

https://dspace.org/

A review of legislative and safety requirements for running the titanium-production pilot plant at Anglo Research

Yumba, Nomsa

2009-05-07T12:08:51Z
http://hdl.handle.net/10539/6932

Downloaded from a DSpace repository. https://dspace.org/

A REVIEW OF LEGISLATIVE AND SAFETY REQUIREMENTS FOR RUNNING THE TITANIUM- PRODUCTION PILOT PLANT AT ANGLO RESEARCH

Nomsa Yumba

A research report submitted to the Faculty of Engineering and Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Masters of Science in Engineering.

Johannesburg, 2007

DECLARATION

I declare that this research report is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University

_____

_____Day of 2007

Abstract

Anglo Research is due to commission a novel pilot plant for the manufacturing of titanium metal from ilmenite ore. The process requires the use of hydrofluoric acid, a very toxic chemical, in large volumes. A health and environmental study and legislative requirements of the process were thus required before commencing with the plant design.

Metallurgical processes have resulted in some degree of environmental impact, from water, air and soil pollution. A prominent example is acid mine drainage, which pollutes ground water. It is therefore important to ensure that proper steps are taken in minimising or mitigating negative environmental effects when developing new process routes.

Hydrofluoric acid (HF) is classified as extremely toxic. This acid is very aggressive physiologically because of the fluoride ion which penetrates the skin and robs the bone tissue of calcium. Because of the hazardous nature of HF, the following legislations were reviewed:

- Hazardous Substances Act 15 of 1973
- Occupational Health & Safety Act of 1993
- National Road Traffic Act 93 of 1996: Chapter VIII
- National Environmental Management Act 107 of 1998
- Environmental Conservation Act 73 of 1989

HF has been used in many other industrial applications including manufacturing of fluorocarbons and other chemicals, aluminium manufacturing, petroleum alkylation and uranium purification.

Steps should be taken to minimise exposure to hydrofluoric acid in areas where there is a likelihood of worker exposure. Control measures include, but are not limited to, elimination/substitution and process modification, isolation, engineering controls, administrative controls, and use of personal protective equipment and hazard communication. HF is corrosive to most metals and materials of construction suitable for HF include fluoropolymers and other metal alloys such as nickel based alloy 400.

Every design aspect of the plant must be done in a way that minimises the environmental and worker exposure to HF. Once safety of the plant design has been extensively reviewed, the pilot plant can then be built. The success of this campaign will be based not only on the achievement of process and product specification, but also on whether it was run without any incidents.

Dedication

For P.K., O.T. and MO

Acknowledgements

I would like to acknowledge:

- My supervisor Prof Marjanovic,
- Eddy Valkenburgh and Alfred Grunnenburg from Necsa for their technical advise
- Anglo Research: Department of Extractive Metallurgy

Table of Contents

1 INTRODUCTION 10

1.1 Background 10
1.2 Objectives 12
1.3 Report outline 12

2 Environmental impact of metallurgical processes 14

3 Nature of HF 17

3.1 Physical and chemical characteristics of HF 17
3.2 Exposure to HF 18
3.2.1 Dermal contact 18
3.2.2 Eye contact 19
3.2.3 Inhalation 19
3.2.4 Ingestion 21
3.2.5 Medical treatment for HF 21

4 Use of HF 25

4.1 Use of HF in Fluorocarbons 25
4.2 HF in aluminium manufacturing 25
4.3 HF in chemical manufacturing 25
4.4 Petroleum alkylation 26
4.5 Metal treatment 26
4.6 Uranium purification 26
4.7 Other HF applications 27
4.8 Use of HF in the mining industry 27
4.9 Environmental impact of industrial use of HF 27
4.9.1 HF release to the environment 28

5 Regulations governing the use of HF 29

5.1 Hazardous substances Act 29
5.2 Occupational Health and Safety Act (OHSA) 30
5.2.1 Major hazard installation requirements 30
5.2.2 Hazardous chemical substances (HCS) regulations 31
5.3 National Road Traffic Act (NRTA) 33
5.4 Environmental management 35
5.5 Environmental conservation 36
5.6 Transportation and offloading 36

6 Handling 38

6.1 Control measures 38
6.1.1 Elimination 39
6.1.2 Isolation 39
6.1.3 Engineering controls 40
6.1.4 Administrative controls 41
6.1.5 Hazard communication 45

