Fatality Statistics

- As little as 7 milliliters (ml) of anhydrous Hydrofluoric acid (HF) in contact with the skin untreated can bind all the free calcium in a normal size adult male.
- With burns involving greater than 25 square inches significant and sometimes fatal hypocalcaemia can occur.
- Exposure of 1% of Body Surface Area (BSA) to 50% or greater HF
- Exposure of 5% of BSA to any HF solution.
- 1% BSA = Palm of hand
- HYDROFLUORIC ACID IS one of the MOST ACUTELY TOXIC CHEMICALS USED AT FERMILAB.
I. HF Acid Uses in Industry

- Plastics Production
- Production & Purification of Radioactive Materials
- Microchip Etching
- Electronic Circuit Cleaners
- Glass Etching

I. HF Acid Uses at Fermilab

- HF is used at Fermilab to Polish Superconducting Radio Frequency Cavities (SCRF) to Remove Impurities and Decrease Surface Roughness
- Buffered Chemical Polish - BCP
  - 2 parts phosphoric acid (85% weight H₃PO₄)
  - 1 part nitric acid (69.5% wt HNO₃)
  - 1 part hydrofluoric acid (49% wt HF)
- Electropolishing Process—“BCP with Current”
  - 89.5% by volume sulfuric acid (96% wt H₂SO₄)
  - 10.5% by volume hydrofluoric acid (40% wt HF)

II. Hydrofluoric Acid Properties

- Colorless liquid with strong irritating odor
- Very strong corrosive inorganic acid
- Nonflammable, very soluble in water
- Pure HF has a boiling point (B.P.) of 65 °F (18 °C)
  - 49wt% HF has a B.P. of 220 °F (104 °C)
  - 49wt% HF has a Freeze Point of -35 °F (-37 °C)
- Vapor Pressure ≈ 7 millimeters of Mercury (mmHg) for 49 wt% at Standard Temperature and Pressure (STP)
II. Hydrofluoric Acid Properties

There is no concentration of HF which can be relied upon as safe!

There is no material that is completely resistant to HF degradation.

II. How Is HF Different from other acids?

- Strong, inorganic acid that on contact with live tissue, produces immediate necrosis and pain at high concentrations but delayed in showing up at low concentrations.
- HF first aid treatment is not limited to washing off the skin (Calcium Gluconate Antidote).
- HF is readily absorbed into skin
- HF binds to the calcium and magnesium in the body to form insoluble salts
  - Insoluble salts interfere with cellular metabolism causing cellular death and necrosis

II. Most Resistant to HF

- High Density Polyethylene (HDPE Container): 75-100% HF at 70 °F to 140 °F (21°C to 60°C)
  - Less than 15% swelling, Less than 20% loss in tensile strength, minor chemical attack
- PTFE (Teflon Container): 100%HF @ 70°F (21 °C) for 6 Months
  - No Change
- Neoprene (Gloves): Resistant to Solution at room temperature for more than 8 hours.
III. Exposure Groups

- **Primary Contact**
  - Accelerator Division
  - AG SCRF Support Group
  - Technical Division
  - SCRF Materials Group
  - Materials Development Laboratory (MDTL)

- **Secondary Contact**
  - Technical Division
  - ESH Groups
  - Business Services
  - Receiving
  - Distribution
  - Fire Department
  - Environment, Safety and Health Section
  - Contractors, Visitors, Summer Students

III. Routes of Entry

- Skin (Absorption)
- Eyes
- Lungs (Inhalation)
- Mouth (Ingestion)

III. Types of Exposure

- Liquid exposure (splash)
- Gas exposure (lungs, skin & eyes)
- Most HF exposures occur by inhalation of the gas or absorption of the liquid
- Employees exposed to HF via inhalation do not pose substantial risks of secondary contamination
- Employees whose clothing or skin are contaminated are risks of secondary contamination (direct contact or off-gas)
III. Worker Airborne Exposure Regulations

- Irritation to nose and throat at 3 parts per million (ppm)
- Time-weighted average (TWA) of 0.5 ppm
- Short-term exposure limit (STEL) 15 min - 2 ppm
- 30 ppm is considered immediately dangerous to life and health (IDLH)

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III. Human Skin – What is going on?

