Pam Koontz
Environmental Health & Safety
University of Tennessee, Knoxville

HYDROFLUORIC ACID SAFETY

What is Hydrofluoric Acid ?

- Hydrofluoric acid is a “weak” inorganic acid.
- Primarily used in industrial processes: glass etching, metal cleaning, laboratory reagents, etc.
- Can be found in household products: rust removers, automotive detailing products, stain removers.

Hydrofluoric Acid – Chemical Properties

- Clear, colorless liquid.
- Density similar to water.
- Distinct ability to dissolve glass.
- May form explosive levels of hydrogen upon contact with many metals.
- It will attack glazes, enamels, pottery, concrete, and leather.
- ACGIH ceiling limit and OSHA TWA is 3 PPM

Dangers of Hydrofluoric Acid

- Hydrofluoric Acid is one of the most dangerous acids known. It needs to be treated differently than even strong acids like Sulfuric and Hydrochloric.
- Hydrofluoric Acid is an acid like no other. It is so potent that contact with it may not even be noticed until long after serious damage has been done. Even very strong acids, and mixtures of acids, like Aqua Forte and Aqua Regia, do not have the power to cause death and injury in the way that Hydrofluoric Acid can.

Why is HF so Dangerous?

- HF has two mechanisms that cause tissue damage:
  - Corrosive Burns from free hydrogen ions
  - Chemical Burns from tissue penetration of the fluoride ion.
- Fluoride ions penetrate and form insoluble salts with calcium and magnesium.
- Soluble salts are also formed with other cations but dissociate rapidly. Consequently, fluoride ions release, and further tissue destruction occurs.

Hydrofluoric Acid vs Other Acids

- Hydrofluoric acid (HF) differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers, including bone. Pain associated with exposure to solutions of HF (1-50%) may be delayed for 1-24 hours. If HF is not rapidly neutralized and the fluoride ion bound, tissue destruction may continue for days and result in limb loss or death. HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid.

HF Mortality/Morbidity

- Local effects include tissue destruction and necrosis. Burns may involve underlying bone.
- Systemic fluoride ion poisoning, from severe burns is associated with hypocalcemia (low calcium levels), hyperkalemia (high potassium levels), hypomagnesemia (low magnesium levels) and sudden death.
- Deaths have been reported from concentrated acid burns involving as little as 2.5% Body Surface Area (BSA).

Storing Hydrofluoric Acid

- Store in a cool, dry place away from incompatible materials. HF reacts with many materials therefore avoid contact with glass, concrete, metals, water, other acids, oxidizers, reducers, alkalis, combustibles, organics and ceramics.
- Store in containers made of polyethylene or fluorocarbon plastic, lead, or platinum. Place storage bottles in polyethylene secondary containment trays.
- **Never store HF in glass containers.**

Spills

- Ensure all areas where HF is used are equipped with proper spill response equipment. Small spills can be neutralized by covering with magnesium sulfate (dry) and absorbed with spill control pads or other absorbent materials. Add sodium bicarbonate or magnesium oxide to an absorbent and place in a plastic container for disposal. Wash the spill site with a sodium bicarbonate solution. Or use a commercial spill kit. Call EHS (4-5084) to dispose of spill clean-up materials. All spill clean-up materials must be placed in a plastic container.

Spills

- 3M's Universal Sorbent is recommended, as it does not react with HF. Organic spill kits that contain Floor-Dri, kitty litter, vermiculite or sand should not be used because HF reacts with silica to produce silicon tetrafluoride, a toxic gas.
- If the spill is large, in a confined space, or in an area where there is not adequate ventilation, or if the acid is concentrated evacuate the room and immediately report the spill to EHS (4-5084) or after hours call 911.

Fire and Explosion Hazard

- Hydrogen fluoride is non-combustible, but may create irritating and corrosive fumes of fluorides when heated or in combination with steam or water. Since hydrogen fluoride does not burn, use an extinguishing agent suitable for surrounding fire. Use water to absorb fumes and keep containers cool. Heat released when water or steam combines with hydrogen fluoride or hydrofluoric acid could be hazardous. For fires involving hydrofluoric acid, apply water in flooding quantities. Hydrofluoric acid and various metals may form hydrogen (extremely flammable gas) creating a fire hazard.

