



# hydrofluoric acid distributors issues

## *guidelines*



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# introduction

1. Hydrogen Fluoride (HF) is essential in the chemical industry and there is a need for HF to be produced, transported, stored and used.
2. HF is a highly toxic and corrosive substance which can provoke acute and chronic poisoning (Detailed information can be found in the EU Risk Assessment of Hydrogen Fluoride, 1999<sup>1</sup>). As also described later in this document HF exposures are different from other acid exposures because HF penetrates all tissue it comes in contact with and does not remain on their surface; and unlike other acids that are rapidly removed or neutralized, the corrosive and toxic effects may continue for days if left untreated. Precautions have to be taken to ensure the safe handling of HF.
3. The HF industry has a very good safety record; nevertheless, the European HF producers, organized in CTEF<sup>2</sup> and the European Chemical Distributors acting within Fecc, have drawn up this document to promote continuous improvement in the standards of safety associated with HF handling.

## The Task

4. The transport, handling and storage of Hydrofluoric Acid (HF) within packages<sup>3</sup>, at any concentration are an area of concern for the distributors sector and CTEF.
5. The following issues are described:
  - Transport infrastructure
  - Storage infrastructure
  - Training and awareness

## Legal Duties

6. Legal duties arise from many sources, and the references contain a number of the most relevant. For the purpose of this guidance those duties may be summarised as requiring safety to be actively managed

through a process that starts with risk assessment. Risk assessment in turn starts with a recognition of the hazards presented by any process, identifying who or what (e.g. the environment) may be affected, and to what extent, and putting in controls that are adequate to eliminate or minimise those risks.

## Risk Assessment

7. Risk assessment is the systematic evaluation of work activities using the following five steps:

- Step 1:** Identify the hazards.
- Step 2:** Identify the exposures. Who and what could be harmed and how?
- Step 3:** Evaluate the risks arising. Decide whether existing precautions are adequate or if more should be done.
- Step 4:** Record the findings.
- Step 5:** Review the assessment regularly and revise if necessary.

8. Advice on carrying out risk assessments is also contained in an UK HSE Guidance leaflet INDG163<sup>4</sup>.
9. The remaining sections of this guidance help to identify many of the hazards associated with the distribution of Hydrofluoric acid solutions, and give guidance on how to reduce the risks. The assessor must ensure that all relevant local factors are taken into account.
10. It is important to set out the limitations of the risk assessment. A complete risk assessment will also have to consider other hazards, which are not within the scope of this guidance. The responsibility for ensuring a suitable and sufficient risk assessment is carried out remains with the employer.
11. The risk assessment should consider adjacent storage, including storage in other forms of packaging and/or bulk, as well as other classes of dangerous goods and low hazard goods.

It is recommended to have a risk assessment recorded.

<sup>1</sup> [http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK\\_ASSESSMENT/REPORT/hfreport002.pdf](http://ecb.jrc.ec.europa.eu/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/hfreport002.pdf)

<sup>2</sup> CTEF – Comite Technique Européen du Fluor. [www.eurofluor.org](http://www.eurofluor.org)

<sup>3</sup> Package goods, within the scope of these discussions, are containers with a capacity of 1000 Litres (Intermediate Bulk Containers (IBCs)) or lower.

<sup>4</sup> <http://www.hse.gov.uk/pubns/indg163.pdf>

## Carriers

12. Due to the nature of the distribution industry within Europe and the variations encountered within each country the following “hierarchy of controls” for transport of Hydrofluoric Acid solutions in packages may be identified:
- Own fleet
  - Partner carriers
  - General carriers
13. Each of the options within the hierarchy involves an increasing degree of risk to be accounted for and the responsibility to apply appropriate control measures for the movement to be undertaken lies with each organisation. It is for each company to decide based on its own criteria how best to be organised.

