UFNF Acid/Base Wet Bench – Physics Room B155

SOP

Bench Features:

The bench consists of 2 independent sides. The left side of the bench is dedicated to non-HF based acids and bases. See Table 1.0 below for acceptable chemicals. No others are allowed without prior UFNF staff approval. The right side is ONLY for HF - hydrofluoric acid. The storage area under the bench is ONLY for Acids including HF, see Table 1.0. Nitrogen guns and 18 M-ohm DI water nozzles are on both sides of the bench. Each side contains an acid process containment area with NO DRAIN and 3 DI water rinse bath compartments (per side) with pneumatic operated drains. Digital stirring hotplate is included for agitation and process heating.

Note: This SOP is to be followed in addition to the UF EH&S Lab Safety Policies found at http://www.ehs.ufl.edu/Lab/default.asp

1.0 **RULES OF OPERATION –**

1.1. This bench may only be used during normal UF hours of operation, Mon-Fri 8-5 and work may only be done with a pre-arranged "Buddy" present. Your "Buddy" must be present in the room with you at all times while using or pouring hazardous chemicals.
1.2. The safety shower is located in the hallway just outside the double doors to the left of the bench. Make sure you know where it is before using this bench.
1.3. All processes must be reviewed by the researchers PI for safety and compatibility issues which include the review of the Material Safety Data Sheets (MSDSs) for all of the materials used in the process.
1.4. Complete a *written* SOP for the procedure. The SOP will include a narrative of the safety and waste remediation issues for the process. The SOP must be present and open during the process run.
1.5. The following Personal Protection Equipment (PPE) must be worn at all times when working with Acids – NO EXCEPTIONS:
1.6. Full Face Shield
1.7. Acid Apron, tied in the back
1.8. Acid Gloves – 12" or longer
1.9. Full coverage street shoes i.e. no open toes
1.10. After donning your gloves, fold the glove back at the wrist to contain drips.
1.11. If diluting acid, **pour acid into water** - "Do like you oughta, add acid to water". Pouring water into acid may cause a very violent reaction.
1.12. Keep all uncapped acids inside the containment area inside the bench deck while you are working. Use pipettes when possible to dispense liquids into working containers.
1.13. If your samples are in process and you need to walk away from the bench, lay the sample containers on top of clean wipes and write the contents of the container and your name on the wipe under your sample.

1.14. Use an appropriately sized funnel to pour waste acid into waste container.
1.15. Clean and remove all items you brought with you. Properly labeled closed containers that include the name of the chemical and owner may be stored in the appropriate area, see Table 1.0. The bench deck is not a storage area. All items left will be discarded and future use of the bench will be prohibited.
1.16. Chemicals not included in Table 1.0 must be approved by laboratory staff prior to use.
1.17. If you intend to use HF, read section 5.0 carefully so that you fully understand the hazardous properties and what to do in case of exposure or spill.
1.18. Rinse all tweezers, containers i.e. anything that may have come into contact with acid inside the front DI Water rinse compartment. Open the drain using the drain toggle switch.
1.19. Rinse your gloves with DI Water before removing PPE. If you intend to re-use your acid apron and face shield (provided it is not contaminated) hang it on one of the hooks provided and attach a name label on the hook. Turn your gloves inside out after removal and dispose. Do not re-use gloves. All contaminated items are to be disposed per section 2.0 Waste Disposal.
1.20. Fill out the Wet bench Excel Logbook on the desktop of the computer near the lab entrance.

Table 1.0

	Storage Location
ACIDS	
H2SO4 - sulfuric Acid	Bench
HNO3 - nitric Acid	Bench
H3PO4 - phosphoric Acid	Bench
CH3COOH - acetic Acid	Bench
HCl – hydrochloric acid	Bench
Transene® Etchants (Aluminum A and D, Gold TFA, Nickel TFB, Chrome).	Bench
BASES	
KOH – potassium hydroxide	Bases Cabinet
H2O2 – hydrogen peroxide	Bases Cabinet
NaOH - sodium hydroxide	Bases Cabinet
NH4OH - Ammonium hydroxide	Bases Cabinet

2.0 Waste disposal:
2.1. Read and review the UF Policy (http://www.ehs.ufl.edu/HMM/HWguide.pdf)
2.2. Ensure that there are existing waste containers for the process materials. If not make a new container using the surplus empty bottles. Choose a bottle that is made of the same material as the original bottle. If these items cannot be found call a staff member. Always Triple rinse and drain waste bottles before

depositing waste in them. This ensures that the user doesn't mistakenly mix incompatible substances. Never fill a waste bottle past the top curve of the bottle.