Symptoms of Hydrofluoric Acid Burns

- The Hydrogen Fluoride molecule is so mobile that it may easily pass through the skin. Because Fluorine has an extremely high affinity for Calcium, bones will be attacked, and this may result in hypocalcaemia. There may be no pain immediately after the burn, leading the injured person to believe that they are not in danger.

Symptoms of Exposure

- CONCENTRATIONS LESS THAN 20% - Erythema (skin redness) and pain may be delayed up to 24 hours, often not reported until tissue damage is extreme. In one study, 7% HF produced symptoms in 1 to several hours, 12% HF in less than one hour, and 14.5% HF immediately.

Symptoms of Exposure

- CONCENTRATIONS 20 TO 50% - Erythema and pain may be delayed from 1 to 8 hours, and is often not reported until tissue damage is extreme.
- CONCENTRATIONS GREATER THAN 50% - Produces immediate burning, erythema, and tissue damage.

Decontamination and First Aid

- Immediately remove all exposed clothing taking necessary precautions to prevent self-exposure (wear gloves) while washing all exposed areas with copious amounts of water.
- Application of 2.5 to 33% calcium gluconate or carbonate gel or slurry, either placed into a surgical glove into which the affected extremity is then placed, or rubbed into the burn, is recommended. *Use calcium gluconate for dermal treatment only.*
- **DO NOT USE CALCIUM CHLORIDE – Calcium chloride is irritating to the tissues and may cause injury.**

Decontamination and First Aid cont.

- While the victim is being rinsed with water, someone should call to arrange treatment by medical personnel. Call 911 and tell the dispatcher the following:
  - There is a person that has been in exposed to Hydrofluoric Acid and the victim is in this location.
  - Please send an ambulance to transport to UT Medical Center.
  - Alert the hospital than someone with HF burns is en route.

Immediately washing off the acid is of primary importance!

Decontamination and First Aid cont.

- After the affected area is flushed with copious amounts of water for at least one minute, calcium gluconate gel is to be applied using these guidelines. A 2.5% calcium gluconate gel will be located inside the HF exposure kit within the laboratory. Apply the gel after putting on the ***NEOPRENE OR NITRILE (22MIL) GLOVES*** in the HF exposure kit. Do not use latex gloves; they are not effective against HF. Note the time when the calcium gluconate gel was first applied to the contaminated site. Provide this information to the EMS team.

Decontamination and First Aid cont.

- The victim must be escorted to the hospital by the responding person or assisting lab personnel
- A copy of the MSDS and the CHP must be also taken to the hospital
- After EMS arrives they shall call the Emergency Room doctor for instructions and for the approval to administer the calcium carbonate tablets (antacid tablets) found in the Spill Exposure Kit

HF EXPOSURE KIT

- Before beginning work involving HF an exposure kit must be available and located in the laboratory area. The exposure kit must contain the following items:
  - Container of calcium gluconate gel
    - This gel must be inspected before each use of HF or at least monthly to ensure the gel has not been removed or has not reached the ***expiration date***. If a tube of the gel has been opened, a new container must be purchased and the old container discarded. No work with HF can be done with an expired tube of calcium gluconate gel.

HF EXPOSURE KIT cont.

- 2 pairs of Neoprene or Nitrile (22mil) gloves
- 1 heavy-duty polyethylene bag to be used for items contaminated by HF
- 1 HF Contaminated Waste Label
- Copy of CHP and MSDS to take to the emergency room
- Calcium Carbonate (antacid tablets)

Other Routes of Exposure - SYSTEMIC TOXICITY

- **Systemic fluoride toxicity may result from ingestion, inhalation, or extensive** dermal burns. Hypocalcemia, hypomagnesemia, hyperkalemia (potassium), pulmonary edema, metabolic acidosis, ventricular arrhythmias, and death are possible.

Other Routes of Exposure - **EYE EXPOSURE**

- May result in severe ocular damage with concentrations greater than 0.5%. Fume exposure commonly causes eye irritation and can also cause ocular injury. Signs and symptoms may be delayed.

