WHEN SECONDS COUNT – A HYDROFLUORIC ACID SAFETY MANAGEMENT PROGRAM FOR FIELD EMPLOYEES AT THE PADUCAH GASEOUS DIFFUSION PLANT

T. A. Deecke
Weston Solutions, Inc.
297 Kentucky Avenue, Kevil, Kentucky 42053

M. Stidham, J. M. Hylko
WESKEM, LLC
297 Kentucky Avenue, Kevil, Kentucky 42053

ABSTRACT

The Paducah Gaseous Diffusion Plant (PGDP) uses a gaseous diffusion enrichment process to increase the percentage of uranium-235 (U-235) above natural concentrations in uranium hexafluoride (UF_6). As part of the safety analysis for the PGDP, a source term evaluation was performed based on various worst-case scenarios releasing UF_6 that undergoes an instantaneous exothermic reaction with atmospheric water to form particulate uranium oxy fluoride aerosols (UO_2F_2) and hydrofluoric acid (HF) vapor. Specifically, HF is a highly corrosive irritant that can cause acid burns to the skin and lungs, and the fluoride ions can cause metabolic poisoning in large quantities. Also, inhaling concentrated HF vapor would likely be fatal. To protect field employees against the adverse effects of HF and other substances found at the PGDP, engineering, administrative and personal protective equipment (PPE) controls are used in concert with the Department of Energy’s Integrated Safety Management System (ISMS). Although an HF exposure event has never occurred on a WESKEM Paducah project, timeliness in response - even applying basic first aid before medical help is available - can reduce injury severity prior to the employee receiving treatment from a physician. Symptom recognition and on-the-spot treatment for HF exposure are very unique and specialized when compared to treating other types of chemical exposures. To address timeliness in response, i.e., when seconds count, WESKEM and Weston Solutions, Inc. Environmental, Safety and Health (ES&H) employees developed an in-house HF safety management program. This program reassures that employees: 1) are informed of the properties, handling, storage and cleanup of HF, and 2) are familiar with interim first-aid measures following an HF exposure. Additional benefits come from reviewing this program with the local medical provider beforehand to verify that they are capable of providing follow-up treatment resulting from any off-normal events involving HF.

INTRODUCTION

The Paducah Gaseous Diffusion Plant (PGDP) uses a gaseous diffusion enrichment process to increase the percentage of uranium-235 (U-235) above natural concentrations in uranium hexafluoride (UF_6). In the process, solid UF_6 containing about 0.7% U-235 is heated to form a gas that is fed through a series of diffusion stages. These stages then concentrate (i.e., enrich) the U-235 to about 3% to 5%. As part of the safety analysis for the PGDP, a source term evaluation was performed based on various scenarios, such as a seismic event. Based on this scenario, certain buildings, roof beams, and equipment are predicted to collapse and expansion joints between piping and equipment are predicted to fail releasing UF_6 into the building. The release can be sudden or dispersed over a period of time depending on plant operating conditions, such that the UF_6 undergoes an instantaneous exothermic reaction with atmospheric water to form particulate uranium oxy fluoride aerosols (UO_2F_2) and hydrofluoric acid (HF) vapor (1, 2) shown in equation 1.

$$UF_6 + 2H_20 \rightarrow UO_2F_2 + 4HF + heat \qquad \text{Eq. 1}$$

Depending on the degree of atmospheric conditions and turbulence induced by other scenario factors, about 61% of the UO_2F_2 aerosols are predicted, based on calculational models, to settle down onto the floor or surrounding equipment during the first 200 seconds; another 25% settles down over the next 300 seconds; and the remaining 14% settles over the next 24 hours.

The HF is the major portion of the release cloud and is buoyed by the heat of reaction and dispersion by atmospheric conditions (e.g., wind). Environmental impacts from UO_2F_2, HF and other radioactive and non-radioactive substances released from the PGDP are discussed elsewhere (3).

The Reaction Produces Compounds with Differing Toxic Effects

Areas coming in contact with the dispersed uranium particulate material require decontamination. In addition, the uranium in the UO_2F_2 acts as a heavy metal affecting the kidneys. Therefore, employees responsible for these efforts would use engineering, administrative and personal protective equipment (PPE) controls to prevent employee exposure. Both radiological and non-radiological bioassay methods are available for monitoring employee exposure to uranium (4).

