National Occupational Health and Safety Commission

# HYDROGEN FLUORIDE

**December 1989**

Australian Government Publishing Service
Canberra

WAP 89/039
GS 001-1989

ISBN 0 644 12820 8



The National Commission's address is:

National Occupational Health and Safety Commission
Level 30, St Martins Tower
31 Market Street
Sydney NSW 2000
GPO Box 58
Sydney NSW 2001
Tel: (02) 265 7555
Facsimile: (02) 265 7538
Telex: 177243

Printed in Australia by Alken Press, Smithfield

# Foreword

The National Occupational Health and Safety Commission, Worksafe Australia, is a tripartite body established by the Commonwealth Government to develop, facilitate and implement a national approach to occupational health and safety.

The National Commission comprises representatives of the peak employee and employer bodies - the Australian Council of Trade Unions (ACTU) and Confederation of Australian Industry (CAI) - as well as the Commonwealth, State and Territory governments.

Since its establishment, the National Commission has produced occupational health guides. Before the National Commission was established, a series of similar guides was published by the National Health and Medical Research Council.

This Guide has been reviewed and endorsed by a working group of the National Commission as part of the co-ordinated effort by the Commonwealth, State and Territory governments and employee and employer organisations to make Australian workplaces safe and healthy.

Although this Guide has been endorsed by the National Commission, it is an advisory document only. It is produced and distributed in the interests of providing useful information on occupational health and safety for employers, employees and others. This document does not replace statutory requirements under relevant State and Territory legislation.

This Guide is aimed primarily at workers and managers but should also be useful to occupational health and safety personnel and others. It may be used in conjunction with appropriate training and consultation, in line with good management practice.

# Contents

# Introduction

This Guide outlines some of the potential health hazards associated with the use of hydrogen fluoride.

This Guide should be read in conjunction with the Worksafe Australia Guide, *Atmospheric Contaminants*, and the National Commission publication, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* (latest edition).

Reference should be made to the manufacturer's specific product information in the form of a material safety data sheet (MSDS). The MSDS should be updated regularly. The MSDS should conform to the National Commission's recommended format and should be freely accessible to all personnel.

# Identification

## Properties

Hydrogen fluoride (hydrofluoric acid) is available industrially in the pure state as a liquid under pressure (anhydrous hydrofluoric acid) or more commonly as an aqueous solution with a maximum strength of 70 per cent (aqueous hydrofluoric acid).

Anhydrous hydrofluoric acid on release from pressure gives off large amounts of gaseous hydrogen fluoride which fumes strongly in moist air. Aqueous hydrofluoric acid also gives off gaseous hydrogen fluoride when open to air but produces visible fume only at concentrations greater than 48 per cent. In both liquid and gaseous form, hydrogen fluoride is extremely reactive, attacking metals, glass, leather and natural rubber.

## Sources of exposure

Important sources of exposure to hydrofluoric acid and other fluorides are aluminium smelting, welding, fertiliser production, fluorocarbon and fluoride production, metal refining and the pickling, etching and polishing of glass and pottery, uranium enrichment, cleaning of metals and cleaning in the building industry.

# Health Hazards

When considering the hazards associated with any workplace, it is essential to understand the relationship between 'hazard', 'exposure' and 'risk'.

'Hazard' is the potential for an agent or process to do harm. 'Risk' is the likelihood that an agent will produce injury or disease under specified conditions.

Health effects can occur only if a worker is actually exposed to the hazard. The risk of injury or disease usually increases with the duration and frequency of exposure to the agent, and the intensity/concentration and toxicity of the agent.

Toxicity refers to the capacity of an agent to produce disease or injury. The evaluation of toxicity takes into account the route of exposure and the actual concentration of an agent in the body.

## Exposure routes

The harmful effects of hydrogen fluoride follow inhalation of vapour, eye and skin contact with liquid or vapour, or ingestion, which are described below:

- *Inhalation* is the most significant route of entry by which harmful substances enter the human body at work.
- Some atmospheric contaminants may be *absorbed* through the skin without any noticeable effect on the skin, while others may cause serious damage to the skin itself. Eyes are especially sensitive.
- *Ingestion* is of relatively minor significance in occupational exposure to toxic materials.

Exposure to hazardous material may be acute or chronic. *Acute exposures* generally refer to single dose, high concentration exposures over short periods, while *chronic exposures* involve repeated or continuous exposures over long periods. These exposures may have acute, immediate effects or chronic, long term effects.

