

Hydrofluoric acid the worst of all acids?



Despite being produced 200 times less than sulphuric acid (1 M vs. 200 M tonnes/year), the ARIA database has recorded nearly 80 accidents involving hydrofluoric acid (HF) (vs. 220 for H_2SO_4). A series of recent accidents serves to recall its hazards, especially the serious consequences in the event of its release..

Why is hydrofluoric acid hazardous?

- **Highly corrosive:** It dissolves the majority of minerals (oxides, silicates), metals and plastics.
- **Highly toxic:** Fluoride ions F^- penetrate deeper tissue layers and fully react with both magnesium and calcium. The resulting salts formed are thus toxic for living cells..
- **Highly soluble in water:** The acid reacts violently with water (releases smoke) and cannot be distinguished from it.
- **Weak acid:** For concentrations of <40%, a chemical burn on the skin is not painful at first, but only once the bone has been reached. It is felt several hours later.
- **Potential fuel source:** Despite being non-flammable, HF in solution reacts with lightweight alkaline metals in releasing hydrogen (H_2 :an extremely flammable and explosive gas).

Product fact sheet

- A colourless, volatile product with a pungent smell.
- Forms : Pure, in anhydrous form (HF-A, gaseous at $T > 20^\circ\text{C}$ under atmospheric pressure) or diluted in water up to 75% (HF).
- Discovered in 1670, derived from fluorine ore (CaF_2)
- Basic industrial consumption for: pharmaceutical product synthesis, fluorinated products, fuel refining (alkylation), glass and metal treatment, production of alumina and uranium fuel.
- Industrial consumption on the rise (by 4-6% a year), notably in semiconductor manufacturing.



The 1st season of the American TV series «**Breaking Bad**» exposed the radical effects of HF on organic tissue as well as on mineral matrices (a bathtub in this case!).

Click here to hear the audio commentary : 
(from Chemistry world magazine, lenght : 334 seconds)

South Korea's «Bhopal like» disaster

On a chemical platform, 8 tonnes of hydrofluoric acid were discharged into the atmosphere via a tanker truck transporting 20 tonnes of 98% HF undergoing transfer by 2 technicians. Five facility employees were killed on the spot, and another 18 intoxicated from its inhalation had to be hospitalised. In the vicinity, a total of 4,195 individuals, including 416 fire-fighters, were medically treated for nausea, skin rash, breathing difficulties and irritations. 212 ha of arable land were contaminated and over 3,900 intoxicated heads of cattle had to be slaughtered. The economic losses tied to the shutdown of 80 chemical plants and damages to installations were appraised at €15 million. The acid wound up corroding more than 1,200 vehicles. 9,100 tonnes of vegetation was burned. All local residents evacuated underwent epidemiological evaluation, and 12,000 inhabitants of the region underwent a medical examination.

Unaware of the hazards of HF, first responders were unable to cope with the situation...

The emergency response did successfully halt the leak after 7 hours of effort. Municipal fire-fighters first arrived without proper protective equipment. They sprinkled the leak with water, which merely served to intensify the rate of product release. Called in as backup, fire-fighters of the nearby American military base set up their own safety perimeter around the plant to prevent local residents and cars from circulating within the toxic cloud. They notified the local police to be relieved of this duty and proceeded to evacuate the population within a 1.5-km radius. Local authorities were heavily criticised for their slow response, as the 300 residents directly concerned were only evacuated 10 days after the accident, as well as for the inadequate resources deployed by first responders and, more specifically, the lack of neutralising agents (lime) applied during the first 22 hours of response..



The human and environmental toll of the **Gumi disaster**, which occurred in the heart of South Korea's «Silicon Valley», accounts for one of the most serious accidents involving a massive release of HF

Cause of this accident: Ignorance of basic best practices

Initial findings from the accident investigation indicated that 2 employees had climbed onto the tanker to hook up the air hose intended to discharge acid into a storage tank. While one of them was connecting the hose, to save time the other one began unscrewing the bolts of the buffer on the acid outlet valve. He then inadvertently bumped into the manual outlet valve arm, which then partially opened, allowing pressurised HF to gush out. During transport of this tanker truck, an internal pressure surge had occurred due to the product's thermal expansion. In violation of procedures imposed by the profession, the tanker had not first been decompressed and flexible hoses had been deployed. Both employees were killed, along with 3 others who were performing works at a neighbouring facility; none of these victims were wearing the appropriate protective equipment. **Aria 43025 - Gumi - 2012/09/27**

[Link to the accident's video](#)



«Metal Attacks !»

