

Hydrogen Fluoride, Hydrofluoric Acid, and Fluorine

Hydrofluoric acid, hydrogen fluoride, and fluorine are one of the most dangerous groups of chemicals used by industry and ranks along side of chlorine as one of the most toxic chemicals that might likely be targeted for intentional release by terrorists using explosives.

Production

Hydrofluoric acid (chemical formula HF) is a solution of anhydrous hydrogen fluoride in water (typically 25%, 38 or 40%, 49%, 70%, or 79%) and is the form usually shipped by railcar or in smaller tanks, and is the form usually stored at a plant site. Anhydrous, 49%, and 70% solutions are the forms of hydrogen fluoride usually encountered in the United States. Concentrations greater than 70% are considered "anhydrous" for regulatory purposes. Anhydrous hydrogen fluoride is usually shipped in railcars under its own vapor pressure. The average U.S. number of railcar shipments of hydrofluoric acid and the anhydrous form during the period 1996-1999 was over 3000 per year. Most hydrogen fluoride is produced by reacting the mineral fluorspar (chemical formula CaF_2) with sulfuric acid, but some may be produced from fluorosilicic acid which is a byproduct of the domestic phosphate industry or from industrial waste or recycled chemicals. In the U.S., fluorine (chemical formula F_2) may be generated at the user site by electrolysis of hydrofluoric acid, but is also shipped to a user site as a compressed gas in cylinders or occasionally as a refrigerated liquefied gas under its own pressure in typically 5000 lb capacity tanks; the U.S. production of fluorine is about 5000 tons per year. The total U.S. consumption of hydrofluoric acid is roughly 350,000 tons per year. The U.S. has the capacity to produce roughly 250,000 tons annually [206,000 tons in 1992]; the balance is imported from other countries. The United States is not the largest producer. The hydrofluoric acid consumption in China in 2009 was 917,000 tons; China also has the capacity to produce over a million tons annually (see <http://www.researchinchina.com/htmls/Report/2009/5703.html>). The U.S. imports fluorspar from China, Mexico, Mongolia, and other countries as it does not have a significant domestic source.

Use

According to an EPA hydrogen fluoride study report to the U.S. Congress in the early 1990's , [see: <http://www.epa.gov/oem/docs/chem/hydro.pdf>], there were 531 facilities that either processed or used hydrogen fluoride in excess of threshold quantities on site. The threshold for reporting to the EPA was 25,000 lbs (processing or manufacturing) or 10,000 lbs (otherwise using HF). The breakdown as to end use (1991 data) was as follows:

- Fluorocarbon manufacture: 152,000 tons (63% of total)
- Alkylation catalyst for gasoline: 16,700 tons (7% of total)

- Nuclear applications, uranium hexafluoride: 13,000 tons (5% of total)
- Aluminum industry to produce aluminum fluoride: 8,000 tons (3% of total)
- Other uses (stainless steel pickling, various chemical derivatives and products, electronics, specialty metal production, etc.): 52,000 tons (22% of total)

Today, hydrogen fluoride consumption is greater than in 1991, with over 1000 facilities that process or use hydrogen fluoride in excess of EPA reporting thresholds. Fluorocarbon manufacture still accounts for about 60% of the total use, mostly refrigerants. Chemical derivatives account for about 18%, aluminum manufacturing 6%, and stainless steel pickling 5%. A major use of fluorine gas is in the production of gaseous uranium hexafluoride from raw uranium, which is the form used for uranium isotope enrichment in the nuclear industry; after enrichment has taken place, the fluorine might be recovered and used again for more uranium enrichment. Other uses of fluorine include sulfur hexafluoride production and treatment of polymer surfaces to reduce permeability to organic liquids (including manufacture of personal protection equipment). Fluorosilicic acid and sodium silicofluoride is commonly used to fluorinate water supplies. Sodium silicofluoride is also used in enamels for china and porcelain, opal glass, as a rodenticide, and mothproofing of wool.

Fifty percent (50%) and greater aqueous hydrofluoric acid is the cutoff concentration for industry providing off-site consequence documentation for hydrogen fluoride under EPA regulations (40 CFR Part 68). Therefore, in the U.S., 49% aqueous hydrofluoric acid is probably the most common concentration stored and shipped. The U.S. OSHA Process Safety Management Rule (20 CFR 1910.119) is required for anhydrous hydrogen fluoride and not for concentrations in water of 70% or less, although good industry practice should incorporate OSHA recommendations for all concentrations (we will give an example where OSHA fined a company following a worker death which occurred when he was sprayed in the face with an HF acid solution). DOT regulations for hazardous chemicals are applicable for all hydrogen fluoride concentrations.

Transportation

The EPA Report to Congress, available at <http://www.epa.gov/oem/docs/chem/hydro.pdf>, presents a detailed listing and specifications for anhydrous hydrogen fluoride and hydrofluoric acid transportation and storage as of about 1992, the date of the report. An updated and proposed specifications published by the Hydrogen Fluoride Industry Practices Institute (a subsidiary of the American Chemistry Council) as of January 2010 is available at <http://www.hfipi.com/guides.asp>, (follow instructions at link). Since the illustrations and information of the 2010 link may be copyrighted, we used the illustration in the Report to Congress for figure 1:

