

Protecting Workers Exposed to Hydrogen Fluoride (HF)

EXPOSURE SHOULD BE CONSIDERED A MEDICAL EMERGENCY

Anhydrous HF is a colorless, corrosive gas above 670 F, and a clear, colorless, corrosive fuming liquid at lower temperatures, with an extremely irritating odor. It readily dissolves in water to form HF acid, which is also a colorless liquid that fumes in higher concentrations. In all forms, HF can be extremely destructive to tissues (e.g., eyes, skin, and lungs) and a wide range of other substances, including most metals, concrete, and glass.

This fact sheet provides some best practices, and a general overview of some HF hazards and their control measures. It does not address all of the **Cal/OSHA** requirements that may apply to workplaces using HF.

Symptoms of Exposure

HF can be absorbed into the body through ingestion, inhalation, and eye or skin contact. It can easily penetrate the skin and cause cellular damage and systemic toxicity. The severity and timing of symptoms are dependent on the concentration and duration of exposure.

Exposure to HF can be fatal:

- Electrolyte imbalances from skin contact.
- Respiratory failure from inhalation.

Generally, exposure to a low concentration of HF vapor for a short time, either in anhydrous form or from water solutions, can cause skin and eye irritation. Severe damage to skin, eyes, other tissues, the respiratory system, and death can occur with exposure to higher concentrations. Burns from HF are particularly dangerous and require immediate and special treatment by trained medical personnel.

WORKING WITH HF SHOULD ONLY BE PERMITTED WHEN A FLUORIDE BINDING AGENT (CALCIUM GLUCONATE GEL 2.5% OR BENZALKONIUM CHLORIDE 0.13%) IS ON HAND

Immediate signs and symptoms

- Ingestion: Swallowing only a small amount of highly concentrated HF will affect major internal organs and may be fatal.
- Inhalation: Breathing HF gas may cause eye, nose, and respiratory tract irritation immediately or up to 36 hours later, even at low levels. Breathing in hydrogen fluoride at high levels or in combination with skin contact can cause death from an irregular heartbeat or from fluid buildup in the lungs.
- Skin: Skin redness, severe burning, and pain may not appear for several hours (up to 24) following exposure to a 20% solution of HF. Burns are apparent within 1 to 8 hours after exposure to 20%-50% HF solutions. Immediate pain and tissue destruction occur following exposure to a 50% solution of HF. Even small splashes of high-concentration hydrogen fluoride on the skin can cause electrolyte imbalances and death. Get medical attention immediately for all skin burns.



- **Eye:** Direct HF splashes to the eye are extremely damaging. Exposure to concentrated HF vapor may result in adverse effects several hours following exposure. Dilute solutions may produce delayed adverse effects as long as four days after the exposure.
- **Systemic Effects:** Exposure to HF can result in severe electrolyte problems, heart arrhythmias, and death.

- NIOSH Immediately Dangerous to Life or Health (IDLH) level for HF is 30 ppm.
- Cal/OSHA Short Term Exposure Limit (STEL) is 1 ppm averaged over a 15-minute period and
- 8-hour Permissible Exposure Limit (PEL) is 0.4 ppm.

Long-term health effects of acute exposures

- People who survive after being severely injured by breathing in HF may suffer lingering chronic lung disease.
- Skin damage caused by concentrated HF may take a long time to heal and could result in severe scarring. Fingertip injuries may result in persistent pain, bone loss, and injury to the nail bed..
- Eye exposure may cause prolonged or permanent visual defects, blindness, or destruction of the eye.
- Swallowing HF can damage the esophagus, stomach, and other organs over several weeks, leading to a gradual and lingering narrowing of the esophagus.

