United States Environmental Protection Agency
Office of Solid Waste and Emergency Response (OS-120)
July 1993
EPA-550-K-93-001
Series 8, No. 3

EPA Chemical Emergency Preparedness and Prevention Advisory

Hydrogen Fluoride

This advisory recommends ways Local Emergency Planning Committees (LEPCs) and chemical facilities can reduce risks posed by the presence of hydrogen fluoride (HF) in their communities. Hydrogen fluoride, a strong inorganic acid, is produced and used as a gas or liquid without water (i.e., in **anhydrous** form), or in a water (**aqueous**) solution. The anhydrous form is potentially more hazardous than hydrogen fluoride in dilute water solutions, because anhydrous hydrogen fluoride has greater potential for fuming and forming vapor clouds. If anhydrous hydrogen fluoride is accidentally released, it may react with water vapor to form a white vapor cloud. Under certain conditions, such a cloud has the potential to travel considerable distances close to the ground and pose a threat to people in its path. EPA stresses that although mishandling of HF can cause harm, there is no cause for undue alarm about its presence in the community when it is properly and safely managed.

Inhalation of hydrogen fluoride vapor, either in anhydrous form or from water solutions, can cause irritation if the exposure is mild (i.e., low concentration in air for a short time), or severe damage to the respiratory system or death in the case of exposure to high concentrations. Contact with the liquid or vapor can severely burn skin, eyes, and other tissue. Burns from hydrogen fluoride are particularly dangerous and require immediate and special treatment by trained medical personnel.

The largest use of hydrogen fluoride is in the manufacture of fluorine-containing chemicals, particularly chlorofluorocarbons (CFCs). Hydrogen fluoride may be used in some petroleum refinery operations, aluminum production, nuclear applications, glass etching and polishing, and metal treating and cleaning.

Although major incidents involving hydrogen fluoride have been rare, one example was an accident at a Texas petroleum refinery. A construction accident at an alkylation unit resulted in the release of 30,000 to 50,000 pounds of hydrogen fluoride and isobutane. The vapors migrated to an adjacent residential area. Eighty-five square blocks and approximately 4,000 residents were evacuated. There were no fatalities. More than 1,000 residents went to three neighboring hospitals. Although about 100 were admitted, most of those reporting to hospitals were treated on an outpatient basis. In some cases, there were reports of skin irritation and irritation to the eyes, nose, throat, and lungs. Some vegetation in the path of the cloud was also damaged.

Federal Requirements:

Hydrogen fluoride's acute toxicity prompted EPA to list it as an extremely hazardous substance (EHS), with a threshold planning quantity (TPQ) of 100 pounds, under Section 302 of the Emergency Planning and Community Right-to-Know Act (commonly known as SARA Title III). OSHA's Process Safety Management Standard, published February 24, 1992, requires facilities with anhydrous hydrogen fluoride in quantities at or above the threshold of 1,000 pounds to implement process safety management to protect employees by preventing or minimizing the consequences of chemical accidents. In addition, OSHA regulations require that facility employees who could potentially be exposed to hydrogen fluoride in any form be trained to handle and use it safely and to recognize and deal with the potential hazards posed by this chemical. EPA regulations required under the Clean Air Act soon will require facilities with HF above a threshold quantity to prepare risk management plans; these plans will be provided to LEPCs and the state.

RECOMMENDED STEPS FOR LEPCS

Section 302 of SARA Title III requires LEPCs to develop comprehensive emergency plans to address facilities where hydrogen fluoride as well as other EHSs are present in excess of their threshold planning quantities (100 pounds for hydrogen fluoride). Because an accidental release of hydrogen fluoride can pose a significant health and safety hazard, EPA suggests that LEPCs take the following steps:

Hazards Analysis/Hazard Identification:

- Know which facilities produce or use hydrogen fluoride. These facilities include:
  - Chemical manufacturers (e.g., chlorofluorocarbons, fluorine, organic and inorganic fluorine compounds, linear alkylbenzenes);
  - Petroleum refinery alkylation units;
  - Aluminum producers;
  - Pharmaceutical companies; and
  - Uranium processors.
- Facilities that produce or use water solutions of hydrogen fluoride, which may be less hazardous than pure hydrogen fluoride, particularly if the solutions are dilute, include:
  - Chemical manufacturers (e.g., some inorganic fluorine compounds);
  - Stainless steel producers;
  - Manufacturers of metal products;
  - Electronic equipment manufacturers;
  - Transportation equipment manufacturers;
  - Aerospace industry; and
  - Glass manufacturers.
- Know routes and methods of HF transportation in the area.

Note: There are many other names for hydrogen fluoride. Hydrogen fluoride without water may be called anhydrous hydrogen fluoride; HF; AHF; HF-A; hydrofluoric acid; hydrofluoric acid, anhydrous; or anhydrofluoric acid. Water solutions of hydrogen fluoride may be called hydrofluoric acid; hydrofluoric acid, aqueous; hydrofluoric acid solution; aqueous HF; HF 70% (or other concentration); hydrofluoric acid 70% (or other concentration); or fluorhydric acid.