Hydrofluoric acid can cause acid burns on the skin and lungs, and fluoride ions can cause metabolic poisoning in large quantities. Also, inhaling concentrated HF vapor would likely be fatal. An exposure event is most likely to occur following a release of either HF vapor or liquid from process equipment, cleaning up a spill, or during remediation activities. For example, even after conducting extensive pre-planning activities and collecting field dose-rate surveys to identify the presence of UO_2F_2 and other radioactive sources, Watson, *et al.* (5) has shown there is always a potential of encountering aqueous HF in containers during remediation of uncharacterized waste collection areas. To address this issue, Watson, *et al.* (5) and Hylko (6) provide engineering, administrative and PPE controls in concert with the Department of Energy's Integrated Safety Management System (ISMS) (7, 8) to protect field employees against the adverse effects of UO_2F_2, HF and other substances found at the PGDP.

Although an HF exposure event has never occurred on a WESKEM Paducah project, timeliness in response - even applying basic first aid before medical help arrives - can reduce injury severity prior to the employee receiving treatment from a physician. Prompt first aid is essential because of the fluoride ion's toxicity and ability to move through the body. Symptom recognition and on-the-spot treatment for HF exposure are very unique and specialized when compared to treating other types of chemical exposures. To address timeliness in response, i.e., when seconds count, WESKEM and Weston Solutions, Inc. Environmental, Safety and Health (ES&H) employees developed an in-house HF safety management program. This program consists of informing employees about the properties, handling, storage and cleanup of HF and interim first-aid measures following an HF exposure. Also, it is recommended that this information be communicated to the local medical provider beforehand to verify that they are capable of providing follow-up treatment resulting from any off-normal events involving HF.

Properties of HF

Hydrofluoric acid, also referred to as hydrogen fluoride, (CAS# 7664-39-3) is a clear, colorless and highly corrosive fuming liquid with a strong irritating, acrid odor that readily reacts with water to form dense white clouds. Hydrofluoric acid is primarily an industrial raw material used in iron and steel foundries, metal finishing, surface cleaning, petroleum refining, mineral processing and digesting, glassmaking (i.e., etching), as well as manufacturing stainless steel, aluminum, inorganic and organic chemicals, electronic components and UF_6. Hydrofluoric acid produces adverse effects at the point of contact (which is usually the skin, eyes, and respiratory tract), is not listed as a carcinogen, and has a National Fire Protection Association (NFPA) hazard rating of Health = 4, Flammability = 0, Reactivity = 1. Table I summarizes the various exposure guideline limits for HF (9, 10).

Table I. Exposure Guideline Limits for HF

Exposure Guidelines	Limits
ACGIH Threshold Limit Value (TLV)	3 parts per million (ppm) – Ceiling
OSHA Permissible Exposure Limit (PEL)	3 ppm – Time-Weighted Average (TWA)
Biological Exposure Index (Pre-Shift)	3 mg (F^-) per gram creatinine in urine
Biological Exposure Index (Post-Shift)	10 mg (F^-) per gram creatinine in urine
OSHA Short-Term Exposure Limit (STEL)	6 ppm (15 minutes)
NIOSH Immediately Dangerous to Life or Health (IDLH)	30 ppm (30 minutes)
Emergency Response Planning Guide 1 (ERPG-1)[a]	2 ppm (60 minutes)
Emergency Response Planning Guide 2 (ERPG-2)[b]	20 ppm (60 minutes), 50 ppm (10 minutes)
Emergency Response Planning Guide 3 (ERPG-3)[c]	50 ppm (60 minutes), 170 ppm (10 minutes)

a: ERPG-1 - The maximum level below which nearly all individuals could be exposed up to one hour without experiencing other than mild, transient adverse health effects.
b: ERPG-2 – The maximum level below which nearly all individuals could be exposed for one hour without developing irreversible health effects or symptoms which would impair taking protective action.
c: ERPG-3 - The maximum level below which nearly all individuals could be exposed for one hour without experiencing or developing life-threatening health effects.

Monitoring of urine for fluorides is an accepted method for determining exposure. Urine fluoride levels above 3 mg/g creatinine at the beginning of a work shift, or above 10 mg/g creatinine at the end of a work shift, may indicate excessive absorption of fluoride. It should be noted that fluorides are often present in significant amounts in persons not occupationally exposed (e.g., dietary sources of fluoride such as tea), and that the urine fluoride determination is not specific for HF (9).