## Health effects

Toxic contaminants may have *local effects*, if they harm only the part of the body they come in contact with, for example, inhalation of silica dust causing pneumoconiosis, or *systemic effects*, causing changes to the function of other organs, as in the case of inhaled particles that are soluble in the fluid of the tissues that line the lung, for example, lead and mercury fumes.

Hydrogen fluoride in both gaseous and aqueous forms is strongly corrosive and causes severe and painful burns to the skin, eyes and mucous membranes and severe respiratory irritation. Chronic exposure to excessive quantities of gaseous or particulate fluoride results in nausea, vomiting, loss of appetite and diarrhoea or constipation. Fluorosis and other chronic effects may result from significant acute exposures. Systemic fluoride poisoning can cause hypocalcaemia, which may lead to cardiac arrythmias and death.

### *Skin*

Burns from a dilute solution (1-20 per cent) of hydrofluoric acid may not be immediately painful or visible. The first symptom is a delayed throbbing, burning pain which is followed by localised destruction of tissue and blood vessels that may penetrate to the bone. Contamination around the nails can give rise to a painful condition and may require amputation of the finger. Healing of the affected area is usually slow.

### *Eyes*

Exposure to hydrogen fluoride causes a burning sensation, redness and secretion. Splashes of dilute acid rapidly produce conjunctivitis, keratitis and more serious destructive effects.

### *Inhalation*

Inhalation of hydrogen fluoride causes an intolerable prickling, burning sensation in the nose and throat, with cough and pain beneath the sternum. Nausea, vomiting, diarrhoea and ulceration of the gums may also occur. In low concentrations, irritation of the nasal passages, dryness, bleeding from the nose and sinus disorders may result, while continued exposure can lead to ulceration and perforation of the nasal septum. Exposure to high concentrations can cause laryngitis, bronchitis and pulmonary oedema (fluid on the lungs) which may not become apparent until 12-24 hours after the exposure.

# Prevention and Control Measures

Following the identification of a hazard, evaluation of work practices and conditions must be undertaken so that effective prevention and control measures can be implemented. This should be considered an integral part of management's responsibilities.

## Evaluation

Environmental sampling and analysis should be undertaken at regular intervals by qualified occupational health and safety professionals in accordance with the methods recommended by the appropriate occupational health authority.

## Exposure standards

The 1990 edition of the National Commission publication, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment*, recommends the time-weighted average exposure level listed below. This level should not be exceeded even instantaneously (peak):

hydrogen fluoride (as F) - 3 ppm, peak; 2.5 mg/m$^3$, peak

The exposure standard was established on the basis of the irritant effects.

The most recent edition of *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* must always be consulted for current values.

The odour threshold of hydrogen fluoride for most people is around 0.1mg/m$^3$. This allows for early warning signs of build-up of hazard levels without the recommended exposure standard being exceeded.

The exposure standards represent airborne concentrations of individual chemical substances which, according to current knowledge, should neither impair the health of, nor cause undue discomfort to, nearly all workers. In certain cases, the exposure standards are believed to guard against narcosis or irritation which could precipitate industrial accidents.

Except where modified by consideration of excursion limits, exposure standards apply to long term exposure to a substance over an eight hour day for a normal working week, over an entire working life.

**The exposure standards do not represent 'no-effect' levels which guarantee protection to every worker.**

## Control measures

Where there is a likelihood of worker exposure to hydrogen fluoride, steps should be taken to minimise that exposure as far as workable. A thorough examination of work practices is essential. Procedures should be adopted to ensure that workers are not unnecessarily exposed to the hazard. Control measures include, but are not limited to, the following, which are ranked in priority of their effectiveness:

- elimination/substitution and process modification;
- engineering controls;
- administrative controls; and
- use of personal protective equipment.

## Engineering controls

Engineering controls should be such that the concentrations of atmospheric contaminants given off by the operations do not exceed the recommended exposure standards.

Care in selection, design, installation, operation and regular maintenance is essential to ensure that ventilation systems adequately control contamination at all times.

The design of an effective ventilation system is a highly specialised area of expertise and therefore should be performed only by those competent to do so. Special care in design is important where combustible, inflammable or potentially explosive materials are involved. Inlets and outlets must not be blocked and must be kept clear at all times.

Air from a local exhaust ventilation system should not be recirculated into the workroom. It should be discharged to the outside air, distant from other work areas, air-conditioning inlets or compressors supplying breathing air.