## Hierarchy of measures

14. The use of ‘own drivers and own vehicles’ for Hydrofluoric Acid deliveries is the preferred choice of many distributors. This way companies could ensure internally that the level of training and competence necessary to safely transport HF is maintained throughout the journey.
15. However, based on the distributor’s capacity and the logistics required to service some remote locations, company fleets (if existing) will often be supplemented by a number of “partner carriers”. “Partner carriers” are chosen based on the individual decision-making and internal criteria of each chemical distribution company.
16. It is strongly advised that these carriers are strictly controlled, audited and monitored to ensure that they are:
- Trained regarding the hazards
  - Trained regarding the extra First Aid necessary
  - Arrive at depots for collection with the correct equipment
17. “Partner carriers” may, if applicable, be restricted to single trip deliveries.
18. However, in some (exceptional) cases the need for trans-shipment<sup>5</sup> of packages and/or use of other carriers may be deemed necessary. In these cases the dis-

tributor should make every effort to ensure that the supply of information, training and material for First Aid, including an antidote kit, is maintained throughout the journey.

## Description of Personal Protection Equipment (PPE) for drivers, including Calcium Gluconate kit

It is highly recommended that:

19. All drivers involved in the carriage of HF in packages to be trained in Emergency First Aid including extra training regarding the need for rapid application of Calcium Gluconate gel.
20. Speed and thoroughness in washing off the acid is of primary importance. Vehicles shall be provided with sufficient water, e.g. in a kind of extinguisher (minimum 20 litres, the more the better).
21. Vehicles carrying HF or sites containing HF shall have immediate access to emergency HF First Aid kit<sup>6</sup>, which contains a minimum of two tubes of Calcium Gluconate gel<sup>7</sup> and if available a copy of the CTEF First Aid Brochure<sup>8</sup> and the legally required documents (ADR/RID). These kits must be regularly audited to ensure they are still suitable for use.

## Procedure for empty packaging

22. All transport and handling of ‘returnable or reusable’ packaging for HF should be treated as if the containers were full. All staff must be trained and have immediate access to HF first aid kits.

## Delivery to customers

23. It is recommended for the distributor to have an account set up with the customer that the material is sold to. The material should be delivered to customers that understand and have a good knowledge of the risks associated with handling HF.

<sup>5</sup> Trans-shipment, within the scope of these discussions, is defined as the removal of packages from a vehicle for either:

- Immediate reloading onto another vehicle; or
- Storage overnight and then onward distributor the next day.

<sup>6</sup> As an example, one of the options for an HF First Aid kit that could be applicable is detailed in the CTEF publication “Management of hydrofluoric acid injury (notes for Health Professional)” available on the website [www.eurofluor.org](http://www.eurofluor.org)

<sup>7</sup> Preparation of Calcium Gluconate Gel is detailed in the CTEF publication “Management of hydrofluoric acid injury (notes for Health Professional)” available on the website [www.eurofluor.org](http://www.eurofluor.org)

<sup>8</sup> CTEF First Aid Brochure is available in different languages on the website [www.eurofluor.org](http://www.eurofluor.org)

# storage

It is highly recommended that:

24. Packaged HF to be stored within controlled sites to ensure the correct level of training and safety when handling the material. The following aspects should also be considered.

## No storage at height, only on ground or first level

28. The storage areas shall be secure external compounds, secure ground level or first level racked storage in warehouses. Adequate ventilation particularly in warehouse storage is needed.

### Pallets

25. The transport and storage of containers other than IBCs require the use of a "pallet" to allow the grouping of containers to aid handling and prevent manual handling of numerous small containers.
26. Distributors can use wooden pallets for HF in containers but must ensure that they have strict rigorous regimes in place to:
  - Use only high quality pallets
  - Check the integrity of the pallet to minimise the potential of nail damage
27. As a desirable option, the use of 'self-bunded' plastic pallets should be promoted.



# information & training

It is highly recommended that:

29. All Distributors implement rigorous control regimes for the training of personnel who deal with HF within their organisations. All staff involved in the supply chain must be given training in hazard awareness so they are informed as to the dangers involved with HF.
30. CTEF has issued specific guidance, which provides training recommendations for HF handling. Fecc and CTEF strongly recommend downloading the document 'STS 98/113 Training Recommendations for HF handling' or its replacing document 'Group 7: Recommendation on safety management for handling of Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions' from the website [www.eurofluor.org](http://www.eurofluor.org).
31. In the document STS 98/111 or its replacing document Group 7 some recommendations for 'Standard Equipment' (Level Delta (d)) can be found. Please refer to the diagram on the right.