2.3. Collect used chemicals and mixes in containers that match the original bottle. Fill out the waste label noting the percentage of the chemicals in the mix; if the material is a metal etch them indicate the metal that is in the solution. Notify lab staff that there is acid waste to be disposed of. Hot solutions should be allowed to cool to room temperature before decanting to waste containers. Always set the bottles in the bottom of the sink and use a funnel for decantation that way spills will be confined to the sink and easily rinsed.

2.4. Contaminated consumables: Laboratory wipes, gloves, arm guards, swabs and other disposable materials that have been contaminated with hazardous substances should be set aside for proper disposal after the user is finished processing. There is a small trash can labeled ACTIVE PROCESS TRASH next to the wet bench which is specifically for process contaminated debris. There should be three trash bags (one inside the other) folded over the rim of the can. Once the work area is cleaned and the debris is placed in the can rinse the gloves and tie the inner most bag, squeezing out as much air as possible. Rinse the gloves again and tie the secondary bag and then the third bag in the same fashion. Once the three bags are securely tied the package can be transferred to the normal trash. Always thoroughly rinse gloves with DI water before removing then inside out and disposal in the normal trash. Similarly, aprons are to be removed so that they are inside out before disposal.

2.5. Broken glass lab ware is to be handled and disposed by staff. All sharp process materials (broken wafers, pipettes, slides, etc) are to be disposed on in the proper container; NOT in the normal trash cans. Sharp objects in the normal trash can compromise the safety of users and cleaning staff.

3.0 Spills Protocol

3.1. Minor spills / droplets on the wipes on the bench top may be cleaned after the process during clean up. Large amounts of material (> 10 ml) require that the process setup be re-done as this amount of material will spread and be difficult to control.

3.2. ANY spill out side of the wet bench top must be cleaned by UFNF staff. Evacuate the processing area and call for clean up, staff will notify users when cleanup is complete.

4.0 Chemical Exposure

4.1. It is the policy of the UFNF that hazardous and or toxic substances will not be used without a safety back-up person present to give emergency aid. This person can give aid and or contact emergency response personnel should the user become incapacitated. Should hazardous chemical exposure happen; response time is critical.

4.2. All direct contact of user's skin to hazardous materials will be reported to the facility staff as soon as is permissible. Severely exposed individuals should be placed under the safety shower with no delay and clothing removed; if there was no initial exposure to the eyes, the eye protection should be removed last. In the event of splash exposure to the eyes, the injured person should be helped to the eyewash station and the eyes be rinsed while holding the eyes open for five minutes while emergency aid summoned.

5.0 Hydrofluoric acid and HF containing solutions

5.1. Tubes of calcium gluconate gel the first aid for HF exposure is kept in all areas where the material is handled.

The following article gives a clear and concise explanation of the safety issues of handling HF:

First aid for a unique acid: HF

Eileen B. Segal

Segal Consults, 2701 Liberty St., Easton, PA 18045-2620

Date: April 30, 1998. An emergency on the popular TV program ER dealing with a security guard exposed to hydrofluoric acid (HF) prompted a good deal of discussion on various first-aid treatments. In the show, the man died. Could he have been saved if proper first-aid and medical treatment had been given promptly?

ER is fiction, but the truth is many deaths have resulted from exposure to HF. In the United States, more than 1000 cases of HF exposures are reported annually, but the actual number of exposures is unknown. Thus, a review of current emergency practices seems prudent, as there are questions regarding the best therapy.

Conventional first aid for exposures to all acids has been to rinse with water for 15 min, even longer for HF, and then get medical treatment from professionals. Although studies and experience have shown that HF requires a different approach from other acids, a review of a significant number of material safety data sheets has revealed the same standard emergency treatment- -water, water, and more water. Newer recommended procedures call for immediate flushing, *but limited to 5 min*, followed by by treatment from emergency responders.

