EUROFLUOR (CTEF, European Technical Committee for Fluorine)

Working Group on Storage, Transport and Safety (STS)

Group 7

RECOMMENDATION ON SAFETY MANAGEMENT FOR HANDLING OF ANHYDROUS HYDROGEN FLUORIDE AND HYDROFLUORIC ACID SOLUTIONS

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PREFACE

Anhydrous hydrogen fluoride/ hydrofluoric acid (AHF/HF) is essential in the chemical industry and there is a need for HF to be produced, transported, stored and used.

The AHF/HF industry has a very good safety record; nevertheless, the European AHF/HF producers, acting within Eurofluor (previously CTEF) have drawn up this document to promote continuous improvement in the standards of safety associated with AHF/HF handling.

This Recommendation is based on the various measures taken by member companies of Eurofluor.

It in no way is intended as a substitute for the various national or international regulations, which should be respected in an integral manner.

It results from the understanding and many years of experience of the AHF/HF producers in their respective countries at the date of issue of this particular document.

Established in good faith, this recommendation should not be used as a standard or a comprehensive specification, but rather as a guide, which should, in each particular case, be adapted and utilised in consultation with an AHF/HF manufacturer, supplier or user, or other experts in the field.

It has been assumed in the preparation of this publication that the user will ensure that the contents are relevant to the application selected and are correctly applied by appropriately qualified and experienced people for whose guidance it has been prepared.

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The contents of this recommendation are based on the most authoritative information available at the time of writing and on good engineering practice, but it is essential to take account of appropriate subsequent technical developments or legislative changes. It is the intent of Eurofluor that this guideline be periodically reviewed and updated to reflect developments in industry practices and evolution of technology. Users of this guideline are urged to use the most recent edition of it, and to consult with an AHF/HF manufacturer before implementing it in detail.

This edition of the document has been drawn up by a Working Group "Storage, Transport and Safety" to whom all suggestions concerning possible revision should be addressed through the offices of Eurofluor. It may not be reproduced in whole or in part without the authorisation of Eurofluor or members companies.

AHF is acronym for anhydrous hydrogen fluoride.

HF is acronym for hydrofluoric acid solutions of any concentration below 100%.

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GENERAL REMARK

This guideline has been developed by the Storage, Transport and Safety Group of the Comité Technique Européen du Fluor (EUROFLUOR). It is intended to offer recommendations on the safety management for handling of anhydrous hydrogen fluoride (AHF) or hydrofluoric acid solutions (HF) at ambient temperatures (from -20°C to +50°C), unless stated otherwise.

All materials of construction, which are mentioned in this document should be double-checked and there should be a search for more information on materials, in our "Recommendation on materials of construction for Anhydrous Hydrogen Fluoride and Hydrofluoric Acid solutions" available from Eurofluor publication webpage www.eurofluor.org.

1. HEALTH AND SAFETY POLICY

1.1 General

To successfully avoid accidents, a multifaceted approach is needed to manage facilities technologies and personnel. The essential elements of this multifaceted approach can be given as follows:

- Management leadership and company commitment
- Process safety information
- Process hazard analysis and assessment
- Safe design and specifications of equipment
- Operating procedures
- Maintenance procedures
- Safe work practices
- Training
- Contractor safety
- Mechanical integrity
- Management of change
- Incident investigation and analysis
- Emergency Management
- Compliance audits

EUROFLUOR Storage, Transport and Safety Working Group (STS) has issued recommendations on elements to be covered by a proper health and safety policy and mainly in the areas of:

- Process Safety Information
- Process hazard analysis and assessment
- Safe design and specifications of all equipment and ancillaries in contact with HF
- Accident investigation and analysis
- Emergency management
- Compliance audits

The present paper is the result of an exchange of experience of the European HF producers and users in the areas of:

- Training
- Safety of operation
- Safe work practices
- Emergency management

1.2 Training Courses Initial and Refresher for Operators

During the introduction period of new personnel, training should be provided by the Safety & Environmental Department and by the operators own department. In addition, refresher courses should be provided for experienced personnel on a regular basis.

Training programs should include:

- HF: product characteristics, hazards, health risk, safe handling, etc...
- General operating rules and safety instructions.
- Main plant procedures and safety procedures.
- First Aid treatment
- Personal Protective Equipment (PPE)

Training programs for first aid and for assistance in case of accident should be carried out. For each department a safety instruction scheme should be in place.

Emergency exercises should be carried out periodically, simulating possible hazardous emergencies which could occur to ensure that operators and maintenance teams are briefed and prepared on their roles. The exercises should audit the followings areas:

- Emergency procedures and implementation of:
    - Use of personal protective equipment.
    - Isolation and decontamination of plant.
    - On site emergency service response.
    - Interplant communication processes.
    - Evacuation and head count procedure.

Periodically the emergency exercise should involve the site safety personnel (fire brigade).

Training courses and refreshers should involve maintenance teams on the following items:

- Hazards linked to the products.
- Safe handling of equipment.
- Personal protective equipment.
- Procedures for maintenance.
- Work permits.

1.3 Procedures

A specific safety handbook should be in place basically covering all aspects of Safety Management.

1.3.1 Main Items

- General and department safety instructions in which responsibilities and competences are laid down.
- Procedure for alterations/changes of process and/or equipment (management of change).
- Safety permit system.
- Safety instructions for third party personnel working on the site.
- Accident reporting procedures.
- Reference to guidelines of the factory inspectorate, which are kept per department.
- Safety information about chemical compounds present on the site (material safety data sheets).

- Internal audit procedures.
- Training programs.

1.3.2 Maintenance Procedures

Procedures for routine maintenance works should be established.

For exceptional works, a specific procedure should be written inside the safety permit system.

As a general rule:

- A plant operator / well-trained operator must be present at any opening of pipe work / equipment.
- No maintenance work can begin without a permit signed by the shift foreman or his delegate.
- Procedures should be in place to aid the selection and control of Contractors - See Section 2.3.7.

1.3.3 Accident and Incident Investigations

Accidents and incidents generally fall under three main headings:

- Local incident, investigated by plant management and operating teams. Actions to prevent a recurrence are handled locally and learning from the incident does not need to be shared with the other production areas on site: "Local Incident".
- Local incident, investigated by plant management and operating teams that bring to light actions to prevent a recurrence that other production areas would learn from: "Learning Events".
- Accidents

Lost time accidents

The investigation is again handled by plant management and operating teams but a detailed report is compiled and issued to site management for comment and approach. After which it will also be issued as "Learning Event" to other production areas and reported to the Company Safety personnel.

All incidents are investigated and the learning communicated locally and to other production areas depending on the nature and severity.

All "Learning Events" should be reported to EUROFLUOR as prevention for others (see Annex I).

Analysis

A detailed analysis of the accident should be done for all lost time accidents and significant near misses.

1.4 Auditing

Auditing of safety instructions, operating instructions, and general operation, should be carried out by all members of staff. Auditing schedules should be agreed with individuals at the beginning of each year and reviewed periodically at local safety meetings.

Auditing of safety instructions and operating instructions basically sets out to test the understanding of managers, supervisors, operators and maintenance staff in the use of safety and operating instructions. Auditing of general operation, i.e. maintenance teams carrying out repairs to plant, or operating teams carrying out general duties sets out to test the awareness of the people when they are working:

- Are they working safely?
- Are they wearing the correct protective clothing?
- Are they aware at the potential hazards?
- Do they have the correct documentation?
- Do they understand fully the work in hand?

1.5 Communication Processes

Periodically line managers should meet with their teams to discuss safety, health and environmental matters. The objective is to positively influence the team and gain commitment to continuous improvement in this area.

The meeting should review the results obtained, the weak points and needs for improvement. A general plant safety improvement program should be established on a yearly basis.

1.6 Safety Equipment Periodic Testing

Each plant should establish a list of equipment which are important for safety and therefore must be subject to periodic checks. This list should be based on the safety analysis.

- Equipment such as storage and pressure vessels and their ancillaries.
- HF piping network, valves, relief valves and instruments.
- Individual safety equipment.
- Emergency communication network.
- Safety equipment such as showers, water curtains, emergency HF absorption systems, emergency power system, shut down systems, HF detectors.

Such tests should be recorded.

1.7 Contractors

Contractors working inside the plant facilities dealing with HF should be subject to selection based:

- on their capability and expertise
- on their ability to cope with the internal safety rules of the site

- on their organization in terms of training and safety, including their results in lost time accident indicators
- on the internal training organization for their specific works and specific risks.

Specific training for the hazards resulting from their works inside the plant (cooperation with the plant or site HSE organization) is required.

To facilitate the above, a system should be established to ensure that contractor workers received the proper training.

As a general rule, important maintenance works involving the use of cranes and engines should be made after emptying the local vessels and pipes to prevent any risk of leakage resulting from equipment falling down or shocks. If not possible suitable protection should be provided.

1.8 Action Plan in the Event of a Major Incident

General principles

4 general principles are applied for the action plan:

- Alarm instructions
- Hazard prevention plan
- Plant operating instructions
- Safety analysis in accordance with major incident regulations.

