FEATURE

# First aid for a unique acid, HF: A sequel

By Eileen B. Segal

**NEWS REPORT**

October 22, 1999: Robert Belk, a 48-year-old business owner, died at Grady Memorial Hospital after an exposure to hydrofluoric acid. Belk owned a company called Chemical Packaging near Atlanta, GA, which produced solutions for high-pressure washing. At the time of the accident, Belk was mixing a solution when a hose slipped out, saturating his clothes with 70% hydrofluoric acid. He hosed off with water, but rather than have his secretary call the paramedics, he drove himself to the hospital! Burns were found on both lower legs and his left arm, but it was the HF which went through his skin that caused his death the following day from respiratory and heart failure.[1]

The above accident, which occurred just before submission of this paper, illustrates a dire consequence of working with hydrofluoric acid without awareness of its extreme hazards and lack of preparedness. From the numerous queries I personally have received after publication of my first paper in 1998,[2] I conclude that there are still many more who could use information. And from a recent spate of inquiries on the SAFETY listserve, it appears that many have not established a protocol for HF exposure or heard of the current recommended methods of treatment. So a review/update to my first paper seems appropriate. In this sequel I want to discuss:

I. Review of HF hazards
II. Emergency procedures
III. Treatments
IV. 5 vs. 15 minutes of irrigation
V. Current status of Hexafluorine

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## I. REVIEW OF HF HAZARDS

Hydrofluoric acid (CAS 7664-39-3) is a high-volume chemical used in at least eight industries (see Figure 1), with production of 375,000 tons in 1998 and demand estimated to be 400,000 tons in the U.S. in 2002.[3] It is considered more hazardous than most chemicals in five out of six ranking systems[4]; it is ranked as one of the most hazardous compounds (worst 10%) to human health. Ray Campbell, REA, CCHO, at Varian, Inc., described his HF injury as "the most painful, disabling, scarring, long-term injury I have ever seen, and I am a Vietnam veteran." Concentrated HF covering 2% of the body can be fatal.

HF is a colorless, fuming liquid or gas with a strong, irritating odor. In concentrated forms it is a strong protonic acid, whereas dilute solutions are weak acids ($pK_a = 3$) that remain relatively nonionized but can penetrate the stratum corneum, the tough waterproof outer skin layer of dead cells, and penetrate deep into tissue layers.[5] Once absorbed HF dissociates rapidly at the physiological pH of 7.4.

$$HF \rightarrow H^+ - F^-$$

Toxic systemic effects occur when the electron-hungry fluoride ion penetrates and migrates into tissue to bind primarily with calcium, but binding to magnesium, sodium, and potassium can also occur.

$$Ca^{2+} + 2F^- \rightarrow CaF_2$$

$$Mg^{2+} + 2F^- + \rightarrow MgF_2$$

Without enough calcium (hypocalcemia) and magnesium (hypomagnesia), nerves fail and cell membranes collapse. In addition, excess potassium (hyperkalemia) can occur, which can lead to life threatening cardiac arrythmias (ventricular fibrillation). The adverse effects can progress for several days after exposure.

Surface involvement of weak solutions is minimal and may even be absent. Burns to the fingers and nail beds may leave the overlying nails intact. An insidious hazard is the fact that dilute solutions are indistinguishable from water.

The time to onset of symptoms is related to the concentration of the HF:

- At concentrations >50%: immediate burns appear with rapid destruction of tissue as noted by a whitish discoloration, usually proceeding to blisters, accompanied by severe pain. The pain is typically described as "deep," "burning," or "throbbing," and often out of proportion to apparent skin involvement.
- At concentrations between 20 and 50%: burns can be delayed 1 to 8 hr.