General ventilation systems are not usually as satisfactory in the control of health hazards as is the use of ventilated process enclosures or local exhaust ventilation, but they may be useful to control minor emissions of contaminants of low toxicity. In designing a mechanical ventilation system

where such contamination occurs, particular attention should be given to fan selection and to the placement of air extractors and fresh air supply openings. In particular, movement of air should be arranged so that clean air streams are drawn past workers and contaminated ones lead away from them. Such systems require rigorous control over all sources of natural ventilation and air movement which may disturb planned air movement, for example, the operation of air-conditioning systems or the opening and closing of doors and windows. Changes or additions to a balanced ventilation system must be implemented in such a way that they will not result in reduced efficiency of the entire ventilation system.

## Personal protective equipment

In certain circumstances, personal protection of the individual may be required as a supplement to other preventive action. It should not be regarded as a substitute for other control measures and must only be used in conjunction with substitution and elimination measures.

Personal protective equipment must be appropriately selected, individually fitted and workers trained in their correct use and maintenance. Personal protective equipment must be checked regularly and maintained to ensure that the worker is being protected.

To protect the eyes and skin, other protective equipment such as safety spectacles, chemical safety goggles, face shields, hats or hoods, overalls with sleeves to the wrist, gloves, long aprons and safety boots should be provided and used as necessary. Where concentrations are expected to be relatively high, supplied air respirators should be used. Supervisors should ensure that employees are adequately instructed in the correct use of personal protective equipment. All personal protective equipment needs to be thoroughly laundered or otherwise cleaned after use.

All protective equipment should be made of materials which are resistant to hydrogen fluoride, for example, PVC, and should comply with the requirements of Australian Standards AS 1715, AS 1716, AS 1336, AS 1337 and AS 2161. Subject to existing facilities, safety showers and eye irrigation facilities should be provided at suitable locations.

When using hydrogen fluoride, personal protective equipment should not be used as a normal control procedure. Personal protective equipment should only be used in emergencies or non-routine operations.

## Storage and transport

Areas where hydrogen fluoride in aqueous or gaseous forms are stored should be provided with efficient ventilation. In enclosed storage areas, hydrofluoric acid vapour may cause serious corrosion of sprinkler systems.

Anhydrous hydrofluoric acid has to be stored and transported in pressure vessels. The aqueous form may be stored or transported in rubber lined or plastic vessels. Tanks and other containers should be protected from heat, direct rays of the sun and from mechanical damage. Transport containers should conform to the appropriate provisions of the Australian Code for the Transport of Dangerous Goods by Road and Rail.

## Labelling

Containers for storage and transport should bear warning labels to indicate the hazardous nature of the compound and the procedures to be adopted in case of emergency. The design of warning labels should consider both the non-English speaking worker and the illiterate, by having a pictorial warning in addition to written information.

## Health assessment

In some occupations, health assessment may form part of a comprehensive occupational health and safety strategy. Where employees are to undergo health assessment, there should be adequate consultation prior to the introduction of any such program. Where medical records are kept, they must be confidential. It is particularly valuable to be able to relate employee health and illness data to exposure levels in the workplace.

## Education and training

All employees working with hydrogen fluoride must be informed of the hazards from exposure to the contaminant and the precautions necessary to prevent damage to their health. Employees should be trained in appropriate procedures to ensure that they carry out their work so that as little contamination as possible is produced, and in the importance of the proper use of all safeguards against exposure to themselves and their fellow workers. Adequate training, both in the proper execution of the task and in the use of all associated engineering controls, as well as of any personal protective equipment, is essential.

Employees exposed to contamination hazards should be educated in the need for, and proper use of, facilities, clothing and equipment and thereby maintain a high standard of personal cleanliness.

Special attention should be given to ensuring that all personnel understand instructions, especially newly recruited employees and those with English-language difficulties, where they are known.

MSDS should be obtained for all substances from the suppliers of such materials before handling.

All employees handling hydrogen fluoride should be fully conversant with emergency procedures and first aid. To achieve this:

- Management should arrange induction programs for new workers and refresher courses should be conducted at least annually.
- MSDS should be obtained from the hydrogen fluoride suppliers and made available to the workforce. All recommendations should be carefully followed.
- Relevant State and Territory legislation should be explained and enforced.