7 Required PPE 48

7.1 Emergency response PPE (level 1) 48
7.2 Increased Risk PPE (level 2) 51

7.3 Routine operational PPE (level 3) 52
7.4 Standard PPE (level 4) 53
7.5 PPE CARE 54
7.6 PPE decontamination 55

8 Material of construction 57

8.1 Metallic alloys 57
8.2 Non metallic materials 61
8.3 Recommendations for storage vessels 62

9 Operating considerations 64

9.1 Sampling 64
9.2 Maintenance 66
9.3 Equipment decontamination 67

10 HF emergencies 68

10.1 First aid 68
10.2 Fire 68
10.3 Spillage handling 69
10.3.1 Small spills 69
10.3.2 Large spills 70
10.3.3 Disposal 72
10.3.4 Emergencies 72
10.3.5 Safety equipment 74

11 Conclusion 77

12 References 78

List of Figures

Figure 1: Examples of placarding for transporting of a single substance and for waste.....35
Figure 2: Front and side views of emergency response PPE.....50
Figure 3: Increased risk PPE.....52
Figure 4: Routine operational PPE.....53
Figure 5: Standard PPE.....54
Figure 6: Schematic diagram of plant layout to accommodate a PPE decontamination bay (Provided by Respirex PPE supplier).....56
Figure 7: A summary iso-corrosion chart for 0.51 mm/yr data in hydrofluoric acid (special metals).....58
Figure 8: HF corrosion data for carbon steel.....60
Figure 9: Condition of stainless steel before and after testing. Photograph sourced from Osborne et al., 2002.....61
Figure 10: Schematic of an online automatic sampler.....65
Figure 11: Flange type manual sampling point.....66
Figure 12: Alkaline materials for neutralisation of HF (Honeywell).....71
Figure 13: Emergency response system.....74

List of Tables

Table 1: Composition of ilmenite ore 11
Table 2: Health effects of respiratory exposure to HF gas 20
Table 3: Treatment for dermal burns 22
Table 4: Treatment for eye exposure 22
Table 5: Treatment for HF inhalation 23
Table 6: Treatment for HF ingestion 24
Table 7: Occupational guidelines for HF gas 32
Table 8: Approximate chemical composition of selected alloys for test work performed by Osborne et al, 2002 59

1 INTRODUCTION

Anglo Research (AR) was involved in the development of a process route for the production of titanium metal from ilmenite ore. Bench scale test work was performed initially to evaluate a process developed by Peruke. A final process flow, including mass balances and energy balances has been developed by AR and is to be tested in a pilot plant campaign.

Before the pilot campaign can be done however, an environmental study needs to be performed and legislative requirements of the process need to be assessed. This is resulting from the fact that hydrofluoric acid (HF), a very toxic chemical, will be used in the process and large volumes will be required. HF will be supplied at 20% concentration for use in the process.

1.1 Background

Titanium is widely distributed and occurs primarily in the minerals anatase, brookite, ilmenite, perovskite, rutile, titanite (sphene), as well as in many iron ores. Although difficult to find in high concentrations, rutile and ilmenite are the only minerals that have any economic importance (Krebs, 2006).

Titanium was discovered combined in a mineral in Cornwall, England in 1791 by amateur geologist William Gregor. He recognized the presence of a new element in ilmenite when he found black sand by a stream in the nearby parish of Manaccan and noticed the sand was attracted by a magnet (Krebs, 2006). The sand was analysed and the presence of two metal oxides was discovered; iron oxide (explaining the attraction to the magnet) and 45.25% of a white metallic oxide he could not identify (Barksdale, 1968). Ilmenite ore produces some difficulties in the recovery of the titanium due to the high content of the unwanted iron in this ore body. The typical composition of this ore is found in Table 1 (Barksdale, 1966).

Table 1: Composition of ilmenite ore

Element	Percentage composition (%)
Ti	28.00%
Fe (Total)	37.00%
Mn	0.60%
Si	1.20%
Al	0.30%
O	28.60%
Misc.	4.30%

As can be seen in Table 1, this ore has a high content of iron, which will have to be separated from the titanium in order to produce a high purity product which can be sold. As mentioned before, another most common ore body which contains titanium is rutile. The ore reserves of rutile are however more limited than those of ilmenite, therefore treatment processes need to be developed for ilmenite (Mackey, 1974).

The use of HF as a lixiviant for titanium production is not a new concept, however, there has never been an attempt to make a full or even pilot scale plant. This is resulting from the challenging chemistry of the downstream processes (Biswas et al, 1992). As stated by Biswas et al (1992), the process which they had attempted to recover titamium lacked an easy and efficient recovery method. Other lixiviants which have been attempted, both recently and in the past, are hydrochloric acid leaching (El-Hazek et al, 2007) and sulphuric acid leaching (Han et al., (1986) and Liang et al., (2005)).

Pyrometallurgical processing is also being practiced, such as the Kroll process (Habashi, (1997)), a complex and expensive batch process. In the Kroll process, the oxide is first converted to chloride through carbochlorination, whereby chlorine gas is passed over red-hot ilmenite in the presence of carbon to make $TiCl_4$. This is condensed and purified by fractional distillation and then reduced with 800 ℃ molten magnesium in an argon atmosphere (Anon, 2006).