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**Hydrofluoric Acid**

| | |
|---|---|
| **CAS No.** | 7664-39-3 |
| **UN 1052** | (anhydrous) |
| **UN 1790** | (solution) |
| **Synonyms:** | hydrogen fluoride, fluoric acid, hydrofluoride, fluorine monohydride |
| **OSHA PEL** | 3 ppm |
| **Description:** | colorless gas or fuming liquid<br>disagreeable, pungent odor at <1 ppm<br>irritation of eyes and throat at 3 ppm |
| **Molecular weight:** | 20.0 daltons |
| **Boiling point** | 68°F (20°C) at 760 mmHg |
| **Specific gravity** | 0.99 at 19°F (−7°C) |
| **Vapor pressure** | 400 mmHg (54°F) |
| **Vapor density** | 0.7 (air = 1) |

**Miscible with water with release of heat**
**Nonflammable**

- At concentrations <20%: painful erythema may be delayed for up to 24 hr. Redness, burning, or pain may not show up until several minutes or even hours have elapsed. Thus the surface area of the burn is not predictive of effects.

## II. EMERGENCY PROCEDURES

Standard first aid for most corrosives is to flush the exposed area with water for 15 min. Then treatment by a professional can be administered. However, because of the dire consequences of HF exposures, the following first aid is recommended (based mainly on procedures used by AlliedSignal[6]).

### A. Skin Contact

1. Immediately (within seconds) shower or flush with plenty of water.
2. Remove all clothing while in the shower (remove goggles last; double-bag contaminated clothes).
3. If 2.5% calcium gluconate gel or 0.13% benzalkonium chloride is available, rinsing may be limited to 5 *min* [this is sufficient time to effectively remove HF from the skin; additional flushing time is unnecessary and will delay further treatment]. If neither neutralizing agent is on hand, continue to flush until medical help is available.
4. Continue with either step a or step b.
   a. Apply calcium gluconate gel (2.5%) while wearing impervious gloves. Massage the gel promptly and repeatedly into burned area until pain is relieved. If pain does not subside within 20 to 30 min, injections of 5% calcium gluconate by a professional may be needed.
   b. Immerse affected area in iced 0.13% benzalkonium chloride (Zephiran). Use ice cubes, not shaved ice in order to prevent frostbite. If immersion is not practical, use towels soaked with iced 0.13% benzalkonium chloride as compresses for the burned area. Change compresses every 2 to 4 min. Continue until pain is relieved (this may require hours).
5. Get medical help.

### B. Breathing Vapor

1. Immediately get to fresh air.
2. Call or have someone call a physician.
3. Breathe 100% oxygen (10 to 12 L/min flow rate) as soon as possible.
4. *Trained* personnel should provide calcium gluconate (2.5%) by nebulizer.
5. Get medical attention.

### C. Ingestion

1. Drink large amounts of water. Do not induce vomiting or administer activated charcoal.
2. Drink several glasses of milk or several ounces of milk of magnesia, Mylanta, Maalox, or similar product, or up to 30 Tums, Caltrate, or other antacid tablet.
3. Get immediate medical attention.

### D. Eye Contact

Because of the ability of HF to penetrate deep into tissue, exposure of HF solution or vapor to the eye can produce more extensive damage than that of other acids in similar concentra-

| Industry | Use |
|---|---|
| Electroplating | Acid Metal Cleaners—Oxide Removers |
| Etching | Glass Etching and Frosting |
| Flotation Agents | Depressants—Nonsulfide Ores |
| Integrated Iron and Steel Manufacturing | Pickling Acids |
| Laboratory Chemicals | Acids, Other Chemicals (non-salts) |
| Oil Refineries | Catalyst to Produce High-Octane Fuel Additives |
| Refrigeration | Manufacture of Fluorocarbons |
| Semiconductors | Wet Chemical Etching |

**Home Use:** Air-conditioning unit coil cleaners; aluminum automotive wheel cleaners; chrome, brass, and crystal cleaners; masonry cleaners; rust stain remover; truck and commercial car washing compounds; water spot remover.

**Figure 1. Uses for HF.**

## FIRST AID FOR HYDROFLUORIC ACID BURNS TO THE EYE(S)

*Bernard Blais, M.D., F.A.A.O., F.A.C.O.E.M., F.A.C.S.*

(1) IT IS IMPERATIVE that immediate and thorough treatment be provided at the EARLIEST possible time.* Alert emergency personnel.

(2) Immediately utilize emergency deluge showers and/or emergency eyewashes† based on the amount or area of contamination to the body.

(3) The employer's first responders must be trained in first aid for hydrofluoric acid burns, including the use of 0.13% benzalkonium chloride and 2.5% calcium gluconate gel and calcium gluconate intravenous solution (first responders per OSHA are to be trained to service the potential hazards).