Mode of action

HF is a mean character or as a professor of chemistry was heard to say, "Fluorine can rip a proton off your grandmother." Hydrofluoric acid is an extremely hazardous liquid; it can cause severe skin and eye irritation or deep-seated, slow-to-heal burns.

The insidious hazard is that symptoms may be slow to appear, depending on the concentration, and thus treatment may be delayed. At concentrations above 50%, immediate skin destruction is apparent by a white, marble-like discoloration accompanied by excruciating pain; the discoloration usually proceeds to blister formation. With 20-50% solutions, burns and pain can be delayed for 1 to 8 h; at concentrations of less than 20%, painful erythema (redness of the skin) may be delayed for 24 h. Concentrations as low as 2% may cause symptoms if skin contact is long enough.

HF's mode of action is to bind calcium whenever contact occurs with skin or other body tissues. In the air-tissue interface, HF penetrates cells as the molecule as the molecule. Once absorbed, it forms soluble salts which are fully dissociable:

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

The dissociation is extremely fast and is highly favored at the physiological pH of 7.4. The fluoride ion is the villain, and it can cause liquefaction necrosis (consistent with alkali damage, not acid damage) of soft tissue and destruction of the supporting tissue by forming insoluble calcium fluoride.

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

Unlike the action of other acids, which are rapidly neutralized, tissue destruction and neutralization of HF may proceed for days. Although flushing is effective in removing surface acid, it does not affect the F– which may have already penetrated. Because calcium is necessary for cell life, its binding can bring about cell death in a short time. If the exposure covers a large amount of skin surface, excessive amounts of calcium may be inactivated, so that inadequate amounts of Ca^{2+} are available for vital body functions. This causes hypocalcemia, in which heart function is diminished, the heart beat becomes abnormal , and cardiac arrhythmia; notably heart function is diminished, heart beat becomes abnormal, and cardiac arrhythmia (ventricular fibrillation) can occur. Liver and kidney damage may also occur.

The fluoride ion can also bind to magnesium to form insoluble MgF_2:

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

The binding of magnesium causes hypomagnesemia, an abnormally low magnesium content of the blood plasma, which can cause neuromuscular hyperirritability (a pathological response of muscles and nerves to slight stimuli).

Also to be considered is the formation of other soluble fluorinated salts:

$$Na^+ + F^- \_ NaF$$
$$K^+ + F^- \_ KF$$

These salts are very toxic at high concentrations. They act as direct cellular poisons by interfering with enzyme mechanisms.

Fingertip injury may cause persistent pain and result in bone loss and nail-bed injury. The healing of skin burns may be prolonged, and extensive scarring may occur.

Acute Toxicity

There are similarities and dissimilarities between the effects of exposure to HF and exposure to other types of acids.