# First Aid

If poisoning occurs, contact a doctor or local or national poisons information centre. Speed in removing the patient from the contaminated atmosphere and in removing hydrofluoric acid from the skin is of primary importance. First aid must be started immediately. The affected person must be referred to a doctor, even when the injury seems slight. Worksites using hydrogen fluoride should have tubes of 2.5-3 per cent calcium gluconate gel, and calcium gluconate tablets in the first aid kit. These should be obtained by contacting the State or Territory occupational health authority.

## Skin

In case of skin contact:

- Remove contaminated clothing using PVC gloves and drench the area with water for a sufficient period of time, usually one to two minutes, to remove all hydrofluoric acid.
- Apply calcium gluconate gel (2.5 - 3 per cent - available in 25 g tubes) to and around the contaminated area and massage it in with clean, preferably gloved, fingers. White specks appearing around the contaminated area indicate that the desired reaction has taken place. (If cloudiness or separation occurs, then the gel must be replaced.)
- Continue massage with repeated application for 15 minutes after the pain has subsided or until medical treatment is available.
- For large or severe burns, four effervescent calcium gluconate tablets (600 mg) should be given by mouth every two hours until the patient is admitted to hospital.

## Eyes

When hydrogen fluoride gets into the eyes:

- irrigate the eyes immediately and copiously with water for at least 15 minutes;
- continue irrigation with isotonic saline or water until the severe pain of the burn is relieved; and
- obtain medical attention, preferably from an eye specialist.

## Inhalation

In cases of inhalation:

- Rescuers should wear respiratory protection.
- Immediately transfer the patient to an uncontaminated location.
- If breathing has stopped, ensure airway is clear and apply artificial respiration as quickly as possible. Oxygen should be given under the supervision of a trained person.
- Four effervescent calcium gluconate tablets (600 mg) should be given by mouth every two hours until the patient is admitted to hospital.
- Obtain medical advice or transport the patient to hospital, explaining that the patient has been exposed to hydrofluoric acid which may cause delayed reaction.
- During resuscitation, examine the patient's skin for burns and treat as shown above.
- The patient is to be kept quiet, preferably lying down, warm and comfortable. Under no circumstances should a patient be permitted to return home or back to work until examined and discharged by a doctor because of the possibility of delayed symptoms.

## Advice to doctor

Specialist medical advice should be sought immediately.

### *Skin*

For dilute solutions of hydrofluoric acid, calcium gluconate gel applied topically will often relieve the pain and reduce the injury. Exposure of subungal tissue may require the removal of the nail in order to treat adequately. Continued pain and destruction may be treated by subcutaneous administration of calcium gluconate. Arterial calcium perfusions have been used.

Systemic fluoride poisoning can result from dermal exposure, particularly with concentrated and extensive exposures. The treatment described above needs to be considered. Early removal of skin may need to be considered in cases of extensive skin damage and refractory hypocalcaemia.

Continue application of the calcium gluconate gel to the skin for 15 minutes after the pain has completely subsided. This may require several hours but, providing improvement in the lesions and symptoms continues, massaging with the gel should be continued. In cases where a thick

necrotic coagulum has formed, it may act as a barrier and prevent the penetration of the gel. This will be indicated by lack of improvement. In these cases, the necrotic tissue should be excised and the gel massaged into the base of the burn, taking usual aseptic precautions.

If the burn fails to respond to the calcium gluconate gel, injection of a sterile 10 per cent solution of calcium gluconate into and under the burn should be considered. Relief of pain is an indication that sufficient solution has been injected. Because of this, an anaesthetic should not be given except in situations where the skin is tightly adherent to the underlying tissues. In these cases, a general anaesthetic should be given as local anaesthesia is contra-indicated.

Once symptoms have subsided, the burn should be covered with a sterile dressing. If the pain recurs, for example, after burn from dilute acid, the patient should return for further symptomatic treatment.

In cases of large areas of skin contamination, for example, greater than 65 sq cm, six effervescent tablets, each containing 400 mg calcium and 20 mg ascorbic acid, should be given in water by mouth every two hours until the patient is admitted to hospital.

Serum calcium and/or magnesium may have to be replaced intravenously if indicated by clinical signs or by electrolyte monitoring. Systemic administration is by the slow intravenous route.

### *Eyes*

Irrigation with water and isotonic saline and obtain an ophthalmologic consultation.

### *Inhalation*

Acute respiratory failure may develop requiring airway support, 100 per cent oxygen and positive end expiratory pressure treatment for pulmonary oedema. In addition, treatments and monitoring for systemic fluoride poisoning described above may be required.