(4) Upon arrival at the scene, first responders should evaluate the victim for potential cardiovascular or pulmonary complications, and initiate emergency medical treatment based on the existing emergency medical services protocol.

(5) Whereas initial irrigation of a corrosive with deluge shower or emergency eyewash generally lasts 15 minutes, in the case of HF burns, it is 5 minutes prior to further medical treatment or until relieved by emergency personnel. Clothing, jewelry, and shoes should be removed during the showering period, removing chemical goggles last over head and eyes closed. Normally, individuals tend to close their eyes when flushing, so it is important to hold the eyelids open and have the victim roll the eyeballs so water will flow to all surfaces.

(6) It is critical to irrigate beneath the eyelids, not just the face and external surfaces of the eyelids. It is important not only to flush away the caustic substance, but also to remove any particulate matter that may have lodged under the eyelids.

(7) A device such as a Morgan Lens or, preferably, an Eye Irrigator can be used with a standard Ringers solution containing 1.0% calcium gluconate and a local anesthetic for HF ocular burns. The Eye Irrigator‡ is a fairly new device, consisting of a slitted loop designed to easily slide up under the upper lid without having to pry open or otherwise traumatize the eye. The procedure is simple but does require some basic training. *Benzalkonium chloride solutions should not be used for ocular burns.*

(8) Eye irrigation should be continued by the first responder until relieved by a physician, preferably by an ophthalmologist. *Calcium gluconate should not be injected subconjunctivally or subtenons,* because it is too toxic for ocular tissue.

(9) The ophthalmologist may elect to continue irrigation with 500–1000 mL of 1% calcium gluconate solution utilizing a local anesthetic. Depending on the severity of the injury, the patient may be admitted to hospital or discharged with a topical application of 1% calcium gluconate eye solution, ophthalmic steroids, antibiotics (systemic or topical), and other treatments for alkali corrosive eye burns such as glaucomatous agents for elevated intraocular pressure.

*Subpart K-Medical and First Aid of OSHA §1910.151 states:

(a) The employer shall ensure the readily availability of medical personnel for advice and consultation on matters of plant health.

(b) In the absence of an infirmary, clinic, or hospital in near proximity to the workplace which is used for the treatment of all injured employees, a person or persons shall be adequately trained to render first aid. First aid supplies approved by the consulting physician shall be readily available.

(c) Where the eyes of body of any person may be exposed to injurious corrosive materials, suitable facilities for quick drenching or flushing of the eyes and body shall be provided within the work area for immediate emergency use.

†See ANSI Z358.1-1998 guidelines, Emergency Eyewash and Shower Equipment.

‡The Eye Irrigator is available from American Health and Safety, P.O. Box 46340, 6250 Nesbitt Rd., Madison, WI 53744-6340, (800) 522-7554. A 5-min. training video is available.

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tions. E.g., hydrochloric acid damages only the superficial structures of the eye, because its penetration is limited by a precipitated protein barrier.[5] In the case of HF, immediate action should be taken with initial flushing and then treatment with sterile 1% calcium gluconate solution. For details, see the inset by Bernard Blais, M.D.

### III. TREATMENTS

Calcium gluconate is the preferred treatment of choice for minor HF exposure for the following reasons:

- It is easy to use.
- It can be self-administered or applied by first aiders.
- It can be applied immediately as soon as the burn is suspected.
- It is painless to apply.
- It produces no risk of increasing tension in the tissues.

- It can be used topically, infiltrated, inhaled, and ophthalmically.
- It reduces the risk of hypocalcemia.
- No sophisticated equipment is necessary.

Pharmascience Inc. is the main supplier of calcium gluconate and can be contacted at 8400 Darnley Rd., Montreal, Quebec H4T 1M4, Canada. In the U.S. the company has a distributor at 175 Rano St., Buffalo, NY 14207 (800-207-4477, orders; 800-363-8805, technical information). Calcium Gluconate Gel is available in 25-g tubes in multiples of 12 for $264.60 in the U.S. Quantities of 6 are available for $165.30. A 5% freight and handling charge is applicable.