Handling, Storage and Cleanup of HF

The handling and storage of HF in incompatible containers can generate considerable amounts of heat, thereby increasing pressure to cause the container to explode. Glass, concrete and other silicon bearing materials can yield silicon tetrafluoride gas. Pressure buildup from this reaction has been known to rupture containers. Carbonates, sulfides and cyanides can yield toxic gases such as carbon dioxide, hydrogen sulfide and hydrogen cyanide, respectively. Alkalis and some oxides can cause strong violent exothermic reactions, and HF can react with certain metals generating hydrogen gas. As a result, wax bottles were routinely used by laboratories (ca. 1950s) for storing HF. Hydrofluoric acid is corrosive to many materials including glazes, enamels, pottery, concrete, leather, natural rubber and many organics. For large-quantity industrial purposes, the HF is typically stored and shipped in special rubber-lined containers (e.g., rail cars and tanks). Figure 1 shows that the preferred types of small-quantity containers for storing HF are made from either polyethylene or Teflon® materials.

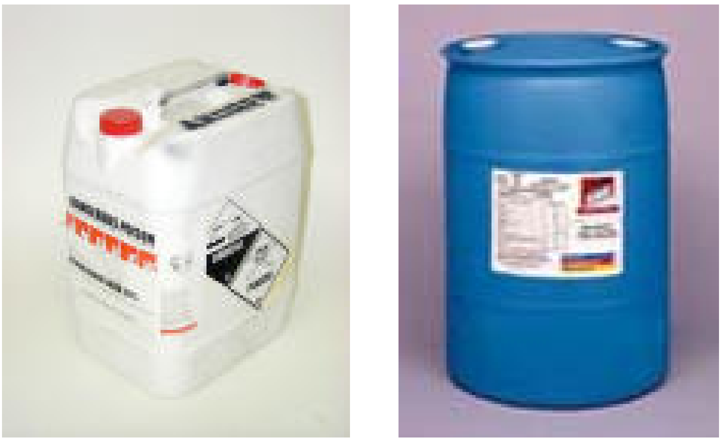

Fig. 1. Preferred types of containers for storing HF

Precautions must also be taken during the cleanup of HF. Adding water to dilute an HF spill would result in a violent exothermic reaction causing the acid to splatter endangering nearby employees. In addition, the reaction would create a large white cloud resulting in an airborne vapor hazard reducing visibility in the cleanup area. When possible, always "add acid" to water when diluting a concentrated acid such as HF. Furthermore, it requires copious amounts of water on a logarithmic scale to increase the pH of the HF. For example, to increase the pH from zero to one (0-1) requires approximately 38 liters (10 gallons) of water; from one to two (1-2) requires approximately 380 liters (100 gallons) of water, etc. However, instead of using water to respond to an HF spill, a common approach in the field is to use a buffer solution, such as KOLORSAFE® Liquid Acid Neutralizer, which consists of a weak base and color indicator to visually show that the acid has been neutralized (11). For small manageable spills, Table II summarizes a variety of alkaline materials (i.e., bases) to neutralize HF (12).

Table II. Typical Alkaline Materials Available to Neutralize HF

Alkaline Material	Common Names	Form Available	Hazards and Reactions	Amount of Material Required for Neutralization
Sodium Hydroxide (NaOH)	Caustic Soda	100% Solid Beads or Flakes, <50% Solution	Very high heat of dilution and neutralization	4.0 kg per kg of 100% HF
Potassium Hydroxide (KOH)	Caustic Potash	85% Solid Beads or Flakes, <45% Solution	Very high heat of dilution and neutralization	6.2 kg per kg of 100% HF
Sodium Carbonate (Na_2CO_3)	Soda Ash	Dry Powder	Rapid evolution of carbon dioxide gas (CO_2)	2.9 kg per kg of 100% HF
Sodium Bicarbonate ($NaHCO_3$)	Bicarb Baking Soda	Dry Powder	Rapid evolution of carbon dioxide gas (CO_2)	4.2 kg per kg of 100% HF
Calcium Carbonate ($CaCO_3$)	Limestone	Pebbles	Slow reaction, slow evolution of carbon dioxide gas (CO_2)	2.7 kg per kg of 100% HF
Calcium Oxide (CaO)	Quicklime	Dry Powder	Very high heat of hydration and neutralization	1.5 kg per kg of 100% HF
Calcium Hydroxide [$Ca(OH)_2$]	Hydrated Lime	Dry Powder Slurry in Water	High heat of neutralization, slippery when wet	2.0 kg per kg of 100% HF

Exposure to HF (13, 14)

The following sections provide symptomatic reactions of the human body following HF exposure to the skin/dermal area and eyes, as well as resulting from inhalation and ingestion.