The FFC Cambridge Process is an electrochemical method in which solid metal compounds, particularly oxides, are cathodically reduced to the respective metals or alloys in molten salts (Chen et al., 2000). This method has the potential of replacing the Kroll process as it is much simpler in operation and uses less energy than the Kroll process. It also promises a great potential for cheap production of useful reactive metals such as titanium (Suzuki, 2005).

The background information proves that there has never been a lack of technologies for the production of titanium. The process developed by AR is also a new technology of which there is hope that it will be embraced by the industry. Success or failure of this campaign will dictate whether a demonstration plant and finally a full scale plant will be commissioned. There is also a possibility of building a new HF plant in South Africa, and should this plant trial be successful, it will greatly impact the capacity of the proposed HF plant (Anon, 2005).

1.2 Objectives

The objective of this report is to provide information regarding hydrofluoric acid to assist the design team and the operations manager of the Anglo Research titanium pilot plant. The aim of the study was to review relevant information which would assist the team to consider all options for the design and safe operability of this pilot plant before commencing with the design and later the commissioning of the pilot plant.

1.3 Report outline

Following this introductory chapter, the content of subsequent chapters is as follows:

Chapter 2: Environmental impact of metallurgical processed, including the use of HF is discussed.

Chapter 3: The nature of HF with regards to its chemical properties as well as the effects of exposure to people working with HF. Treatment for exposure is also included in the discussion. This will provide an explanation on why proper planning for the use of this chemical is important.

Chapter 3: The industrial applications of the acid are discussed in this chapter. The use of HF in other industries will prove that it is possible to use this chemical, and even ensure an incident free campaign by learning from other operations.

Chapter 4: The South African legislation will also be discussed regarding the use of HF as well as the required actions before the industrial use of the chemical or any hazardous installation.

Chapter 5: The handling of HF, including control measures which include engineering and administrative controls as well as hazard communication will be found in this chapter.

Chapter 6: Personal protective equipment necessary for HF use is discussed in this chapter. This includes the different levels of PPE based on the risk of exposure to the hazardous chemical.

Chapter 7: Materials which may be used for construction of equipment and pipelines for HF applications are reviewed in this chapter.

Chapter 8: A discussion of operability considerations which include sampling of process streams as well as equipment maintenance will be found in this chapter.

Chapter 9: The nature of HF requires proper emergency and first aid planning to ensure prompt response to emergencies, which is discussed in this chapter.

Chapter 10: Conclusions drawn from the conducted review can be found in this chapter.

2 ENVIRONMENTAL IMPACT OF METALLURGICAL PROCESSES

Metallurgical processes involve processing of natural resources, which may impact the environment at any stage of the life cycle of the process. Mining and metallurgical processes involve:

- Finding ore bodies through geological explorations.
- Extracting the ore from underground or open pit mining.
- Beneficiation of the desired metals through hydrometallurgical and pyrometallurgical processes in order to manufacture the required product.
- Transporting of the manufactured product.
- Use of the product.
- Recycling and disposing of minerals and metals products.

All these processes result in some degree of environmental impact, from water, air and soil pollution. Environmental laws were not very strict in the past as mining was the main economic driver. This led to environmental neglect on the part of mining companies, resulting in mining and metallurgical processes having negative connotations with regards to the impact they cause on the environment.

An example of the impact that processing of metals can cause on the environment is acid mine drainage. This process involves the oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}), which then reacts with sulfide-bearing minerals resulting in the formation of sulphuric acid. This acid dissolves metals such as lead, zinc, copper, arsenic, selenium, mercury, and cadmium, into ground and surface water. Acid mine drainage can poison ground and drinking water and destroy aquatic life and habitat. Commonly mined ore bodies that pose the risk of acid rock drainage include gold, silver, copper, coal, iron, zinc, and lead (Bureau of land management, 1999). There are numerous abandoned and non operating mining sites where acid mine drainage is still causing ground water pollution, even though attempts are made to combat this problem.

The degree in which mining has polluted the environment has led to environmental laws becoming more stringent, and therefore the use of toxic chemicals will be banned or where no replacements can be found, control will be even more stringent. The mining industry has however become more diligent, as a result of government intervention, in taking ownership

with regards to protecting the environment. Mitigation plans include performing life cycle analysis as one of the tools with which the mining industry hopes to prove that it has become a responsible citizen of the modern environmentally- conscious world (Monhemius, 2006).