### A. Mixing Your Own Solutions

This method can be considerably cheaper or a local pharmacy can make up a solution.

*1. Topical Gel (2.5%).* Mix one 10-mL ampule (10%) per ounce of surgical gel (K-Y Lubricating Jelly; Johnson & Johnson). The gel must be kept above 40°F. Do not freeze.

The latest DuPont MSDS (Nov 1998) supplies another formulation as well: Mix 3.5 g of USP calcium gluconate powder with a 5-oz tube of surgical water-soluble lubricant (e.g., K-Y Lubricating Jelly).

*2. Calcium Gluconate Solutions for Topical Injections.* Mix one 10-mL ampule (10%) with an equal amount of saline solution to give a 5% calcium gluconate concentrate.

*3. Nebulizer.* Mix one 10-mL ampule (10%) per 30 mL of saline solution to give a 2.5% calcium gluconate solution.

*4. Eye Wash.* Mix one 10-mL ampule (10%) per 90 mL of saline to get a 1% calcium gluconate solution. If you take 100 mL out of a 1000-mL bag of normal saline and put in 100 mL of calcium gluconate, you will have the proper mixture.

*Note:* The shelf-life for all mixtures has not been determined, but a periodic replacement period should be established; the recommendation on the DuPont MSDS is 6 months. If the ingredients are stored separately until needed, the shelf-life is less of a concern.

Be aware that even following emergency treatment with calcium gluconate, delayed life-threatening burns can still occur. Followup treatment at a medical facility is necessary. It is wise to warn the hospital of your intentions to bring folks to them for HF burn treatment and to make sure that they are informed of its specific treatment.

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### B. Benzalkonium Chloride (Zephiran Solution)

This product can be obtained from Sanofi Inc., 90 Park Ave., New York, NY 10016 (800-446-6267). It is available in gallon containers as a 1:750 (0.13%) solution. The material has a limited shelf-life and should be stored in light-resistant containers. A 17% solution is also available but should only be diluted by a qualified individual. Since benzalkonium chloride is a nonprescription drug, it should be available through most local pharmacies. They can obtain it from pharmaceutical wholesale distributors such as McKesson Pharmaceuticals, Cardinal Health Inc., or the local pharmaceutical wholesaler. Assorted basins should be kept on hand for immersions.

## IV. 5 vs. 15 MINUTES OF IRRIGATION

After my first paper was published,[2] a letter to the editor was published in the Jan./Feb. 1999 issue of *CH&S* entitled, "Another viewpoint on the treatment of HF skin exposure."[7] The purpose of the letter was to "provide an interpretation of these different procedures and offer a practical response for HF skin procedure." Points brought out follow:

- It is straightforward to train employees in a *single* emergency response treatment (i.e., the common 15-min wash protocol).
- Recommendations in MSDSs are inconsistent.
- There is a real possibility that a confused employee will attempt to apply HF treatment to another acid, (e.g., HCl).
- Community-involvement programs stress communication with industrial users of HF and hospitals.

All the above are valid statements, but considering DuPont's claim,

*Flushing with water thoroughly for 5 min is sufficient to effectively remove HF from skin. Additional flushing time is unnecessary and will delay further treatment. Although flushing is effective in removing surface acid, it does not affect the F that may have already penetrated.*

we have a dilemma. Will an exception to the rule for HF cause confusion? The solution is, of course, to have a plan in effect *ahead of time*, and to provide training to implement that plan. All potentially exposed personnel should be trained in first-aid care for HF burns before beginning work with HF. Calcium gluconate gel should be readily accessible in areas where HF exposure potential exists.

DuPont provides all its potentially exposed personnel with a (3" × 5") booklet and card (2.25" × 3.75"), easily carried on their persons. These are routinely provided free of charge to companies purchasing HF and to anyone who requests a single copy (call 800-441-9408).

My contact at DuPont informed me that the 5-min wash procedure began in 1990 and since that time at least 75% (it might be as high as 98%) of companies using anhydrous HF have adopted the 5-min wash. Further, he

tells me that the 5-min wash is being applied to other *water-soluble* substances such as hydrochloric acid and chlorine. The DuPont MSDSs for hydrochloric acid and chlorine state for skin contact, "Flush the skin thoroughly with water at least 5 minutes." Preliminary tests show that the 5-min time frame is effective in many cases; this is especially fortuitous in cold areas where a 15-min cold shower wreaks its own hazards.

