“Hydrofluoric Acid and Ammonium Bifluoride are much more dangerous than you think!”

by Patrick DeFlorio
Yankee Glassblower
Concord MA

Abstract

Many glassblowers are unaware that there are many fatalities and permanent disabilities due to unsafe use of hydrofluoric acid and ammonium bifluoride. Examples of deaths and injuries are listed in this article along with the chemistry of why these are such toxic materials. Most of the information relates to hydrofluoric acid.

The “fluoride” in hydrofluoric acid (HF) and related acids is deadly! To illustrate this point: consider that an Australian geology student spilled 100-230 ml of HF and HCl on his lap while working alone under a fume hood. He was etching samples to examine the grain structure. After rinsing with a limited 6 l/minute source of water he immersed himself in a pool for a little over a half hour while waiting for an ambulance. Seven days later a leg was removed in a valiant effort to save his life. His painful injury lasted only another eight days until he died of massive organ failure. Only nine percent of his body was exposed to the acid. By not using a shower with high volume he may have actually spread the contamination. He did not take off the soaked clothes or have any first aid gel applied to the burn.(1)

A safety shower could have saved his life. A regulation eye wash and shower should be within reach, 10 seconds, at most, from the fume hood. The flow from the shower should be 25 gallons per minute. This is not a suggestion, it is the law! In addition, gloves and an apron should be worn at all times when using chemicals.

It is important to understand why the fluoride compounds are so dangerous. Many man-made compounds want to return to their natural state. Iron ore is heated, fluxed and alloyed to form steel. If the steel is unprotected in a humid environment it quickly returns to iron ore, more commonly referred to as rust. We are familiar with the same cycle with sand and quartz. HF is formed by heating fluorspar (CaF_2) and sulfuric acid (H_2SO_4). The hydrogen and fluoride combine to form the acid, which condenses at room temperature. Since much of the energy was used to break up the fluorspar compound, it always tries to combine with either calcium or magnesium to return to its stable state. (2)

Calcium is not only found in bones and teeth, but is an essential element in all our cells. Fluorine combines with the calcium and magnesium to form salts that can not be dissolved by cells themselves. This both robs them of critical minerals and poisons them at the same time. HF dissolves perfectly in water allowing it to penetrate the protective shield of the skin and freely travel the circulatory system, reeking havoc: “hypocalcaemia should be considered a potential risk in all instances of inhalation or ingestion and whenever skin burns exceed 25 square inches.” (3). Hypocalcaemia is when fluoride has lowered the body’s natural level of calcium, an effect similar to what happens with magnesium. This causes health problems including regulating heart beat and breathing.

Vertical columns, on the periodic chart, group elements by their available, or valiance electrons for combining with other elements. Members of groups have similar but not identical properties. Fluoride belongs to the halide group with both bromine and chlorine. Chlorine is used to kill algae in swimming pools and bromine is also used in swimming pools as well as to kill insect larvae commonly found in flour. Fluorine, the 17th most common element, is used in insecticides and to kill unwanted yeast in brewing beer and wine. (4)

Another example of just how deadly this material can be comes from New York City, where two garbage men picking up trash accidentally crushed a gallon of 70% HF, obviously not knowing its contents. One man was hit in the face and mouth and the second was injured less extensively. The accident was across the street from an ambulance company. Despite immediate attention, the first victim died in the hospital. His face was so badly burned that his wife was not allowed to visit him. Police classified the incident as a murder investigation. The acid spraying in the victim's mouth caused enough damage to kill him.

An ounce of prevention is worth a pound of flesh! All MSDS listings insist on protecting your skin and body from exposure to HF.(5) At this time I cannot find an independent recommendation for gloves. Commercial sites do compare their gloves to various chemicals and acids. The ASGS does not endorse these products or verify results so it is important to evaluate the gloves you are using to determine if they offer adequate protection. Remember that is the information you see on these websites represent the average expectancy of a glove; some may be defective or can easily be compromised by a small cut. Government test of gloves showed a life expectancy of half the manufacturer's claim of 8 hours. In comparison to the use of more protective gloves, Nitrile gloves lasted less than a minute. A mean (average) penetration time of less than a minute is not acceptable. This is why; if at all possible, a basket should be used to submerge glass in solution instead of directly using a glove.