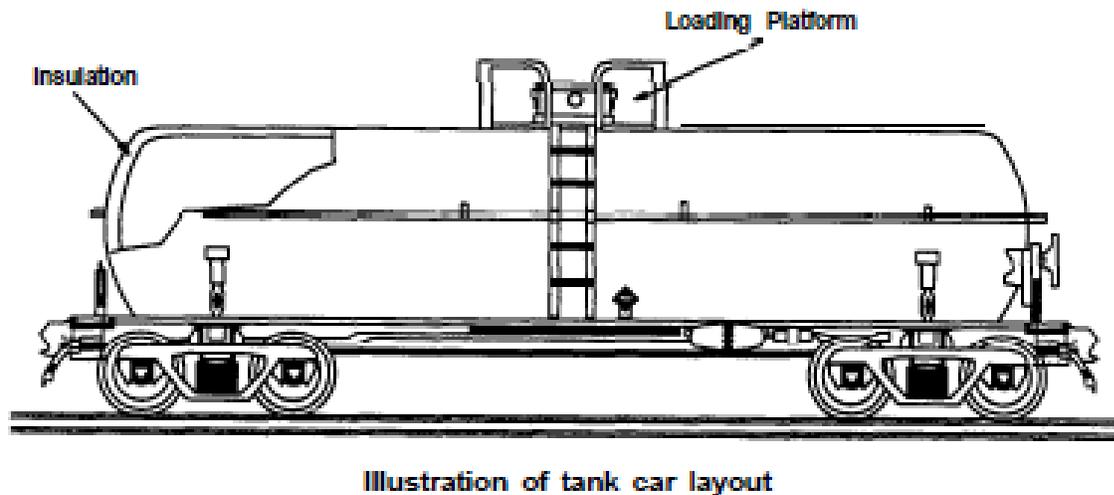
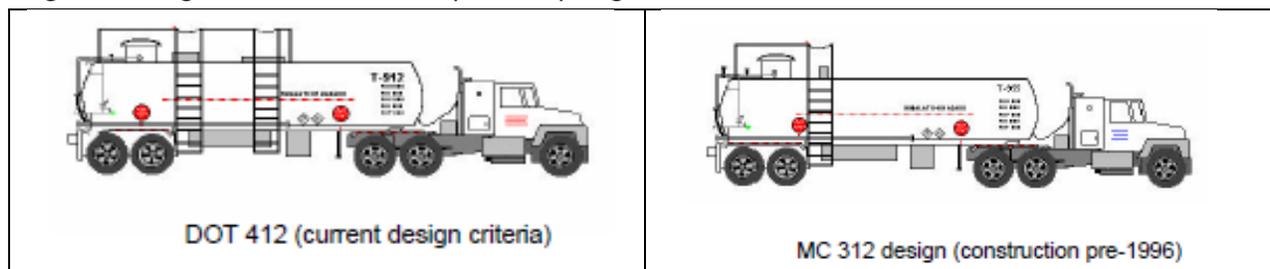


Figure 1. Class 105A300W Rail Road Tank Car Commonly Used for Anhydrous Hydrogen Fluoride

Figure 1 shows a cut of the 105A300W tank car commonly used to transport anhydrous hydrogen fluoride, which has a capacity range of 4,000 to 16,000 gallons. Other tank specification numbers are also allowed by the U.S. Department of Transportation (and also in Canada), but all are similar in appearance and design, and all have test pressures of 300 psig or greater (burst pressure 750 psig for 105A300W). The only opening permitted is a single man way at the top. There are five valves inside the dome cover, one of which is a safety valve designed to vent in case of over pressurization. Rail road tank cars for transporting aqueous hydrofluoric acid look similar and have different capacities, and may be lined with rubber or chlorobutyl rubber or a fluoropolymer. A typical rail car for transporting aqueous hydrofluoric acid has capacities ranging from 4,500 to 8,000 gallons, although larger capacities are possible.

Cargo tank trailers (transported by motor vehicle) are similar for both anhydrous and 70% aqueous hydrogen fluoride, and illustrated by figure 2. Similar to railroad cars, the chemical is loaded and unloaded from the top and must meet DOT specifications (DOT-412 if current or MC-312 if constructed before 1995, see 40 CFR 178.348). Bottom outlets are not allowed. Figure 2 for DOT-412 illustrates a manhole "nozzle" at the top with 20-inch diameter minimum. A typical container capacity is 5000 gallons. The tank may be constructed of carbon steel or SA240 type 316L Stainless Steel (specification UNS S31603). The degree of corrosion is roughly the same for stainless and carbon steels in contact with anhydrous and 70% aqueous hydrogen fluoride at ambient temperatures, except that anhydrous hydrogen fluoride can result in hydrogen stress corrosion cracking and embrittlement of carbon steel at low temperatures requiring additional testing and repairs. Direct contact of carbon steel with more dilute hydrofluoric acid solutions is not recommended because of corrosion; carbon steel tanks are lined with chlorobutyl rubber (or a fluoropolymer such as PTFE if below 49% concentration).

Figure 2. Cargo Tank Trailer for Anhydrous Hydrogen Fluoride



Images from Honeywell International as used in http://www.americanchemistry.com/s_acc/sec_directory.asp?CID=1457&DID=5883.

Anhydrous hydrogen fluoride ISO containers are carbon-steel framed tanks and normally come in two sizes (20 feet long and 6000 to 6700 gallon capacity or 30 feet long and 8,900 to 10,000 gallon capacity), both sizes 8 to 8.5 feet high. Aqueous hydrofluoric acid intermodal ISO containers meet IM101 DOT 51 specifications, are of carbon or 316L stainless steel, and is lined with either chlorobutyl or fluoropolymer material.