HF Characteristics:

- Be aware of the characteristics that make hydrogen fluoride hazardous, including:
  - It is highly toxic;
  - Depending on temperature and concentration, it may be highly corrosive to many substances (e.g., dilute HF attacks most common metals);
  - It can become airborne if released above its boiling point of 67° F; and
  - Anhydrous hydrogen fluoride may form a vapor cloud containing aerosol if released under certain conditions. Depending on the conditions, the cloud may travel considerable distances while remaining close to the ground.

Vulnerability Analysis:

- Example exposure guidelines include:
  - IDLH (30 ppm for 30 minutes) and
  - ERPG-3 (50 ppm for 1 hour).
- When modeling potential releases of hydrogen fluoride, take into account its important properties, such as possible behavior as a dense gas (heavier than air), aerosol formation (HF vapor and droplets), and reaction with water vapor. In addition to including the chemistry of HF in vulnerability analysis, it is important to include other factors such as release rate, release quantity, meteorological conditions, and area topography.
- Note that the physical and chemical behavior of hydrogen fluoride is complex upon release and models not designed to address this behavior may provide inaccurate estimates of dispersion and downwind concentrations.
- Identify vulnerable populations in potentially high concentration areas.

Emergency Planning/Testing the Plan:

- Ensure that the facilities covered by Sections 302, 311, and 312 of SARA Title III have provided to the LEPCs and local fire departments adequate information about hydrogen fluoride at their location. Gather information about smaller quantities of hydrogen fluoride as well. (Not all facilities using or storing hydrogen fluoride will meet the reporting thresholds.) The LEPC can request material safety data sheets (MSDSs) for hazardous chemicals present at a facility in amounts below the threshold.

- Review methods facilities use to detect and respond to releases.

- Engage in a dialogue with facilities regarding methods for preventing accidental releases of hydrogen fluoride and systems in place to reduce the off-site risk if release should occur. On-site means of reducing off-site risks may include emergency transfer systems, water spray mitigation systems, remotely-operated isolation valves, HF detectors, and HF inventory reduction. Be aware that the effectiveness of these methods may be site specific. For example, reducing inventories could possibly lead to an increase in transportation-related risk.

- Regularly exercise and review Title III plans to ensure that facilities handling large quantities of hydrogen fluoride are covered, and that emergency response issues concerning possible releases of hydrogen fluoride have been addressed. Consider whether plans should include protection in place and/or evacuation in case of a hydrogen fluoride release.

- Determine if the local emergency response plan is consistent with the facility's response plan.

- Ensure that local hospitals and physicians are properly trained and prepared to treat victims of hydrogen fluoride exposure; in particular, ensure that they are aware of the special hazards of hydrogen fluoride exposure and are equipped to treat such exposure.

Right-to-Know/Risk Communication:

- Inform the community of the potential hazards of HF, as well as emergency response methods for treating victims of hydrogen fluoride exposure.

- Send a copy of this advisory to all fire departments, medical facilities, and hydrogen fluoride facilities in your LEPC jurisdiction, calling their attention to the recommended steps for facilities in the section below.

RECOMMENDED STEPS FOR FACILITIES

In cooperation with LEPCs and local response officials, facilities should take the following steps:

Handling and Storage:

- Protect HF-containing vessels and piping from impact by vehicles, machinery, or falling objects. Heavy objects should not be lifted over equipment containing hydrogen fluoride if it is possible to avoid doing so. If not possible, potentially affected equipment should be emptied prior to the lift.

- Ensure that all containers, piping, valves, and fittings contacting hydrogen fluoride are constructed of hydrogen fluoride-resistant materials. These materials may include special alloys (such as Monel), specially-treated metals, corrosion-resistant substances such as Teflon, and Hastelloy-B. Carbon steel is generally used for anhydrous hydrogen fluoride. Hydrogen fluoride is incompatible with glass, concrete, and other silica-based materials. Even dilute solutions of hydrogen fluoride should not be stored in glass containers.

- In industrial use, anhydrous HF may contain some water. Improper control of moisture may result in accelerated corrosion.

- Carry out regular inspections of equipment used for hydrogen fluoride (including transfer hoses) for thickness and cracks, fractures, or defects due to corrosion or mechanical stress. Include welds in the inspection.

- Refer to Department of Transportation (DOT) regulations for shipping, packaging, marking, and labeling requirements.

Employee Safety:

- Ensure that adequate training is provided to all facility employees concerning the safe handling, storage, and use of hydrogen fluoride.

- Ensure that adequate training is provided to all employees concerning the need to wear personal protective clothing and equipment that is appropriate to the task for both emergency and non-emergency situations.

- Ensure that adequate training is provided to all employees concerning emergency and notification procedures in the event of an accident.

- Ensure that the proper protective equipment is easily accessible in case hydrogen fluoride is released. Train employees in the proper use of the equipment. Inspect and test the equipment regularly.