In a rolling mill, employees attempted to open the manhole lid on a hydrofluoric acid tank with a grinder in order to improve handling control. An explosion occurred at 1:25 pm, killing 2 employees and injuring 2 others. An explosion involving hydrogen, triggered by acid attacking the metal, caused this accident. The tank had been emptied but still not cleaned; moreover it had been disconnected from both the filling and ventilation lines. **Aria 39794 - Krefeld - Germany - 2010/05/05**

Small bump / big damages

Inside a plant manufacturing ultra-pure chemical compounds, a forklift operator accidentally struck a 50% HF container being stored in the warehouse. The acid pooled on the floor, releasing a thick cloud of white vapour. The 3.5 m³ of HF held in the retention basin plus the 45 m³ of water used to rinse the storage zone were pumped. 6 tonnes of solid waste had to be discharged: individual protective equipment and pallets were contaminated, electrical/electronic devices and steel partitions were corroded, and 2 forklifts were destroyed. Property damage totalled €250,000.

On the day of the accident, the operator had attempted to reposition a container without having complete visibility of the forks on his forklift due to the warehouse being highly stocked. The container slid downwards, with the forks on the lift getting stuck in place and puncturing the container stored just behind. These plastic containers had been designed with only a single shell. The risk of a container sliding and being punctured by the forks on a lift had not been taken into account in the risk analysis [...]. **Aria 45930 - Saint Fromond - France - 2014/11/04**

For further informations :

- Eurofluor: « *HF Data sheet* » and « *Guideline in case of HF exposure* », (download at www.eurofluor.org/publications-and-recommendations/)
- Loss prevention Bulletin n° 232 / 2013: « *Anatomy of HF acid tanker unloading* » pages 4-9, a set of good practices for safely loading and unloading HF mobile tanks (download at www.icheme.org)
- BARPI / 2011: « *Inadequate use of available feedbacks* », in several accidents the steel attack by acid led to the formation of a highly-explosive atmosphere ([download link here](#))

Questions to ask to mitigate risks tied to the use of hydrofluoric acid (HF)...

Reducing risks at their source

1. Minimise the quantities of HF being stored on-site
2. Limit the risks of HF contact with incompatible products: water, humidity, highly basic compounds
3. Store HF under the least physically constraining conditions possible (e.g. pressure, temperature).

Simplifying the design and maintenance of equipment using HF

4. Design streamlined facilities: minimise the number of valves, pipes, flanges, etc.
5. Always use compatible materials: steel for HF-A and HF>70%, otherwise use fluorinated polymers and resins
6. Use non-intrusive instrumentation, protect the equipment and parts against external aggressors
7. Implement a rigorous preventive maintenance protocol on all machinery and parts in contact with HF

Preventing and protecting

8. Assign the appropriate individual protective equipment: type 1 full-body suit for personnel maintaining or operating equipment with HF, and type 3 suit for those in the vicinity during an operation (see EN 943 / 14605)
9. Make sensors available adjacent to equipment (HF sensors activating alarms, surveillance cameras)
10. Allocate neutralisation and rinsing devices in the event of a leak: water curtains for vapours, an abundant water reserve - *insufficient sprinkling increases vapour release!* - Ensure that alkaline neutralising products are on hand (preferably derived from calcium, which forms non-hazardous salts with HF)
11. Set up a safety perimeter for all operations performed on equipment with HF (15 m), and a protection perimeter in case of accidental discharge, extending from 30 m (small leak) to 200 m (large leak)
12. Use a work permit system for maintenance, accounting for all possible accident scenarios; anticipate the potential drift of vapours towards adjoining areas in the event of a leak (means of alarm, wind direction)
13. Know and respond with best practices: use guidelines and recommendations for the transport / storage / equipment design / materials / individual protective equipment (see www.eurofluor.org/publications-and-recommendations/ or API-RP-751)

For all comments / suggestions or to notify an accident or incident : srt.barpi@developpement-durable.gouv.fr

Accident summaries recorded in the ARIA database may be consulted on www.aria.developpement-durable.gouv.fr