1.8.1 Preventive Measures

Preventive Measures should at least contain:

- Display of alarm instructions throughout building (stairwells, notice-boards, emergency exits, platforms).
- Designation of emergency team and guide for the Fire Brigade.
- Continuous training of all personnel in alarm instructions, safety instructions and hazard prevention plan so as to prevent panic in the event of a major incident.
- Regular drills (recommended to be at least once a year) involving Fire Brigade and plant personnel.
- Investigation of possible major incidents and appropriate action.
- Training of all personnel working in the plant (including those from subcontractors) using videos, safety instructions and verbal instruction.
- Updating of the documentation and specially the communication system.

1.8.2 Procedure in the Event of a Major Incident

Alarm

- Sound internal alarm in the plant.
- Notify Fire Brigade which will in turn notify neighbouring plants, Plant Security and Environmental Protection via the Central Site Warning System.

- Notify all relevant personnel according to a communication list.

Action to be taken in plant

- Proceed in accordance with alarm instructions.
- All persons (except emergency team) to leave the area as trained.
- Proceed to designated assembly area.
- Await further instructions.

Emergency team

- The emergency team for the plant may include the shift foreman and the control room supervisor of the plant.

Equipment for the emergency team

Equipment for each member of the emergency team should at least consist of:

- Heavy-duty breathing apparatus.
- Protective suits.
- Communication devices.

1.9 Health

Level of exposure of the personnel may be monitored by wearing from time to time personal monitoring devices.

Occupational exposure limits (OEL) are according to national standards (please check latest Safety Data Sheet for the must up to date values).

2. HF SAFETY

HF is a highly toxic and corrosive substance, which can cause acute and chronic poisoning.

ANYONE WHO KNOWS OR EVEN SUSPECTS THAT HE HAS COME IN CONTACT WITH HF SHOULD IMMEDIATELY SEEK FIRST AID, AND BE REFERRED TO A DOCTOR EVEN THOUGH THE INJURY SEEMS SLIGHT.

More information on First Aid and Medical treatment see STS First Aid Brochures (www.eurofluor.org).

2.1 Special safety facilities

The following facilities should be strategically positioned readily accessible (below 30 sec) and easily identifiable in all areas where hydrofluoric acid or solutions of hydrofluoric acid are to be found.

Safety showers

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).

Eye wash fountains

As per safety showers above, but each with a rated capacity of 10 to 15 litres per minutes for at least 10 minutes.

Eye wash bottles

Additional to eye wash fountains sealed bottles containing a saline solution (isotonic NaCl 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.

Calcium gluconate gel

Quantities of calcium gluconate gel should be located on the plant in the emergency cabinet and must be available for everybody.

Care must be taken that gel and eye wash solution have not expired.

3. TRAINING RECOMMENDATION FOR HF HANDLING

3.1 General Overview

- All HF handling facilities should have written policies and procedures covering the appropriate training requirements for each task or role. All employees and contractors involved with HF handling facilities should understand the risks associated with handling HF and should be provided with the training required to complete their task or role. Specific training should include hazard awareness, risk assessment, the correct way to fit, wear and decontaminate personal protective equipment as well as first aid and emergency procedures as a minimum. These training requirements should be strictly enforced and implemented.
- **Note: In order to ensure that the appropriate standards are achieved and maintained a policy detailing the re-training of personnel should be implemented.**
- HF is a very toxic and corrosive chemical which, when exposure occurs, can lead to severe health risks and can, if the correct treatment is not quickly and efficiently applied, prove to be fatal. However, it should be noted that, despite the hazards associated with handling HF, the European industry has a good safety record and has shown that HF can be safely handled, that the associated risks can be accurately identified and suitable personal protective equipment provides sufficient protection when worn in the correct manner. The largest proportion of injuries is due to a failure in the Risk Assessment process or to a lack or incorrect use of the appropriate personal protective equipment. It is recommended that users of this guideline also use the information contained in the Chemical Safety Data Sheet for HF (See www.eurofluor.org) and work in conjunction with a recognised and experienced supplier/producer of HF to ensure adequate design standards.
- This guideline attempts to describe typical training requirements of an HF handling facility and the appropriate level of retraining. All training discussed in this document refers to additional training above and beyond that which would normally be expected for each employee, i.e. Secondary First aid concentrates on HF specific actions and assumes that the recipient understands and is qualified in some way in the basics of first aid e.g. a doctor or a nurse. The guideline also assumes that training in standard procedures for a chemical plant, e.g. Permit to Work, has been identified and given as appropriate.

3.2 Training Recommendations

Training recommendations for all personnel involved with the manufacture, storage, transport and use of Hydrogen Fluoride have been summarised in Table 1.

The training program has been structured as modules of training each of which is intended to build upon the training already given and should be used to re-emphasise key points. Each facility manufacturing or using HF should produce suitable packages to meet these requirements. Some of the required training is generic, e.g. HF Awareness or Initial First Aid, but much of the training is specific to the plant and, as such, may vary from site to site within a single company, e.g. Operating Procedures, Maintenance procedures.

Consideration must also be given to re-training. The requirements and frequencies for retraining will vary with the activities and experience of personnel but the importance of positive reinforcement of good practice by retraining should not be under-estimated.

For each module of training provided the understanding of the individual should be validated. In some packages practical training as well as classroom training is appropriate and this should also be tested. In this way the trainer can ensure that the messages have been received and understood and any misconceptions can be identified and clarified.

All training or re-training given, together with the identity of the trainer should be formally recorded and these records should be readily available for checking and auditing.

3.2.1 Site Induction Module

Purpose

The Site Induction Module is intended to raise the awareness of the potential risks associated with the site for all individuals working on the site. This training will be site specific.

Content

The Site Induction Module should include the basic requirements of an individual who wishes to enter the site boundary and should, as a minimum, cover the following topics:-

- General Introduction to site
- Site policies, rules and regulations
- On-site Vehicle policy
- Parking requirements
- Signing in and out policy
- Fire & Emergency Procedures (including, where possible examples of alarms, etc.)
- Wind direction indicators
- Evacuation routes and assembly points
- Personal protective equipment requirements
- Instructions on entering plant areas
- Identification of any specific equipment requirements (e.g. intrinsically safe, etc.)
- Hygiene Issues
- Permit to Work Arrangements (additional training may be required)
- The importance of reporting incidents

Audience

The Site Induction Module should be given to all employees, contractors and internal or external visitors who will be working on or visiting the site. Additionally, consideration should be given to making any close neighbours aware of these systems and procedures, in particular the testing, use and meaning of any emergency alarm systems and the appropriate actions required.

One exception may be temporary visitors who are accompanied on site at all times by an experienced site person. Under this circumstance the host will be responsible for the visitor's behaviour and will ensure that the site procedures and systems are followed.

Individuals having completed the site training module should then be given a pass or badge which clearly shows that the training has been successfully completed.

3.2.2 Plant Induction Module

Purpose

The Plant Induction Module is intended to build upon the Site Awareness module by detailing the requirements of the plant. Each plant handling HF will have specific requirements and alarms the correct response to which should be fully understood by all personnel working in or visiting the plant. This training will be plant specific though there may be areas common to more than one plant within a site boundary.

Content

The Plant Induction Module should build upon the basic information contained in the Site Awareness module and should identify the requirements for an individual who wishes to enter inside the plant boundary and should, as a minimum, cover the following topics:

- General Introduction to plant (geography, areas of special concern, etc.)
- Plant rules and regulations
- Signing on and off policy
- How to raise an alarm
- Fire & Emergency Procedures (including, where possible examples of alarms, etc.)
- Wind direction indicators
- Evacuation routes and assembly points
- Personal protective equipment requirements (i.e. the levels of personal protective equipment on plant and the acceptable activities)
- Identification of any specific equipment requirements (e.g. intrinsically safe, etc.)
- Hygiene Arrangements
- Permit to Work Issue Points (if applicable)
- The importance of reporting incidents, however minor
- The location of safety equipment (e.g. First aid kit; safety showers, etc.)

Audience

The Plant Induction Module should be given to all employees, contractors and internal or external visitors who will be working on the plant. For larger sites this will mean that employees or contractors working on more than one plant will require more than one plant induction module.

Individuals having completed the site training module should then be given a pass or badge which clearly shows that the plant-specific training has been successfully completed.

3.2.3 HF Induction Module

Purpose

The HF Induction Module is intended to raise the awareness of the specific hazards associated with handling HF. This training could be a generic package used at more than one HF handling plant.

Content

The HF Induction Module should build upon the basic information contained in the Plant Induction module and give detailed information about the hazards associated with HF and its use together with any mitigation systems (e.g. Calcium Gluconate gel). The training should cover the following topics:

- A description of the hazards associated with HF
- A description of the initial first aid measures
- A description of the delayed onset of symptoms associated with HF
- A description of the site personal protective equipment and its suitability, limitations, etc.
- The location of Safety, Health & Environmental information (e.g. Safety data sheet)
- The location of first aid equipment on site
- The correct response to involvement in an HF incident
- Decontamination procedures
- How to raise further help if required
- How / where to get further advice
- The importance of ceasing work and reporting back to the control room if in doubt
- The importance of cleaning up when work is complete
- The most effective way to decontaminate tools, equipment and personal protective equipment
- The role of the individual in a plant emergency
- Assembly points
- The importance of labelling samples or contaminated equipment
- The importance of reporting all incidents or near misses so that learning can prevent a recurrence

Audience

The HF Induction Module should be given to all employees, contractors (including contract hauliers, drivers, etc.) and internal or external visitors who could potentially be exposed to HF either directly or indirectly.