The following information was found on the OSHA Web-Site http://www.osha.gov/SLTC/healthguidelines/hydrogenfluoride/recognition.html

. **Please consider the note below the table warning of inconsistencies between manufacturers' claims and test results.**

"Workers should use appropriate personal protective clothing and equipment that must be carefully selected, used, and maintained to be effective in preventing skin contact with hydrogen fluoride. The selection of the appropriate personal protective equipment (PPE) (e.g., gloves, sleeves, encapsulating suits) should be based on the extent of the worker's potential exposure to hydrogen fluoride. The resistance of various materials to permeation by 30 to 70 percent solutions of hydrogen fluoride is shown below:"

Material	**Breakthrough time (hr)**
Saranex	>8
Barricade	>8
Chemrel	>8
Responder	>8
Butyl Rubber	>4

Natural Rubber	Caution 1 to 4
Neoprene	Caution 1 to 4
Polyethylene	Caution 1 to 4
4H (PE/EVAL)	Caution 1 to 4
Nitrile Rubber	<1(*)
Polyvinyl Alcohol	<1(*)
Polyvinyl Chloride	<1(*)

(*) Not recommended, degradation may occur

To evaluate the use of these PPE materials with hydrogen fluoride, users should consult the best available performance data and manufacturers' recommendations. Significant differences have been demonstrated in the chemical resistance of generically similar PPE materials (e.g., butyl) produced by different manufacturers. In addition, the chemical resistance of a mixture may be significantly different from that of any of its neat components."(6)

Protective clothing is easier to research. The National Institute of Occupational Safety and Health, a division of the United States Health and Human Services Department, recommends Tychem, claiming a 4 hour mean penetration time. This material is similar in appearance to Tyvac, which is used to sheath a house. The American Conference of Governmental Industrial Hygienists recommendations includes: "Polyvinyl Chloride as a good to excellent protective material."(7) Wearing goggles without a face shield is not very effective and can lead to eye injuries. Breathing or swallowing HF is usually fatal, meaning that touching or adjusting goggles with wet hands could lead to serious, potential health risks. When working with HF you need to wear gloves, facemask and goggles along with sleeve protection and an apron fabricated of Tychem.

HF is used in many industries and it is helpful to look at their particular publications for guidance. Since 1670, HF has left its mark on the glass industry, beginning originally with decorative etching. In the metal industry, it is used to clean Aluminum and stainless steel. Geologist use small samples of HF to study grain structure or as a means of freeing precious minerals from sandy rock. The car wash industry cleans aluminum wheel rims with HF and ABF. Graffiti is removed from concrete and stone with HF as well. Some art supplies use these toxic compounds even though the label promotes the safety of the product.

Housework can be dangerous as well. A healthy, 26 year old woman attempted to remove a stubborn stain from a bathtub in a very small bathroom with no ventilation. She tried several household cleaners but thoroughly rinsed the tub between different products. One of the cleaners contained 8% HF. She was crouched over the tub, giving her maximum exposure. HF fumes in humid environments and the action of physically scrubbing thoroughly, released more noxious fumes into the air. HF fumes are denser than air and tend to settle in vats and tubs. Many publications claim that there is little fuming in dilute HF, but that was not the case. The woman complained of burning eyes and tasting the acid fumes. The next day she did not wake up and slept through the entire day; she was admitted to the hospital on her second visit to the emergency room. The

