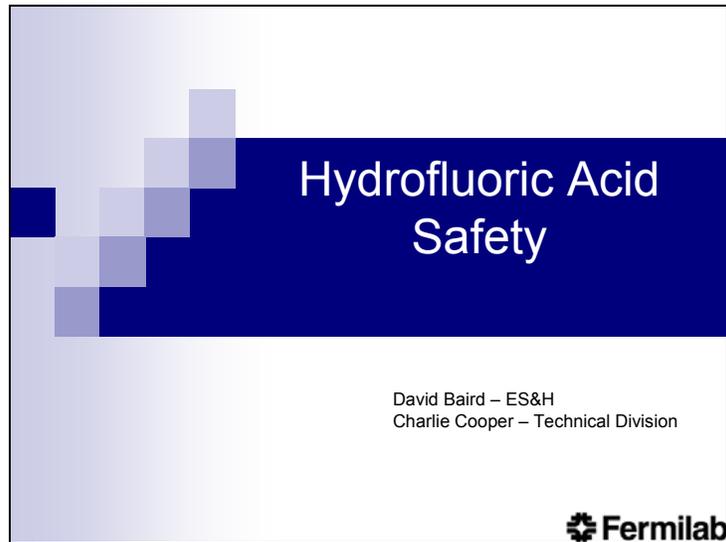


Slide 1

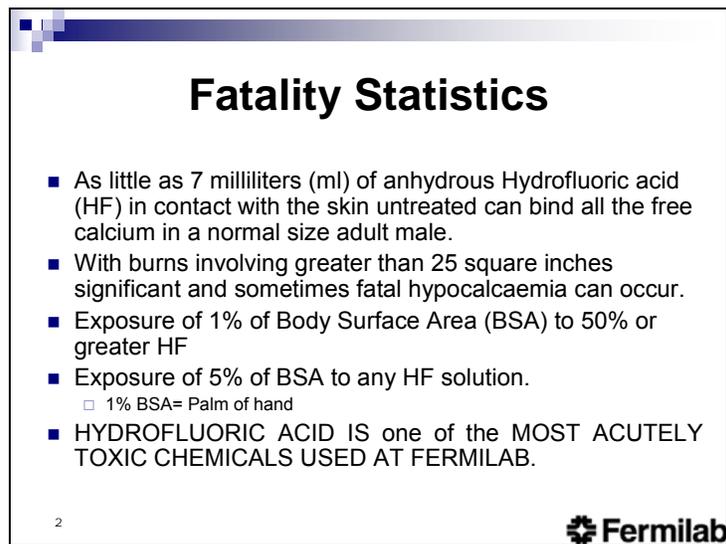


Hydrofluoric Acid  
Safety

David Baird – ES&H  
Charlie Cooper – Technical Division



Slide 2



## 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.

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## Outline

- I. Hydrofluoric Acid Uses
- II. Hydrofluoric Acid Properties
- III. Hydrofluoric Acid Exposure
- IV. Safe Work Practices
- V. What to do for Hydrofluoric Acid exposure
- VI. Chemical Concern Contact Numbers
- VII. Questions & Answers

 Fermilab

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## I. HF Acid Uses in Industry

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

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Slide 5

## I. HF Acid Uses at Fermilab



- HF is used at Fermilab to Polish Superconducting Radio Frequency Cavities (SRF) to Remove Impurities and Decrease Surface Roughness
- Buffered Chemical Polish - BCP
  - 2 parts phosphoric acid (85% weight (wt)  $H_3PO_4$ )
  - 1 part nitric acid (69.5% wt  $HNO_3$ )
  - 1 part hydrofluoric acid (49% wt HF)
- Electropolishing Process—"BCP with Current"
  - 89.5% by volume sulfuric acid (96% wt  $H_2SO_4$ )
  - 10.5% by volume hydrofluoric acid (40% wt HF)

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## 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  $\approx$  7 millimeters of Mercury (mmHg) for 49 wt% at Standard Temperature and Pressure (STP)

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## 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.**

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Slide 8

## 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

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## 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.



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## III. Exposure Groups

<ul style="list-style-type: none"><li>■ <b>Primary Contact</b><ul style="list-style-type: none"><li>□ Accelerator Division<ul style="list-style-type: none"><li>■ A0 SCRF Support Group (M. Foley/M. Frett)</li></ul></li><li>□ Technical Division<ul style="list-style-type: none"><li>■ SCRF Materials Group (C. Antoine)</li><li>■ Materials Development Laboratory (MDTL) (C. Cooper)</li></ul></li></ul></li></ul>	<ul style="list-style-type: none"><li>■ <b>Secondary Contact</b><ul style="list-style-type: none"><li>□ Technical Division<ul style="list-style-type: none"><li>■ ESH Group (R. Sood/R. Ruthe)</li></ul></li><li>□ Business Services<ul style="list-style-type: none"><li>■ Receiving (G. Davidson/B. Niesman)</li><li>■ Distribution (G. Davidson/B. Niesman)</li><li>■ Fire Department (J. Steinhoff)</li></ul></li><li>□ Environment, Safety and Health Section<ul style="list-style-type: none"><li>■ HCTT (Billy Arnold)</li></ul></li><li>□ Contractors, Visitors, Summer Students</li></ul></li></ul>
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Slide 11