First Aid for Eye Exposure

- Immediately flush eyes for at least 5 minutes with copious cool flowing water. The victim should then be transported to a medical facility. If a sterile 1% calcium gluconate solution is available and MEDICAL PERSONNEL are available then following the 5 minutes wash time, 1% calcium gluconate irrigation should be started.
- Call 911 and inform them of Hydrofluoric Acid exposure and instruct them to notify hospital of person in transport.

Other Routes of Exposure - **ORAL EXPOSURE**

- Ingestion may result in vomiting and abdominal pain; painful necrotic lesions, hemorrhagic gastritis, and pancreatitis have been reported after significant exposure.

Other Routes of Exposure - **INHALATION EXPOSURE**

- Inhalation of hydrofluoric acid vapors may cause severe throat irritation, cough, dyspnea, cyanosis, lung injury and pulmonary edema resulting in death.

First Aid for Inhalation Exposure

- If a large volume of Hydrofluoric Acid gas is inhaled:
  - Immediately remove the victim to clean air. Call 911
  - Inform 911 operator of Hydrofluoric Acid exposure and instruct them to notify hospital of person in transport
  - Inhalation of Hydrofluoric Acid fumes may cause swelling in the respiratory tract up to 24 hours after exposure. Persons who have inhaled Hydrofluoric Acid vapors may need prophylactic oxygen treatment and must be seen by a physician as soon as possible

HF Accidents

- 1981 – At the Sullivan Park Research Facility of Corning, Inc., an HF tank leaked. A clean-up crew went in without proper respirators and 2 workers died.
- 1994 – A lab tech in Western Australia died from burns sustained when he accidentally spilled concentrated (70%) HF on himself.
- 1996 – A NYC sanitation worker died of toxic fumes released when HF blew up in the back of his truck.

HYDROFLUORIC ACID FATALITY TO LAB WORKER IN PERTH

- *Extract from Australian Institute of Occupational Hygienists Newsletter, December 1994:*
- An accident in Perth highlighted just how hazardous this acid can be and it is worth recounting for the benefit of any lab working or hygienists whose work may involve advising others who use this substance.
- On November 12, a 37 year old man died in the Intensive Care Unit of Fremantle Hospital after he accidentally splashed about 100 ml of a 70% solution on his right leg on October 28. It was estimated that the extent of the spill covered about 10% of his total body area. The individual was working as a technician in a small paleontology laboratory, which was attached to a private residence. HF is used in the industry to digest silicates in ore samples. The victim immediately attempted to remove the spill from his clothing hosing himself down with a hose attached to a sink in the laboratory. He then ran from the laboratory to the swimming pool in the garden, and he remained in the pool until the ambulance arrived within the hour. At the time he appeared confused, possibly as a result of shock. The following week his right leg was amputated, however despite this, the individual eventually succumbed to the toxic effects of the hydrofluoric acid 2 weeks after the initial spill.

Minimum Lethal Exposure - ORAL

- Death has occurred after ingestion of 1.5 grams of hydrofluoric acid (concentration unknown) within 6.5 hours of ingestion. Postmortem findings in this case revealed no gross tissue damage and a liver fluoride level of 165 micrograms/100 gram.
- A 33-year-old man who ingested 3 to 4 ounces of a rust remover (unstated HF concentration) died within 45 to 60 minutes. At autopsy, severe mucosal edema of the stomach and hemorrhage and necrosis of the pancreas were noted. The postmortem blood fluoride level was 56.2 milligrams/liter.
- Ingestion of 15 milliliters of a 9 percent solution was reported to cause death.

Minimum Lethal Exposure - DERMAL

- A dermal exposure to 70 percent hydrofluoric acid over a 2.5 percent total body surface area resulted in death. The serum calcium level was 2.2 milligrams/deciliter.
- An adult patient who developed 25 percent total body surface area second degree burns after exposure to a 70 percent hydrofluoric acid preparation died in cardiac arrest. Ionized serum calcium level was 1.7 milligrams per deciliter (normal: 4 to 4.8) immediately premortem.
- Two workers died following a splash exposure of 70 percent hydrofluoric acid to the face, chest, arms and legs. Both workers were promptly removed from site of exposure. Clothing was removed and burns were initially treated at the workplace with a cold shower and alcohol was applied to burn areas. Suitable protective clothing was not worn at the workplace.

