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Research Article

Lessons Learned—Fluoride Exposure and Response

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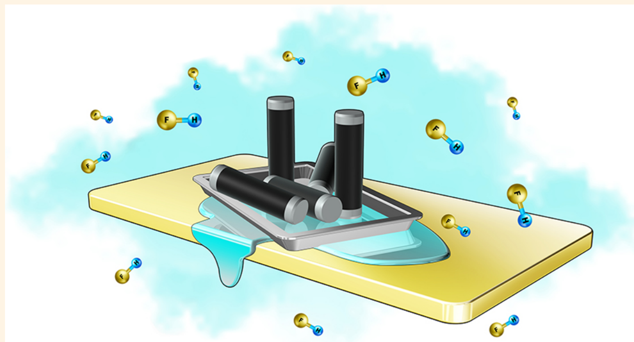
ABSTRACT: Laboratory research can expose workers to a wide variety of chemical hazards. Researchers must not only take personal responsibility for their safety but also inevitably rely on coworkers to also work safely. The foundations for protocols, requirements, and behaviors come from our history and lessons learned from others. For that reason, here, a recent incident is examined in which a researcher suffered hydrofluoric acid (HF) burns while working with an inorganic digestion mixture of aqueous HF (8%) and nitric acid (HNO_3, 58%). HF education is critical for workers because delays in treatment, improper treatment, and delay of symptoms are all factors in unfavorable outcomes in case reports. While the potential severity of the incident was elevated due to bypassed engineered controls and lack of proper personal protective equipment, only minor injuries were sustained. We discuss the results of a causal analysis of the incident that revealed areas of improvement in protocols, personal protective equipment, and emergency response that could help prevent similar accidents from occurring. We also present simple improvements that anyone can implement to reduce the potential consequences of an accident, based upon our lessons learned.



KEYWORDS: *hydrofluoric acid, exposure, personal protective equipment, lessons learned*

■ HF HAZARDS AND PREVIOUSLY REPORTED HF INCIDENTS

Hydrofluoric acid (HF) is an important chemical in a variety of industries worldwide. Most hydrofluoric acid is consumed in the manufacture of fluorine-containing chemicals, metal pickling, and petroleum alkylation. However, HF is used in a multitude of applications requiring manual manipulation of the acid and can also be produced during various chemical reactions, for example, alkyl carbonate solutions of lithium hexafluorophosphate.[1]

HF exists as a gas or as an aqueous liquid with concentrations ranging from parts per million levels to nearly 100% anhydrous acid. While HF is very corrosive to human tissue, it is also a powerful systemic toxin, directly destroying skin, eye, bone, and tendon tissue. Acute fluoride poisoning from dermal, ocular, respiratory, or gastrointestinal exposure can cause severe organ damage, gross electrolyte imbalance in the blood, cardiac arrest, and even death.[2−5]

At any concentration, the HF molecule can be drawn through the skin. Aqueous solutions greater than 70% HF can penetrate the dermis layer of the skin within 5 min, while symptoms of solutions weaker than 14.5% acid can have a significant delay in presentation.[5,6] Decontamination to mitigate damage from exposure needs to be prompt and specific to address both corrosive and toxic aspects of exposure. Due to the severity, multisystem affliction, and the possibility of delayed harm, HF exposures often result in inpatient treatment and monitoring.[7] Table 1 lists select case studies to illustrate the dangers of HF and the varying long-term outcomes based on response and treatment.

While large quantities of HF are used in a variety of industries, HF is present in academic and national laboratories as well. It is commonly used in materials research, chemical research, metallurgical/environmental/geological laboratories, silicon chip etching, and ceramics production, among others. The high risks of HF use, illustrated in academic and industrial exposures,[1−11] have driven some, such as Carnegie Mellon University, to implement comprehensive hydrofluoric acid safety programs outlining guidelines, standard operating procedures (SOPs), training, and first aid kits.[12]

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Table 1. Case Study Illustrating the Dangers of Hydrofluoric Acid

concentration	description	treatment	outcome
10%	Dermal hand exposure for several hours. 1st and 2nd degree burns.	Calcium gluconate infiltration after burns appeared.	Full resolution after 3 week recovery from damage to index finger tendon.[8]
5%	Pin-hole in glove used for protection during a 4 h task.	Sought help at a doctor's office after burn appeared, no calcium applied.	Pain continued for 4 days; severe pain under the fingernail. Affected finger amputated due to bone demineralization.[8]
anhydrous gas	Full-body exposure, ocular exposure, inhalation.	Calcium gluconate to all burned surfaces of skin, nebulized calcium gluconate for lungs.	Full recovery in 3 months.[8]
concentrated	Acid spray to the eyes, severe damage to the eyes and eyelids.	Immediate and profuse water irrigation.	Full recovery after 35 days.[9]
20%	3% body area burns to the thigh.	Immediate irrigation and application of calcium gluconate gel.	Cardiac arrest 16 h after exposure from systemic toxicity, resuscitated successfully, and successfully treated with calcium, magnesium, and potassium supplementation.[10]
60%[a]	Dermal exposure of about 30% of the body.	None documented.	Death from systemic toxicity/cardiac arrest 30 min after exposure.[11]

[a]The 60% concentration case study is a fatality.

