
From Honeywell, "Recommended Medical Treatment for Hydrofluoric Acid Exposure"
https://www.honeywell-hfacid.com/document/hf-medical-book/?download=1