In order to mitigate environmental impacts of processes in mining industries, it is important to have an environmental policy, which should include, but not be limited to, the following principles:

- All relevant environmental risks should be identified and prioritised;
- Environmental issues relating to potentially serious environmental impacts should be dealt with promptly;
- The best practicable environmental option; that is, the option that has most benefit, or causes the least damage to the environment, at a cost acceptable to society and affordable to the company must be adopted.

Control measures need to be put in place to ensure that processes which are being developed will have minimal impact on the environment. These measures include:

- Elimination/substitution and process modification;
- Isolation
- Engineering controls;
- Administrative controls; and
- Use of personal protective equipment.
- Hazard communication

As mentioned in section 1.1, there have been many attempts in developing new process for the production of titanium. These include both hydrometallurgical and pyrometallurgical routes. Hydrometallurgical processes involve the use of chemicals for the dissolution of the targeted metal from solid into solution. This process typically involves the use of large volumes of water, which if not contained in a closed loop in the process, could result in excessive use of water as well as pollution. Pyrometallurgical processes required high inputs of energy, which also have negative environmental impacts such as carbon emissions.

The process which is proposed by Anglo Research requires the use of HF, which is one of the most toxic chemical which can be used, both to people and the environment. The process also uses both hydrometallurgical and pyrometallurgical treatment. Other lixiviants which can be used in this process are sulphuric acid and hydrochloric acid, which also have detrimental effects if exposed to the environment.

Part of the reason why this option of processing was chosen was that it has allowed for regeneration of all the reagents in the system, with fresh reagents being added for topping up. The financial incentive of this process is that unlike other processes which produce titanium oxide (TiO_2) as the product, this process produces titanium metal, which can be sold directly to various titanium metal users such as the motor manufacturing industry

Although the South African government might agree on the use of HF in the proposed process, there is a possibility that environmentalist will protests this. An example of a similarly toxic chemical used in metallurgical processes is cyanide. Cyanide has been used in gold processing for over fifty years and now various states in the United States (SERC, 2004), as well as European countries have either banned the use of HF or made it very difficult for new operations to be commissioned in order to discourage the use of this chemical. It is possible that the use of HF will also be banned in the future as there are currently attempts to stop the use of this chemical in certain industries such as the petrochemical industry, and therefore its use is questionable.

3 NATURE OF HF

The nature of HF is discussed in this chapter. Discussions include the physical and chemical characteristics of HF, repercussions of exposure to this chemical as well as treatment actions to be taken in case of exposure.

3.1 Physical and chemical characteristics of HF

Hydrofluoric acid (HF), the inorganic acid of elemental fluorine, is a colourless gas or fuming liquid with a strong, irritating odour. It is produced from the reaction between calcium fluoride and sulphuric acid. When present in its purified form (>99%) it is referred to as anhydrous HFA, and as aqueous HFA in its more diluted forms (Kirkpatrick, 1995).

Hydrofluoric acid (HF) is classified as extremely toxic and is very aggressive physiologically because of the fluoride ion. When exposed to air, concentrated solutions and anhydrous hydrofluoric acid produce pungent fumes which are especially dangerous. Unless heated, dilute concentrations of less than 40% HF do not produce significant vapor concentrations (Honeywell, 2006).

Hydrogen fluoride is strongly corrosive in both gaseous and aqueous forms and causes severe and painful burns to the skin, eyes and mucous membranes and severe respiratory irritation. This acid is particularly dangerous because of its ability to penetrate tissue. This ability is attributed to the high electronegativity of the fluoride anion which holds on tightly to the hydrogen (H) cation. The bond with the H cation results in a weak acid that exists predominantly in the undissociated state compared to other acids (1000 times less dissociated vs. hydrochloric acid (HCl)). The undissociated state allows the HF molecule to penetrate skin and soft tissue by non-ionic diffusion. Once in the tissue the F anion is able to dissociate and cause liquefactive necrosis of soft tissue, bone erosion, as well as extensive electrolyte abnormalities by binding the cations Ca^{2+} and Mg^{2+}. Other acids cause damage via the free H cations resulting in coagulative necrosis and poor tissue penetration (Bertolini, 1992).

The ability to penetrate tissue enables HF to cause severe systemic toxicity from even small dermal exposures. Exposure to this compound should therefore be treated with extreme caution. The amount of toxicity depends, like every other toxin, on four factors:

- Concentration of the agent
- The route of exposure
- The length of exposure and
- The amount of surface area affected.

Two different hazard exposures exist, acute and chronic, depending on the duration of exposure. High concentration exposures over short periods are called acute exposures, while chronic exposures involve repeated or continuous exposures over long periods.