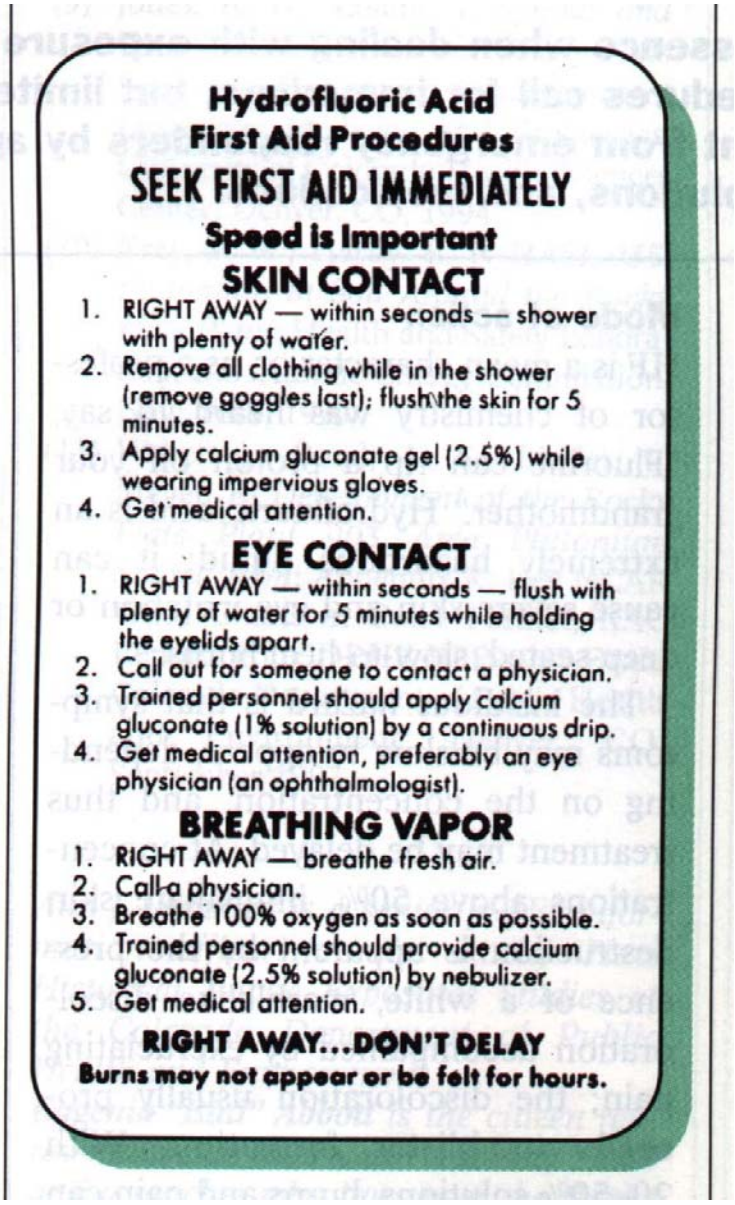
Skin. Like other acids, the extent of injury depends on the amount, concentration, duration of contact, part of the body contacted, and temperature. The toxic effects of HF are primarily due to F^-, which can penetrate tissues and bind intracellular calcium and magnesium. Severe burns can be caused by exposure to concentrated HF (≥50%) on 1% or more of the body surface, and to any concentration of HF on at least 5% of the body surface. Initial signs of damage are redness, edema, and blistering. The severe throbbing pain of burns is thought to be due to irritation of nerve endings by increased levels of potassium ions entering the extracellular space to compensate for the reduced levels of calcium ions, which have been bound to the fluoride. Dilute solutions of HF penetrate deeply before dissociation. Surface involvement is minimal and may even be absent.

Respiratory tract. Concentrated solutions and anhydrous hydrofluoric acid produce pungent fumes upon contact with air. These fumes can cause nasal congestion and bronchitis, even in low concentrations. Burns that occur when the vapors or liquid contact to the oral mucosa or upper airway may cause severe swelling, to the point of airway obstruction requiring a tracheostomy. Acute symptoms from inhalation exposure are coughing, choking, and nose and throat irritation, followed (after an asymtomatic period of 1-2 days) by chills, fever, difficulty in breathing, and cyanosis. Anyone with symptoms should be hospitalized for observation and/or treatment. As with dermal exposure, pulmonary edema may be delayed for several hours, even up to two days. This is likely in patients with burns of the face and neck. Pulmonary edema that does not respond to medical treatment may be fatal.

Gastrointestinal tract. If HF is ingested, severe burns to the mouth, esophagus, and stomach can result, with severe pain, bleeding, vomiting, diarrhea, and collapse of blood

pressure. Systemic effects can also occur. A number of deaths have occurred after even small amounts of HF.

Eyes. Hydrofluoric acid can cause severe eye burns, with destruction or opacification of the cornea. Blindness may result from severe or untreated exposures. Immediate first aid and specialized medical care are necessary.



Hydrofluoric Acid
First Aid Procedures

SEEK FIRST AID IMMEDIATELY

Speed is Important

SKIN CONTACT

1. RIGHT AWAY — within seconds — shower with plenty of water.
2. Remove all clothing while in the shower (remove goggles last); flush the skin for 5 minutes.
3. Apply calcium gluconate gel (2.5%) while wearing impervious gloves.
4. Get medical attention.

EYE CONTACT

1. RIGHT AWAY — within seconds — flush with plenty of water for 5 minutes while holding the eyelids apart.
2. Call out for someone to contact a physician.
3. Trained personnel should apply calcium gluconate (1% solution) by a continuous drip.
4. Get medical attention, preferably an eye physician (an ophthalmologist).