Hydrofluoric acid may be shipped in smaller packages, including 1 gallon containers, 55 gallon drums, and intermediate packages up to 300 gallons. For regulatory purposes for hazardous materials, the U.S. Department of Transportation regards bulk packages as having a capacity of 119 gallons or greater. Cylinders up to about 400 lbs capacity may be used to transport anhydrous hydrogen fluoride or aqueous hydrogen fluoride. Laboratories are the primary user of smaller cylinders. On-site storage tanks for 49% hydrofluoric acid may be constructed of lined carbon steel (corrosion-resistant lining) or molded plastic tanks.

Physical Properties

Table 1 presents physical properties of fluorine, anhydrous hydrogen fluoride, 70% hydrofluoric acid, and 49% hydrofluoric acid. In this table, 70% hydrofluoric acid means a solution of 70% anhydrous hydrogen fluoride and 30% water by weight.

Table 1. Physical Properties

Chemical	Melting Point	Boiling Point	Sp. Gravity (water =1) of liquid	Vapor Pressure @ specified temp.
Fluorine	-363°F (-219.6°C)	-307°F (-188.1°C)	Gas @ 25°C; liquid 1.5127 @ -188°C	0.1214 atm @ -203°C 51.4 atm @ -128°C
Anhydrous hydrogen fluoride	-118°F (-83.6°C)	67°F (19.5°C)	Gas @ 25°C Liq: 1.015 @ 0°C	1.03 atm at 20°C
70% hydrofluoric acid	-95.8°F (-71°C)	151°F (66°C)	1.243 @ 16°C	0.145 atm at 21°C
49% hydrofluoric acid	-34°F (-37°C)	224°F (106°C)	1.175 @ 16°C	0.037 atm at 24°C

Notes: Anhydrous hydrogen fluoride: see I. Sheft et al, *Journal of Inorganic and Nuclear Chemistry*, 35(11) 1973 pp 3677-3680; 49% and 70% from Hydrogen Fluoride Industry Practices Institute website; fluorine properties from <http://www.atsdr.cdc.gov/toxprofiles/tp11-c4.pdf>.

Fluorine is a gas under normal temperatures and pressures. It is normally shipped as a compressed gas in cylinders or generated by the user on site by electrolysis of hydrogen fluoride or by recycling chemical products containing fluoride. The gas can be liquefied and stored on site, but only if pressurized and refrigerated. To liquefy fluorine, the temperature must be below its critical temperature (127°C or 197°F) and even then about 51 or 52 atm (741 psig) pressure will be inside the container. [psig = pounds per square inch gage]. If chilled further, for example, to -203°C (-333°F), a container of liquefied fluorine will have a vapor pressure of 0.1214 atmospheres. In the U.S., fluorine is not currently shipped in rail cars.

Anhydrous hydrogen fluoride boils at 67°F (19.5°C) under normal atmospheric pressure. The chemical is normally stored as a liquid in containers under its own vapor pressure, which at 67°F (19.5°C) is equal to 1 atmosphere. If the temperature in a storage container rises above its normal boiling point, the vapor pressure increases. Railroad tank cars have a safety valve set to vent at 300 psig; the vapor pressure would normally not get this high unless the tank car was subjected to a fire. Anhydrous hydrogen fluoride is withdrawn from the top of the tank car using a transfer pump.

Solutions of hydrofluoric acid in water have higher boiling points and lower vapor pressures. The vapor pressure of 49% (or lower concentration) hydrofluoric acid at ambient temperature is considered by the EPA not to pose a significant risk from a toxic vapor cloud for the purposes of users doing an off-site consequence analysis under 40 CFR Part 68. However, any spill of hydrofluoric acid regardless of concentration can result in significant environmental damage.

Anhydrous hydrogen fluoride is very soluble in water. Tests at the Nevada HazMat Test Facility by industry have demonstrated that over 90 percent of hydrogen fluoride released to the atmosphere in case of an accident can be knocked down by water sprays incorporated as a safety feature at facilities that store or use hydrogen fluoride. This is now a standard safety feature employed by refineries and others that use large volumes of hydrogen fluoride.

Example Hydrogen Fluoride and Hydrofluoric Acid Accidents

EPA hydrogen fluoride study report to the U.S. Congress summarized information on 10 anhydrous hydrogen fluoride and 13 hydrofluoric acid release accidents at fixed facilities in the U.S. from their "Accidental Release Information Program" during the period from September 1986 through 1991. This data base is not a complete list of all releases; it only contains release information that industry is required by law to report and for which EPA sent a questionnaire to the industry, and the questionnaire has not been independently verified. The U.S. Department of Transportation reported another 19 hydrogen fluoride release accidents during 1980 through 1990, including one railroad tank car derailment, two tank car weld failures or piping failures, eight valve failures on tank cars, and eight packaging failures. The study report to Congress also looked at other U.S. hydrogen fluoride release incidents bringing the total to 155 accidents.