## Level Delta (δ) Personal Protective Equipment



Delta Level is the minimum level of personal protective equipment (PPE) required to enter an HF handling facility and is not designed for use when there is a risk of potential exposure to HF.

Delta Level of PPE is specified when the risk assessment has indicated that no physical contact with acid containing equipment is likely and, therefore, only minimal protection is needed. It is intended to give protection against potentially small, unforeseen incidents e.g. drips, surface contamination, etc.

Delta Level personal protective equipment is defined as:

- Standard hard hat.
- Safety spectacles with side shields or chemical goggles.
- HF resistant boots, overboots or safety shoes with steel toe.
- HF resistant gloves may also be required.

Escape air packs or suitable filtration systems should also be readily available to enable an escape in the unlikely event of a leak.

### First aid measures/plan

Fecc and CTEF strongly recommend downloading the document 'STS 98/111 Personal protective equipment for use with HF' or its replacing document 'Group 7: Recommendation on safety management for handling of Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions' on website [www.eurofluor.org](http://www.eurofluor.org).

DO's and DON'Ts when working with HF			
	Always treat HF with the Greatest Respect.	Don't eat, drink or smoke when wearing work clothes or PPE.	
	Always assume chemical contamination exists even after decontamination, therefore wear appropriate PPE.	Don't store or re-use contaminated PPE without completely decontaminating it first.	
	Carefully inspect and test Personal Protective Equipment (PPE) before wearing it.	Don't delay with HF First-Aid. Don't forget to protect yourself and those administering aid or assistance.	
	Remove immediately, with caution and without hesitation any work clothes contaminated with HF.	Don't store work clothes with personal clothes.	
	Neutralise any spillage of HF immediately.	Don't carry out any maintenance or work on a HF system against a single isolation valve.	
	Always follow up HF First-Aid Treatment and go to the Medical Department, even if any pain has receded.	Don't touch any liquid in the workplace. Don't assume it's harmless.	
	Apply HF First-Aid Treatment with any suspected HF contamination. "Better to be Safe, than Sorry"	Don't share Personal Protective Equipment (PPE).	

**CTEF – Comité Technique Européen du Fluor**

CTEF (Comité Technique Européen du Fluor) represents the major producers and users of hydrogen fluoride (HF) and fluoride chemicals in Europe. CTEF aims to assure safe production, storage, transportation and use of hydrofluoric acid.

32. Hydrofluoric Acid exposures are different from other acid exposures because:

- HF penetrates all tissue it comes in contact with and does not remain on their surface.
- Once absorbed HF rapidly dissociates into ionic Hydrogen and Fluoride.
- Hydrogen is in this context of little importance, Fluoride migrates and continues to destroy deep tissue layers as it migrates and will create soluble and insoluble compounds that are the basis for the systemic toxic effects.
- Unlike other acids that are rapidly removed or neutralized, the corrosive and toxic effects may

continue for days if left untreated.

- In case of contact with HF, control or treatment by medical personnel is needed.

33. Hydrogen Fluoride is corrosive to the skin, eyes, and the mucous membranes of the respiratory and digestive tracts. HF is readily absorbed into the body causing acute and severe toxic systemic effects, mainly attributable to a rapidly developing serum hypocalcemia caused by the formation of calcium fluoride or fluoroapatite, serum hypomagnesemia and serum hyperkalemia.

34. HF skin burns are usually accompanied by se-

vere pain, which is thought to be due to irritation of nerve endings by increased level of potassium ions entering the extra-cellular space to compensate for the reduced levels of calcium ions, which have been bound to the fluoride. Relief of pain is an important guide for the success of the treatment; therefore local anaesthesia should be avoided.

