Chemical Safety for SRF Work

Introduction

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USPAS Course:

SRF Technology: Practices and Hands-On Measurements

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HF Safety

Non-HF Acid Exposures

- Treated with First Aid typically 3 degree burns
- Protection from infection
- Plastic Surgery
- Risk of fatality is Low

HF Acid Exposures

- Risk of fatality is very high, many hours after initial exposure
- Even after first aid and medical treatment

Why is HF Needed?

- Niobium surface has a very robust native oxide (Nb_2O_5)
- Hydrofluoric Acid has a good ability to destabilize Nb_2O_5 and form soluble niobium fluorides and niobium oxifluorides

$$Nb_2O_5 + 14HF \rightarrow 2H_6NbO_2F_7 + H_2O$$

$$Nb_2O_5 + 12HF \rightarrow 2HNbF_6 + 5H_2O$$

$$Nb_2O_5 + 10HF \rightarrow 2NbF_5 + 5H_2O$$

$$Nb_2O_5 + 10HF \rightarrow 2H_6NbOF_5 + 3H_2O$$

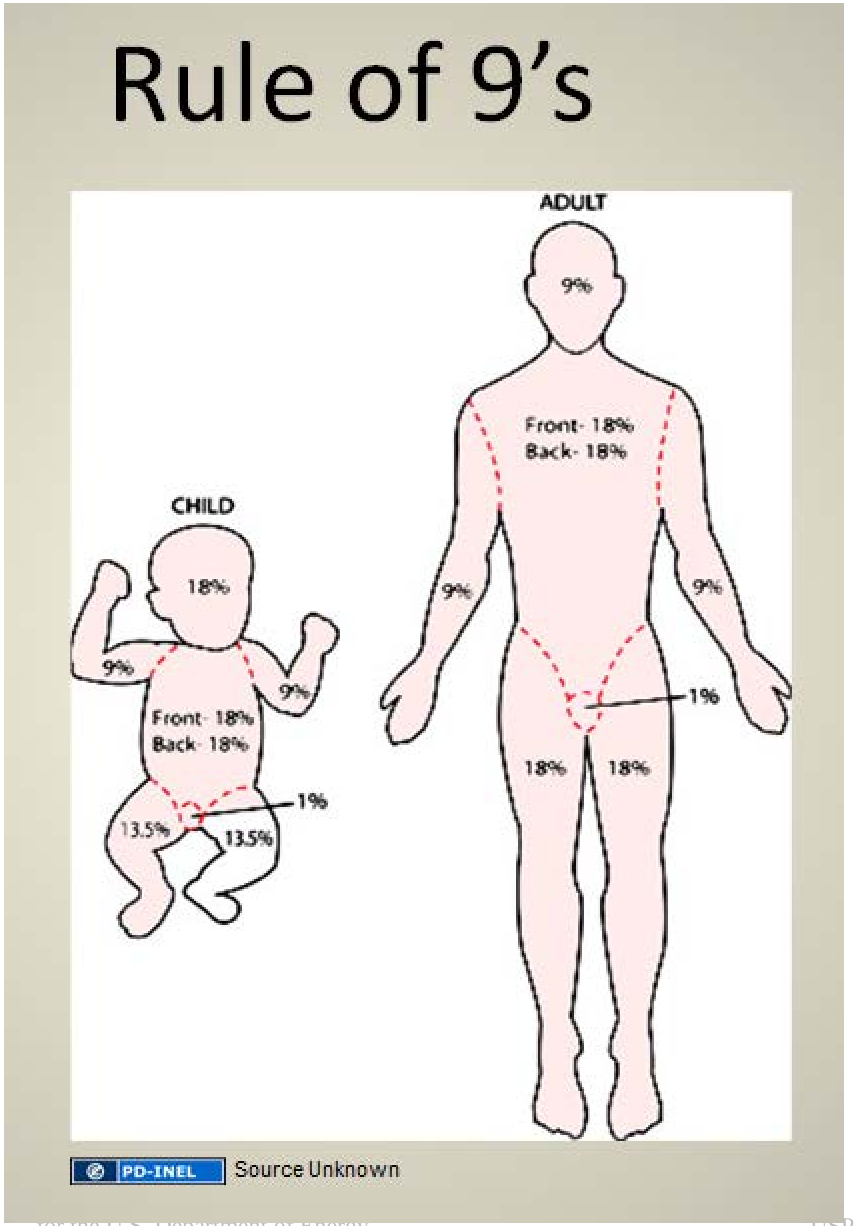
$$HNbF_6 + HF \rightarrow H_2NbF_7 \,.$$