BREATHING VAPOR

1. RIGHT AWAY — breathe fresh air.
2. Call a physician.
3. Breathe 100% oxygen as soon as possible.
4. Trained personnel should provide calcium gluconate (2.5% solution) by nebulizer.
5. Get medical attention.

RIGHT AWAY...DON'T DELAY

Burns may not appear or be felt for hours.

Chronic toxicity

The fluoride ion is considered the major concern from a chronic toxicity standpoint. Long-term, exposure to high levels of fluoride salts in water can cause mottling of teeth

in children, fluorosis of bone, and sometimes osteosclerosis in adults and children. HF is not considered a developmental or reproductive hazard, although there have been rare cases of mottling of first teeth in infants born to mothers who had high daily intakes of fluoride during pregnancy. However, low doses of fluoride are thought to be essential for normal fetal development in humans. HF is not listed as a carcinogen or suspected carcinogen by the International Agency for Research on Cancer, the National Toxicology Program, OSHA, or the American Conference of Governmental Industrial Hygienists.

First-aid treatments

When exposures are promptly and successfully treated, results are generally favorable. Improper treatment can result in permanent damage, disability, or death. Treatment is directed toward binding of the fluoride ion to prevent tissue destruction. *Speed is of the essence.* All potentially exposed personnel should be trained in its handling, and first-aid actions should be planned before beginning work with HF.

AlliedSignal. AlliedSignal Inc., the world's leading supplier of HF, provides a pamphlet, "Recommended Medical Treatment for Hydrofluoric Acid Exposure" (latest edition, July 1996). The company has shared its information broadly and has provided hundreds of free copies of the informative booklet (call 1-800-622-5002 for a copy). The treatments specified for contact or suspected contact follow.

• **Skin contact**

1. Move victim immediately to safety shower or other water source and flush affected area thoroughly with large amounts of cool running water.

2. Remove all contaminated clothing while flushing.

3. Rinsing may be limited to 5 min if 0.13% benzalkonium chloride solution or 2.5% calcium gluconate gel is available, with the soaks or gel applied as soon as the rinsing is stopped. If not available, rinsing must continue until medical treatment is rendered.

4. While the victim is being rinsed with water, someone should alert first-aid or medical personnel and arrange for subsequent treatment.

5.Immediately after thorough washing, use *one* of the measures below:

a. Begin soaking the affected areas in iced 0.13% benzalkonium chloride solution. Use ice cubes, not shaved ice, in order to prevent frostbite. If immersion is not practical, towels should be soaked with iced 0.13% benzalkonium chloride solution and used as compresses for the burned area. Compresses should be changed every 2 to 3 min. Soaks or compresses should be continued until pain is relieved or until more definitive medical

treatment is provided. Relief of pain is an indication of the success of treatment; therefore, local anesthetics should be avoided.

b. Start massaging 2.5% calcium gluconate gel into the burn site. Apply gel every 15 min and massage continuously until pain and/or redness disappear or until more definitive medical care is given. It is advisable for the applier to wear surgical gloves.

Note: Clinical experience has shown that both benzalkonium chloride and calcium gluconate gel are effective when used correctly in appropriate situations. In an animal model, benzalkonium chloride soaks appear to be superior to calcium gluconate gel under the experimental conditions used (see Dunn et al., 1992, 1996).

6. After treatment of burned areas is begun, the victim should be examined to ensure there are no other burn sites which have been overlooked.

7. Arrange to have victim seen by a physician. Continue soaks or massaging.

Ocular exposure

Because of the seriousness of exposure to HF and the fact that treatment of HF contact differs from that of other inorganic acids, it is important that all potentially exposed personnel and medical staff be trained ahead of time in these chosen procedures. If eye exposure occurs, use the following procedures:

Emergency eyewash and/or deluge shower shall be used, as appropriate, for flushing the affected area thoroughly with large amounts of fluid.

Remove clothes, shoes, and jewelry. Remove goggles last by pulling them over the top of injured individual's head.

Irrigate eyes using an eyewash station until first responders arrive. If on hand, use the state-of-the-art Eye Irrigator (available from American Health & Safety, Inc., 6250 Nesbit Rd., Madison, WI 53744).