Skin/Dermal Area

Direct exposure to either HF liquid or concentrated vapors can cause immediate severe burning, pain and a whitish discoloration of the skin which usually proceeds to blistering, necrosis (i.e., a mortification or gangrene of bone, or the death of a bone or portion of a bone *en masse*, as opposed to its death by molecular disintegration) or ulceration. Table III summarizes the time it takes to observe clinical signs or symptoms following exposure to varying HF concentrations.

Table III. Time to Observe Clinical Signs or Symptoms Following Exposure to Varying HF Concentrations

HF Concentration	Time to Observe Clinical Signs or Symptoms
>50%	Immediately apparent
20% - 50%	1-8 hours
<20%	Up to 24 hours

Furthermore, because HF is absorbed into the bloodstream, large or multiple burns totaling over 160 square centimeters (25 square inches) of body surface area can be fatal if not treated promptly and properly. The fluoride ion readily penetrates the skin causing deep tissue destruction and reacts with body calcium, as shown in equation 2.

$2HF + Ca^{2+} \rightarrow CaF_2$ Eq. 2

This is one of the major toxic effects of HF on body calcium that forms the basis for treatment. There is evidence that fluoride may combine with calcium and phosphate, so that five calcium ions are tied up for each fluoride ion [e.g. $Ca_5F(P0_4)_3$]. Unlike other acids that are rapidly neutralized, this process may continue for days if left untreated, causing changes to the exposed tissue, bones and joints.

The burns are usually accompanied by severe, throbbing pain from the irritation of nerve endings resulting from increased levels of potassium ions entering the extracellular space to compensate for the reduced levels of calcium ions causing hypocalcemia. Another major systemic poisoning is hypomagnesemia that alters the normal heteroionic exchange of calcium and magnesium at the bone surface. Magnesium is critically important in maintaining normal cell function, and symptomatic magnesium depletion is often associated with multiple biochemical abnormalities, including hypocalcemia. The organ systems commonly affected by magnesium deficiency are the cardiovascular system and the central and peripheral nervous systems.

Exposure to hydrofluoric acid has not been the subject of long-term toxicity studies or testing because it is a very strong irritant producing immediate symptoms. Instead, chronic toxicity studies following long-term exposure to other forms of fluoride (e.g., fluoride salts) have reported tooth mottling (i.e., characterized by white spots that do not reflect light or teeth turning yellow or brown) in children and sometimes osteosclerosis (i.e., abnormal hardness and density of bone) in adults and children. Skeletal fluorosis (i.e., a complicated illness caused by the accumulation of too much fluoride in the bones) is known to be associated with excessive exposure to fluoride compounds, but has not been reported as a consequence following exposure to HF.

Eyes

Both HF liquid and concentrated vapor can cause irritation or corneal burns to the eyes.

Inhalation

Mild exposure can result in irritation of the nose, throat and respiratory system and can cause swelling in the respiratory tract up to 24 hours after exposure. Onset of symptoms may be delayed for several hours. Severe exposure can cause nose and throat burns, lung inflammation and pulmonary edema (i.e., abnormal accumulation of fluid in the lungs often caused by congestive heart failure caused by the inability of the heart to maintain adequate blood circulation in the peripheral tissues and the lungs) including hypocalcemia.

Ingestion

Ingestion of HF can cause severe mouth, throat and stomach burns and may be fatal if swallowed. Even with small amounts of dilute solutions, profound and possibly fatal hypocalcemia is likely to occur unless medical treatment is promptly initiated.

On-the-Spot Treatment Recommendations Following HF Exposure

The following sections provide on-the-spot treatment recommendations following HF exposure to the skin/dermal area and eyes, as well as resulting from inhalation and ingestion. The treatments mentioned herein can be started while waiting for advanced medical treatment from a physician or during transport to a hospital.

Skin/Dermal Area

On-the-spot treatment, for example, is directed towards binding the fluoride ions to prevent deep-tissue destruction. Treatment consists of washing the area with plenty of water for approximately 5 minutes and then applying 2.5% of calcium gluconate gel that is continuously massaged into the burn area until pain is relieved. A responder must wear gloves when applying the gel to prevent secondary HF burns.