The worst accident cited in the EPA data base in terms of quantity released was the 30 October 1987 release of hydrogen fluoride from a pressurized tank at the Marathon Corporation refinery at Texas City,

Texas. This release was also discussed in the AristaTek newsletter for April 2005. The EPA in their data base estimated that 65,200 lbs of hydrogen fluoride total was released; another release estimate (cited in the Dayal study) was 36,000 lbs during the first hour and 4,000 lbs during the next hour. The accident was caused by an overhead crane dropping a convection unit onto the pressurized hydrogen fluoride tank severing the top piping. The resulting toxic plume cloud was reported to be two to three miles long and 0.5 to 1 mile wide. Winds were from the southeast at 5 to 10 mph. At least 3000 people in 52 city blocks were evacuated (the EPA estimated 5800 people evacuated and another estimate was 4000 people, and another EPA report said 85 city blocks evacuated). The effects on community exposure were published in a paper, H. Dayal et al, "A Community-based Epidemiological Study of Exposure to Hydrofluoric Acid (HF)", *Annals of Epid.*, vol 2, pages 213-230, (1992), available at <http://www.ncbi.nlm.nih.gov/pubmed/1342272>. The EPA reported 1037 people off-site were treated for eye and respiratory problems, which persisted for over two years with some individuals; no deaths were reported. The accident could have been a lot worse in terms of injuries and fatalities, if the bottom of the tank had severed or the toxic plume cloud drifted into a more populated area.

Deaths have occurred due to hydrogen fluoride exposure in other accidents. Fortunately, there have been no instances of mass casualties due to hydrogen fluoride or fluorine inhalation (at least not in public records based on available information from the Internet). An OSHA investigation of workplace accidents due to inhalation or skin exposure is available at <http://www3.interscience.wiley.com/journal/85006258/abstract?CRETRY=1&SRETRY=0>. Several other countries have also provided documentation. Some examples of worker deaths follow:

- 12 May 2000, Hunter's Sales Inc., Twin City GA: An employee was sprayed with hydrogen fluoride solution due to rupture of a hose while the chemical was being transferred from a 55-gallon drum to a mixing vat. Although the employee used the emergency shower, he returned to work and died later as symptoms of exposure were delayed. OSHA fined the company \$22,000 for failure to have an adequate hazard communication program to protect workers handling hydrogen fluoride. Details at http://ehstoday.com/news/ehs_imp_33811/.
- 6 March 1991, Kerr-McGee Southwestern Refinery, Corpus Christi, TX. Two workers died and five injured when they inhaled hydrofluoric acid vapors escaped from a gasoline blending unit. The company did not make public economic losses.
- 28 October 1994, Perth Australia. A 37-year-old technician working in a small paleontology laboratory accidentally splashed himself on his right leg with 100 ml of 70% hydrofluoric acid solution, and immediately washed himself using a hose attached to a laboratory sink. He then ran outside to a nearby pool filled with water and remained in the pool until the ambulance arrived. The hospital amputated his leg one week later, and on 12 November, he died.
- 2 January 2007, Bayer Alumina Plant, Point Comfort, TX. A 37 year-old technician opened a valve in the piping system of a vacuum monitoring line during a routine stem cleaning operation, and hydrogen fluoride discharged in his face. The technician walked over to the control room operator and said he had hydrogen fluoride in his face. The operator summoned help and applied calcium gluconate gel to his face, and the technician was taken shortly afterward to the hospital at 2 PM. He was airlifted to another hospital at 6 PM and was pronounced dead at 8:07

PM. The cause of death was chemical inhalation, according to the attending physician. The Mine Safety and Health Administration investigative report (<http://www.msha.gov/FATALS/2007/FTL07m01.asp>) revealed deficiencies in company procedures for checking and cleaning vacuum monitoring lines, among them being that the procedure did not **require** technicians to wear a respirator or face shield to perform this work. A standard work instruction on stem cleaning dated 9 January 2002 warned of potential hydrogen fluoride drips, leaks, and sprays, and said that a hardhat, safety glasses, hydrogen fluoride cartridge respirator, face shield, and rubber gloves **should** be worn, and required the use of a special wash out tool designed to prevent hydrogen fluoride from escaping during this procedure. The technician who died did not wear a respirator or face shield, and management did not **require** the wearing of a respirator and face shield.

These reports all have in common that exposure to hydrogen fluoride or hydrofluoric acid by skin contact or inhalation can result in death, and that the effects of exposure are often delayed. The person may feel fine after exposure and take precautions to wash the affected part and even seek hospital treatment, only to die sometime later.

First Aid and Health Effects

Hydrogen fluoride is readily absorbed through the skin and is toxic by inhalation and ingestion. The U.S. Department of Health Services, Agency for Toxic Substances & Disease Registry (ATSDR), has published guidelines for Hydrogen Fluoride (see <http://www.atsdr.cdc.gov/toxpro2.html> and Appendix I of http://www.americanchemistry.com/s_acc/sec_directory.asp?CID=1457&DID=5883). The ATSDR recommends that all persons who have eye exposure or serious skin exposure (i.e. fingertip exposure or skin exposure greater than the size of the total surface area of the palm, or any evidence of burns or blistering) be transported to the hospital as soon as possible, and that continuous skin and eye irrigation or treatment be administered during transport. Adsorption of fluoride ions can result in hypocalcemia and cardiac arrest. Rapid decontamination with copious amounts of water is recommended. Eyes should be flushed for at least 20 minutes with plain water or saline solution in case of eye exposure. This must be done immediately after exposure. Calcium-containing gels (e.g. calcium gluconate), solutions, and medications can be used to “neutralize” the fluoride ion [Calcium fluoride is insoluble and is not readily absorbed]. The gel form of calcium gluconate should not be applied to the eyes.

In case of ingestion, emesis should not be induced as first aid. If the patient is able to swallow, 4 to 12 ounces of water should be administered to dilute the acid; a one-time dose of several ounces of Mylanta, Maalox, or milk of magnesia may be given to bind the fluoride in the stomach. Activated charcoal or sodium bicarbonate should not be administered.

The ATSDR websites cited present information on advanced life support and treatment under the care of qualified medics.