Minimum Lethal Exposure - **DERMAL**

- A woman died from severe chemical burns of the skin and lungs, with intense pulmonary hemorrhagic edema after having acid thrown onto her face during an attack.
- A patient with HF burns involving 8 percent of his body died from intractable cardiac arrhythmia secondary to the depletion of ionized calcium.

Minimum Lethal Exposure - **INHALATION**

- Estimates of the lowest lethal concentrations for hydrogen fluoride range from 50-250 ppm for 5 minute exposure and are based on accidental, voluntary and occupational exposure information.

Study of Fatal HF Poisonings

- AMERICAN JOURNAL OF INDUSTRIAL MEDICINE 40:215±220 (2001)
- From 1984 to 1994 9 deaths were investigated from 8 industrial incidents
- Unsafe work practices were implicated in each incident
- Calcium chloride or gluconate was noted to have been administered to 5 of the 9 victims

Study of Fatal HF Poisonings - Use of Calcium Treatment

Case no.	Approximate time from exposure to death	Calcium gluconate administered? (Y/N)	Time from exposure to administration
1	30min	N	
2	3 h 30min	N	
3	15 h	Y	6 h
4	4 h	Y	1h 30 min
5	30min	N	
6	30min	N	
7	2 h 30min	Y	Unknown
8	4 h	Y	1.5 h
9	4 h	Y	30min

HF Burn - Grade 1

Grade 1 – a white burn mark and/or erythema and pain.

HF Burn – Grade 3

Grade 3 - a white burn mark and/or erythema

and pain, edema, blistering and necrosis.

Mild HF burn to thigh from commercial rust stain remover.

Handling Hydrofluoric Acid

- Familiarize yourself with the hazards specific to HF before handling.
- HF should never be handled by anyone who has not been trained to use it.
- Always handle HF in:
  - *A properly functioning fume hood*
  - *An area equipped with a Safety Shower/Eye Wash*
- Calcium Gluconate should be available for skin treatment.

Handling Hydrofluoric Acid

- Recommended Personal Protective Equipment:
  - **Goggles**
  - **Face shield** (plastic)
  - **Gloves**: Thin disposable gloves (such as 4, 6, or 8 mil blue Nitrile glove) used in laboratory operations provide a contact barrier only and should be disposed of immediately when contamination is suspected. Thicker (10-20 mil) PVC or neoprene gloves provide good resistance to HF but do not provide the necessary dexterity for most lab procedures. Thinner PVC or poly ("food" handling) gloves can provide some resistance to HF, but should also be changed immediately at the first sign of contamination. Disposable gloves should never be worn without double gloving because of the potential for pinholes and exposure. A combination of double gloves, Nitrile and poly, can be used to provide greater protection from a broader range of materials.
  - **Acid resistant apron**
  - **Long pants, sleeves, and closed toe shoes** (always required when working with corrosives)

Working With HF Safely

- ***Never use Hydrofluoric Acid when working alone or after hours.*** Always ensure that knowledgeable laboratory personnel have been alerted and at least one is in the general vicinity.
- All lab personnel, not just those who will be using Hydrofluoric Acid, should be informed of the dangers of this chemical and the emergency procedures necessary in case of an accident. A sign should be posted to alert people that work with Hydrofluoric Acid is in progress.

Working With HF Safely

- All persons who will be using Hydrofluoric Acid must be made aware of its properties and trained in proper procedures for use and disposal.
- Laboratories which keep or use Hydrofluoric Acid gas or concentrated solutions (>1% Hydrofluoric Acid) should have emergency procedures on hand as well as an MSDS.

Working With HF Safely

- Laboratories which keep or use Hydrofluoric Acid gas or concentrated solutions (>1% Hydrofluoric Acid) must have an operational safety shower and eye wash in their laboratory.
  - Before beginning any procedure involving Hydrofluoric Acid, make sure the access to the emergency shower and eyewash is unobstructed.