- Fluoride ion binds calcium ions
- Potassium (K+) enters extra cellular space to compensate for calcium loss
- Nerve endings are irritated by increased levels of K+
- Severe pain occurs from this irritation
- Fluoride ions move rapidly through the skin causing deep tissue damage.

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III. How Corrosive is it?

- The initial extent of the burn depends on the concentration, temperature, duration of contact, quantity exposed to

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time of pain onset</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20</td>
<td>Up to 24 hours</td>
</tr>
<tr>
<td>20-50*</td>
<td>1-6 hours</td>
</tr>
<tr>
<td>&gt;50</td>
<td>&lt;1</td>
</tr>
<tr>
<td>99</td>
<td>immediate</td>
</tr>
</tbody>
</table>

*Maximum concentration used at lab
III. HF Skin Exposure
- Assess for pain
- Assess for redness/whiteness of skin/blisters
- Assess area of burn
  - If >25 in² or 160 cm² then risk for serious systemic toxicity is present

III. HF Exposure to Eyes
- Severe burns
- Opacification of cornea
- Blindness

III. Inhalation of HF
- Coughing/Choking
- Inability to breathe / Chest tightness
- Chills/Fever
- Cyanosis (blue lips)
- Delayed reactions can occur
- Can cause
  - Laryngeal edema
  - Bronchospasm
  - Pulmonary edema
  - Respiratory arrest
III. Systemic Toxicity of HF

- Main concern is for HYPOCALCEMIA
- Can cause your heart to stop
- Other blood/tissue abnormalities
  - ↓ Magnesium (Mg)
  - ↑ K+
  - ↑ Fluoride levels in blood and organs

IV. Safe Work Practices

- Never use HF alone (two-man rule)
- Training
- Always Wear Personal Protective Equipment (PPE)
- Documentation & Signs
- Develop an Hazard Analysis or Standard Operating Procedures
  - Acid Etching (TD)
  - Post Etching Disassembly (AD)
  - HF Waste Pick-up and Transport (HCTT)
- Always use HF in the lab hood
- Do not eat or drink in the lab

IV. Documentation & Signs

- MDTL/SCRF Materials Lab Chemical Hygiene Plan
- Buffered Chemical Polish Procedure
- Develop Operating Procedure for Electropolishing (and any other new procedure that involves HF)
- Signs
  - Safety Shower
  - HF Acid
  - Calcium Gluconate Antidote
  - What to do in case of exposure sign (Shown Next Slide)
- Training Completion List
- Safety Data Sheet (SDS)
- Chemical Inventory
- Chemical Labels
- Informational Sheet to take to the Emergency Room
IV. What to do in Case of HF Exposure

Emergency Response Plan for Hydrofluoric Acid Exposure

<table>
<thead>
<tr>
<th>Ingestion</th>
<th>PPE Only</th>
<th>Skin</th>
<th>Eyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drink 1 Glass of Water</td>
<td>Call 3131</td>
<td>Wash Area with Water for 2-3 Minutes</td>
<td>Apply 2.5 % Calcium Gluconate Gel</td>
</tr>
<tr>
<td>Take up to 30 Tablets</td>
<td>Call 3232</td>
<td>Do not Induce Vomiting</td>
<td>Call 3131</td>
</tr>
<tr>
<td>Do not Induce Nausea</td>
<td>Call 3131</td>
<td>Remove Visible Liquid</td>
<td>Remove / Check / Get New PPE as Needed</td>
</tr>
<tr>
<td>Call 3232</td>
<td>Remove any PPE</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Small Spill
- Pour Soda Ash or Uni-Safe Sorbent

Large Spill
- Leave the Area
- Call 3131 Remotely

IV. Personal Protective Equipment

Operation Specific that may include all or some of the following. All are needed for etching operations.
- neoprene gloves
- Saranex coated coveralls
- rubber aprons and knee-boots
- a face shield
- goggles

IV. Face Shield Goggles

- Acid Resistant – Not Designed for Immersion but for Splash Resistance
IV. Gloves