Following successful completion of this training some companies have elected to give employees a tube of calcium gluconate to keep at home.

3.2.4 PPE Module

Purpose

The PPE Module is intended to describe the requirement for personal protective equipment. When, where and how it should be used. The module should identify the correct personal protective equipment and how this was derived.

For additional information see Chapter 7.

Content

- A description of the hazards associated with HF
- A review of past incidents and learning
- A description of the personal protective equipment required
- A description of the decontamination systems
- A description of the initial first aid procedures
- A practical demonstration showing how to put the personal protective equipment on
- A practical demonstration of the decontamination procedures
- A practical demonstration of the use of calcium gluconate gel
- A discussion on potential pitfalls identified
- Validation of the understanding of each part of the procedure
- A check that each attendee has a tube of gel available at home (if applicable)
- The importance of reporting any exposure, either whilst at work or home
- The importance of reporting the use of gel and requesting a replacement

Note: PPE supplied by external contractors or visitors should not be used within the plant boundaries unless it has been shown to be suitable for use with HF.

Audience

This training is intended for any individual who has the potential to be exposed to HF either directly or indirectly. This includes individuals who are not expected to work on contaminated systems but who could potentially be contaminated by the actions of others, e.g. drivers.

3.2.5 Initial First Aid Module

Purpose

The Initial First Aid Module is intended to describe the actions which should be taken in the event of a potential exposure to HF. The training should emphasise the need for prompt and correct action to be taken in order to minimise the impact of the exposure.

For additional information see *EUROFLUOR Guidelines in case of AHF/HF exposure.*

Content

- A description of the hazards associated with HF
- A review of past incidents and learning

- The importance of fast and effective first aid
- The importance of self-protection to prevent additional casualties
- The importance of getting help & how this is achieved – particularly if more than one casualty is present
- A description of the personal protective equipment required when treating a casualty
- A description of the need to remove all contaminated clothing
- A description of how to decontaminate a casualty
- A description of the correct first aid procedures for each potential exposure, i.e. Skin contact, Ingestion, Eye contact and Inhalation
- A practical demonstration of the use of calcium gluconate gel
- Validation of the understanding of each part of the procedure
- A check that each attendee has a tube of gel available at home (if applicable)
- The importance of reporting any exposure, either whilst at work or home
- The importance of reporting the use of gel and requesting a replacement
- The importance of passing on casualties who are injured to medical professionals as soon as possible
- The importance of giving full and accurate information to medical professionals upon their arrival e.g. Safety data sheet if available, history, treatment given, etc. is very high.

Note: This training should only be given by medical professionals or those with extensive knowledge of HF first aid procedures

Audience

This training is intended for any individual who has the potential to be exposed to HF either directly or indirectly in his workplace, e.g. plant operators, laboratory, etc. This includes individuals who are not expected to work on contaminated systems but who could potentially be contaminated by the actions of others, e.g. drivers, maintenance personnel.

Suppliers of HF will ensure that customers handling HF have the necessary first aid equipment in place and the necessary training is understood and given as appropriate.

Support personnel, e.g. Emergency response teams, also require this module.

3.2.6 Secondary First Aid Module

Purpose

The Secondary First Aid Module is intended for medical professionals and describes the actions which should be taken in the event of an exposure to HF. The training should emphasise the need for the correct medical care to be given to serious and minor exposures in order to minimise the long term effects. Secondary medical treatment may be provided by an on-site facility or by a local hospital or doctor.

For additional information see *EUROFLUOR Guidelines in case of AHF/HF exposure.*

Content

- A description of the hazards associated with HF
- A review of past incidents and learning
- The importance of fast and effective treatment
- A description of the effects of HF on the human body
- A description of the correct symptomatic treatment required.
- The importance of self-protection to prevent additional casualties
- A description of the personal protective equipment required when treating a casualty
- A description of the need to remove all contaminated clothing
- A description of how to decontaminate a casualty
- A description of the first aid procedures which will have been followed by the initial response
- A practical demonstration of the use of calcium gluconate gel
- A check that gel is available at the facility
- The importance of reporting all incidents and the treatments given so that learning can prevent a recurrence

Note: This training is intended for medical professionals and should be given by suitably qualified personnel only.

Audience

This training is intended for those with a higher level of medical training e.g. medical professionals. Suppliers of HF will ensure that customers handling HF have access to a suitable secondary first aid resource.

3.2.7 Operating Procedures Module

Purpose

The Operating Procedures Module is intended to describe the structure of the detailed plant operating instructions. Complex plants are normally broken into a number of discrete areas, e.g. fluorspar drying, each of which have a number of operating procedures associated. Once an operator has been trained and validated in all of the procedures within an area the individual is competent to operate in that area. Additional training is required for each process area.

Detailed procedures describing the tasks and activities required to operate the plant area safely shall be available. The area operating teams shall be fully trained in these procedures.

For new operators joining the plant a structured training plan should be developed.

Operating procedure training involves both classroom and practical training with validation for each part. Individuals have to prove understanding in the classroom before being allowed to watch the procedure for real and only then, are they allowed following the procedure under supervision. Once the individual has shown an appropriate level of

competence the supervisor will sign off the practical validation and only then will the individual be considered fully competent.

Many companies appoint a 'mentor' for an operator moving into an area for the first time. The mentor's role is to help, guide and support the new starter through the training program by sharing knowledge and experiences. In this way new operators gain a high level of training and knowledge and the plant management team gain a confidence in the new operator.

Individuals will be expected to have undergone the Site, Plant, HF Induction, PPE and Initial First Aid modules before completing operating procedures on plant.

Content

- A description of the hazards associated with HF
- A description of the process and the individuals role
- A description of the personal protective equipment required when following each procedure
- A description of the emergency procedures and the individuals role in these
- A description of the initial first aid procedures
- A detailed description of each procedure, the safety, health and environmental issues associated, the personal protective equipment required and the most effective way to do the task safely.
- The importance of reporting all incidents or near misses so that learning can prevent a recurrence

Audience

This training is intended for the plant operating team and should be given to all operators and supervisors on the plant. Supervisors should be given the full training module covering all of the plant; operators may be given all or parts of the module as appropriate.

3.2.8 Tanker Procedures Module

Purpose

The Tanker Procedures Module is intended to describe, in detail, the steps needed to connect and disconnect a tanker in order to load or unload. It will also cover the design features associated with the various tankers within the fleet and their valving systems, relief's, etc.

Detailed procedures describing the tasks and activities required to operate the plant area safely shall be available. The tanker loading or unloading teams shall be fully trained in all of these procedures.

For new operators moving into this area a structured training plan should be developed.

Tanker procedure training involves both classroom and practical training with validation for each part. Individuals have to prove understanding in the classroom before being allowed to connect or disconnect a tanker under supervision. Once the individual has shown an

appropriate level of competence the supervisor will sign off the practical validation and only then will the individual be considered fully competent.

Many companies appoint a 'mentor' for an operator moving into an area for the first time. The mentor's role is to help, guide and support the new starter through the training program by sharing knowledge and experiences. In this way new operators gain a high level of training and knowledge and the plant management team gain a confidence in the new operator.

Content

- A description of the hazards associated with HF
- A description of the tank design features (valves, reliefs, etc.) both inside and outside
- A description of the personal protective equipment required at each stage of the procedure
- A description of the emergency procedures
- A description of the initial first aid procedures
- A detailed description of the procedure for loading a tanker
- A detailed description of the procedure for unloading a tanker
- A detailed description of the procedure for preparing a tank for maintenance
- A detailed description of the procedure to change a valve or a relief valve on a tank
- A detailed description of the procedure for re-commissioning a tank following maintenance
- The importance of reporting all incidents or near misses so that learning can prevent a recurrence

Audience

This training is intended for the supervisors and operators responsible for the loading or unloading of HF tankers.

3.2.9 Decontamination Procedures Module

Purpose

The Decontamination Procedures Module is intended to describe, in detail, the principles to be followed when decontaminating or preparing equipment for maintenance and when maintaining equipment. The module should cover the specific issues associated with 'dirty' break-ins where it is identified that full decontamination cannot be guaranteed.

Special attention should be given during the training to ensure that where equipment is being moved either on site or off site the wider issues of the transportation are included.

Some companies use a predetermined checklist to ensure that all possible outcomes are considered, i.e. a HAZOP study, prior to beginning work on the plant. Following the decontamination the procedure is then reviewed and any learning incorporated.

For equipment which is regularly maintained, e.g. vessels, some companies record the method of decontamination, the HAZOP and the report for reference each time the equipment is decontaminated.

Content

- A description of the hazards associated with HF
- A description of the equipment to be decontaminated (with diagrams if possible)
- A description of any equipment needed to effect the decontamination (hoses, water lines, etc.)
- A description of the personal protective equipment required at each stage of the procedure
- A description of the potential issues which may arise, their likelihood and how these would be dealt with if they arise
- A description of the initial first aid procedures
- A description of the isolation standards necessary (locks, spades, etc.)
- An overview of the Permit to Work system
- A paper example preparing a system for decontamination
- A practical example where the individual prepares a system for maintenance under supervision
- The importance of reporting all incidents or near misses so that learning can prevent a recurrence

Audience

This training is intended for the supervisors, operators and maintenance personnel responsible for preparing or working on HF plant equipment.