The U.S. EPA has published Acute Exposure Guideline levels (AEGs) for hydrogen fluoride inhalation, in terms of parts per million (ppm) for different times of exposure (Table 2).

Table 2. Acute Exposure Guideline Levels (AEGLs) for Hydrogen Fluoride, from EPA National Advisory Committee, for different exposure times

AEGL-Level	10-minute	30-minute	60-minute	4-hour	8-hour
AEGL-1 nondisabling	1 ppm (0.8 mg/m ³)	1 ppm (0.8 mg/m ³)	1 ppm (0.8 mg/m ³)	1 ppm (0.8 mg/m ³)	1 ppm (0.8 mg/m ³)
AEGL-2 disabling	95 ppm (78 mg/m ³)	34 ppm (28 mg/m ³)	24 ppm (20 mg/m ³)	12 ppm (9.8 mg/m ³)	12 ppm (9.8 mg/m ³)
AEGL-3 lethal	170 ppm (139 mg/m ³)	62 ppm (51 mg/m ³)	44 ppm (36 mg/m ³)	22 ppm (18 mg/m ³)	22 ppm (18 mg/m ³)

CITGO Corpus Christi, TX, Refinery Explosion, 10 July 2009

On 19 July 2009, highly flammable hydrocarbon vapors were released from process piping at the CITGO Corpus Christi east refinery hydrogen fluoride alkylation unit. The vapor cloud of released hydrocarbons reached an adjacent unit and ignited and exploded. The resulting fire caused multiple failures, including release of hydrogen fluoride from the alkylation unit, and burned for two (another report said several) days. One employee was critically injured by the fire and a second employee was treated for possible hydrogen fluoride exposure during cleanup operations. CITGO reported to the Texas Commission on Environmental Quality that approximately 21 tons (42,000 lbs) of hydrogen fluoride was released from the alkylation unit piping and equipment, and all except 30 lbs was captured by the company HF water mitigation system. The alkylation unit was restarted on 1 November 2009.



Chemical Safety Board video clip taken of the hydrocarbon vapor cloud a second before ignition, video from a CITGO surveillance camera.

The accident was investigated by the U.S. Chemical Safety Board (CSB), which used footage from two company surveillance cameras to help determine the root cause of the accident; the 4 minute sequence can be viewed at <http://www.csb.gov/investigations/detail.aspx?SID=83&Type=1&pg=1&>. The footage indicated violent shaking in the process recycle piping which broke two threaded connections releasing hydrocarbon vapor. The shaking was caused by nearby flow blockage, which occurred due to a sudden failure of a control valve. The control valve failed when an internal plug untreaded from the valve stem closing the valve. A manually operated bypass valve became inaccessible due to the hydrocarbon release.

The CSB notified CITGO on 24 November 2009 of their intent to release a video clip based on portions two CITGO surveillance videotapes on the CSB website. CITGO objected, citing issues of national security and conflicts with other ongoing investigations by other agencies. After consulting with the Department of Homeland Security for a ruling, CSB posted the video on their website along with the Department of Homeland Security response [Ruling: The limited footage shown in the video clip did not require Sensitive Security Information (SSI) protection; camera footage may be SSI if it reveals insight into a specific security process].

The CSB also disputed the CITGO estimate of 30 lbs of hydrogen fluoride not captured by HF water mitigation system, and came up with their own estimate of at least 4000 lbs escaping the HF mitigation system. The CITGO estimate was based on ground-based monitors which CSB maintained could not see most of the fluorides released because of updrafts resulting from the two-day fire. The CSB estimate of at least 4000 lbs was based on tests reported in the literature showing a 90% capture (95% at best) with water mitigation systems and the CITGO estimate of 42000 lbs of hydrogen fluoride released from the alkylation unit piping and equipment. Regardless of release amount not captured by the water sprays, the prevailing winds resulted in the smoke-cloud moving toward the Corpus Christi ship channel and Nueces Bay away from population areas. The CITGO refinery also nearly exhausted their stored water supply for their water mitigation system during the first day, and after 11.5 hours following the incident CITGO began pumping salt water from the ship channel into their fire-water supply.

The CSB also recommended that CITGO conduct independent, third-party audits of the safety of its two HF alkylation units at refineries in Corpus Christi, TX, and Lemont, Illinois. CITGO had never conducted a safety audit of their units at either refinery as recommended by American Petroleum Institute Recommended Practice 751, "Safe Operation of Hydrofluoric Acid Alkylation Units". Another recommendation was that CITGO develop and initiate plans to ensure an adequate water supply for the refinery HF mitigation system.