The gel is prepared by heating 395 grams of K-Y Jelly® to 50-60^{o}C and adding 2.5% by weight (9.9 grams) of reagent grade calcium gluconate slowly while stirring thoroughly until dissolved. The finished gel will be clear. Air bubbles can be removed by letting the bubbles rise to the surface after standing. The gel should be replaced every six months. The medications must be prepared ahead of time and available to be effective. They are not to be used in lieu of medical treatment.

For extensive burns where pain is present longer than 30 minutes, 5% aqueous calcium gluconate is injected beneath, around and in the burn area. Figure 2 provides examples of prepared solutions of calcium gluconate. Using local anesthetics is not recommended since a reduction in pain is an indicator of treatment effectiveness. Also, a small burned area (e.g., finger, hand) can be treated temporarily by immersion in Milk of Magnesia® while in transit to a hospital.

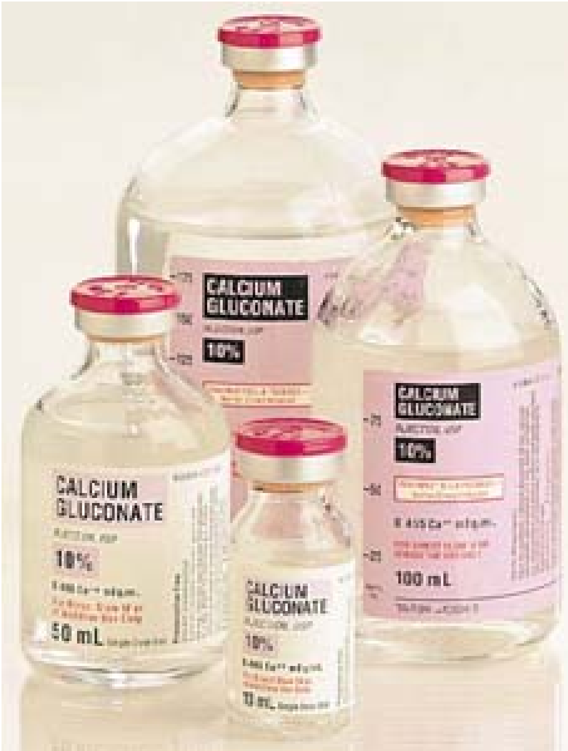

Fig. 2. Examples of prepared solutions of Calcium Gluconate.

Eyes

Treatment for this type of exposure consists of irrigating the eyes for at least 15 minutes with copious quantities of water, keeping the upper and lower eyelids apart and away from the eye during irrigation. Rubbing of the eyes is to be avoided. The next step is to seek competent medical attention immediately, preferably from an eye specialist. Although the solution described for skin treatment should not be used, it is acceptable to irrigate with 1% calcium gluconate in normal saline for 1 to 2 hours to prevent or lessen corneal damage.

Inhalation

Treatment for this type of exposure consists of moving the employee to fresh air, then keeping them lying down, quiet and warm. If breathing has stopped, artificial respiration should be started immediately. If available, 2.5% calcium gluconate in normal saline should be given using a nebulizer with oxygen.

Ingestion

A variety of treatments are available for this type of exposure consisting of drinking: 1) large amounts of water, 2) several glasses of milk, 3) several milliliters (ounces) of Milk of Magnesia®, or 4) grinding up and administering up to 30 antacid tablets with water. These treatments yield a soothing effect by diluting the ingested HF without inducing vomiting.

CONCLUSION

Hydrofluoric acid has a number of chemical, physiological and toxicological properties that make handling difficult and dangerous. In addition to severe acid burns on the skin/dermal surface, the fluoride toxicity can cause metabolic imbalances and life-threatening cardiac arrhythmias (i.e., a disturbance in the regular rhythm of the heartbeat). Even moderate exposures to concentrated HF can be fatal if left untreated. Furthermore, medical treatment is very specialized and differs from the treatment of other types of acid exposures. This HF safety management program was developed based on a review of the available literature and personal knowledge of the authors who have dealt with the health effects of HF directly. Although work control processes are already in place to prevent an HF exposure from occurring during routine field operations (7, 8), this program reassures that employees: 1) are informed of the properties, handling, storage and cleanup of HF, and 2) are familiar with interim first-aid measures following an HF exposure. Additional benefits come from reviewing this program with the local medical provider beforehand to verify that they are capable of providing follow-up treatment resulting from any off-normal events involving HF.

