

HF SAFETY

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IIT – M

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.

HF – 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 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).

Symptoms of HF 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.

No Immediate effect,
but AFTER 24hours.



- 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.

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.

- **INHALATION EXPOSURE**

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

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.

- 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.

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.

HF Accident at Perth, 1994

- 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.
- 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**

- 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 pre-mortem.
- 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.
- 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.

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

Personal Protective Equipment for HF

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- Eye protection in the form of chemical splash goggles and a face shield should be used.
- Two (2) pairs of regular Blue Nitrile gloves should be worn.
- Neoprene or Nitrile (22mil) gloves or other HF resistant gloves should be worn.
- An acid-resistant apron should be used (Some clothing can absorb the chemical and maintain it close to the skin).
- A warning sign indicating the use of HF should be posted nearby to warn other users.
- A Material Safety Data Sheet (MSDS) on HF should also always be kept in the immediate work area where HF is used.
- BUDDY System

HF Storage

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- Store all HF and HF waste in labeled chemically compatible containers (e.g. polyethylene, polypropylene, teflon, wax, ~~lead or platinum~~ containers).
- Glass, metal, and ceramic containers are not compatible with HF.
- HF should never be stored with incompatible chemicals such as ammonia or other alkaline materials.
- Always place HF on a low protected shelf or other location where it will not be accidentally spilled or knocked over.
- Use secondary containers whenever possible to minimize and contain areas of leaks and spills.

HF Exposure Kit

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- Container of calcium gluconate gel.
- This gel must be inspected before each use of HF or at least weekly to ensure the gel has not been removed or has not reached the expiration date. No work with HF can be done with an expired tube of calcium gluconate gel.
- 2 pairs of Neoprene or Nitrile (22mil) gloves.
- Copy of these procedures and MSDS to take to the emergency room.
- Calcium Carbonate in case of spills. Do not apply Calcium Carbonate on your skin.

HF - First Aid

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- **Skin Exposure**

- Move the victim immediately under an emergency shower or other water source and flush the affected area with large amounts of cool running water for at least 15 minutes.
- While the victim is flushing with water, they should also take off all clothing, shoes and jewelry, removing goggles last. Close your eyes, face water flow and pull goggles over head.
- **Be extremely careful not to contaminate yourself (use Neoprene or Nitrile (22mil) gloves located in the hf exposure kit to assist).** Some clothing can absorb the chemical and maintain it close to the skin.
- While the victim is being rinsed with water, the person assisting should call to arrange treatment by medical personnel – CALL 8333/8888. Immediately washing off the acid is of primary importance!
- After contacting the Medical Personnel, the person assisting should call C. Rajendran (97908-54825), Kousik Sivakumar (96770-20628) AND the victim's Thesis Advisor to inform the accident irrespective of what time of the day it is.

HF - First Aid

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- **Skin Exposure (cont.)**

- After the affected area is flushed with copious amounts of water for at least 15 minutes, 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.
 - In order to prevent cross contamination, the victim should self apply the calcium gluconate gel. If the victim is unable to self apply, anyone present can 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. Reapply every 15 minutes.
 - Provide this information to the Emergency Medical Personnel.
- The victim must be escorted to the hospital by the responding person or assisting lab personnel.
- A copy of the MSDS and these emergency procedures must be also taken to the hospital.

HF - First Aid

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- **Eye Exposure:**

- Immediately flush eyes for at least 15 minutes with copious amounts of cool flowing water.
- While the victim is being rinsed with water, someone should call to arrange treatment by medical personnel – CALL 8333/8888. Immediately washing off the acid is of primary importance!
- After contacting the Medical Personnel, the person assisting should call C. Rajendran (97908-54825), Kousik Sivakumar (96770-20628) AND the victim's Thesis Advisor to inform the accident irrespective of what time of the day it is.
- 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 15 minutes wash time, 1% calcium gluconate irrigation should be started.

HF - First Aid

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- **Inhalation:**

- Immediately remove the victim to clean air.
- Call to arrange treatment by medical personnel – CALL 8333/8888.
- Call C. Rajendran (97908-54825), Kousik Sivakumar (96770-20628) AND the victim's Thesis Advisor to inform the accident irrespective of what time of the day it is.
- 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 – Spills

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- If HF is spilled outside a chemical hood –
 - Evacuate the area
 - Close the doors
 - Post the area with a sign to prevent others from entering
 - Call C. Rajendran (97908-54825) and Kousik Sivakumar (96770-20628)
- If a larger amount is spilled, or the acid is concentrated, contain the spill as best you can, evacuate the area, and call C. Rajendran (97908-54825) and Kousik Sivakumar (96770-20628).
- Small spills of HF inside a chemical fume hood can be cleaned up by laboratory staff if they
 - Have received spill clean-up training
 - Have the correct equipment
 - Understand the hazards
 - Are confident in their ability to clean up the spill safely and dispose off the waste properly.

Using Hydrofluoric acid safely

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- Never use Hydrofluoric acid when working alone or after hours. Hydrofluoric acid may be used when working alone during normal working hours provided knowledgeable laboratory personnel have been alerted and at least one is in the general vicinity.
- When working with Hydrofluoric acid:
 - Work in a fume hood with the sash as low as possible.
 - Wear goggles and a face shield.
 - Two (2) pairs of regular Blue Nitrile gloves should be worn.
 - 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 should be worn.
- 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.

Using Hydrofluoric acid safely

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- A sign must be posted to alert people that work with Hydrofluoric acid is in progress.
- 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 vapor or concentrated solutions (>1% Hydrofluoric acid) must have these emergency procedures on hand as well as an MSDS.
- Laboratories which keep or use Hydrofluoric acid vapor 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.

Using Hydrofluoric acid safely

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- New students should never be given the task of mixing Hydrofluoric acid solutions. Only experienced persons familiar with its properties should handle the concentrated acid.
- A supply of calcium carbonate or calcium hydroxide for spills must be available near the fume hood where the work will be conducted.
- A HF exposure Kit with Calcium gluconate gel (not expired) must be available in any lab that contains HF. Calcium gluconate gel is a topical antidote for HF skin exposure. Calcium gluconate works by combining with HF to form insoluble calcium fluoride, thus preventing the extraction of calcium from tissues and bones.
- It is safe to dump unused HF in the Wet Bench drain provided the acid has been diluted by flowing large amounts of water. Never store used HF.
- Any exposure to Hydrofluoric acid must be medically evaluated.



Thank You