Role of The PEAC Tool

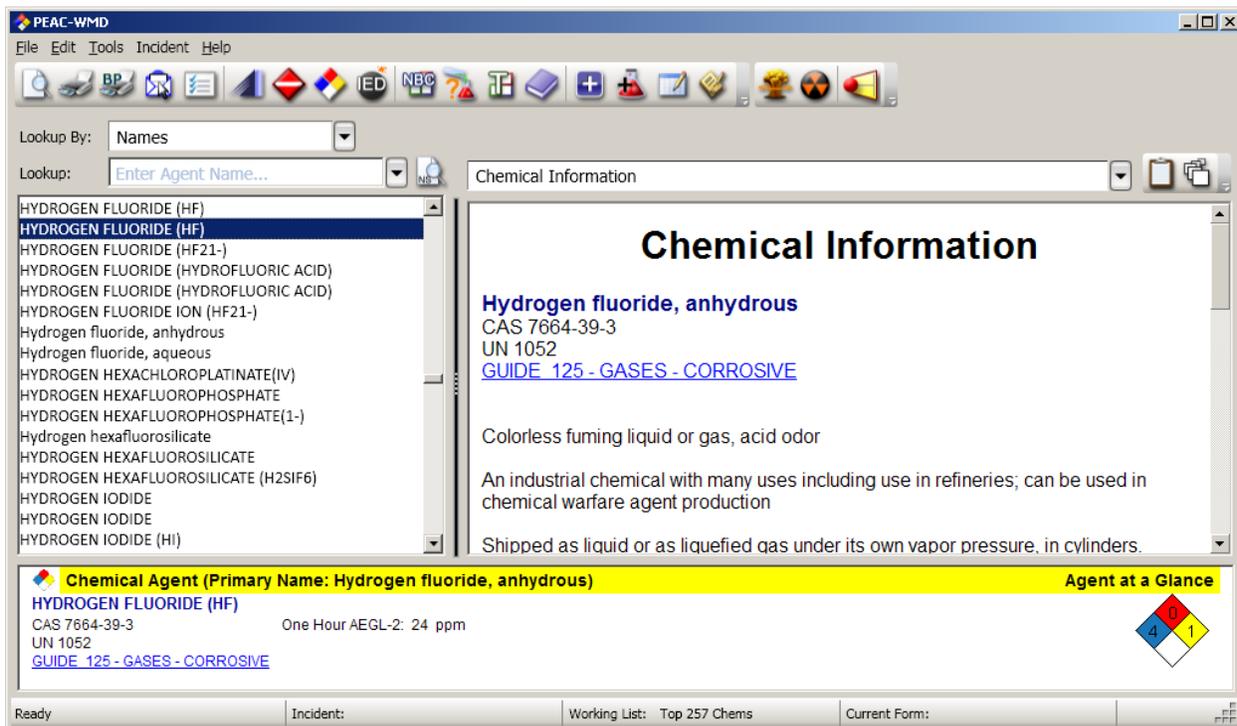
While industrial accidents happen, industry as a whole is cognizant of the hydrogen fluoride hazards and practices safe engineering practices. The PEAC tool is valuable to industry and responders to look at "what if" situations. A major concern in today's world is the potential for terrorists to purposely release a dangerous chemical in a populated area. We will consider two hypothetical scenarios:

- A railcar containing 10,000 gallons (83,000 lbs) of anhydrous hydrogen fluoride is blown up with explosives releasing its entire contents at once.
- A railcar stationary on the track containing 10,000 gallons (83,000 lbs) of anhydrous hydrogen fluoride is fired upon resulting in anhydrous hydrogen fluoride leaving a half-inch diameter hole near the bottom of the railcar.

What is the "minimum" safe evacuation protective action distance (PAD) in the case of inhalation exposure? "Evacuation" may mean "Shelter in Place" if there is not enough time to evacuate people. There could still be fatalities closer to the source. We will assume a 1 PM release, June 30, daytime release, St. Louis MO location, winds from the southwest at 5 mph, outdoor temperature at 80°F, and mostly overcast (80% overcast) skies.

Comment: The PEAC tool asks the user to select a date, time, and latitude and longitude. This allows the protective action distance to be displayed on a map. Also, the protection action distance calculated depends upon the angle of the sun for a daytime release, which in turn depends upon the date, latitude, cloud cover, time of day, and location, and wind speed. Other gas dispersion models such as ALOHA ask the same kind of information.

The first step is to pull up Hydrogen fluoride in the PEAC tool. Earlier, under “options” [open  on the tool bar] we had specified that we wanted to work in the English system and set the date and time rather than use the PEAC tool internal clock; we also specified that we wanted to input the total mass released. To get “hydrogen fluoride”, we type in or select “hydrogen fluoride” in “lookup” under “Names”. We can get a lot of information about hydrogen chloride using the scroll-down bar at the right.



The screenshot shows the PEAC-WMD software interface. The main window is titled "PEAC-WMD" and has a menu bar with "File", "Edit", "Tools", "Incident", and "Help". Below the menu bar is a toolbar with various icons. The "Lookup By:" dropdown is set to "Names". The "Lookup:" field contains "Enter Agent Name...". The "Chemical Information" dropdown is open, showing a list of chemical names. The selected item is "HYDROGEN FLUORIDE (HF)". The right pane displays the "Chemical Information" for "Hydrogen fluoride, anhydrous", including its CAS number (7664-39-3), UN number (1052), and a link to "GUIDE 125 - GASES - CORROSIVE". The bottom status bar shows "Ready", "Incident:", "Working List: Top 257 Chems", and "Current Form:".

Chemical Information

Hydrogen fluoride, anhydrous
CAS 7664-39-3
UN 1052
[GUIDE 125 - GASES - CORROSIVE](#)

Colorless fuming liquid or gas, acid odor

An industrial chemical with many uses including use in refineries; can be used in chemical warfare agent production

Shipped as liquid or as liquefied gas under its own vapor pressure, in cylinders.