ACKNOWLEDGEMENT

The authors want to recognize and thank Carl Walter and Doris Becker for their assistance in preparing this paper.

REFERENCES

6. S. H. Kim, N. C. J. Chen, R. W. Schmidt and R. P. Taleyarkhan, Source Term Evaluation During Seismic Events in the Paducah Gaseous Diffusion Plant, ORNL/TM-13260. Oak Ridge National Laboratory/Lockheed Martin Energy Systems, Inc. Oak Ridge, TN. December 30, 1996.

7. Depleted UF6 Management Information Network, <http://web.ead.anl.gov/uranium/>.

8. Public Health Assessment - Paducah Gaseous Diffusion Plant (U.S. DOE), Paducah, McCracken County, Kentucky. Prepared by Energy Section, Federal Facilities Assessment Branch, Division of Health Assessment and Consultation, Agency for Toxic Substances and Disease Registry. Atlanta, GA. May 21, 2002. <http://www.atsdr.cdc.gov/hac/pha/paducah2/pgd_p6.html#envirg1.4.1>

9. Guide to Good Practices for Occupational Radiological Protection in Uranium Facilities, DOE-STD-1136-2000, Change Notice No. 3. U.S. Department of Energy, Washington, DC. December 2001.

10. D. D. Watson, J. F. Walter, J. M. Hylko, C. E. Johnson, and C. T. Wagner, “Experiences Using Level A and B Personal Protective Equipment to Remove High-Hazard Radioactive and Hazardous Constituents from a USDOE Material Storage Area.” Waste Management ’01 - HLW, LLW, Mixed Wastes and Environmental Restoration - Working Towards a Cleaner Environment. Tucson, AZ. February 25-March 1, 2001. Paper appearing in CD-ROM <21a\21a-5.pdf>.

11. 6. J. M. Hylko, “Using Engineering, Administrative and Personal Protective Equipment Controls to Remediate Hazardous and Radioactive Constituents.” The 9th International

Conference on Environmental Remediation and Radioactive Waste Management (ICEM ’03). Examination Schools, Oxford, England. September 21-25, 2003. Paper appearing in CD-ROM <D:\icem03\pdfs\4652.pdf >.

7. T. T. Potts, J. M. Hylko, and T. A. Douglas, “An Advanced Tool for Applied Integrated Safety Management.” Waste Management ’03 - HLW, TRU, LLW, Mixed, Hazardous Wastes and Environmental Restoration Waste Management, Energy Security, and a Clean Environment. Tucson, AZ. February 23-February 27, 2003. Paper appearing in CD-ROM <\wm03\pdfs\307.pdf>.

8. B. Bell, J. Ellington, L. Smith, and J. M. Hylko, “A Practical Approach for Integrating ISMS Into Everyday Waste Management Field Activities.” Waste Management ’04 - HLW, TRU, LLW, Mixed, Hazardous Wastes and Environmental Restoration Waste Management, Energy Security, and a Clean Environment. Tucson, AZ. February 29-March 4, 2004. Paper appearing in CD-ROM <D:\wm04\pdfs\4318.pdf >.

9. 2000 TLVs® and BEIs® – Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. The American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, OH. 2000.

10. Online NIOSH Pocket Guide to Chemical Hazards – Hydrogen Fluoride, <www.cdc.gov/niosh/npg/npgd0334.html >.

11. “KOLORSAFE® Liquid Acid Neutralizer,” Material Safety Data Sheet No. 1006. NPS Corporation, Green Bay, WI. July 16, 2002.

12. “Typical Alkaline Materials (Bases) for Neutralization of HF.” Download Technical Document Link HF Neutralization, <www.honeywell.com/sites/sm/chemicals/hfacid/>.

13. “Material Safety Data Sheet, Hydrofluoric Acid, Anhydrous.” Download Technical Document Link MSDS Number HF-0001, MSDS – Anhydrous HF, <www.honeywell.com/sites/sm/chemicals/hfacid/>. January 2004.

14. “Recommended Medical Treatment for Hydrofluoric Acid Exposure,” Download Technical Document Link HF Medical Book, <www.honeywell.com/sites/sm/chemicals/hfacid/>. May 2000.