### *Ingestion*

Nasogastric suction with calcium gluconate solution may reduce systemic fluoride toxicity. The possibility of chemical burns to the gastrointestinal tract needs to be kept in mind. Acute systemic fluoride poisoning may cause profound hypocalcaemia (hypomagnesemia) requiring intravenous calcium (magnesium) therapy. Electrocardiogram results and blood calcium/magnesium need to be monitored in acute systemic fluoride poisoning.

# Emergency Procedures

## Spills or leaks

In cases of spills or leaks:

- move people upwind from the area and cordon it off;
- keep clear of liquid and visible fumes;
- do not enter the contaminated area unless wearing protective clothing. (For minor leaks, wear full PVC clothing, including boots, gloves and face shield. For major leaks, wear protective liquid and vapour-proof PVC clothing and self-contained breathing apparatus); and
- isolate the source of the leakage.

With small leakages or spills of liquid hydrogen fluoride:

- use water only when it can be applied at a rate very much higher than the hydrogen fluoride leakage rate so that it will very rapidly dilute the hydrogen fluoride and suppress most of the vapour released - dilution of the liquid by a factor of at least ten is desirable; and
- water should be directed from a point upwind of the leakage and the downwind area should be cleared of people before action is taken.

With large leakages or spills of liquid hydrogen fluoride:

- Water should not be applied, but the spillage should be contained as far as possible. If retention walls have not been installed in the plant operating area, temporary bunds with sand or earth may be improvised. The spillage should be run off at a controlled rate for dilution as above.
- A large amount of fume will be given off from the pool of hydrogen fluoride. This fume should be suppressed as far as possible using 'fog nozzles' downwind of the pool.

In all cases, the dilute aqueous hydrogen fluoride should be neutralised using the most readily available source of alkali - the use of ground limestone is recommended since the reaction rate is likely to be limited and the fluoride is retained as insoluble calcium fluoride.

## Fire

Although hydrogen fluoride is non-flammable, its action on metal containers and metal piping can result in the formation of hydrogen, thus creating a fire and explosion hazard. Potential sources of ignition should be excluded from areas around such equipment.

Hydrofluoric acid cannot catch fire. When heated, however, hydrofluoric acid emits highly corrosive fumes of fluorides. Fire fighting personnel should therefore wear self-contained breathing apparatus. If hydrofluoric acid is exposed to fire, and there is no spillage, proceed as follows:

- move people upwind from the area and notify the fire brigade and police of the location, type and quantity of material;
- if available, spray water on the tanker or containers to keep them cool; and
- put out the fire with dry powder, carbon dioxide, vapourising liquid or foam extinguisher or water delivered as a fine spray, if available.

If hydrofluoric acid is exposed to fire and there is spillage, treat the spillage first.

# Further Reading

American Conference of Governmental Industrial Hygienists, *Documentation of the Threshold Limit Values and Biological Exposure Indices,* 5th Edition, American Conference of Governmental Industrial Hygienists, Cincinnatti, 1986.

Bretherick, L., *Handbook of Reactive Chemical Hazards*, 2nd Edition, Butterworths, London, 1979.

Clayton, G. and Clayton, F., *Patty's Industrial Hygiene and Toxicology*, 3rd Edition, John Wiley and Sons, New York, 1982.

Commonwealth of Australia, 'Australian Code for the Transport of Dangerous Goods by Road and Rail', *Commonwealth of Australia Gazette,* No. P15, 7 April 1987.

Environmental Protection Agency, *Chemical Emergency Preparedness Program Interim Guidance - Chemical Profiles,* Environmental Protection Agency, Washington, 1985.

Gosselin, R.E., Smith, R.P. and Hodge, H.C., *Clinical Toxicology of Commercial Products,* 5th Edition, Williams and Wilkins, London, 1984.

Standards Australia, AS 1336-1982 *Recommended Practices for Eye Protection in the Industrial Environment*, Sydney.

- AS 1337-1984 *Eye Protection of Industrial Applications*, Sydney.
- AS 1678.8.0.008 *Hydrofluoric Acid*, Sydney.
- AS 1715-1982 *Selection, Use and Maintenance of Respiratory Protective Devices*, Sydney.
- AS 1716-1984 *Respiratory Protective Devices*, Sydney.
- AS 2161-1978 *Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves)*, Sydney.
- AS 2508.8.013 *Hydrofluoric Acid*, Sydney.