■ WHAT HAPPENED?

On a late Friday afternoon, a researcher was performing a microwave acid digestion of a refractory metal alloy using an 8% HF solution, made from a combination of 10 mL of HNO_3 (70%) and 2 mL of HF (48%). During the workup of digested replicates, the researcher was in a seated position while at a scale transferring, diluting, and weighing the finished samples. The samples were in digestion vessels, loosely capped, on an unsecured tray. While transferring, one of the top-heavy, unsecured microwave vessels containing concentrated HNO_3 and HF was knocked over, causing a chain reaction resulting in 4 vessels (48 mL of 8% HF/58% HNO_3) spilling and landing in the lap of the researcher (Figure 1). The sitting researcher, who was not wearing a face shield, had liquid splash up onto their chin and mouth area. Feeling the burn of the HNO_3, they made their way to a sink where, with the help of a second researcher (with only nitrile gloves as personal protective equipment, PPE), the individual's face and mouth were rinsed with copious amounts of water, and calcium gluconate gel was applied to the area. The uninjured researcher removed the individual's contaminated PPE and retrieved two researchers from an adjoining laboratory. With the additional support, one researcher continued to apply calcium gluconate gel; one called the onsite emergency personnel, and one went to meet paramedics, briefing them on the way to the laboratory. Following initial assessment and treatments, the paramedics proceeded to transport the injured researcher to the hospital for additional treatments. Fortunately, the only permanent injury was the loss of tooth enamel from the tooth that encountered the acid. At the time of the incident, the researcher was wearing a laboratory coat, plastic laboratory apron, splash goggles, and acid-resistant gloves.

Figure 1. Post-accident photo of the spill area. Unsecured vessels were transferred using an insufficient secondary containment (similar to a lunch tray) which was incapable of containing a spill. Discoloration on the chair is due to acid damage.

■ WHAT WAS THE CAUSE?

As a Department of Energy subsidiary, a root causal analysis was conducted by Environment, Safety, and Health (ES&H) personnel using a barrier analysis method,[13] determining causal factors and context surrounding the accident. These were examined through the lens of the "Hierarchy of Controls" which includes elimination/substitution, engineering controls, administrative controls, and personal protection equipment. Regarding elimination/substitution, the researcher did reduce the HF concentration from 25% HF to 8% HF in HNO_3/water; however, complete acid digestion of the refractory metal alloy was not possible without the presence of HF. This is due to fluoride mediated solubility of refractory elements in water and its role in preventing the production of insoluble oxides.[14]

The remaining hazard controls were examined in-depth through interviews, an examination of the laboratory space/equipment, and causal meetings with ES&H and emergency response teams. At the time of the incident, all researchers involved in the spill and emergency response met the minimum restrictions in place to work with HF, including the researcher performing the digestion. One of these requirements was an HF hazard safety course provided to educate on HF hazard awareness, accident prevention, and emergency response, which each researcher had taken within the year. In addition to the safety course, researchers were required to illustrate in a laboratory setting their understanding of a laboratory-specific HF work control authorization agreement, primary hazard screening assessment, and standard operating procedure (SOP). These documents described not only HF hazards and procedures but also the engineering controls and PPE required to perform HF activities. In addition, there were no previous

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"near misses", incidences, or laboratory inspection findings involving HF.

Despite the training, hazard screenings, operating procedures, engineered controls, and available PPE, the causal analysis revealed that a multitude of issues contributed to the incident and the severity of the incident, including the following:

- The fume hood, designed to protect from the respiratory threat of HF and provide some splash protection, was not utilized to dilute samples during the incident.
- The "secondary container" meant to prevent and contain spills was insufficient for this task, providing no support to prevent vessels from tipping and insufficient volume to hold spills. This issue was compounded by the risk of the microwave digestion vessels themselves, which when outside of their cartridges, as in this case, did not provide any type of seal.
- Due to bypassing engineered controls, PPE was critically relied upon as a control, even though PPE is the least effective control in the hierarchy of controls. During the incident, the face shield required for HF laboratory use was not worn. The only injury caused by the spill was to the face.
- The laboratory established a two-person rule to ensure emergency support in the case of an HF incident, which was not implemented. The researcher handling HF was fortunate another researcher was passing through the laboratory at the time of the incident.
- Due to the timing of personnel turnover, there was very little overlap between the researcher and their predecessor. Longer on-the-job training should have been implemented to instill the importance of the hazard controls and procedures.
- Postincident laboratory inspection revealed tidiness/space issues on laboratory countertops.