35. The extent and the intensity of these systemic complications are directly related to the amount of HF absorbed, and the concentration of the HF when in solution. There are also indications that subcutaneous deposits of HF under the burnt area may be responsible for a slow supply of fluoride ions to the circulation.
36. Symptoms of serious intoxications include hypotension, hypocalcemia tetany, and/or laryngospasm, often-respiratory failure (possibly due to pulmonary hypertension), ventricular tachycardia, ventricular fibrillation and cardiac arrest. Renal and hepatic functions may be impaired and muscular damage may be secondary to tetany.
37. Fecc and CTEF strongly recommend downloading the document 'First Aid Brochure' from the website: [www.eurofluor.org](http://www.eurofluor.org)
38. All personnel involved in the physical handling of HF (Drivers, Fillers and warehouse staff) must be trained in Emergency First Aid and then given extra training regarding the application of Calcium Gluconate gel.
39. Speed and thoroughness in washing off the acid is of primary importance. Vehicles should be provided with sufficient water, e.g. in a kind of extinguisher (minimum 20 litres, the more the better). Sites shall install a safety shower. Each shower should be capable of delivering approximately 100 litres of clean water per minute for 15 minutes. Deluge initiation should be simple and rapid. The water supply pipe work should be protected from frost (e.g. by insulation and/or trace heating). Additional sealed eye wash bottles containing a saline solution or clear water can be contained in suitable cabinets. Each cabinet should contain about one litre of solution and be regularly checked to ensure their contents are up to standard.
40. Distributors should offer hazard awareness training material to customers who purchase HF and advise all customers to inform the local hospital that they handle the substance so they can plan for an incident.
41. All organisations involved in the handling of HF either in filling or storage must have a written emergency plan to ensure that effective treatment of HF contact is given immediately and that the local hospital is aware of the likelihood of an HF incident. All involved personnel should be aware of this plan. Industrial experience indicates that prompt treatment, as described, will prevent the development of serious injury. In the majority of cases caused by industrial accidents, little more than skin effects results after prompt treatment.
42. Therefore, speed is essential. Delays in first aid care or medical treatment or improper medical treatment will likely result in greater damage or may, in some cases, result in a fatal outcome.
43. Fecc and CTEF strongly recommend downloading the document 'STS 94/96 Guidelines in case of HF Exposure', where there are concise flowcharts detailing the correct treatment for each exposure route (skin, eyes, inhalation and ingestion). The document can be found on the website [www.eurofluor.org](http://www.eurofluor.org).
44. High concentrations of hydrofluoric acid (above 60%)

## site security

are classified for transport and assigned to packing group I of class 8. As such, these concentrations will fall within scope of the High Consequence Dangerous Goods (HCDG) provisions of ADR chapter 1.10 and require security provisions.

45. ADR 1.10 requires those involved in the transport of HCDG to adopt, implement and comply with a written security plan. Local competent authority guidance on these security plans may be available in Member States and may be subject to local enforcement inspections.
46. Because of the hazardous nature of the chemical, distributors are recommended to adopt aspects of such a security plan for solutions of hydrofluoric acid below 60%. As a minimum requirement, all solutions of HF should be stored in a secure area with limited access to trained personnel only.

## Glossary

**Hazard** - That property of a material that has the potential to cause harm to people, property or the environment.

**Risk** - The chance that somebody or something could be harmed by the hazards, together with an indication of how serious the harm could be

**IBC** (for the purpose of this guide) - "Intermediate Bulk Container" (IBC) means a rigid or flexible portable packaging.... that:

- has a capacity of not more than 3 m<sup>3</sup> for solids and liquids of packing groups II and III;
  - is designed for mechanical handling;
  - is resistant to the stresses produced in handling and transport as determined by the tests specified in Chapter 6.5 of ADR
- Composite IBC with plastic inner receptacle: These are IBCs comprising a rigid outer structure encasing a plastic inner receptacle. It is constructed so that the outer and inner assemblies are used as an integrated single unit to be filled, stored, transported or emptied.

## References

1. INDG163 - Guidance 5 Steps To Risk Assessment – ISBN-0-7176-6189-X
2. The Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations
3. ADR – European Agreement concerning the International Carriage of Dangerous Goods by Road – ISBN 92-1-139112-1

## Guidance

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Number	Publication title	Info
First Aid Brochure	Management of hydrofluoric acid injury (notes for Health Professional) Second Edition	Available in seven languages
STS 94/96	Guidelines in case of HF exposure	Detailed Medical Guidelines
Group 7	Recommendations on safety management for handling of Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions	Available in 2010, replacing STS 98/111 and STS99/113
STS 98/111	Personal protective equipment for use with HF	Available until mid 2010
STS 99/113	Training Recommendations for HF handling	Available until mid 2010



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