3.2.10 Maintenance Procedures Module

Purpose

The Maintenance Procedures Module is intended to describe, in detail, the principles to be followed when maintaining equipment. The module should cover the specific issues associated with 'clean' and 'dirty' equipment.

For equipment which is regularly maintained, e.g. pumps, some companies use standard procedures and generate a report on the effectiveness of the decontamination procedure, the condition of the equipment and the work carried out each time the equipment is worked on.

Content

- A description of the hazards associated with HF
- A description of the equipment to be maintained (with diagrams if possible)
- A description of the personal protective equipment required at each stage of the procedure
- A description of the potential issues which may arise, their likelihood and how these would be dealt if they arise
- A description of the initial first aid procedures
- The importance of reporting all incidents or near misses so that learning can prevent a recurrence

Audience

This training is intended for the supervisors and maintenance personnel responsible for working on HF plant equipment.

3.2.11 Sampling Procedures Module

Purpose

The Sampling Procedures Module is intended to describe, in detail, the steps to be followed when sampling systems containing HF.

Sampling HF containing streams is a hazardous activity which should be undertaken as little as necessary. Customers wishing to ensure the quality control of HF should be encouraged to do this in partnership with their supplier by auditing rather than by re-sampling and additional analysis.

Content

- A description of the hazards associated with HF
- A description of the equipment to be used (with diagrams if possible)
- A description of the personal protective equipment required at each stage of the procedure
- A description of the potential issues which may arise, their likelihood and how these would be dealt if they arise
- A description of the initial first aid procedures
- A description of the site method for transporting samples to the laboratory, if this is not located on the plant.
- The importance of reporting all incidents or near misses so that learning can prevent a recurrence

Audience

This training is intended for the supervisors, operators and laboratory personnel responsible for taking samples on an HF plant.

3.2.12 Laboratory Handling Module

3.3 Purpose

The Laboratory Handling Module is intended to describe, in general, the requirements for using HF in a laboratory environment. This may be a Quality control laboratory or a Research and Development environment.

Due to the nature of the work carried out in laboratories relatively small amounts of HF may be present at any one time. However, the sometimes specialist activities, e.g. dilution, transfers, etc., do have a high risk factor associated with them and should not be overlooked. Also, the personnel involved may not be experienced in the use of personal protective equipment, etc.

Content

- A description of the hazards associated with HF
- A description and practical exercise in the personal protective equipment required
- A description of the initial first aid procedures
- A detailed description of each analytical technique to be followed and the risks associated.
- The location of emergency equipment.
- Detailed descriptions of any generic procedures done repeatedly, e.g. dilution of Anhydrous HF.
- Detailed descriptions of any waste disposal requirements.
- The importance of reporting all incidents or near misses so that learning can prevent a recurrence
- Detailed description of the paperwork required prior to initiating a new experiment involving HF

Audience

This training is intended for laboratory personnel involved with handling HF and their supervisors. It should also be provided for analysts working alongside colleagues handling HF.

Table 1: Training Guidelines Matrix

	Visitors	Plant Engineer	Plant Supervisor	Plant Operator	Tanker Operator	Plant/ Contract Maintenance	Laboratory Staff	Occupational Health (Internal or External)	Emergency Response Team	Hauliers	Other Companies in close proximity	Customers
Site Induction	+	*	*	*	*	*	*	*	*	*	+	N/A
Plant Induction	+	*	*	*	*	*	*	*	*	*	N/A	N/A
HF Induction	+	*	*	*	*	*	*	*	*	*	N/A	N/A
PPE	N/A	*	*	*	*	*	*	*	*	*	N/A	*
Initial First Aid	N/A	*	*	*	*	*	*	*	*	*	N/A	*
Secondary First Aid	N/A	N/A	N/A	N/A	N/A	N/A	N/A	*	+	N/A	N/A	+
Operating Procedures	N/A	*	*	*	*	+	N/A	N/A	*	N/A	N/A	N/A
Tanker Procedures	N/A	*	*	*	*	+	N/A	N/A	*	*	N/A	N/A
Decontamination Procedures	N/A	*	*	*	*	*	N/A	N/A	*	N/A	N/A	N/A
Maintenance Procedures	N/A	*	*	*	*	*	N/A	N/A	*	N/A	N/A	N/A
Sampling Procedures	N/A	+	*	*	*	N/A	*	N/A	N/A	N/A	N/A	+
Emergency Procedures	N/A	+	*	*	*	*	+	+	*	*	*	*
Laboratory Handling	N/A	+	+	+	+	N/A	*	N/A	N/A	N/A	N/A	+

* Recommended Training **+** Optional Training N/A - Training not Applicable

4. HF HANDLING LABORATORIES

4.1 Safe Systems of Work

4.1.1 Planning

The handling of HF is in itself a hazardous operation and should be completed only in dedicated locations within laboratories which should be clearly labelled as HF handling areas. This chapter is intended only for laboratories handling HF and where referred to a 'laboratory' is an HF handling laboratory.

4.1.2 Alternatives to HF

Before an experiment with HF is started thought should be given to the possibility of using an alternative fluorinating agent. However, it should be remembered that these substitutes are not free of their own hazards and can produce free HF during the course of a reaction.

4.1.3 Unforeseen HF Formation

It is important to consider the reaction products and the possibility of formation of HF during the reaction, when fluorine-containing compounds are in use e.g. by hydrogenation of halocarbons, reaction of fluorides with acid or thermal breakdown of compounds, the same hazards as a reaction with HF are present and therefore the same precautions should be observed.

4.1.4 Scale of Experiments

For safety reasons experiments should be performed on as small scale as possible. Be aware, however, that for continuous experiments, equipment such as pumps and rotameters have lower limits on rates of flow.

4.2 Risk Assessment

Each laboratory handling HF should prepare a full Risk Assessment prior to initiating each new experiment or task. The Risk Assessment process should be completed by the laboratory team and should include an independent representative to provide an alternative viewpoint. The Risk Assessment may include the following details:

- Clear identification of the task to be done and the individuals involved.
- Clear identification of the equipment required.
- A review of the competence and understanding of the individuals involved.
- An evaluation of the risks associated with each step of the task.
- Clear identification of the possibility of exposure to all hazards.
- Elimination or mitigation of as many hazards as possible.

- A review of the appropriate level of personal protective equipment required for each step of the task and at what point the personal protective equipment should be worn.
- Clear identification of any health implications associated with the task, the individuals involved in the task and the personal protective equipment to be used.
- Clear identification of the expected duration of the task and any hygiene implications.
- Clear identification of the decontamination procedures required.
- Clear identification of any back up emergency plan, if necessary.

One stipulation of the Risk Assessment shall be that all individuals involved will have undergone specific training in the handling of HF in a laboratory.

4.3 Calcium Gluconate Gel

Tubes of calcium gluconate gel to treat HF burns shall be located where the experiment is being carried out.

There is an expiry date on each tube, the tube should be discarded and a new one obtained before this date. A procedure to ensure that tubes are replaced prior to their expiry date should be in place.

It is suggested that anyone using HF, or who could possibly come in to accidental contact with it (e.g. people working in the same laboratory), shall keep a fresh tube of gel at home at all times and got instructions how to use it. This is for application in the event of any observed delayed effects.

This tube should also have the out of hour's medical emergency telephone number noted on the box. It is suggested that a member of the laboratory team should be designated to order new supplies and re-issuing the gel kept at home.

Note: It is important to begin treatment with gel as soon as possible if HF contamination is suspected. This tube of gel retained in the home is intended for individuals to begin treatment at the earliest opportunity. However, it is important to report any incident, whether actual HF contamination or not, and to receive follow up advice from an occupational health specialist and a fresh tube of gel should be supplied.

Gel is available from a number of suppliers. For additional information see *EUROFLUOR Guidelines in case of AHF/HF exposure.*

4.4 Signs and Labelling

It is important that others should be aware of people working with HF in the immediate vicinity. To this end signs should be exhibited where HF is in use.

4.5 Personal Protective Equipment (PPE)

The correct personal protective equipment should be available within the laboratory. The degree of personal protective equipment worn at any time is dependant upon the nature of the task being performed.

Note: In all cases, under normal conditions, personal protective equipment should NOT be relied upon as the primary or only defence mechanism. The primary personal protection should always be the design standards which must eliminate or minimise the risk of exposure to HF wherever possible.

It is highly recommended that an emergency locker containing a full set of the equipment required in case an emergency is situated away from the laboratory handling HF. This will allow easy access to the correct equipment (personal protective equipment, tools, etc.) needed to mitigate an emergency.

Gloves should be tested for pin holes before each use e.g. by inflating with air and/or immersing in water.

Note: It is important to note that "normal" laboratory type gloves may be completely unsuitable for any work with HF. ALL gloves used in handling HF must be resistant to HF.

4.6 Materials of Construction

Examples of common materials compatible with varying strengths of HF at room temperature are tabulated below. **Note that their suitability depends greatly upon the temperature and pressure they will be subjected to and the nature of other components present e.g. HCl or organic compounds.**

Note: Consultation with a Design Engineer is strongly recommended.