Working With HF Safely

- Undergraduate students should never be given the task of mixing Hydrofluoric Acid solutions. Only experienced persons familiar with its properties should handle the concentrated acid.
- Clean up all spills promptly.
- Purchase HF in limited quantities. Keep as little on hand as possible (3 month or less supply).

Working With HF Safely

- When working with Hydrofluoric Acid or concentrated HF solutions (> 1%):
  - Work in a fume hood with the sash as low as possible. Wear goggles and a face shield. Wear a long-sleeved, buttoned lab coat, pants or long skirt, and closed-toe shoes. Wear Neoprene or Nitrile (22mil) gloves or other Hydrofluoric Acid resistant gloves (Hydrofluoric Acid burns around the fingernails are extremely painful, difficult to treat, and may require surgical removal of the nail). A chemically resistant apron is also recommended.

Working With HF Safely

- Double gloving is highly recommended. Make sure your gloves have no pin-holes.
- Any exposure to Hydrofluoric Acid must be medically evaluated.
- Do not leave tongs, stirrers, etc., which have been contaminated with HF in fume hoods where other people may pick them up or otherwise come into contact with them.

Working With HF Safely

- Any unattended containers must be labelled. If it is not feasible to do this, and containers must be left in the laboratory fume hood unattended by the HF user, place a placard or sign in the fume hood indicating the HF hazard.
- When the work has been completed and personal protective equipment has been removed, wash hands thoroughly with soap and water.

Working With HF Safely

- Properly dispose of contaminated disposable gloves, aprons, etc in a plastic container and close it so it is spill proof. All waste containers must be labeled with a hazardous waste label with the chemical name written out.
  - eg: hydrofluoric acid - NOT HF!!

Working With HF Safely

- The principle investigator shall supply a CHP for the processes involving HF to affected employees and verify that they understand it.
- Employees should understand the health and physical hazards of HF. The ability of HF to inflict damage without initial pain should be emphasized.

Working With HF Safely

- Solutions with concentrations > 50% may release hazardous concentrations of HF vapor under conditions of poor ventilation and require respirator use. If employees wish to use respirators when using HF, such respirators shall ONLY be obtained after proper training in respirator use. The principle investigator shall ensure that only employees who have received respirator training and have received appropriate medical exams by an Occupational Health Physician are allowed to wear respirators. Persons wearing respirators must also be fit tested for their respirator annually.

Summary of Hydrofluoric Acid Safety

- Hydrofluoric Acid is an extremely dangerous chemical, and can cause death from a skin exposure of less than 3% of body area. Special training, preparation, Personal Protective Equipment, and handling precautions are needed at all times.
- This training is not a substitute for medical advice, Risk Assessments, Chemical Safety Data Sheets, or any other professional service that needs to be used before dealing with Hydrofluoric Acid.
- **If you are exposed to hydrofluoric acid seek medical attention immediately, even if you do not feel pain.** It may take up to 24 hrs to feel the pain from <20% HF exposure.
- In order to warn and protect others from the hazard of HF, a warning sign indicating the use of HF should be posted.
- http://www.powerlabs.org/chemlabs/hydrofluo.htm - demo

Sources

- http://www.osha.gov/SLTC/healthguidelines/hydrogenfluoride/index.html
- http://www.utsouthwestern.edu/vgn/images/portal/cit_56417/52/7/328156Hydrofluoric_Acid_Safety_Training.pdf
- http://ehs.unc.edu/environmental/docs/hydrofluoricacid.pdf
- http://calgonate.com/
- http://www.udel.edu/ehs/hfsop.html

Sources

- http://www.fap.pdx.edu/safety/hydrofluoric_acid/
- http://ehs.sc.edu/HF/USC-HF.pdf
- http://www.ehs.indiana.edu/LabSafety/Chemical%20Fact%20Sheets/Hydrofluoric%20Acid.pdf
- http://www.udel.edu/ehs/hfsafety.html
- http://www.powerlabs.org/chemlabs/hydrofluo.htm