Chronic exposure to excessive quantities of gaseous or particulate fluoride (see Table 2) results in nausea, vomiting, loss of appetite and diarrhoea or constipation. Fluorosis, a syndrome characterized by weight loss, bone embrittlement, anemia, and general ill health (Anon, 2004) and other chronic effects may result from significant acute exposures. Systemic fluoride poisoning can cause hypocalcaemia, which may lead to cardiac arrythmias and death (Anon, 1989).

As already mentioned, exposure to HF can lead to fatalities, and therefore it is important for people working with this acid to understand the effects of exposure to the acid. The different routes of exposure are dermal contact, eye contact, inhalation and ingestion. Any person who comes into contact with the acid, via any route of entry, must seek medical attention immediately.

3.2 Exposure to HF

The different routes of exposure, being dermal contact, eye contact, inhalation and ingestion are discussed in the subsections to follow.

3.2.1 Dermal contact

HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, the duration of contact with the acid and the size of the burn. The acid, however, differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers by binding to the calcium in the body (Anon a, 2003).

Tissue destruction is accompanied by severe pain variously described as "unbearable", "excruciating" or "intense". This is probably due to immobilisation of calcium resulting in an excess of potassium ions and subsequent potassium nerve stimulation (Anon b, 2003). Pain is usually followed by localized 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. Unlike other acids which are rapidly neutralized, this process may continue for days if left untreated. Death of skin, tissues, blood vessels and even bone may follow.

In contrast to the immediate effects of concentrated HF, the effects of contact with more dilute hydrofluoric acid or its vapours may be delayed, and this is one of the problems with the recognition of some HF burns. Skin contact with acid concentrations in the 20% to 50% range may not produce clinical signs or symptoms for one to eight hours. With concentrations less than 20%, the latent period may be up to twenty-four hours before any pain is felt. HF concentrations as low as 2% may cause symptoms if the skin contact time is long enough (Hatzifotis et al., 2004). It is therefore important to apply treatment if any contact with the acid is suspected, regardless of how minor it may seem.

3.2.2 Eye contact

Eye exposure is due to exposure to vapors or to splash injury. While eye exposure itself is not likely to cause systemic problems, a possibility of inhalation or face burn will be there. The type of exposure and concentration will dictate the time it takes for patients to experience pain.

Exposure to hydrogen fluoride causes a burning sensation, redness and secretion. Splashes of dilute acid rapidly produce conjunctivitis, corneal opacification, corneal sloughing, keratitis and necrosis of the anterior chamber (Anon b, 2003). If not properly treated, the burns may result in scarring and blindness. The prognosis is not good if first aid treatment is delayed or inadequate.

3.2.3 Inhalation

HF is a volatile liquid with a boiling point of only 19.5 ^{0}C at 1 atmosphere for anhydrous HF. The more concentrated the aqueous HF, the lower the boiling point and the higher the vapour pressure (WGSTS, 1997). The volatility of HF makes it a high risk compound for inhalation

injury. Severity can range from mild airway irritation to severe burning and dyspnea. With inhalation of HF concentrations > 50% there is a significant risk that pulmonary edema/ARDS and pulmonary hemorrhage will develop (Dunser et al., 2004).

For burns involving face and neck, burns covering more than 5% body surface area and burns with HF concentration of more than 50%, inhalation must be assumed even if the patient is initially only mildly symptomatic. Soaked clothing is also a strong predictor of inhalation injury (Sheridan et al., 1995). All inhalation injury patients are at high risk for systemic complications. Patients with inhalation exposures should therefore be observed for signs of systemic absorption and fluoride toxicity.

Exposure to hydrofluoric acid fumes can cause 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 edema (fluid on the lungs) which may not become apparent until 12-24 hours after (Dunser et al., 2004). Table 2 summarises the health effects of respiratory exposure to hydrogen fluoride gas for different exposure limits (IVHHN, year unspecified).

Table 2: Health effects of respiratory exposure to HF gas

Exposure limits (ppm)	Health effects
< 3	Irritation of nose and eyes
> 3	Pronounced eye and respiratory symptoms, including burning throat and cough after 1 hour
30	Respiratory symptoms worsen. Can be tolerated for several minutes
50 – 250	Dangerous even for brief exposure
120	Maximum concentration in air that can be tolerated for 1 minute. Smarting of the skin, conjunctivitis and irritation of the respiratory tract occur

3.2.4 Ingestion

Ingestion of the acid should be given immediate medical attention as it is a life threatening emergency as the acid could corrode the internal organs. The patient is likely to have acute nausea, vomiting and abdominal pain. Besides the systemic risks the patient is also at risk for viscous perforation and hemorrhagic gastritis. It is estimated that the minimal toxic dose from ingestion is 5 - 10 mg HF/kg body mass and the minimal lethal dose is 15 - 30 mg HF/kg body mass (Bertolini, 1992).