	Grade of HF		
Material	Anhydrous	> 70 %	< 70 %
Mild steel	Yes	No	X
Stainless steel	*	No*	X
PTFE ^	*	*	*
FEP	*	*	*
PFA	*	*	*
Monel	*	*	O*
Inconel	*	*	O*
Hastelloy	*	*	O*
Polyethylene	X	*	*
Polypropylene	X	X	*
PVDF	X	X	X
Glass or glass fibre	X	X	X
Silica containing ceramics	X	X	X
Natural rubber	X	X	X
Silicone rubber	X	X	X
Polyamides e.g. Nylon	X	X	X

"" - Acceptable "X" – Not acceptable "O" to be checked if suitable*

Note: PTFE, if filled, must be filled with a suitable material (e.g. CaF_2 but not glass).

Lead washers can be used with the fittings on HF cylinders. It is safe to use in this manner, but should not be considered for rig building.

Note: When considering materials of construction consideration should also be given to other components which may be present or which may be formed during the experiment. For example, some of the materials above, though compatible with HF would not be suitable for use with organic components and this loss of containment of HF may not have been considered during the risk assessment. This may be of particular importance when considering the purchase of standard equipment, e.g. peristaltic pumps.

Mechanical properties must also be considered when choosing materials e.g. copper would not be selected for building a rig due to its lack of mechanical strength.

Care should be taken when handling HF around wooden surfaces as the HF can absorb into the surfaces leaving it unsafe to touch. If HF is thought to have come into contact with a wooden surface then it should be scrubbed with a potassium carbonate solution.

It is important to keep PTFE, FEP etc., which are compatible with HF, away from materials like polyamides, which are incompatible with HF. It is recommended that only HF compatible tubing is used and stored in laboratories using HF.

It is also important to keep HF compatible lubricating agents away from lubricants which are incompatible with HF. It is recommended that only HF compatible lubricating agents are used and stored in laboratories using HF. This is particularly important where valves are to be used under severely corroding conditions, they must be supplied lubricated with PTFE / perfluoroether greases instead of the standard silicone grease.

Labelling of METAL tubing is essential to avoid confusion where differing materials of similar appearance are used in one rig (e.g. Monel and stainless steel). In cases where confusion arises, an alloy detector should be used to determine the composition of the material of construction.

Experiments using HF under reflux can be carried out by using PTFE equipment which includes a condenser.

Experiments at reasonably low temperatures (0-15°C) can be carried out using PTFE, PFA or FEP. FEP is particularly suitable due to its translucence, although it is expensive and equipment constructed in this material is not as widely available as PTFE.

More information should be obtained by the STS Group 4 document materials of construction.

4.7 Working Practices

- All work using HF will involve only trained personnel
- Lone working with HF is not recommended.
- Experiments involving HF shall not be left unattended.
- All staff starting to work with HF for the first time should undergo a medical examination for lung function capability and base fluoride in urine level.
- Other workers in the laboratory or visitors, even if not directly concerned with the HF experiments, shall be informed of its hazards and the precautions necessary to

avoid contact with HF. The adequate and correct labelling of the area where the experiment is located, equipment, pipe work, reactants and products is an important part of this process.

- It is recommended that permanent members of staff who are not working directly with HF but are working in an "HF Lab" should at least attend an HF awareness course.
- Care should be taken to prevent contamination spreading outside the fume cupboard e.g. via equipment and protective equipment. Special care should be taken not to touch equipment whilst wearing HF-contaminated gloves e.g. taps, door handles etc.
- Before starting any experimentation a neutralization agent (e.g. calcium carbonate or potassium carbonate) should be on hand so HF contamination can be dealt with speedily.
- Gloves (or equipment) should be rinsed immediately after use. If any contamination is suspected the gloves should be trashed.
- Consider restrictions to enter offices or control rooms whilst wearing protective equipment. No samples are allowed within these areas.
- Workers involved in maintaining equipment which could be contaminated with HF should have the job fully explained to them. The laboratory staff and the maintenance team should complete a Risk Assessment. If it is deemed necessary a full Permit to Work Certificate may be appropriate.
- Local screening of high risk joints / restrictors should be given some thought when designing experimental rigs.
- HF shall never be discharged into a fume cupboard, down a drain or into the atmosphere. All HF shall be neutralised prior to disposal.
- Experiments involving complex high pressure rigs using HF shall always undergo a hazard study, the results of which shall be retained. Such hazard studies shall always involve a member of the appropriate laboratory team and will have methods of containment built into them (e.g. dump tanks/scrubbers) to cope with a major release owing to equipment failure.
- When planning an experiment or a series of experiments the inventory of HF that the lab holds should be governed by the frequency that the HF cylinder may need to be changed. It is recommended that cylinders should be sized to keep quantities as low as possible.

4.8 Fumecupboard Practices

- Polycarbonate screens should be fitted to all fumecupboard doors where there is HF in use
- The fumecupboards should not be located next to the laboratory doors.
- Fumecupboard vents should be designed to ensure that ‘suck back’ from vents into other fume cupboard in-takes is not feasible.
- The safe use of fumecupboards should always be considered to prevent any exposure.

4.9 HF Rig Building

- Any rig that is to operate at higher than atmospheric pressure should be referred to a design engineer and the rig under-go a full HAZOP.
- The correct materials of construction should be used to prevent corrosion. See STS recommendation Group 4 materials of construction.
- Pipe work should be supported. This is particularly relevant to valves, where there is mechanical stress when opening and closing and to HF manifold lines used to feed more than one rig in a laboratory.
- Where there is an HF manifold, a clear line diagram of the apparatus connected to the cylinder and instructions for purging the lines shall be readily available. The laminated diagram and instructions should be clearly visible close to the manifold.
- HF pipe work should be characteristically labelled or colour coded.
- Care should be taken in the positions of sample points for streams containing HF. A minimum of two isolation valves is preferred and the sample point should point away from the operator in the event of the sample valves failing.
- The sampling procedure for any experimentation should be prepared and included in the Risk Assessment.
- Care must be taken to avoid liquid HF being trapped in a closed length of pipe e.g. between two valves. **Under no circumstances lines suspected to contain trapped HF should be heated.**

4.10 Anhydrous HF in Use

Anhydrous HF is a low boiling liquid (boiling point 19.5°C) which fumes on contact with air and reacts violently with water and bases, evolving a considerable amount of heat. Due to its low boiling point, its use is limited for liquid phase work at atmospheric pressure.

- See STS document Group 5 on general properties of HF.

4.10.1 Cylinders

4.10.1.1 Inventory & Use Control

- Incidents have been reported where cylinders of HF have “exploded” due to over-pressurisation because of hydrogen build-up caused by the reaction of HF / water impurity with the metal of the cylinder. This increase in pressure generally takes several years to reach a dangerous level. To prevent such occurrences, an inventory should be held and exhibited of HF cylinders stocked in the workplace. Cylinders over two years old should be checked for excessive pressure build up before use (according to local regulations).
- Store cylinders in a DRY, COOL, VENTILATED place away from direct sunlight or where there is a risk of fire.
- If excessive pressure is found in a cylinder it should be vented through an appropriate scrubbing train with a nitrogen bleed to prevent suck back. For cylinders

with dip-pipes it may be necessary to invert the cylinder to ensure that the gaseous head space is vented rather than liquor.

4.10.1.2 Connecting New Cylinders

Where an HF cylinder is connected to a permanent rig or manifold thought should be given at the design stage to facilitate the changing of the cylinder.

Note: HF is invariably trapped in pipe work, so never take chances when changing even apparently empty cylinders. When breaking into any line that may have contained liquid HF the correct level of personal protective equipment should be worn.

Always keep the main valve on HF cylinders closed when not in use. Remember to decontaminate all tools and gloves when finished.

4.10.1.3 Cylinders with Seized/Stuck Valves

Do not attempt to open seized/stuck valves on HF cylinders. Replace the blanking nut and dome, fix a label and arrange for the cylinder to be returned to the supplier.

4.11 Aqueous HF in Use

Aqueous HF can be more hazardous than its anhydrous form because of its lower volatility and therefore higher persistence, it does not fume at lower concentrations making it hard to distinguish from other chemicals or water. The burns caused by aqueous solutions can be serious because often they have delayed symptoms which cause late treatment and therefore the effect of a burn may be more pronounced.

Therefore greater thought must be given when ordering aqueous grades. The greatest care must be taken in handling this material, with the appropriate personal protective equipment being worn, as described earlier. The smallest volume required should be ordered to prevent unnecessary disposal problems at the end of an experiment.

A number of concentrations are readily available. For HF concentrations below 40% or between 40 and 60 %, dilute the next highest strength HF to the required strength with water, adding the acid to the water. Always carefully add acid to water possibly as ice in a suitable vessel with stirring and cooling, wearing the appropriate personal protective equipment.

For concentrations between 60 and 100 %, dilution of anhydrous HF with aqueous HF is required. Wear the appropriate personal protective equipment.

Cool the aqueous acid in a plastic container held in ice, then add the anhydrous HF with stirring, at a very slow rate. A violent reaction occurs with evolution of heat with a loud crackling sound and spitting if the addition is uncontrolled or the temperature is too high. Not only is this potentially hazardous, but the required concentration will not be achieved as HF will be lost as vapour.

The prepared solution should be stored in a labelled and proper sample bomb (depending upon the vapour pressure of the prepared solution) in a safe place, e.g. in a bundled container enclosed in a ventilated area.

4.12 Disposal

The correct level of personal protective equipment should be worn during this procedure.