Considering all of these causal relationships, the root cause of the incident was determined to be a low level of regard for the dangers of HF by the researcher performing the HF digestion procedure, leading to inconsistent use of the protective controls. Often the respect researchers give to dangerous chemicals comes from mentors and lessons learned stories. In this case, the healthy fear most carry for HF was not displayed.

WHAT CORRECTIVE ACTIONS WERE TAKEN?

By determining the causal relationships that led to the incident, solutions were developed to prevent future acid-related incidences:

- An automated liquid handler/dispenser has been added to the laboratory. This robotic system operates in a closed, ventilated box and has the capability of dispensing and diluting acids, including HF, while separating the operator completely from exposure during these steps. This system reduces acid handling and reliance on PPE.
- New microwave vessels can now be used as a separation device. They can be safely sealed, secured in a specially designed tray (Figure 2), and handled outside the hood at room temperature.
- The HF hazard training, a work control agreement, operation procedures, and primary hazard screening have been updated and clarified to ensure fewer "judgment calls" on the correct engineering and PPE controls to use.

Figure 2. Specially designed Teflon microwave vessel holder. The weight and shape of the holder decrease tipping hazards.

- The number of signs warning of HF use and identifying the emergency response stations has been greatly increased.
- On-the-job training has intensified, ensuring not just a clear understanding of the dangers and requirements but also supervision during digestion procedures. This includes continued use of the "two-person rule".
- Administrative procedures continue to dictate that HF work must never be performed alone or after hours. One challenge during the incident was that an onsite clinic was closed (3:00 PM Friday), and the injured individual was taken to an offsite, city hospital which was further away.
- Procedures now require that any HF exiting the fume hood or liquid dispenser must be diluted to less than 1% HF concentration and less than 20% total acid concentration or be fully sealed in a microwave digestion tube, all while dawning full HF designated PPE and continuously practicing good laboratory behaviors. Training on proper sealing of microwave tubes is provided.
- PPE was reviewed and improved, and researchers were trained in the correct use of multilayered protection (Figure 3). Improvements to the PPE included replacing older acid gloves with new Trionic O-240 long-cuffed chemical gloves, chosen due to the glove's high breakthrough times (390 min) specifically for concentrated HF and acid solutions.[15] Note: Trionic gloves should only be used once and should be sealed until the time of use, as long exposure to air will degrade the gloves, allowing the potential for pin-hole formation.
- The incident was presented at an internal "lunch-n-learn", illustrating the incident and the corrective actions to other material and chemical research groups. This resulted in improvements in the type of PPE used in multiple other laboratories.

HOW CAN INCIDENCES LIKE THIS BE PREVENTED?

Although this incident was the result of improper or lack of utilization of safety controls, the causal analysis revealed areas for significant improvements to controls and emergency protocols to prevent HF incidences from occurring while ensuring that any HF incident or exposure will be responded to correctly. Moving beyond the specifics of this incident, Table 2 provides recommendations for safe utilization of HF in a laboratory setting, and are all actions that have been implemented since the incident.

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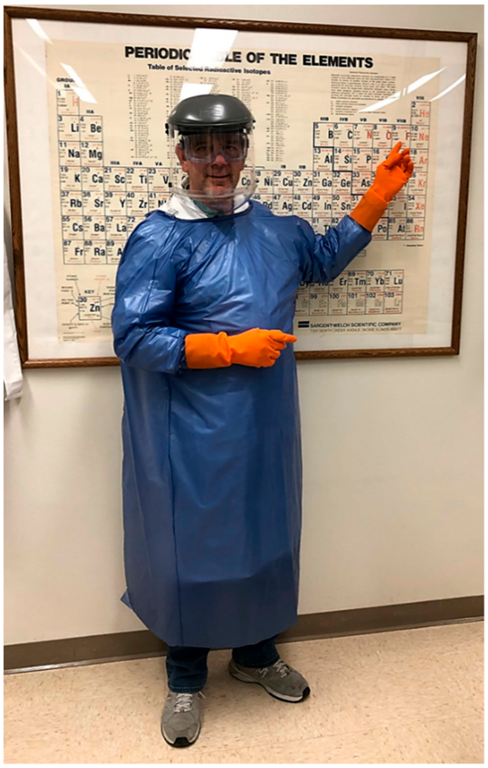

Figure 3. Demonstration of essential PPE required for protection from HF spills. These include close-toed shoes, long pants, vapor protecting chemical splash goggles, plastic apron with full-length sleeves and upper chest protection, face shield with chin splash protection, and nitrile gloves under HF-resistant gloves (Trionic O-240).