P. Kneisel, Jlab

Hydrofluoric Acid Safety

- **Hydrofluoric acid is an anomaly**
  - **It does not react like all other acids, readily absorbed into the skin**
  - **Absorption is deep into the body, it destroys everything in its path, then slowly releases into blood stream bonding all calcium and magnesium**
  - **Calcium is needed to control your hart function → cardiac arrest can result in as little as 8 hours after the exposure**
  - **Time to proper first aid (removal of and bonding of fluorine) is the most important detail and will determine the outcome**
  - **Large exposures always lead to death even with first aid and medical treatment, rare cases have survived > 8% of body**

Percent of body surface area



Learning From Real Exposures - Perth

- **37 Year old Male spilled 100-210ml of 70% w/w concentrated HF on his lap while seated**
- **PPE Worn – wrist length rubber gloves and PVC sleeve protectors**
- **Was working alone**
- **Sustained burns 9% of his body**
- **Washed legs with water (6 l/min) and did not remove clothing → went into shock**

FATALITY DUE TO ACUTE FLUORIDE POISONING FOLLOWING DERMAL CONTACT WITH HYDROFLUORIC ACID IN A PALYNOLOGY LABORATORY

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Abstract: A fatal accident involving concentrated hydrofluoric acid in a palynological laboratory is described. Similar deaths due to dermal exposure to concentrated hydrofluoric acid have been reported in the literature. It is evident that rigorous control measures including proper personal protective equipment and first aid are of utmost importance in the prevention of death and injury when handling hydrofluoric acid. Possible factors that may have contributed to the accident are reviewed. Copyright © 1996 British Occupational Hygiene Society.

INTRODUCTION: Hydrofluoric acid is a corrosive and toxic liquid that is potentially toxic even following dermal exposure to small amounts (Burke et al., 1973). The fatality described below highlights the potential for relatively small quantities of concentrated hydrofluoric acid to produce acute systemic toxicity and it is clear that laboratory personnel underestimated the risks associated with the acid. The purpose of this paper is to raise awareness of the inherent dangers associated with dermal contact with concentrated hydrofluoric acid, and of the importance of observing strict precautions when handling it.

ACCIDENT DESCRIPTION: A palynological technique used by geologists involves the dissolving of sedimentary rock with mineral acids (hydrochloric and hydrofluoric acid) to liberate acid-insoluble microscopic fossils. The fossils are then examined by microscopy to determine the age of the rock and oil potential.

A 37-year-old male laboratory technician was performing acid digestion of oil well core and ditch samples with 70% w/w concentrated hydrofluoric acid in a fume cupboard. He was believed to be seated when he knocked over a small quantity (100-230 ml) of hydrofluoric acid onto his lap, splashing both thighs. The only personal protective equipment (PPE) worn was two pairs of wrist length rubber gloves and a pair of polyvinyl chloride (PVC) sleeve protectors. As a result of the fact that the technician was working alone, it is unclear whether the spill was from the digestion cup or the 2-l bulk acid container.

The technician sustained burns to 9% of his body surface area, despite washing his legs with water from a makeshift plumbing arrangement that supplied water at 6 l. min -. No calcium gluconate gel was applied to the affected area and contaminated clothing was not removed during the flushing with water.

Following flushing, the technician, who appeared to be in severe pain and shock, immersed himself in a chlorinated swimming pool at the rear of the workplace, where he remained for approximately 35-40 min before ambulance help arrived.

The injured man was hypothermic and hypocalacaemic on admission to an intensive care unit at a nearby hospital, and soon became unconscious. His condition continued to deteriorate despite subcutaneous injections of calcium gluconate and administration of intravenous calcium and magnesium. His right leg was amputated 7 days after the incident. He subsequently died from multi-organ failure 15 days after hydrofluoric acid spill.