Protection from HF Exposure

The best way to prevent exposure is to substitute with a less toxic chemical. However, if working with HF is the only option, then implement engineering and administrative (including work practice) controls. Where such controls are not feasible or do not adequately reduce HF exposures, then conduct a hazard assessment that meets T8CCR section 3380 requirements and select suitable personal protective equipment (PPE) accordingly. The following are some best practices:

- Pump from closed containers or reagent bottles whenever feasible.
- Wear a long-sleeved shirt, long pants, and closed toe shoes even when working with small quantities of dilute forms of HF. Add PPE (eyes, face, hands)

based on the risk of worker exposure, quantities, and the concentration of HF being used.

 Always protect the eyes and face with goggles and a face shield whenever there is risk of exposure. While there is no absolute



recommendation against wearing contact lenses, employers should assess the risk of eye exposure and develop a policy in this regard.

- Where feasible, work in a chemical fume hood that meets T8CCR section 5154.1 requirements, or use other forms of ventilation that control HF vapor emissions at the source. Besides PPE, consider using a barrier to reduce risk of exposure to splashes.
- Wear an HF-resistant full-body apron and chemicalresistant boots anytime there is a risk of splash. Ensure there is no splash intrusion between the boot tops and legs.
- Use appropriate HF-resistant gloves.
- Select chemical boots, aprons, and gloves based on potential exposures to HF and the nature of the work, taking into consideration concentration and contact time. Consult the safety data sheet (SDS) and manufacturer of the PPE being considered to help determine adequate material, breakthrough protection, and permeation times.
- Wash hands and arms at the end of procedures involving HF—after PPE has been removed.
- Make sure the SDS for the HF being used is readily available. Ensure containers are properly labeled, and consider posting warning signs in the work area.



Exposure Evaluation and Medical Surveillance

Worker skin and airborne exposures to HF must be evaluated by a qualified individual. A physician who is board certified in occupational medicine should provide consultation to develop an appropriate medical program for management of exposures and monitoring of employees working with HF.

Handling & Storage Precautions

Before starting work:

- Consult the SDS for the specific concentration and form of HF being used and confirm with your medical service provider what procedures should be implemented, such as:
 - **Skin exposures**: which fluoride binding agent

(calcium gluconate 2.5% gel or benzalkonium chloride 0.13% solution soak) should be used for first aid. In most cases, using calcium gluconate will be more practical.

- **Eye exposure**: 1% calcium gluconate irrigating solution.
- **Inhalation**: nebulized calcium gluconate 2.5% solution.
- Confirm the location and adequate stock levels of fluoride binding agents and spill cleanup materials.
- Ensure that emergency eyewashes and showers are functioning properly and are immediately accessible to exposed workers—at most within 10 seconds.
 Emergency eyewashes and showers must meet T8CCR, section 5162 requirements. Train employees on the duration of emergency eyewash/shower use for HF exposures according to the SDS, or your medical service provider's recommendations.
- Ensure that there are individuals trained in first aid according to T8CCR, section 3400 requirements (equivalent to the American Red Cross or the Mine Safety and Health Administration criteria).

What to do if there is exposure to HF

- When exposure to HF occurs—**or is suspected** implement the procedures provided in the SDS,or by your medical service provider. Don't wait for symptoms to appear. Seek urgent care from your medical service provider, or if necessary, a hospital. Ensure the SDS goes with the exposed worker.
- Skin. Remove contaminated clothing and jewelry carefully to avoid additional contact. Flush exposed skin with water for at least 15 minutes before applying a fluoride binding agent. If a fluoride binding agent is not available, flush for at least 30 minutes. Double-glove to apply a fluoride binding agent such as calcium gluconate gel 2.5% as soon as possible after washing, and while the exposed worker is being taken to the hospital. Calcium gluconate gel should be reapplied frequently and massaged into the affected area. Systemic toxicity has occurred with relatively small burns, so medical consultation is advised in all cases.
- Eye Exposure: Immediately rinse eyes using an emergency eyewash that meets T8CCR, section 5162 requirements, and continue for at least 30 minutes. Remove and discard any contact lenses, if possible. Lift eyelids and move eyes to ensure complete irrigation. Urgently transport the injured person to medical care. Continue irrigation while transporting, if possible. Use of a 1% calcium gluconate irrigating solution can be beneficial.