It is believed that several glasses of milk or several ounces of milk of magnesia, or any other calcium containing fluids or other antacid tablets can be given to a conscious person. The calcium content is believed to be able to bind with the fluoride ion and act as an antidote. This however has not been supported in the literature (Heard and Delgado, 2003).

3.2.5 Medical treatment for HF

It is important to react promptly to any case of HF exposure to minimize local tissue injury and destruction while at the same time monitoring for and treating any systemic effects of the exposure. The following represent types of treatment that are most consistently employed based on the recent literature for the various types of exposure. There have been differences of opinion with regards to the type of treatment to administer to casualties exposed to HF. This was found particularly in Burd (2004), where he discussed points of disagreement regarding HF treatment specified in a paper written by Hatzifotis et al (2004).

Due to this treatment dispute, treatment guidelines provided by Honeywell, the largest HF producer in the world, are included in this review. A summary on the treatment methods can be found in Table 3, Table 4, Table 5 and Table 6. The information in the tables was extracted from Honeywell, 2006. Treatment methods include both first aid and medical treatment information. The concentration of the acid also plays a role in the extent of harm caused by exposure. The information in the tables also includes different treatments depending on whether the casualty was exposed to concentrated or dilute acid. In some cases, such as eye exposure and ingestion, damage caused by exposure to HF is irrespective of the concentration, and therefore the same treatment is administered for both concentrated and dilute HF.

Table 3: Treatment for dermal burns

	Concentrated acid	**Dilute acid**
First aid	Wash with water, then apply 0.13% iced soaks of Benzalkonium Chloride (BC) OR Calcium Gluconate 2.5% Gel	Wash with water, then apply 0.13% iced soaks of Benzalkonium Chloride (BC) OR Calcium Gluconate 2.5% Gel
Medical treatment	Continue BC soaks OR Calcium Gluconate 2.5% - 5% Injection if soaks don't relieve pain, especially for deep/large burns AND Observe for/Treat systemic effects (especially if > 160 cm^2)	Continue BC soaks OR Calcium Gluconate 2.5% Gel OR Calcium Gluconate 2.5% - 5% Injection Systemic effects unlikely

Table 4: Treatment for eye exposure

	All HF concentrations
First aid	Water or saline wash
Medical treatment	Topical tetracaine hydrochloride THEN 1% calcium gluconate irrigation (dilution can be made with saline solution) AND Consult an ophthalmologist

Table 5: Treatment for HF inhalation

	Concentrated acid	**Dilute acid**
First aid	Oxygen AND 2.5% Calcium gluconate by nebulizer	Oxygen AND 2.5% Calcium Gluconate by nebulizer
Medical treatment	Continue Calcium Gluconate by nebulizer Observe and treat for respiratory distress, bronchoconstriction, pulmonary edema and systemic effects by monitoring cardiac monitoring, monitoring serum calcium, fluoride, magnesium, and electrolytes.	Continue calcium gluconate by nebulizer Observe Serious effects unlikely. Inhalation of HF fumes from dilute acids is uncommon

In addition to the usual medical history, the following information should be given to the medical practitioner following any of the routes of exposure:

- Concentration of HF,
- Date and time of exposure,
- Duration of exposure,
- How exposure occurred,
- Body parts exposed/affected,
- First aid measures instituted (what, when, how long).

This information is important because injuries due to dilute HF solutions or low concentrations of vapors may result in delays in clinical presentation up to 24 hours following exposure.

Table 6: Treatment for HF ingestion

	All HF concentrations
First aid	DO NOT INDUCE VOMITING Milk or Water THEN Milk of Magnesia
Medical treatment	Lavage with Calcium Chloride or Calcium Gluconate AND Treat systemic effects by monitoring cardiac monitoring, monitoring serum calcium, fluoride, magnesium, and electrolytes.

Rapid removal of the acid and an immediate visit to the hospital are important steps the patient can take to help minimize injury. For physicians, toxicologists, nurses and other health care personnel, early aggressive treatment of local tissue damage and appropriate vigilance for systemic symptoms are the keys to reducing morbidity and mortality.

4 USE OF HF

Although the use of hydrofluoric acid in the mining industry is not very extensive, there are some applications in the metal's industry as well as other industrial sectors which are discussed in this chapter.

4.1 Use of HF in Fluorocarbons

Hydrofluoric acid is an intermediary in the manufacture of fluorocarbons. Prior to the 1987 Montreal Protocol, chlorofluorocarbons (CFCs) were the dominant fluorinated hydrocarbon and are now replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as the dominant fluorocarbons (TURI, 2000).

Refrigerants such as R-134a and R-125, which are used in refrigeration and cooling applications, contain HF as an ingredient. Approximately 6 000 tons of refrigerants are currently imported into South Africa annually (Anon, 2005).