Learning From Real Exposures: Highlights

Learning From Real Exposures- Perth

- **Jumped into a chlorinated swimming pool was removed after 30-40 min**
- **Ambulance took him to the hospital**

- **Received subcutaneous injections of calcium gluconate and intravenous calcium and magnesium**

- **Right leg amputated after 7 days**

- **Died from multi-organ failure after 15 days**

Result: Acute Systemic Toxicity of Hydrofluoric Acid

Toxicity Comparison:

Carbon Monoxide: LC50=1807ppm, 4 hours
Hydrogen Fluoride: LC50=342ppm, 60 minutes
Arsine, Arsenic Hydride: LC50=94ppm, 15 minutes
Hydrogen Cyanide: LC50=63ppm, 40 minutes

Contributing Factors

- **Dermal exposure of 9% concentrated hydrofluoric acid**
- **PPE inadequate for safe work**
- **Duration of exposure**
  - **Did not remove contaminated clothing**
  - **No safety shower**
  - **Rinsing flow rate very low and may have spread the HF exposure**
  - **No calcium gluconate applied just after the exposure**
  - **Inhalation may have played a factor, unknown**
- **Work environment**
  - **Height of fume hood required deceased to sit not stand**
  - **Acid digestion cups were instable base dia. = 59mm, top dia. = 78mm height 75mm and lightweight 2 mm polyethylene**
  - **Fume hood opening and work space limited pouring from 2 l bottle**

Another Exposure Example This Time Survival

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Hydrofluoric Acid Burn

Martin W. Dünser, M.D., and Josef Rieder, M.D.

N Engl J Med 2007; 356:e5 | February 8, 2007 | DOI: 10.1056/NEJMicm055763

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A 45-year-old healthy man was involved in demolishing an industrial plant in which glass had been etched. He was exposed to a reservoir of 70% hydrofluoric acid while repairing a pipeline. He was admitted to the intensive care unit for second-degree and third-degree burns from hydrofluoric acid affecting 30% of his body-surface area, including both hands, both forearms, the chest, back, scalp, and neck. After penetrating tissue, hydrofluoric acid dissociates into hydrogen and fluoride ions, of which particularly fluoride is toxic. Since fluoride ions are inactivated by means of precipitation with calcium and magnesium, the infusion of calcium and magnesium is considered a therapy in patients with hydrofluoric acid burns. In this patient, magnesium was infused intravenously, and calcium was infused intravenously and intraarterially (through the brachial artery) and was applied topically to the burned skin. The blood magnesium level was always within the normal range during substitution therapy. Blood levels of ionized calcium were initially elevated to up to 1.75 mmol per liter but were within the normal range after 36 to 48 hours. As a result of this intense calcium and magnesium therapy, cutaneous calcification developed on the fingertips by 36 to 48 hours, as well as on the dorsal and palmar aspects of the hand (Panels A and B, respectively). Three months later, the patient had regained an almost full range of motion, was free of symptoms, and had a good =40065020 etic result.

Details:

- 70% HF exposure
- 30% body surface area
- Magnesium was infused in his blood stream intravenously
- Calcium infused intravenously and intraarterially
- And calcium applied topically
- Patient fully recovered most range of motion and survived incident mainly due to the procedure applied

What you should expect once at the hospitals

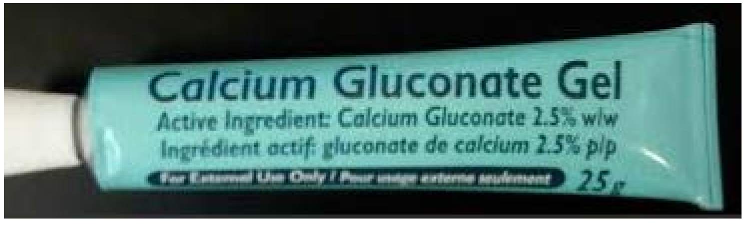
- **They may not connect the seriousness of the HF exposure**
  - **Please bring HF Honeywell protocols to guide their response**

- **Doctors will have to look up the protocol and you may have to insist on the time urgency with an HF exposure**

- **Constant application of calcium gluconate is prudent so bring a supply with you**

HF Safety cont.