■ QUICK ACTION TIPS AND HF EXPOSURE EMERGENCY PROTOCOL

Every emergency will be different. This incident highlights the need to have additional personnel prepared for and trained in HF exposure emergency protocol. During the emergency response, the researchers implemented correct response protocols, even introducing some steps that later became protocol. With this fast, proper response, injuries were minimal and permanent damage limited. With an exposure of skin to HF, the following steps are crucial to limiting permanent injury:

(1) Immediately wash affected areas with copious amounts of water. If possible, use an emergency shower to ensure that no exposed areas are missed. Remove all clothing and jewelry to ensure that trapped HF is also removed.
(2) Immediately after the water rinse, apply a generous amount of Calgonate gel and continuously massage into the exposed areas. Reapply every 10−15 min until medical support arrives. If Calgonate gel is unavailable, rinse with water for at least 15 min or until medical support arrives.
(3) If the exposed individual can rinse and apply the calcium gluconate themselves, a supporting individual should call 911 and inform the dispatcher/medical personnel of the exposure to HF. If the individual is incapable of rinsing and applying calcium gluconate, the supporting individual should help rinse and apply gel prior to calling 911. (Note: The assisting individual should wear appropriate PPE before helping the exposed individual. This ensures that they do not contaminate themselves in the process.)

Note: Privacy curtains and after-shower kits can make emergency response more comfortable and reduce hesitation to disrobe. Kits can include flip-flops, robes, towels, and bags for contaminated clothes and shoes.

Additional Exposure Tips. Emergency personnel and physicians will be able to better treat the injuries and situation with the following information:

(1) Summary of first aid given.
(2) What body parts were known to be exposed? When and how was the individual exposed? How long was the exposure?
(3) What concentration of HF was the individual exposed to?
(4) Areas of the laboratory that may have residual HF.

■ CONCLUSION

Accidents happen. Understanding the dangers of what you are working with, having safety protocols in place, following those protocols, and knowing how to respond in the case of an accident are what saves lives. Learning from not just your history but also lessons learned from others can lead to simple improvements in procedure and response which can reduce

Table 2. Recommendations to Ensure the Safe Utilization of Hydrofluoric Acid (HF) in a Laboratory Setting

preparation	Review the MSDS for hydrofluoric acid (HF) and any byproducts that could be formed in the specific process in which HF is being utilized.[16]
	Create/review the SOP for the use of HF in the specific process being performed.
	Ensure Calgonate (2.5% calcium gluconate gel[17,18]) and spill kits are on hand, and review first aid procedures.
	Review the location of the safety shower and eyewash.
	Ensure that these water sources are functioning properly and have been routinely flushed.
	Never work with HF after hours.
	Ensure "buddy" is present, trained, understands the risks of HF, and can provide first aid in the case of emergency. Review operating procedures with them.
	Inspect PPE for pinholes or excessive wear.
during use	Don the PPE, both operator and "buddy", inspecting again for pinholes or wear.
	Use clearly labeled HF compatible containers, such as Teflon, that have sufficient support to ensure that the containers cannot tip over.
	Work within HF compatible secondary containment capable of containing spills.
	Keep containers with HF closed when not actively in use.
	Post signage, "HF in use", on doors.
	Alert additional personnel, and make sure they are available for support (e.g., calling 911, meeting and directing emergency responders to the laboratory).
transportation	Do not transport unsealed HF containers.
	Use HF compatible secondary containment to contain potential spills.

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the potential consequences of an incident. Here, we openly shared a traumatic incident in which a researcher was exposed to hydrofluoric acid. While engineering controls, administrative controls, and personal protective equipment were bypassed, the quick, proper emergency response minimized the injury to the researcher, with tooth enamel loss being the only permanent effect. Even though it was determined that the bypassing of the hierarchy of controls was the cause of the accident, we strive to make continual improvements to the control and response protocols.

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Author Contributions

The manuscript was written through the contributions of all authors.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

HF, hydrofluoric acid; HNO_3, nitric acid; PPE, personal protective equipment; SOP, standard operating procedure

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