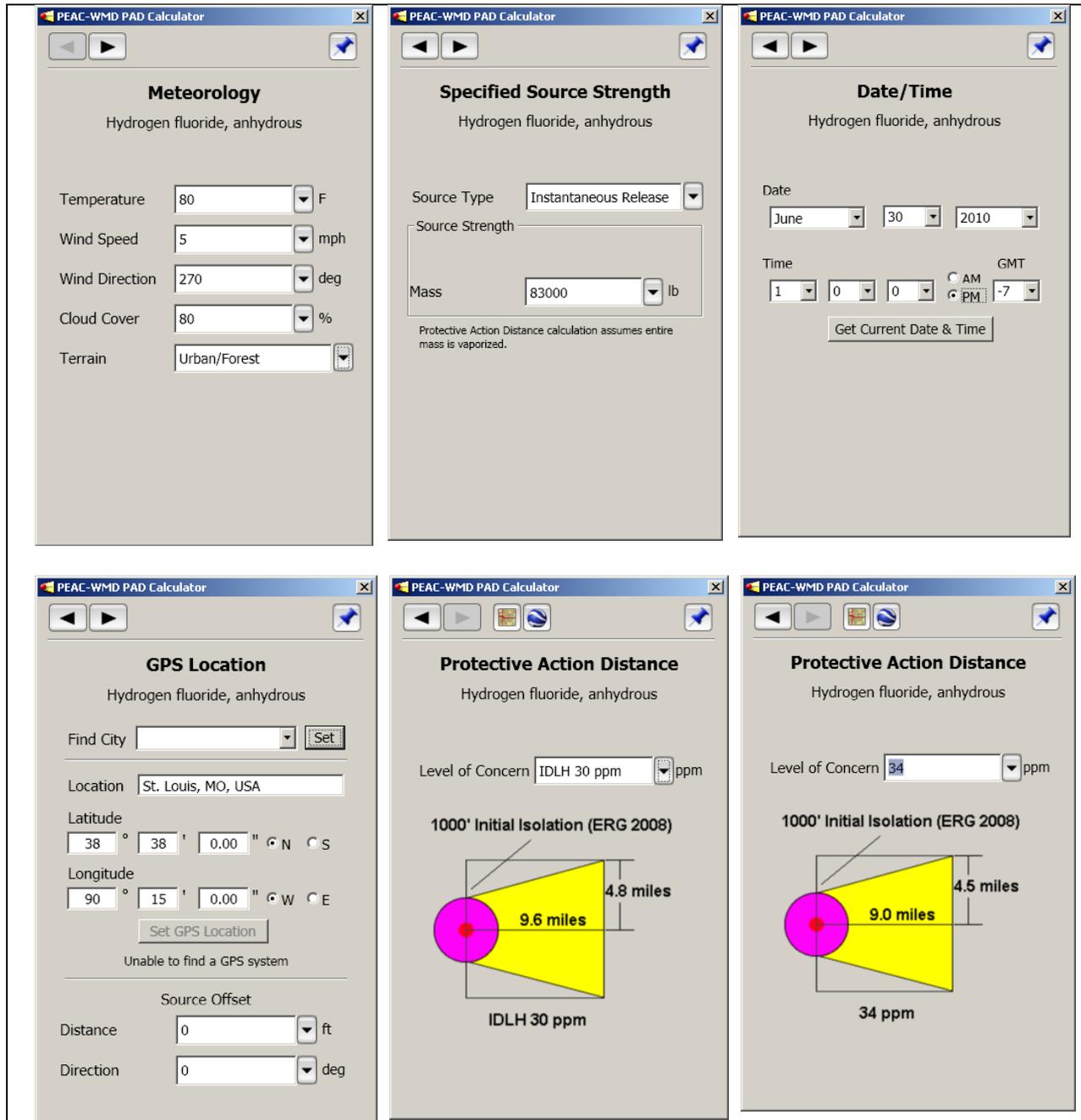
Chemical Agent (Primary Name: Hydrogen fluoride, anhydrous) **Agent at a Glance**

HYDROGEN FLUORIDE (HF)
CAS 7664-39-3 One Hour AEGL-2: 24 ppm
UN 1052
[GUIDE 125 - GASES - CORROSIVE](#)

Ready Incident: Working List: Top 257 Chems Current Form:

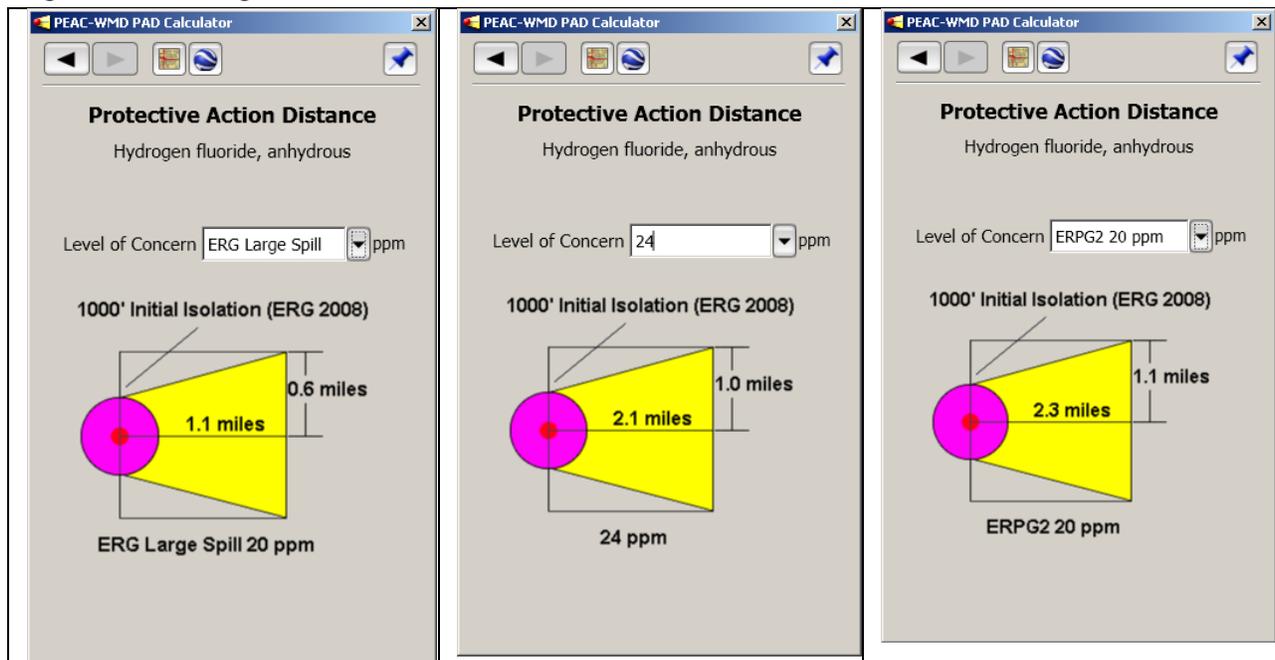
To determine the minimum” safe evacuation protective action distance (PAD), we open the  icon on the tool bar. An “acknowledgement” statement pops up acknowledging limitations of the model. This is followed by a “Meteorology Screen” where the user enters temperature, wind speed and direction, and cloud cover. For the “Explosion” scenario, all 83,000 lbs is assumed to be released at once (a worst case). We then enter the date and time, and St. Louis MO location. The PEAC tool entered a default latitude and longitude since we did not specify an exact location.