And consider this! In 1998 Pharmascience introduced a new product, a sterile 2.5% isotonic calcium gluconate wash packaged in a plastic container (480 mL). In the event of an exposure, the solution was to be applied immediately to affected areas until thoroughly washed. It was claimed that the wash removed more HF than a pure water wash and significantly reduced the quantity of HF that penetrated the skin. After washing, calcium gluconate gel was to be applied repeatedly while seeking medical attention. Evidently HF users weren't ready for this innovation and as of Aug. 6, 1999, the wash was no longer available.

## V. CURRENT STATUS OF HEXAFLUORINE

At the 1998 spring meeting of the Semiconductor Safety Association, Hall et al. delivered a paper[8] that presented impressive results about the use of Hexafluorine, a proprietary product manufactured by Laboratoire PREVOR in France, claimed to be an amphoteric, hypertonic, chelating agent specifically designed to detoxify hydrofluoric acid. It has chemical bond energy greater than that of eye/skin receptors and does not produce a significant exothermic reaction with release of heat that could further damage exposed tissue. In addition, it is claimed to be safe to use in the eyes. Hall describes five cases in his paper. Two of those cases follow:

1. A worker fell into a bath containing 1505 L of water, 30 L of concentrated hydrochloric acid, and 233 L of 59% HF (calcd bath concn, 9.2% HF), immersing his entire body and face. Hexafluorine, as well as a regular water eyewash, was immediately used for decontamination by coworkers. Only minor burns developed on the back and abdomen, there was a significant corneal burn of the left eye, but the right eye remained normal.

2. At a facility using a chemical dipping bath containing nitric acid and HF for producing stainless steel for construction and machine tools, a worker sustained an eye splash with 38% HF. He rinsed his eye immediately with Hexafluorine and did not develop any eye injury, returning to work the next day.

Experimental animal data on rats and rabbits as well as in vitro data are compelling. One such case is shown in Figure 2. To simulate the effects of decontamination without flushing, 10 mL of 0.1 N HF (0.2%) was placed in a beaker and either water, 10% calcium gluconate, or Hexafluorine was added. The pH and the pF (pF = negative logarithm of the fluoride ion concentration) were measured. As noted, water had little effect. Both calcium gluconate and Hexafluorine absorbed or neutralized $H^+$, although Hexafluorine bound the hydrogen ion 100 times greater than calcium gluconate. The final pH for Hexafluorine was 6.5 vs. 4.5 (still acidic) for calcium gluconate.

| | pH | pF |
|---|---|---|
| Water | Little change | Little change |
| 10% calcium gluconate | 4.5 | 3 |
| Hexafluorine | 6.5 | 6 |

**Figure 2. Experimental Results.**

I recently spoke with Alan Hall, M.D., one of the authors of the 1998 paper on Hexafluorine, who has been hired as a consultant for PREVOR. He was very skeptical about the product at the beginning, but new incidents of 11 exposed workers at Mannesmann AG (headquartered in Dusseldorf, Germany) have shown the effectiveness of the product. These case studies will be presented at the Semiconductor Safety Association 2000 spring meeting and published.[9]

*One should always try to keep up to date to learn of new innovations in safety, especially when working with nasty chemicals such as HF, and then institute those changes if they can save lives.*

Hexafluorine is being widely used in France and Germany; Ireland, Italy, Sweden, and the United Kingdom are giving serious consideration to its use. In the U.S., PREVOR is actively seeking FDA approval, armed with the new compelling data from Germany. One "sticky" issue is whether the product should be considered a drug or, preferably, a medical device (as it is in Europe).

For more information on PREVOR, check out the web site at http://www.prevor.com.