doctors quickly determined that she had a problem with her lungs. The suspicion was that she had pneumonia and she was treated accordingly. She was given Lasix in an attempt to remove the fluid in her lungs. Her condition worsened until on the eighth day when she was placed on a mechanical ventilator. The next day she was given steroids to improve her breathing and a scrapper was inserted into her lungs to remove samples to help find the cause of her problems. The lab showed the small air sacks ruptured and lungs filled with fluids. This condition is known as pulmonary edema, wherein the lungs which are damaged eventually fill up with fluid. Oxygen from the air is prevented from entering the small chambers where it is dissolved into the blood stream. The body runs at a deficit, eventually cells are turned off and die. The scraping procedure was repeated on day 21. Finally on the twenty fifth day, she was able to breathe without use of a ventilator and was discharged from the hospital. She now breaks into uncontrollable coughing fits after climbing a single flight of stairs. Her lungs are permanently damaged enough to limit her mobility at age 26. The threshold limit for HF is 3 parts per million of air, and 22 ppm over an 8 hour day is considered a fatal dose.(8)

Scott Bankroff wrote an excellent article in the February 2005 Fusion: "*Polypropylene Glassblower's Sink*." The article has pictures of the cleaning area before and after the renovations, including numbered changes. The item listed as #1 was the installation of a regulation eye wash.(9) Eye wash and safety showers are mandatory if you are working with corrosive materials! You should be able to reach a shower and eye wash within ten seconds of the fume hood. The path should be clear of any obstacles. Regulations state that an eyewash should be between 33–45″ high and be able to deliver 0.4 gallons of clean water per minute. The water quality and flow need to be tested on a scheduled basis. If the water is stagnant, it will compound the injury by applying bacteria to the skin where it has lost its protective capability. Employees should practice both pieces of equipment. Hold the eyelids apart when using the eye wash and roll the eye to expose all traces of acid. Present advice is to flush for between 10 and 15 minutes with a vigorous flow. Discuss the exact length of rinse with your safety officer and physician. Please note that this is a controversial topic.

The acid sink in Scott'Bankroff's photograph used in Fusion has ventilation directly over the top of the sink where it skims the fumes off the surface of the liquid. If the vent were installed on the wall or ceiling, it would actually increase the amount of fumes in the room; the fumes would be pulled off of the acid across the working space, in order to travel to the exit. A hinged lid was placed on the tank so that it would not be out-gassing fumes when not in use. Acid warning signs were posted on the walls of the improved sink, advising visitors of the potential hazards.

Many glassblowers have switched to ammonium bifluoride to avoid the dangers of HF. The Solvay Chemical web-site states: "Mixing ammonium bifluoride with water will produce HF."(10) The second chemical produced would be the ammonium ion. A direct comparison between the compounds is difficult. HF is a gas which condenses at 20°C to form a colorless liquid. This 100% strength chemical is referred to as anhydrous HF. This is unlike other acids which are gasses dissolved into water. When diluted with water, it is named by the percent of solution such as 70% HF solution. The recommended strength to clean quartz is "10% by solution of ABF or 7% by volume of HF. (11) ABF, is a white powder that is dissolved in water; users must be careful to mix to the prescribed concentration.

MSDS sheets using the HMIS or NFPA rating systems list HF as a 4, meaning accidental exposure can cause injury or death. This is the most severe classification. ABF is either listed as a 3 or 4. The lower rating may be because a powder offers some protection over a corrosive liquid. However, it is still fatal. An ABF salesman in New York City died because he was handling the powder without using gloves. Both compounds are acids and exposure should be treated in the same way. The pH varies depending on the concentration of ABF in water 10 mg/l water will produce 3.38 and 100 mg/l will produce 2.88 pH. HF is 3.18 pH at near 1% concentration by weight, and 4.5 at 8%. A neutral solution of water is 7 pH.

If you are injured and have not previously contacted your emergency medical responders or emergency room about your use of HF, you will endure severe pain longer than needed and you may have longer lasting injuries. A common problem is confusion by the medical staff about the acid that caused the injury. Do not say: ”I was burned by hydrofluoric acid,” because this is commonly misconstrued as hydrochloric acid. One glassblower was treated incorrectly for a hydrofluoric acid injury and had to go to the emergency room three times because of this type of misunderstanding. By the time he was finally treated, he had lost his thumb down to the first knuckle. Use the term “HF acid” and make sure that you are being treated correctly.