- **Before using HF**
  - **Ensure the lab has a functioning safety shower**
  - **Calcium gluconate cream or equivalent**
  - **Proper PPE to cover all exposed skin**
  - **Additional personnel trained in providing first aid and available**



- **Before using a System**
  - **Review and understand the hazards**
  - **Know what to do when an accident happens**

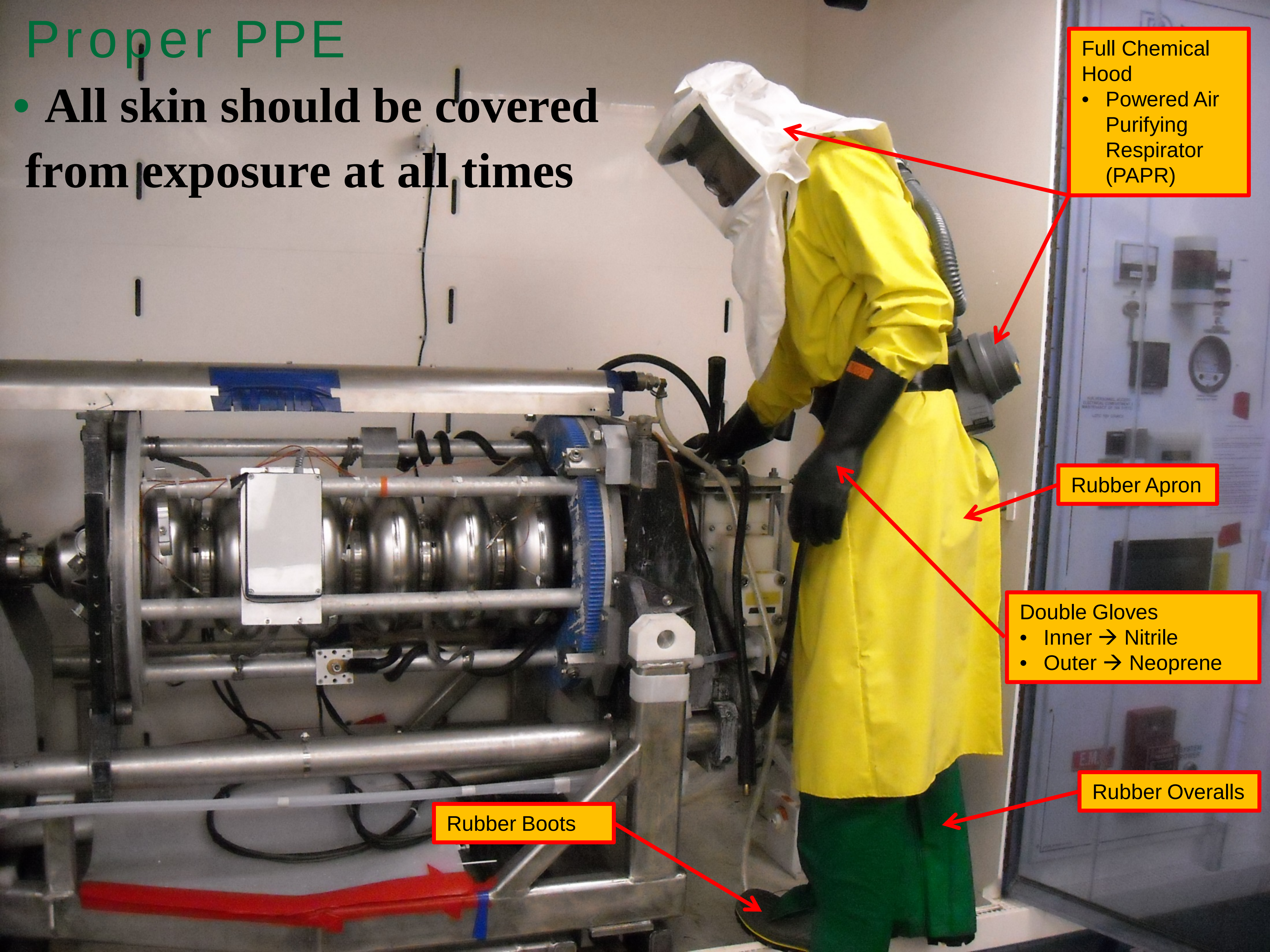
What we know about HF exposures and resulting injuries

- **It can be avoided with:**
  - Proper PPE
  - Local Safety showers with eye wash stations
  - Calcium gluconate readily available
  - First aid protocols posted in areas of need
  - Training of first responders
  - Facility safety Protocols (extreme care during maintenance actives)
  - Design of acid facilities and systems
    - Fume hoods, wet benches
    - Automated equipment