Solutions containing HF should be neutralised by pouring slowly, with stirring, into a solution of sodium or potassium carbonate (20 % w/w with ice) contained in a plastic vessel.

Carbonate is preferable to hydroxide since the evolution of CO_2 has the advantage of removing heat, although the resultant frothing must be controlled by the rate of addition and constant stirring. After neutralisation (checked by pH paper/indicator), any organic should be separated and disposed of by suitable methods.

HF containing vapour should be neutralised by passing the vapour, diluted with an air or nitrogen stream to prevent suck back, into a suitable scrubber using pH control. Thought should be given as to the need for an anti-suck back device in case there is an interruption in the air or nitrogen supply. Visible traps should be used wherever possible so that any 'suck-back' can be traced visibly.

4.13 Decontamination

It is important that everything that has possibly been in contact with HF should be thoroughly decontaminated after use. HF has a tendency to form a layer on metallic surfaces; it is readily absorbed into wood and will dissolve and form an aqueous layer on moist surfaces. Tools should be immersed into a sodium or potassium carbonate bath before washing with water.

All personal protective equipment used during an experiment should be assumed to have been contaminated with HF and should be thoroughly decontaminated e.g. by use of a safety shower. Particular care should be taken with removing personal protective equipment to ensure that secondary contamination does not occur. Where personal protective equipment is known to have been contaminated it should be decontaminated and disposed of.

Wooden surfaces should be wiped with carbonate solution. Known spillages of HF onto wooden surfaces should be treated with carbonate solid followed by washing with carbonate solution and finally water.

5. HF SAMPLING

5.1 General

- Sample taking frequency should be kept to a minimum
- The amount of HF taken for the sample shall be minimised.
- Sampling operations shall, where possible, be performed when site personnel numbers are at a minimum.

5.2 Layout

- The sampling area will be within the boundaries of the HF acid unit.
- The sample point will be clearly labelled an HF sample point.
- The sample area will be well lighted.
- There will be suitable access to the area for emergency response.
- The area around the sample point will be constructed of material of an adequate chemical resistance to enable spillage collection and prevent ground contamination.
- The sample area, when sampling, should be preferably controlled using a physical barrier to prevent unauthorised access.

5.3 Equipment

A safety shower will be adjacent to the sample point with if possible an alarm relayed to a manned area.

- A first aid kit will be provided adjacent to the sample point. This will contain HF burn treatments.
- The appropriate level of clothing will be worn when sampling, considering pressures, temperatures and sample streams.
- A method of communication or monitoring between the sample takers and the control room shall be provided.
- The sample bomb or sample container will be overhauled, inspected and tested on a regular basis
- (Vacuum test) and replacement of seals within the bomb or container will take place before each new sample is taken.
- The bomb or container will be transported to and from the sample site in a carrier, which will prevent leakage during transportation.
- The sample carrier will be clearly labelled as to the contents of the bomb or container.
- Only sample bombs or containers designated for HF sampling will be used in this service.
- Inspection of metallic sample bombs or containers by a thickness determination method should take place at least once every 12 months and records kept of any thinning detected.
- Only approved sample bombs or containers must be used.

5.4 Operation

Sampling operations shall be carried out following a prescribed procedure, which will as a minimum cover the following:

- Safety equipment operational and in good condition
- List PPE requirements
- A step-by-step guide, listing operation of valves
- A sampling pipe work integrity test will be done before each sample
- The sample will be delivered to an approved sample testing area
- The disposal of the sample material left after sampling
- Control of the area during sample taking

5.5 Emergency Procedures

- An emergency plan and alarm system shall be written down and all personnel shall be trained.
- Emergency clothing suitable for leak isolation will be accessible.
- Emergency first aid information will be provided.
- Qualified first aiders will be trained in treating HF burns.

5.6 Training

Staff will be trained and a record kept in the following topics:

- System design
- Operational hazards and risks
- Operating procedures
- Emergency procedures
- Exposure control methods

5.7 Auditing

In order to ensure that relevant procedures and standards are maintained, regular auditing of HF sampling procedures and methods is imperative. Periodic auditing will confirm that systems are working correctly and are being followed.

Auditing should be considered at a number of different levels, e.g. frequent audits from within the work group and less frequent, external auditing by non-facility personnel. All audits and actions generated should be fully documented with individual actions and responsibilities clearly identified and followed up.

6. PERSONAL PROTECTIVE EQUIPMENT FOR USE WITH HF

6.1 General Overview

All HF handling facilities should have written policies and procedures covering the use of personal protective equipment by all employees, contractors and visitors. An appropriate training policy must be in force at the facility. All employees and contractors involved with HF facilities should have appropriate training, to include hazard awareness, risk assessment, the correct way to fit, wear and decontaminate personal protective equipment as well as first aid and emergency procedures as a minimum. These policies should be strictly enforced and implemented.

Note: In all cases, under normal conditions, personal protective equipment should NOT be relied upon as the primary or only defense mechanism. The primary personal protection should always be the design standards which must eliminate or minimise the risk of exposure to HF wherever possible.

HF is a very toxic and corrosive chemical which, when exposure occurs, can lead to severe health risks and can, if the correct treatment is not quickly and efficiently applied, prove to be fatal. However, it should be noted that, despite the hazards associated with handling HF, the European industry has a good safety record and has shown that HF can be safely handled, that the associated risks can be accurately identified and suitable personal protective equipment provides sufficient protection when worn in the correct manner. The largest proportion of injuries is due to a failure in the Risk Assessment process or the lack or incorrect use of the appropriate personal protective equipment. Therefore, it is recommended that users of this guideline work in conjunction with a recognised and experienced supplier of HF to ensure adequate design standards. This guideline attempts to describe typical duties of an HF handling facility and the appropriate level of PPE. The risks of exposure associated with each task will be identified by the Risk Assessment prior to commencing work.

Many materials have been tried and tested following recognised procedures for resistance to HF. Many materials have also been shown to be acceptable through years of experience. When selecting personal protective equipment the material of choice should be shown to be resistant to HF. It is recommended that handlers of HF select only reputable personal protective equipment suppliers who can give documentary evidence of resistance to HF or rely on their supplier of HF to advise on suitable equipment.

It should be noted that all materials have some permeability to HF, particularly liquid HF, and direct contact should be avoided. Personal protective equipment known to have been exposed to liquid HF should be decontaminated as soon as possible.

This guideline is intended to complement the Risk Assessment and to detail the potential personal protective equipment available which has been used successfully at the members' operating facilities. For abnormal situations, for example during emergencies, a level of complete protection should always be specified, details of which can also be found in this recommendation.

The health aspects associated with the wearing of personal protective equipment should not be under-estimated and should form part of the Risk Assessment. For example, it may

not be appropriate for personnel suffering from asthma to be asked to wear full protective equipment with breathing apparatus.

In order to select the most appropriate material the user should contact the various companies supplying personal protective equipment and should request the up to date data on breakthrough times for the various products, the test procedure followed and the recommended maximum working time. Alternatively, contact your supplier of HF and request information on suitable personal protective equipment.

6.2 Legislative Standards

Within the European Community ALL personal protective equipment is required to carry the 'CE' marking. PPE falls into one of three categories:

6.2.1 Simple Design

This equipment is designed for minimal risks only and where the effects of any hazard are of minimal risk and the consequences of any exposure are reversible.

6.2.2 Intermediate Design

Personal protective equipment which has been tested against at least one hazard and is approved by a notified body.

6.2.3 Complex Design

This equipment is designed for hazards which cause irreversible effects or mortal danger.

For use in tasks where contact with HF may occur only Complex Design personal protective equipment is acceptable. Where personal protective equipment does not display the relevant CE mark it cannot be employed at a European facility handling HF.

Relevant test protocol and standards are referred to where possible. A summary of this information is provided in Appendix 1: European Personal Protective Equipment Standards.

Note: There is a recognised standard for reporting degradation of test materials. However, the chemical permeation test requires the condition of a test fabric to be noted including any degradation. However, permeation can occur without any obvious sign of degradation and it would be unsafe to assume that, because degradation was not obvious, there was no damage due to exposure. The only method acceptable is to test the personal protective equipment for permeation of the specific chemical(s).

6.3 Personal Protective Equipment Policy

Each operating site should have a clear, written policy describing the use and requirements of individuals with regard to personal protective equipment. The policy, which should be reviewed periodically, should comply with all local, national and international legislation where appropriate and, as a minimum, should include the following areas:

6.3.1 Risk Assessment

Each site handling HF should have a procedure which demands a Risk Assessment is completed prior to initiating each new task or job. The Risk Assessment process should be completed by the operating team and should include a representative of the team expected to complete the task.

The Risk Assessment should include the following details:

- Clear identification of the task to be done and the individuals involved.
- Clear identification of the equipment required.
- A review of the competence and understanding of the individuals involved.
- An evaluation of the risks associated with each step of the task.
- Clear identification of the possibility of exposure to all hazards.
- Elimination or mitigation of as many hazards as possible.
- A review of the appropriate level of personal protective equipment required for each step of the task and at what point the personal protective equipment should be worn.
- Clear identification of any health implications associated with the task, the individuals involved in the task and the personal protective equipment to be used.
- Clear identification of the expected duration of the task and any hygiene implications.
- Clear identification of the decontamination procedures required.
- Clear identification of any back up emergency plan, if necessary.