4.2 HF in aluminium manufacturing

Aluminium manufacturers use cryolite, manufactured from hydrofluoric acid, in the smelting of primary aluminium (Beck, 2001). In the African context, HF is used to manufacture aluminium trifluoride (ATF), used in the production of aluminium metal at the three aluminium smelters in South Africa and Mozambique, but ATF currently has to be imported (Anon, 2005)

4.3 HF in chemical manufacturing

The major fluorine-containing chemicals manufactured from hydrofluoric acid are inorganic fluorides, fluoborate salts, fluoboric acid, and fluoborates (Sievert, 2002). HF is also used in the manufacturing of fluoropolymers. An example of this is the Teflon coating and other fluoropolymer resins manufactured by DuPont (DuPont, 2006)

4.4 Petroleum alkylation

Hydrofluoric acid is a catalyst in petroleum alkylation catalysis, a process for producing high-octane components for use in motor fuels (Anon, 1999). There has however been a push to ban hydrofluoric acid in refineries (Drosjack, 2003). In a newspaper article, Drosjack (2003) stated that the U.S. Public Interest Research Group wants Congress to require refinery operators to stop using hydrofluoric acid in favor of alternative chemicals that would pose less risk if released by accident or during a terrorist attack. HF is currently still being used.

4.5 Metal treatment

Another primary use of hydrofluoric acid is etching. Etching prepares the surface for further processing in various ways, including increasing wettability, changing the appearance or texture of the finish and removing contaminants (Segal, 2000). The primary use for etching is for silicon in the manufacture of microelectronic circuits. The electronics industry uses high purity, 49% hydrofluoric acid solution to etch silicon (PEC, 2003).

The acid is also used in metal surface treatments, including pickling of stainless steel (ATSDR, 2006) and desmuting. Metal pickling is the process by which manufacturers remove surface oxides (scale) from stainless steel and other metals. A variety of acids can be used to accomplish this task, including nitric and sulfuric acids. Desmuting is necessary to remove the gray-to-black residual film deposited on the surface during cleaning and etching processes. Hydrofluoric acid is used for desmuting high-silicon aluminium alloys and aluminium die castings (Strachan, 1999).

4.6 Uranium purification

HF is used in the production and purification of radioactive chemicals. In the uranium context, HF is used in the conversion process for the enrichment of uranium, where Uranium manufacturers use hydrofluoric acid to produce uranium hexafluoride (UF_4), separating U-235 from other uranium isotopes (Settle, 2005). Low-enriched uranium (LEU) is used in nuclear reactors for the generation of electricity worldwide. It could also be used as fuel for the proposed nuclear pebble-bed modular reactor in South Africa (Anon, 2005).

4.7 Other HF applications

Other applications for HF include:

- Calibration of environmental emission monitors and trace impurity analyzers. Cement and glass industries are more particularly concerned by the analysis of HF in their releases (TURI, 2000)
- Dry cleaning as rust removal agent or stain remover, meat packing industry and stonework surfaces (OSHD, 2004)

4.8 Use of HF in the mining industry

The use of HF in the mining industry has been and is still in under investigation for various ore bodies. HF has been used as a modifier in the separation of quartz from feldspar (a class of aluminium-containing silicates). Other modifiers are however being tested because of the growing awareness of environmental and health problems associated with HF (Shehu and Spaziani, 1999).

Work has also been done in the past to extract titanium from ilmenite using HF. The challenge with the work however was that there was no easy method of recovering the metal, resulting in a lack of motivation to continue with this process. (Biswas et al., 1992).

Other leaching work done in the mining industry which involves the use of HF is the production of ultra clean coal. The work was performed on an Australian black coal which was isolated using a low-temperature ashing (LTA) procedure (Steel et al., 2001). Leach work has also been done in the recovery of Nb, Ta, Fe and Mn from ferrocolumbite with hydrofluoric acid solutions (Rodriguez et al, 2007). Although various applications of HF as lixiviant in leaching processes have been investigated, there have been no pilot tests to confirm the laboratory scale work.

4.9 Environmental impact of industrial use of HF

There are a number of other industries which are linked to HF as incidental producers of HF. These industries do not use HF as part of their input streams but the processes involved result in the production of HF. A summary of these industries in Australia, together with the reported fluoride emission quantities can be seen in Table 7.

Table 7: Summary of incidental releases of fluorides for industries in Australia

Industry	Emission rate (kg total fluorides/ton product)
Phosphate manufacturing	1.9 kg fluorides per ton of superphosphate (NPI, 1999a)
Bricks, clay and ceramics industry	0.295 kg fluorides per ton of ceramic product (NPI, 1999b)
Fossil fuel combustion for power generation	0.08kg HF per ton black coal and 0.075kg HF per ton brown coal (NPI, 1999c)

4.9.1 HF release to the environment

HF is expected to be rapidly transformed into various fluoride compounds once released to the environment.