- Neoprene: Resistant for more than 8 hours
- Inside Pair Purple Nitrile Gloves: Little to no resistance to HF

IV. Foot Protection

- Boots or Spat

IV. Full Body Suit

- HF Resistant - The Suit is Hot
V. Planning for Emergency

- Training
- Standard Operating Procedures Highly Toxic Materials
  - Assistant System
  - Engineering Controls
  - Emergency Equipment
  - Personal Protective Equipment (PPE)
  - Label all containers
  - Post your area while working

V. Emergency Happens
What Now?

- Do not panic! Think Think Think
- Assistant response
  - Help individual to eyewash/safety shower flush the area with large amounts of water for 5 minutes. Have the employee remove all contaminated clothing while under the shower.
- DO NOT CONTAMINATE SELF or Assistant

V. Primary Decontamination

- Immediately go to eyewash/safety shower
- Remove all clothes, shoes and jewelry
- Remove goggles last, face water and pull over head
- Maximum time is 5 minutes
V. Emergency Happens
What Now?
- The assistant should call 3131 and 3232
  - Let Fire Department and Medical Department know you have an HF exposure and give the exact location
- The employee should self administer calcium gluconate
- The employee must not be transported to the hospital without being decontaminated
- Assistant should bag all contaminated supplies (USE PPE)
- The employee must be escorted to the hospital by the responding person or assisting lab personnel
- A copy of the SDS and Recommended Medical Treatment for HF Exposure must go to the hospital

V. First Aid: Absorption
- Minor burn-less than 2 square inches (13 cm²)
- Major burn-more than 2 square inches (13 cm²)
- Start self application of 2.5% calcium gluconate gel every 15 minutes
  - NOTE THE TIME OF INITIATION OF THE APPLICATION
  - 0.13% benzalkonium chloride may also be used for skin contact
- Must seek medical attention

V. Calcium Gluconate Antidote
- All Areas that Store/Ship/Use/Handle any amount of HF must have an appropriate amount of antidote readily available.
- Primary users of HF are given a tube of antidote to self administer at home for cases of dilute HF exposure with delayed onset symptoms.
V. Treatment of Choice

- Calcium Gluconate Gel
- Neutralizes the HF
  - Binds the fluoride ion to prevent deep tissue destruction and systemic absorption
- Easy to use
- Recently became easier to obtain
- Treatment should be started after flushing with water for 5 minutes
- Treatment fast and effective
  - Relief of pain is an indication of the efficiency of the antidote

Note: Bring a tube of calcium gluconate home after working with HF/BCP as a safety precaution.

V. Treatment of Choice

- Resulting reaction produces glucose as compared to ammonium fluoride and acetic acid in the case of other treatments
- Worst case scenario is it MAY cause minor irritation

Note: Bring a tube of calcium gluconate home after working with HF/BCP as a safety precaution.

V. First Aid: Eyes

- Use eyewash for 5 minutes
- Eye must be kept open
- Must seek medical attention

Caution: Do not apply calcium gluconate gel to eyes
V. First Aid: Inhalation

- Inhalation hazards result from exposure to gas as well as vapors from contaminated items
  - Decontaminate everything contaminated and move to fresh air
  - Thoroughly flush the face with water, particularly the areas around the nose and mouth
  - Apply Calcium Gluconate Gel around the nose and mouth
  - Emergency personnel should begin oxygen
  - Must seek medical attention

V. First Aid: Ingestion

- A conscious patient may be given high amounts of calcium or magnesium based antacid or only water
- Do not induce vomiting
- Must seek medical attention

V. Secondary Decontamination

- May include examining and decontaminating the following:
  - Ear canal, mouth, nose, anus, vagina
  - Folds of neck, knees, groin
  - Below nails, hand, feet
  - Areas covered with hair, scalp and pubis
- Employees exposed to HF vapors only do not pose a significant risk of secondary contamination
- Employees whose clothing or skin is contaminated with HF liquid or solution can secondarily contaminate response personnel by direct contact or through off-gassing vapors.

Fermilab
Best Treatment for Exposures is Prevention

- Administrative controls
- Engineering controls
- Personal Protective Equipment
- Training

What questions do you have?