6.3.2 Levels of Personal Protective Equipment

All areas and associated hazards of the facility should be considered when evaluating the

Suitability and use of personal protective equipment: The areas considered when preparing this recommendation included production units, decontamination and maintenance areas, loading and unloading facilities, transit, sampling and laboratory handling, pilot plant, on- and off-site medical facilities including emergency responders.

When defining personal protective equipment consideration should also be given to any potential health implications for the wearer and suitable standards should be applied, for example, it may be appropriate to define a maximum work time for some equipment. Heating and cooling systems for personnel required to wear personal protective equipment in extreme conditions are available and should be considered where necessary. Also, certain tasks, for example scaffolding in areas of high risk, may require a heavy duty glove which is not only chemically resistant but will also resist mechanical damage.

Note: All materials used to manufacture personal protective equipment are permeable to HF, in particular liquid HF. Procedures should therefore ensure that, where contact with liquid HF may have taken place, the wearer should endeavour to decontaminate and inspect the equipment at the earliest possible opportunity. Also, once HF has penetrated the outer protective layer it cannot be removed by the decontamination process, therefore a suitable operational lifespan should be determined where appropriate.

Four potential 'Levels' of personal protective equipment have been identified for use on HF handling facilities. The Risk Assessment will clearly identify the PPE required for each task. :

- Level Alpha (α) Emergency Response
- Level Beta (β) Operational Equipment for Increased Risk Activities
- Level Gamma (γ) Routine Operational Equipment
- Level Delta (δ) Standard on-plant Equipment

The naming nomenclature has been used in order to provide a unique identification label

6.3.2.1 Level Alpha (α): Emergency Response (See Fig 1)

Level Alpha personal protective equipment is used for emergency response or where the risk assessment has identified a high degree of probability that the task could result in a significant exposure and when an airline is not a practical option, for example, the airline will not give sufficient mobility. Alpha Level should use equipment designed to prevent ingress of HF and should give full protection from potential HF exposures. The health impact of using this level of personal protective equipment should not be under-estimated. The wearing of fully encapsulated suits and breathing apparatus (BA) whilst working, particularly in hot climates, can lead to additional health risks for the employees involved. The additional risks associated should be identified and assessed in the risk assessment.

Alpha Level personal protective equipment is defined as:

- Fully encompassing HF resistant suit.
- Suitable gloves either built in or completely sealed at the wrists
- Breathing apparatus (BA) set or, if practicable, airline providing suitable supply of breathing air
- Standard hard hat or bump cap worn inside the suit.
- HF resistant boot with steel toe and shank worn inside outer leg seal.

Alpha Level personal protective equipment is used for emergency response and is designed to be gas tight and to provide full protection against the ingress of HF. Specific training is required to ensure correct fitting.

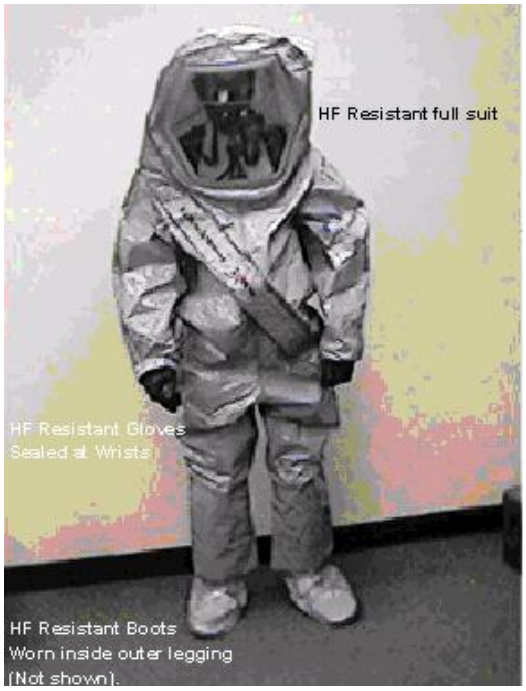

Fig 1.1: Front View

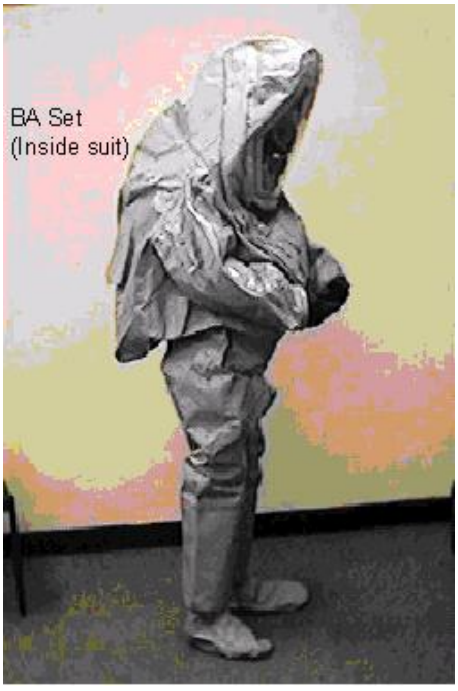

Fig 1.2: Side View

Fig 1.3: Front View showing BA Set

6.3.2.2 Level Beta (β): Operational Equipment for Increased Risks See Fig 2)

Beta Level personal protective equipment is used for routine operational tasks involving invasive interactions with process equipment or for non-routine interactions which have been identified as requiring a higher level of protection. β Level equipment is designed to prevent the ingress of HF and should give full protection against likely HF exposures.

Beta Level personal protective equipment is defined as:

- HF resistant one piece suit.
- Standard hard hat or bump cap worn inside the suit.
- HF resistant gloves sealed with the suit.
- External air supply or in the suit integrated gas mask (resistant to HF attack) providing suitable supply of breathing air
- HF resistant boots or over-boots with steel toe and shank sealed with the suit. Boots permanently attached to a one-piece, gas tight suit may also be worn.

Training is required to ensure that Beta Level personal protective equipment is fitted correctly.

Fig 2: Level Beta Personal Protective Equipment

6.3.2.3 Level Gamma (γ): Routine Operational Equipment (See Fig 3)

Level Gamma (γ) personal protective equipment is used for routine operational tasks involving non-invasive interactions with process equipment in designated areas. It is designed to give a greater degree of protection against incidental contact with process fluids for individuals working in the HF handling area.

Level Gamma personal protective equipment is defined as:

- Standard hard hat with HF resistant nape and face visor. Visor MUST be in the down position. Ventilated full protection helmet may also be worn.
- Chemical goggles. Goggles MUST be worn under visor.
- HF resistant gloves.
- HF resistant jacket with the gloves overlapping the sleeves.
- HF resistant high waisted trousers overlapping HF resistant boots.
- HF resistant boots or over-boots with steel toe and shank (Wellington type boots).

Training is required to ensure that γ Level personal protective equipment is fitted correctly.

Fig 3: Level Gamma Personal Protective Equipment

6.3.2.4 Level Delta (δ) Standard on-plant Equipment (See Fig 4)

Delta Level is the minimum level of personal protective equipment 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.

Delta Level personal protective equipment is defined as:

- Standard hard hat.
- Safety spectacles with side shields or chemical goggles.
- Jacket with long sleeves and long trousers.
- HF resistant boots over-boots or safety shoes with steel toe.
- HF resistant gloves may also be required.
- Escape air packs or suitable filtration systems should be considered.

Fig 4: Level Delta Personal Protective Equipment

6.4 Protective Equipment Care

Facilities to enable the decontamination of used personal protective equipment should be provided. Initial decontamination should take place immediately on leaving the area, for example, by use of a shower. All personal protective equipment used on plant should be assumed to be contaminated with HF and treated with appropriate care.

Care should also be exercised during the removal of all personal protective equipment. In particular, where others provide assistance, the Risk Assessment should have identified suitable personal protective equipment for the assistant.

Secondary systems to ensure complete decontamination by neutralisation should be available for use by the operating teams. Where protective equipment is not issued to individuals as equipment for their personal use care must be taken to ensure that hygiene issues are adequately addressed.

All cleaned personal protective equipment should be tested for integrity prior to re-use within the HF facility. This testing may be completed in a number of ways and will depend upon the personal protective equipment, for example, gloves should be tested before each trip onto the plant by inflating with air and/or submerging in a water bath, suits should be visually inspected using a light source to determine minor defects, etc.

Personal protective equipment should be stored and routinely maintained by trained personnel in accordance with the manufacturer's recommendations. In all cases defective or untested equipment must not be used within the facility. All repairs to personal protective equipment should only be carried out by trained and authorized individuals and the level of approved repairs adequately described by the personal protective equipment policy, for example, no equipment with more than one repair can be used for high risk duties. Care should be taken to ensure that all decontamination liquors are treated in a suitable facility prior to discharge to the local waterways.

6.5 Training

In all cases personal protective equipment should only be worn by those trained in its use, application and decontamination. The training requirements for operators, maintenance, contractors, management and visitors should be clearly identified and must be strictly followed. Periodic re-training should also be provided.

In all cases training and re-training should be recorded and these records maintained for a suitable period. Training should, as a minimum, include the following areas:

6.5.1 Product Introduction

All individuals working on or visiting facilities handling HF should understand the toxicity and hazards associated with the product.