The best antidote at this time for HF and ABF burns is calcium gluconate in a cream. The gel has a shelf life that may be extended by placing it in the refrigerator. A supply should be near the acid sink for immediate use in case of injury. Liquids are used in the treatment of eyes and for injections. Treatments are being reviewed and improved constantly; check with your safety officer for the latest information. Current recommendations for the initial water rinse vary between 5 and 15 minutes of water. Start treatment as soon as possible. Damage will be minimized by removing and neutralizing the fluorine as quickly as possible. If clothing is contaminated, quickly remove it. Rescuers should wear protective gloves themselves, so they do not become injured. Call an ambulance as soon as somebody is injured. Apply calcium gluconate gel immediately after the rinse. The gel is quite slippery so it is not recommended that you drive yourself to the hospital. All HF and ABF burns should be treated medically.

In conclusion, HF and ABF are helpful chemical cleaners that must be treated with respect. It is advisable to avoid their use if at all possible. If you are going to use these compounds, make sure you follow the latest safety precautions starting with notifying your local medical providers.

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Footnotes:

- 1) Bob Kell, "Fatality due to acute HF exposure Adapted from*:* *Universities Safety Assn. Digest,* Vol. 59, April 1997*,*" *University of Houston Environmental and Physical Safety.* April 29, 2006 <www.uh.edu/admin/srmd/hfexposure.html>
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- 2) "Honeywell Hydrofluoric Acid" (PDF file page 7), *Honeywell International Inc*., 2006. June 15, 2006 http://www.honeywell.com.merx.npoint.servlets.DocumentServlet?docid=DC63633A9-2871-90C6-BD48-1EE9B2F67D38

- 3) "Honeywell Hydrofluoric Acid" (PDF file page 6), *Honeywell International Inc.*, 2006. June 15, 2006 <http://www.honeywell.com.merx.npoint.servlets.DocumentServlet?docid=DC63633A9-2871-90C6-BD48-1EE9B2F67D38>

- 4) "Occupational Safety and Health Guideline for Hydrogen Fluoride," *Occupational Safety & Health Administration* (Circa 1996). June 15, 2006 <http://www.osha.gov/SLTC/healthguidelines/hydrogenfluoride/recognition.html>

- 5) "A Companion to the NIOSH Pocket Guide to Chemical Hazards , Table H, 12," *National Institute for Health and Safety,* April 1999. June 19, 2006 <http://www.cdc.gov/niosh/ncpc/hcpc.html

- 6) "Occupational Safety And Health Guideline For Hydrofluoric Acid," *U.S. Department of Labor Occupational Health and Safety*, 1996. June 15, 2006 <http://www.osha.gov/SLTC/healthguidelines/hydrogenfluoride/recognition.html>

- 7) *Hazardous Substance Fact Sheet (Hydrogen Fluoride,* New Jersey Department of Health and Senior Services (1992). Trenton: NJ.

- *8)* James R. Bennion, MD, MPH, Major USAF & Alfred Franzblau, MD, "Chemical Pneumonitis Following Household Exposure to Hydrofluoric Acid," *American Journal of Industrial Medicine* 31 (1997): 474-478.

- 9) Scott Bankroff, "Polypropylene Scientific Glassblower's Sink," Fusion. LII.1 (February 2005): 25-26.

- 10) "Solvay Fluorides," *Ammonium Bifluoride,* page 3 (2003). June 15, 2006 <http://www.solvaychemicals.us/static/wma/pdf/5/1/0/3/ABF.pdf>

11) "Fused Quartz Properties & Usage Guide GE Type 214, 214LD and 124, guidelines for usage and cleaning," *National Scientific*, 1995. August 17, 2006 <http://www.quartz.com/gedata.html#guide>