Contaminated clothing and jewelry.

- Place inside a polyethylene bag. Avoid touching contaminated areas of the clothing. If that's not feasible, or extent of contamination is not known, use tongs, tool handles, sticks, or similar objects to place clothing in a bag. Anything that touches contaminated clothing should also be placed in the bag.
- Seal the bag, and then seal that bag inside another polyethylene bag. Steps must be taken to ensure anyone else that may handle the bag is aware of the hazard so they can protect themselves as well.
- When local or state health department or emergency personnel arrive, tell them what you did with the clothing.

Eyeglasses should be removed and washed with soap and water before they are re-worn.

- Airborne Exposure. If HF is released into the air, evacuate the area or shelter in place as directed by your supervision and according to your workplace emergency action plan. Emergency transport to a hospital is required even when symptoms are not initially obvious. Supplemental oxygen may be provided if the victim is having difficulty breathing. If available, administer nebulized calcium gluconate 2.5% solution. Initiate CPR as needed.
- **Ingestion**. Transport immediately to medical care. Do not induce vomiting.

Spill Clean-up

Cleanup must be done only by workers who have the necessary equipment and training to do it properly, but only after immediately notifying supervisors. If the spill is large or in an area where there is inadequate ventilation, evacuate the room immediately and await help from individuals with adequate training and equipment. Consult the SDS for recommended cleanup methods and materials.

Waste Disposal

Used HF and HF-containing solutions, as well as contaminated clothing and other articles, should be collected in a polyethylene container and separated from other types of waste. Do not mix with solvents, organic acids, oxidizers, or other chemical waste. The container must be labeled according to California hazardous waste regulations. Store the container separate from incompatible materials in a secondary container. Spill clean-up waste should also be collected for disposal as hazardous waste.

Resources

Some of the information and graphics in this fact sheet are from the University of Illinois at Chicago (UIC), **Environmental Health and Safety Office, Hydrofluoric Acid Chemical Safety Fact Sheet**, provided by Kevin Cisner (creator) and the UIC, published with permission.

Title 8, California Code of Regulations (T8CCR)

- Article 10: Personal Safety Devices and Safeguards
- Section 3400: Medical Services and First Aid Section 5189: Process Safety Management of Acutely Hazardous Materials www.dir.ca.gov/Title8/5189. html
- Section 5144: Respiratory Protection Section 5194: Hazard Communication www.dir.ca.gov/Title8/5194. html
- Section 5154.1: Ventilation Requirements for Laboratory-Type Hood Operations
- Section 5162: Emergency Eyewash and Shower Equipment
- Section 5189: Process Safety Management of Acutely Hazardous Materials
- Section 5194: Hazard Communication

American Chemistry Council Emergency Preparedness and Response for Anhydrous Hydrogen Fluoride and Hydrofluoric Acid

American Chemical Society Hydrogen Fluoride

Cal/OSHA Respiratory Protection in the Workplace – A Guide for Employers

CDC Emergency Preparedness and Response - HF

EPA Chemical Emergency Preparedness and Prevention Advisory: Hydrogen Fluoride

EPA Hydrogen Fluoride (Hydrofluoric Acid) Fact Sheet

2020 Emergency Response Guidebook: Guide No. 157. U.S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration.

Health and Human Services (U.S.) Toxicological Profile for Fluorides, Hydrogen Fluoride, and Fluorine

Honeywell Corporation: Recommended Medical Treatment for Hydrofluoric Acid Exposure

International Labor Organization (ILO) Hydrogen Fluoride (hydrofluoric acid, anhydrous)

NIOSH Emergency Response Card

NIOSH IDLH Values (HF)

NIOSH Pocket Guide

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This document is available with active links at www.dir.ca.gov/dosh/PubOrder.asp For assistance regarding this subject matter, employers may contact Cal/OSHA Consultation Services at: 1-800-963-9424 or InfoCons@dir.ca.gov www.dir.ca.gov/dosh/consultation.html