6.5.2 Plant Induction

All individuals working on facilities handling HF should, as a minimum, be trained in the operation, the general layout of the plant, its emergency equipment locations, the alarm systems and what to do in an emergency.

6.5.3 Personal Protective Equipment

All individuals working on or visiting facilities handling HF should be trained in the use and limitations of the personal protective equipment available within the facility. Training in the use of personal protective equipment should also cover the health and hygiene issues associated with wearing the equipment.

6.5.4 Job Specific

Training should be given appropriate to the individual's role on the facility. The level of training given should be appropriate to the role of the individual and the level of risk associated with the task, for example, sampling of HF systems would demand a high degree of training and experience from the operator involved.

6.5.5 Emergency Response

All individuals working on or visiting facilities handling HF should be trained in their role in an emergency. This will be part of the site emergency planning procedures and the roles will vary from leaving the area and reporting to a central location to being part of the response team – all individuals should understand and be prepared to fulfil their roles.

All individuals should know the location of emergency first aid equipment, for example, calcium gluconate gel. All individuals should understand their responsibility to report all incidents, exposures or potential exposures to HF.

6.5.6 First Aid

All individuals working on or visiting facilities handling HF should have an understanding of the effects of HF on the human body and should be trained in the symptoms of all potential exposure types (skin, airways, eyes, ingestion) and in the correct response, which may depend upon their role within the emergency procedures, to an exposure incident. An understanding of the need for prompt treatment should be given during the training program.

All individuals should be trained in the use of calcium gluconate gel, some companies have elected to provide each individual exposed to potential risks with a tube of calcium gluconate gel at home to begin immediate treatment should delayed effects become apparent. It is imperative, however, that 'home treatment' be supplemented by medically trained staff and that any use of calcium gluconate gel at home to be reported to the workplace at the earliest opportunity.

An appropriate number of individuals should have more detailed first aid training in the use of first aid equipment and these individuals should be responsible for administering the

initial treatment to any HF exposure. These individuals should be clearly identified within the facility.

6.5.7 Neighbouring Facilities

Additional training may be appropriate for personnel in adjacent facilities, potentially including other companies, on the correct response to alarms.

6.5.8 Auditing

In order to ensure that relevant procedures and standards are maintained regular auditing of personal protective equipment systems is imperative. Periodic auditing will confirm that systems are working correctly and are being followed.

Auditing should be considered at a number of differing levels, for example, frequent audits from within the work group and less frequent, external auditing by non-facility personnel. All audits and actions generated should be fully documented with individual actions and responsibilities clearly identified and followed up.

7. HF DETECTION

7.1 General Overview

All HF handling facilities should consider the use of HF detectors for the following purposes:

- Personal exposure monitoring
- Leak detection
- Quantification of release concentrations at site / plant boundaries during an incident

Further guidance with respect to emergency / incident response and personnel monitoring (including exposure levels), can be found in the STS recommendation Group 5 General Properties on HF and Group 6Emergency Response (on site). Facilities should have written policies and procedures covering the use of personal exposure monitoring and medical monitoring programs for all employees, and contractors. An appropriate training and maintenance policy must be in force at the facility. All employees and contractors involved with the maintenance of HF detectors should have appropriate training, to include hazard awareness, risk assessment (appreciation of the impact of working on the equipment), detailed knowledge on the testing and maintenance of the equipment as well as first aid and emergency procedures as a minimum. These policies should be strictly enforced and implemented.

7.2 Detection Technology

Members of EUROFLUOR currently employ two types of technology for the detection of HF leaks:

- Electrochemical cell
- Laser

Whilst the detection equipment is installed at the facility the user must maintain regular contact with the supplier to ensure that the equipment is up to date.

7.3 Design, Installation, Operation and Maintenance

At all stages of the detectors life cycle i.e. design, installation, and operation the following should be considered:

- Range (minimum and maximum detection limits)
- Alarm (values and functionality, i.e. fail safe, high / high high, management e.g. auto repeat)
- Response time (plus any changes with time / use / exposure, post / during calibration)
- Calibration (method, procedures, frequency, durations)
- Interferences (chemical, humidity, temperature)
- Back-up power (both for the field instrument and the alarm / reading)
- Mechanism to display alarms, detection status and results
- Number and location of detectors

ANNEX I - HF ACCIDENTS REPORT

1. GENERAL INFORMATION

Name of people reporting	
Date of the accident	
Country	

2. CIRCUMSTANCES

2.1. Generalities

HF type

☐ Anhydrous

☐ Aqueous [ ] %

☐ Other (please specify) [ ]

Quantity [ ] kg

Where?

☐ HF factory

☐ Industrial user

☐ At end user

☐ On the road

☐ On the railway

☐ Other (please specify)

[ ]

Type of operation

☐ Analysing

☐ Sampling

☐ Producing

☐ Maintenance

☐ Loading

☐ Unloading

☐ Transportation

☐ Other (please specify)

[ ]

2.2. Description

(NB: don't hesitate to add drawings or pictures to clarify the situation!)

[ ]

3. CONSEQUENCES

3.1. Number of persons concerned? Injury?

3.2. In case of injury, describe it in detail: size and type of the burn, apparent severity, pain etc.

Describe thoroughly all the phases of the treatment (if any): delay before first water rinsing, duration of rinsing, delay before applying calcium gluconate gel, duration of massage, other treatment if any (calcium gluconate injection? surgery? etc.)

3.3. Pollution?

3.4. Media information?

3.5. Other?

4. ACCIDENT ANALYSIS

4.1. Root causes?

4.2. Corrective actions?

ANNEX II - PPE RECAPITULATIVE TABLE USA/EUROPE

	USA	EUROPE (EUROFLUOR)
Emergency	• Positive pressure, full-facepiece self-contained breathing apparatus (SCBA) or positive pressure supplied air respirator with NIOSH approved escape SCBA • Totally encapsulating, vapor-tight, chemical protective suit (*picture: suit with built-in socks, underneath footwear fully encapsulated*) • HF resistant inner gloves • HF resistant outer gloves • HF resistant boots, with steel toe and shank • Standard hard hat or bump cap worn inside the suit 	• Breathing Apparatus (BA) Set (EN132: 1990 Annex A) or, if practicable, air line providing suitable supply of breathing air (EN132: 1990 Annex A; EN270: 1994; EN137) • Fully encompassing HF resistant suit (prEN943-2) • Suitable gloves either built in or completely sealed at the wrists (EN488) • HF resistant Wellington-type boot (EN943-2: 1995) with steel toe and shank worn inside outer leg seal • Standard hard hat or bump cap worn inside the suit (EN397) 
Increased Risk	• Positive pressure, full-facepiece self-contained breathing apparatus (SCBA) or positive pressure supplied air respirator with NIOSH approved escape SCBA. • Hooded HF resistant clothing, like overalls and long-sleeved jacket, coveralls, or one or two piece splash suit. • HF resistant inner gloves. • HF resistant outer gloves. • HF resistant boots, with steel toe and shank. • Standard hard hat or bump cap worn inside the suit 	• Air line (resistant to HF attack) providing suitable supply of breathing air (EN132: 1990 Annex A; EN270: 1994; EN137) • Airfed HF resistant jacket with high waisted trousers (EN467: 1995) sealed at Wellington-type boots and gloves with integral, air fed hood (Visor to EN146; air fed hood to EN270) or fully encompassing HF resistant one piece suit (Visor to EN146; prEN943-2). • HF resistant gloves (EN374-3). • HF resistant Wellington-type boots or overboots with steel toe and shank (EN345 with additional testing to EN369 [specifically for HF]). Boots permanently attached to a one-piece, gas tight suit may also be worn (EN943). • Standard hard hat or bump cap worn inside the jacket (EN397). 

Routine	• Full-face NIOSH approved air purifying respirators for HF service or NIOSH approved hood assembly respirators. NIOSH approved halfmasks may also be used with chemical splash goggles in certain situations. • Hooded HF resistant clothing, such as overalls, two-piece chemical splash suit, or disposable HF resistant overalls. • HF resistant inner gloves. • HF resistant outer gloves. • HF resistant boots, with steel toe and shank, or disposable HF resistant outer covers. • Hard hat, face shield, and chemical splash goggles. • NIOSH-approved escape mask (if no other respiratory protection is required). 	• HF resistant jacket with sleeves sealed at gloves (EN467: 1995). HF resistant high waisted trousers sealed at Wellington-type boots (EN467: 1995). • HF resistant gloves (EN374-3). • HF resistant Wellington-type boots or overboots with steel toe and shank (EN345 with additional testing to EN369 [specifically for HF]). • Standard hard hat (EN397) with HF resistant nape (EN467: 1995) and face visor (EN166-B). Visor MUST be in the down position when within the HF handling area. • Chemical goggles (EN166-345-B). Goggles MUST be worn under visor when within the plant boundaries. 
Visitor	• Coveralls. • Gloves. • HF resistant boots, with steel toe and shank, or disposable HF resistant outer covers. • Hard hat and face shield. • Safety glasses with side shields or chemical splash goggles. • Available escape respirator.	• HF resistant gloves (EN374-3) may also be required. • HF resistant Wellington-type boots, overboots or safety shoes with steel toe (EN345). • Standard hard hat (EN397). • Safety spectacles with side shields or chemical goggles (EN166-345-B). • Escape Air packs or Suitable filtration systems should also be readily available to enable an escape in the unlikely event of a leak.