### III. Routes of Entry

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

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### 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)

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### **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<sup>+</sup>) enters extra cellular space to compensate for calcium loss
- Nerve endings are irritated by increased levels of K<sup>+</sup>
- 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

<u>Concentration</u>	<u>Time of pain onset</u>
0-20	Up to 24 hours
20-50*	1-8 hours
>50	<1
99	immediate

\*Maximum concentration used at lab

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### III. HF Skin Exposure



- Assess for pain
- Assess for redness/whiteness of skin/blisters
- Assess area of burn
  - If >25 in<sup>2</sup> or 160 cm<sup>2</sup> then risk for serious systemic toxicity is present

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### III. HF Exposure to Eyes

- Severe burns
- Opacification of cornea
- Blindness

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### 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

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### III. Systemic Toxicity of HF

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

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### 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

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Slide 21

## 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
- Material Safety Data Sheet (MSDS)
- Chemical Inventory
- Chemical Labels
- Informational Sheet to take to the Emergency Room



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## IV. What to do in Case of HF Exposure

Emergency Response Plan for Hydrofluoric Acid Exposure									
Inhalation	Skin	Eyes	Ingestion	PPE Only	Room				
<ul style="list-style-type: none"> <li>•Leave Area with HF Vapors</li> <li>•Call 3131</li> <li>•Call 3232</li> </ul>	<ul style="list-style-type: none"> <li>•Remove Contaminated Clothing</li> <li>•Wash Area with Water for 2-3 Minutes</li> <li>•Begin Applying 2.5 % Calcium Gluconate Gel</li> <li>•Call 3131</li> <li>•Call 3232</li> </ul>	<ul style="list-style-type: none"> <li>•Flush Continuously with Water</li> <li>•Call 3131</li> <li>•Call 3232</li> </ul>	<ul style="list-style-type: none"> <li>•Drink 1 Glass of Water</li> <li>•Take up to 30 Tums</li> <li>•Do not Induce Vomiting</li> <li>•Call 3131</li> <li>•Call 3232</li> </ul>	<ul style="list-style-type: none"> <li>•Remove any Visible Liquid with Red pH Sensitive Towels</li> <li>•Remove / Check / Get New PPE as Needed</li> </ul>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr style="background-color: #cccccc;"> <th style="text-align: center;">Small Spill</th> </tr> <tr> <td style="padding: 2px;"> <ul style="list-style-type: none"> <li>•Pour Soda Ash or Uni-Safe Sorbent</li> </ul> </td> </tr> <tr style="background-color: #cccccc;"> <th style="text-align: center;">Large Spill</th> </tr> <tr> <td style="padding: 2px;"> <ul style="list-style-type: none"> <li>•Leave the Area</li> <li>•Call 3131 Remotely</li> </ul> </td> </tr> </table>	Small Spill	<ul style="list-style-type: none"> <li>•Pour Soda Ash or Uni-Safe Sorbent</li> </ul>	Large Spill	<ul style="list-style-type: none"> <li>•Leave the Area</li> <li>•Call 3131 Remotely</li> </ul>
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## 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

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Slide 24

## IV. Face Shield Goggles



- Acid Resistant – Not Designed for Immersion but for Splash Resistance

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Slide 25

### IV. Gloves



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

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Slide 26

### IV. Foot Protection



- Boots or Spat

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Slide 27

## IV. Full Body Suit



- HF Resistant - The Suit is Hot

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Slide 28

## 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

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## 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

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## 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

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## 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 MSDS and Recommended Medical Treatment for HF Exposure must go to the hospital

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## V. First Aid: Absorption

- Minor burn-less than 2 square inches (13 cm<sup>2</sup>)
- Major burn-more than 2 square inches (13 cm<sup>2</sup>)
- Start self application of 2.5% calcium gluconate gel every 15 minutes
  - NOTE THE TIME OF INITIATION OF THE APPLICATION
- Must seek medical attention

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## 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.



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## 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

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Slide 35

**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.

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**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

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## 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

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## 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

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## 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.

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## Best Treatment for Exposures is Prevention

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

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**VI. Chemical Concern Contact Numbers**

- **Accelerator Division**
  - Richard Rebstock (3499)
- **ESH Section**
  - Dave Baird (3945)
- **Technical Division**
  - Richard Ruthe (5424)
- **Business Services Section**
  - Greg Mitchell (8002)

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**What questions do you have?**

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