Irrigate eye(s) with isotonic saline or Ringer's solution, using Eye Irrigator for 5 min or until arrival of first responders with calcium gluconate.

Irrigate eye(s) with 500–1000 mL of 1% calcium gluconate solution for each eye.

Transfer to ophthalmologist while continuing irrigation with 1% calcium gluconate solution.

—Bernard Blais, M.D., FAAO, FACOEM, FACS, Blais Consulting, Ltd.

Eye contact.

1. Immediately flush the eyes for a least 15 min with large amounts of gently flowing water. Hold the eyelids open and away from the eye during irrigation to allow thorough flushing of the eyes. *Do not use benzalkonium chloride solutions described for skin*

treatment. If sterile 1% calcium gluconate is available, washing may be limited to 5 min, after which the 1% calcium gluconate solution should be used repeatedly to irrigate the eye using a syringe.

2. Take the victim to a doctor, preferably an eye specialist, as soon as possible. Ice-water compresses may be applied to the eyes while transporting the victim (see the box on eye treatment).

• **Inhalation**

1. Immediately move victim to fresh air and get medical attention.

2. Keep victim warm, quiet, and comfortable.

3. If breathing has stopped, start artificial respiration at once. Make sure mouth and throat are free of foreign material and the airway is open.

4. Oxygen should be administered as soon as possible by a trained individual. Continue oxygen while awaiting medical attention.

5. A nebulized solution of 2.5% calcium gluconate may be administered with oxygen by inhalation.

6. Do not give stimulants unless instructed to do so by a physician.

7. The victim should be examined by a physician and held under observation for at least 24 h.

8. Vapor exposures can cause skin and mucous membrane burns as well as damage to pulmonary tissue. Vapor burns to the skin are treated the same as liquid HF burns.

• **Ingestion**

1. Have the victim drink large amounts of water as quickly as possible to dilute the acid. Do not induce vomiting. Do not give emetics or baking soda. Never give anything by mouth to an unconscious person.

2. Give several glasses of milk or several ounces of milk of magnesia, Mylanta, Maalox, or the like. The calcium or magnesium in these compounds may act as an antidote.

3. Get immediate medical attention.

Other first-aid information

DuPont. DuPont's MSDS, dated Sept. 19, 1995, states, "*Flush skin thoroughly with water for 5 minutes.* Flushing with water thoroughly for 5 minutes is sufficient to effectively remove HF from skin. Additional flushing time is unnecessary and will delay further treatment."

DuPont has a technical information booklet, "Hydrofluoric Acid/ Anhydrous, Technical: Properties, Uses, Storage, and Handling," which it shares with the public. In addition, DuPont has prepared a 3 x 5" booklet and a 2.25 x 3.75" card with first-aid information for distribution to its customers and potentially exposed personnel.which can easily be carried on their persons (see box for a copy of the card).

Mallinckrodt Baker. This company is another supplier of HF; its MSDS advises a 15-20-min wash and then treatment with Hyamine 1622 (tetracaine benzethonium chloride) or 0.13% Zephiran Chloride (benzalkonium chloride). However, the MSDS provides a "Note to Physician" in its section on first-aid measures for an alternative first-aid procedure, stating:

"It has been conclusively shown [references given] that flushing the affected area with water for *one* minute and then massaging HF Antidote Gel (contains calcium gluconate) into the wound until there is a cessation of pain is the most effective first aid treatment available. HF Antidote Gel is available in 25-g tubes....We recommend that any person in contact with HF should carry, or have access to, a tube of HF Antidote Gel at all times; ideally with one tube at the workplace, one on the person" and one at home. For safety's sake, we believe that HF Antidote Gel should be issued to all employees who may come into contact with HF."

To obtain an MSDS from Mallinckrodt Baker, call 1-800-JTBAKER or 908-859-6911 and follow the voice prompts to obtain information by fax (the catalog number is 6904).