Figure 3. Modeling for Explosion, Entire Rail Car Contents of 83,000 Pounds Released at Once



Note that the Protective Action Distance is modeled to two levels of concern, the 9.6 miles is based on the Immediately Dangerous to Life and Health (IDLH) value of 30 ppm for a 30 minute exposure, from the NIOSH Pocket Guide to Chemical Hazards, and the 9.0 miles is based on EPA's Acute Exposure Guideline Level for threshold of disabling effects, AEGL-2, for a 30 minute exposure. The 1000 foot initial isolation diameter came from the 2008 Emergency Response Guidebook.

Figure 4. Modeling for 0.5-inch Diameter Hole in Bottom of Rail Car



At left in Figure 4 is the 2008 Emergency Response Guidebook recommendation of 1.1 miles for “Large Spills”. In the center is a PEAC tool prediction of 2.1 miles for AEGL-2 of 24 ppm, 60 minute exposure. At right is the PEAC tool prediction based on the Emergency Response Planning Guideline Level 2 (ERPG2) of 20 ppm for the one hour exposure. The ERPG2 value is published by the American Industrial Hygiene Association, and is the allowable concentration for serious health effects or impaired ability to take protective action.

Some points need to be made here:

- The PEAC tool has chosen to use the same format for display of the Protective Action Distance (PAD) results as the 2008 ERG but allows the user to select different levels of concern and give flexibility to select a release situation and meteorology.
- The 2008 Emergency Response Guidebook (2008 ERG) is designed for “typical” transportation accidents, not for terrorist incidents. While there is a section for chemical warfare agents “when used as a weapon”, this logic does not extend to toxic chemicals used by industry. We are looking at a couple of hypothetical terrorist incidents in these examples, and therefore the release rate or amount is greater in these hypothetical incidents than what was used in the 2008 ERG release scenarios used in the ERG Guidebook.
- The PEAC tool models the centerline concentration near a man’s height. This concentration falls off as one moves crosswind away from the centerline; however, because of possible shifting winds and variable terrain and buildings, the concentration cannot be predicted except in an idealized situation.

- The EPA AEGL-2 levels seem to be the most popular criteria for selecting a Level of Concern for plume cloud modeling. The ERPG-2 (one hour exposure) is another popular criteria for selecting the PAD. Historically, IDLH values have been used and sometimes still used if ERPG or AEGL values are not available.
- The PEAC tool lists the IDLH, ERPG, and AEGL values, and other published criteria for each chemical, or the user can select a distance for other levels of concern. This gives the user a flexibility of choice.
- Responders can quickly work through many “what if” situations, create reports, files, and E-mail results to decision makers using the PEAC tool.

How good are the modeling numbers? No one has completed validation tests for distances far from the hydrogen fluoride release source, but there have been tests (called the “Goldfish Series”) at the Nevada HazMat Spill Center near Mercury Nevada comparing “measured plume cloud concentrations resulting from hydrogen fluoride spills” to other models up to 0.3 km from the source. PEAC tool comparisons are in the April 2005 AristaTek Newsletter. Comparisons of the tests with other models are available in a paper: Hanna, S.R., D.G. Strimaites, and J.C. Chang. 1991. “Evaluation of Fourteen Hazardous Gas Models with Ammonia and Hydrogen Fluoride Field Data” Journal of Hazardous Materials 26 pp. 127-158.

For the “explosion” example, where all of the hydrogen fluoride is released into the atmosphere within a few minutes, the duration of exposure should be short. “Shelter in Place” is the most durable option barring extraneous circumstances.

Conclusion

The possibility of toxic industrial chemicals (TICs) and toxic industrial materials (TICs) released as the result of terrorist activity must be considered by industry, emergency responders, and law enforcement. Industry and government agencies as a whole have done a reasonably good job at protecting workers and the public against releases, although accidents can and do occur. The PEAC tool can be a valuable aid to responders and responder training to quickly evaluate consequences of “what if” and “worst case” situations.