- **Minimizing use where possible !**

Proper PPE

- **All skin should be covered from exposure at all times**



HF Exposure

General Rules – Skin Exposure

Time for removal and binding of fluorine is the most critical factor to the outcome

1. Don PPE, remove clothing, contact medical help
2. Rinse exposed area and remove all remaining acid, check all possible areas
3. As soon as acid is removed start applying calcium gluconate (proper PPE required)
4. Apply calcium gluconate until hospital staff takes over

- **The need for training first responders is evident**
  - Accident victim will most likely be in shock
  - It takes multiple personnel to apply proper first aid
  - Immediate area may be risk to others due to accident

Ansell Chemical Resistance Guide
Permeation & Degradation Data

This Information Applies Only to Ansell Occupational Healthcare Glove Brands

CHEMICAL	LAMINATE FILM BARRIER			NITRILE SOL-VEX			UNSUPPORTED NEOPRENE 29-865			SUPPORTED POLYVINYL ALCOHOL PVA			POLYVINYL CHLORIDE (Vinyl) SNORKEL			NATURAL RUBBER CANNERS AND HANDLERS*			NEOPRENE/ NATURAL RUBBER BLEND CHEMI-PRO*		
	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate	Degradation Rating	Permeation: Breakthrough	Permeation: Rate
77. Hydrofluoric Acid, 48%	E	>480	—	E	334	—	E	>480	—	NR	—	—	G	155	—	E	190	—	E	153	—
112. Nitric Acid, 70%	E	>480	—	NR	—	—	E	>480	—	NR	—	—	F	104	—	NR	—	—	G	90	—
113. Nitric Acid, Red Fuming	▲	>480	—	NR	—	—	NR	—	—	NR	—	—	P	—	—	NR	—	—	NR	—	—
142. Sulfuric Acid, 95%	E	>480	—	NR	—	—	F	105	—	NR	—	—	G	70	—	NR	—	—	NR	—	—
127. Phosphoric Acid, conc.	▲	>480	—	E	>360	—	G	>480	—	NR	—	—	G	>360	—	F	>360	—	G	>360	—
138. Sodium Hydroxide, 50%	E	>480	—	E	>360	—	E	>480	—	NR	—	—	G	>360	—	E	>360	—	E	>360	—

Key to Degradation Ratings

E – Excellent; fluid has very little degrading effect.
G – Good; fluid has minor degrading effect.
F – Fair; fluid has moderate degrading effect.
P – Poor; fluid has pronounced degrading effect.
NR – Fluid was not tested against this material.

NOTE: Any test samples rated P (poor) or NR (not recommended) in degradation testing were not tested for permeation resistance. A dash (–) appears in those cases.

Key to Permeation Breakthrough

> Greater than (time) < Less than (time)

Specific Gloves Used for Testing

	Degradation	Permeation
Nitrile	Sol-Vex® 37-145 (11 mil/0.28 mm)	Sol-Vex® 37-165 (22 mil/0.54 mm)
Neoprene Unsupported	29-865 (18 mil/0.46 mm)	29-865 (18 mil/0.46 mm)
Polyvinyl Alcohol Supported	PVA™	PVA™
Polyvinyl Chloride Supported	Snorkel®	Monkey Grip™
Natural Rubber Latex	Canners 392 (19 mil/0.48 mm)	Canners 392 (19 mil/0.48 mm)
Neoprene/Latex Blend	Chemi-Pro 224 (27 mil/0.67 mm)	Chemi-Pro 224 (27 mil/0.67 mm)
Laminated LCP™ Film	Barrier 2-100 (2.5 mil/0.06 mm)	Barrier 2-100 (2.5 mil/0.06 mm)

Single palm thickness is listed in both mil and metric millimeter (mm) for Unsupported Gloves. Supported Gloves are specified by glove weight, not thickness.

One type glove does not solve the problem

Follow Jlab's Chemical Safety Guidelines and Recommendations

- **They have good success dealing with large quantities of HF on a daily basis**

- **Systems in place**
  - **Alarming safety showers (call goes to security) established procedures take over from there**
  - **Large number of first responders trained in HF first aid**
  - **Yearly training by medical staff with many years of experience with HF**