Sources and recommended reading

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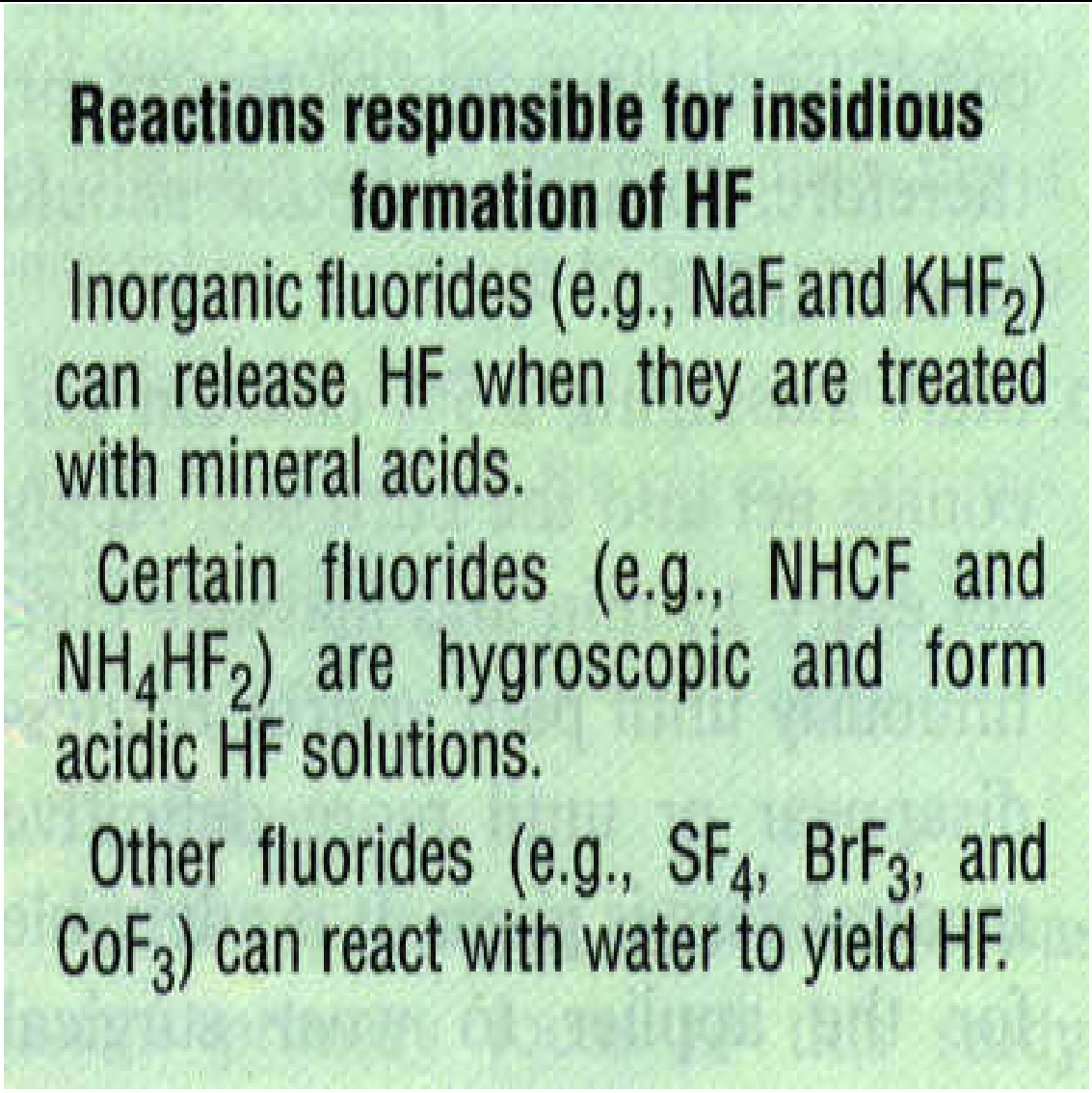

Back to the fictitious security guard on *ER*: All we know is that the victim was beyond saving by the time he reached the hospital. Would he have been spared if emergency responders had begun treatment at the scene? It makes one wonder. Anyone dealing with HF should be prepared for that type of emergency. You don't want to change fiction into reality.

Acknowledgment. I am especially grateful to personnel at AlliedSignal and DuPont for stimulating discussions and materials. Both companies were generous in sharing their information. Thanks are due to Dr. Bernard Blais for many personal discussions and his contribution to this article.