## CONCLUSION

Because HF is a unique acid and its emergency treatment is specialized and different from that of other inorganic acids, all exposed and poten-

tially exposed personnel should be made familiar with its properties and hazards and trained *ahead of time* to deal with emergency situations. In the case of the HF fatality mentioned in the introductory news report, the victim evidently was not aware of the internal damage that the fluoride ion could inflict. Protocols should be set up, appropriate supplies should be on hand, and arrangements should be made with nearby hospitals and professionals because not all physicians may be aware of the unique treatments. In addition, one should *always* try to keep up to date to learn of new innovations in safety, especially when working with nasty chemicals such as HF, and then institute those changes if they can save lives. Even if you've already converted to a 5-min rinse and have calcium gluconate on hand, don't get complacent; new and better changes may be coming. Stay on top of safety!

**Acknowledgments**

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References

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2. Segal, E. B. "First aid for a unique acid: HF", *Chem. Health Saf.* **1998**, *5*, 25–28. Also on the Web: http://dchas.cehs.siu.edu/Magazine/hf.
3. "Chemical Market Reporter", Chemical Profile of Hydrofluoric Acid, Oct. 1999, Schnell Publishing, New York, NY.
4. Chemical Scorecard, Environmental Defense Fund, New York, NY, 1999.
5. Caravati, E.M., *Am. J. Emerg. Med.* **1988**, *6*(2), 143.
6. "Recommended Medical Treatment for Hydrofluoric Acid Exposure," Dec. 1998, AlliedSignal Inc., P.O. Box 1053, 101 Columbia Rd., Morristown, NJ 07962-1053. This booklet can be obtained at no charge by calling 800-622-5002 or faxing your request to 973-455-6141. For more information, check out AlliedSignal's web site at http://www.specialtychem.com/ha/.
7. Langerman, N. *Chem. Health Saf.* **1999**, *6*(1), 5.
8. Hall, A. H.; Blomet, J.; Gross, M.; Nehles, J. "Hexafluorine® for Emergency Decontamination of Hydrofluoric Acid (HF) Eye/Skin Splashes." Presented at the Semiconductor Safety Association Meeting, San Diego, CA, March 1999. Funded by Laboratoire PREVOR, Moulin de Verville, Valmondois, France.
9. The meeting will be held in Arlington, VA, April 25–28. For more information, check out the SSA web site: http://semiconductorsafety.org.

**Additional Resources**

• *Interesting case studies*

1. Brown, J., "An Invisible Fire", *Discover*, April 1996, pp 88–90.
2. Detailed Coroner's Report of a Fatal Accident in Australia, 1994: McCann, D. A., Coroner, Coroner's Court, Grain Pool Building, 172 St. George's Terrace, Perth 6000, West Australia.

• *For large-volume users*

Guidelines from the Hydrogen Fluoride Industry Practices Institute (HFIPI), a subsidiary of the CMA: *Recommended Practices for the Hydrogen Fluoride Industry*, 3 vols. These guidelines are only sold in sets of $100 each, including shipping and handling (additional cost for international shipping); they cannot be purchased individually. For more information or to order, contact Hydrogen Fluoride Practices Institute, Attn. Reid Dennis, 3050 K St., NW, Suite 400, Washington, DC 20007; tel 703-741-5619; fax 703-741-6091.

• *Sample Protocols*

The following have offered to share their protocols, which can be adapted to your work site.

Thomas J. Shelley at Cornell University, 607-255-4285; e-mail tjs@cornell.edu. URL: http://www.ehs.cornell.edu/lrs/cheminfo/infopackets/hf.htm.

Debbie M. Decker at University of California, Davis, 530-754-7964; dmdecker@ucdavis.edu. URL: http://ehs.ucdavis.edu. Check on "Safety Nets" and search for #70.

• *Medical Information*

U.S. Department of Human Services, Public Health Service, Agency for Toxic Substance and Disease Registry, "Medical Management Guidelines for Acute Chemical Exposures," 8/1/92; updated 4/12/99: http://acpo-xdv-www.epo.cdc.gov/wonder/prevguid/p0000016/body015.htm#head00500 6000000000.

Wilkes, G. "Hydrofluoric Acid Burns," updated 4/11/99: http://emedicine.com/emerg/topic804.htm.

• *Slide presentation*

A set of 40 slides on HF geared toward the laboratory worker is available from the University of Delaware: http://www.udel.edu/OHS/chemical/hfpresent/sld001.htm.