- Have trained medical and/or emergency response personnel and adequate supplies (including first aid supplies) on site, or quickly available, to provide proper first aid in case of exposure.

Hazard Awareness:

- Avoid unintended contact between hydrogen fluoride and other chemicals. Hydrogen fluoride may react with other substances (e.g., alkalies, some oxides, sulfides, and cyanides), sometimes violently, and sometimes producing toxic gases.

Risk Minimization:

- Use good design and engineering practices for locating equipment containing hydrogen fluoride to minimize damage from possible equipment ruptures, explosions, or fires.

- Control access to hydrogen fluoride areas to avoid entry by untrained personnel.

- Ensure that no containers are leaking or broken, and conduct regular maintenance checks of all equipment and containers coming in contact with hydrogen fluoride, particularly checking for evidence of corrosion.

- Design hydrogen fluoride facilities with systems to minimize releases in the event of a leak or malfunction (e.g., by providing valves to isolate the area of the leak or providing the means to rapidly transfer the hydrogen fluoride to a different vessel).

- Have procedures in place for quick, organized response in case of a release of hydrogen fluoride.

Emergency Notification:

- In the event of a release, contact the National Response Center [(800) 424-8802], your SERC and LEPC, the local fire department, police department, and other local emergency responders.

- When contacting these organizations, provide the following information: chemical name, estimate of quantity released, time and duration of the release, affected media (e.g., air, surface water, groundwater), potential health risks, and the name and telephone number of a contact person at the facility.

CLEAN AIR ACT AMENDMENTS

Hydrogen fluoride is specifically mentioned in the accidental release provisions of the Clean Air Act Amendments of 1990. This law requires EPA to promulgate an initial list of at least 100 substances that may cause death, injury, or serious adverse effects to human health or the environment. Congress has identified the first 15 substances to be included on this list; hydrogen fluoride is among them. Where regulated substances above the threshold quantity are present at a facility, the owner/operator will be required to prepare a risk management plan that includes a hazard assessment, an accidental release prevention program, and a response program. The law requires that EPA publish regulations under the amended Clean Air Act within three years, and allows facilities an additional three years to comply. Facilities will be required to provide copies of the risk management plan to the LEPC, as well as to the state. Under the Clean Air Act Amendments of 1990, EPA also was directed by Congress to carry out a study of the potential hazards of hydrogen fluoride to the public and to make recommendations for the reduction of such hazards.

OTHER INFORMATION

The following is a list of some sources of information about hydrogen fluoride and the Emergency Planning and Community Right-to-Know Act.

- The American Petroleum Institute (API) Recommended Practice 751, "Safe Operation of Hydrofluoric Acid Alkylation Units." Call API at (202) 682-8375.

- API background paper, "The Use of Hydrofluoric Acid in the Petroleum Refining Alkylation Process." Call API at (202) 682-8163.

- CHEMTREC, a 24-hour emergency hotline that provides information and assistance to responders during an emergency. Contact (800) 424-9300 or (202) 483-7616. (**Note: CHEMTREC is *for emergency use only*.**) A call to CHEMTREC will also activate the Chemical Manufacturers Association's HF Mutual Aid Group, comprised of specially trained teams that respond to emergencies involving hydrogen fluoride.

- Response Information Data Sheets (RIDS) that include hydrogen fluoride response information are found in CAMEO™, a computer-based planning and response management program that is available from:

  The National Safety Council
  444 N. Michigan Avenue
  Chicago, IL 60611
  (312) 527-4800 (x6900)

- Your County or State Health Agency.

- Your State Emergency Response Commission.

- Your EPA Regional CEPP Coordinator. EPA Regional offices are located in Boston, New York, Philadelphia, Atlanta, Chicago, Dallas, Kansas City, Denver, San Francisco, and Seattle.

- EPA's Emergency Planning and Community Right-to-Know Information Hotline at (800) 535-0202, or (703) 920-9877 from Monday to Friday, 8:30 a.m. to 7:30 p.m., Eastern time.

- Chemical Manufacturers Association, Hydrogen Fluoride Panel. For further information, contact Fernando Leiva (202) 887-1100.

- "Hydrofluoric Acid Anhydrous - Technical: Properties, Uses, Storage and Handling," DuPont Chemicals and Pigments. Contact (800) 441-9442.

- "Recommended Medical Treatment for Hydrofluoric Acid Exposure," Allied-Signal, 1991. Contact Allied-Signal Technical Services, (800) 622-5002.

This advisory is the third of a new series which EPA is publishing to alert LEPCs to hazards posed by hazardous substances that have resulted in accidents where death, injury, or evacuations have occurred. LEPCs are responsible for emergency planning for hazardous materials and for collecting and managing data on hazardous chemicals present in their community.

Please send comments on this Advisory and suggestions for future topics to:

CEPP Advisory
EPA OS-120
401 M Street, SW
Washington, DC 20460

Additional copies of this advisory and the earlier advisories on swimming pool chemicals and ammonia are available from the above address or by calling (800) 535-0202 or (703) 920-9877.