Aquatic release: HF will react differently depending on the type of water HF is released into. If water is at pH 7, HF will be ionized and will not degrade. The fluoride ions will be immobilised by the presence of calcium. In fresh water of pH 5 and above, the fluoride ion is dominant and decreases with decrease in pH. Undissociated HF_2^- and HF are dominant at low pH. The presence of phosphates, insoluble phosphate compounds form and are transferred to bottom sediments. Metal fluorides form when HF is released to sea water.

Dissolved fluorides are typically removed by precipitation with calcium carbonate which insoluble fluorides can be removed by sedimentation.

Atmospheric release: HF is released to the atmosphere as gaseous HF or as solids in the form of aerosols. Removal from the environment can be done by dry or wet deposition

Terrestrial release: HF can enter soil media through atmospheric deposition, and other fluoride containing compounds such as sludge and phosphate fertilisers. One detrimental effect of HF release is that it can reacts with silica in soil, forming silicate fluoride (SiF_4), which is potentially as dangerous as HF. Fluorides bind with other fluoride containing minerals, such as fluorspar, cryolite and apatite and clay minerals in soil and is therefore immobile. When soil has low clay content, leaching of these minerals is possible, resulting in the increase of aluminium and iron in ground water.

5 REGULATIONS GOVERNING THE USE OF HF

In order to ensure legal compliance with respect to the legislative requirements for building a pilot plant involving HF, a review of the South African Acts and regulations was conducted. A discussion of the important requirements based on the relevant acts can be found in the subsections to follow. The most applicable acts that where reviewed are the:

- Hazardous Substances Act 15 of 1973
- Occupational Health & Safety Act of 1993
- National Road Traffic Act 93 of 1996: Chapter VIII
- National Environmental Management Act 107 of 1998
- Environmental Conservation Act 73 of 1989

It should be noted that in addition to the acts, it is important to find out about the provincial or municipality by laws regarding the different aspects discussed.

5.1 Hazardous substances Act

According to the hazardous substances regulations, HF is classified as a Group II hazardous substance under the following description: *Hydrofluoric acid solution (fluoric acid, hydrogen fluoride solution) containing 60 per cent or more hydrogen fluoride* (Department of Health, 1992). Although the process uses dilute concentrations of HF, this will also be included in this classification due to its hazardous nature and the description of group I and II hazardous substances.

Under the declaration of grouped hazardous substances (chapter 2), a group I or II hazardous substance is any substance or mixture of substances which, in the course of customary or reasonable handling or use, including ingestion, might, by reason of its toxic, corrosive, irritant, strongly sensitizing or flammable nature or because it generates pressure through decomposition, heat or other means, cause injury, ill-health or death to human beings (Department of Health, 1992). The declaration of hydrofluoric acid as a hazardous substance led to the review of other government acts.

There are other chemicals which will be used in the pilot plant, such as ammonium chloride. However, HF is regarded as the most hazardous, and therefore all safety considerations will be based on HF.

5.2 Occupational Health and Safety Act (OHSA)

The OHSA provides guidelines for employers to ensure that the activities involved in their company processes do not harm their employees. Under the OHSA, the major regulations which are covered are the major hazard installation requirements and the hazardous chemical substances regulations.

5.2.1 Major hazard installation requirements

The pilot plant can be classified as a major hazard installation due to the hazardous nature and the volumes of HF which will be used in the pilot plant. According to section 43 of the Occupational Health and Safety Act under major hazard installation regulations, a written application needs to be submitted to the relevant local authority and the provincial director, for permission to erect the pilot plant within 12 months before the installation (Department of labour, 2001). The details to be included in the application are:

- Address of the installation
- Material safety data sheets of the chemicals resulting the classification of the pilot plant as a major hazard (in this case, HF)
- The volumes of HF to be stored on site for the duration of the campaign
- The risk assessment of the plant to be installed

The surrounding community also needs to be notified through advertising in at least one local newspaper. A risk assessment of the plant should also be conducted and submitted to the relevant local emergency services (Department of labour, 2001). Details to be included in the assessment are:

- A general process description of the plant
- A description of the major incidents associated with that type of installation and the consequences of such incidents, which shall include potential incidents

- An estimation of the probability of a major incident as well as it's potential effects;
- A copy of the site emergency plan;
- An estimation of the total result in the case of an explosion or fire and concentration effects in the case of toxic release
- the potential effect of a major incident on any other installation, members of the public and residential areas
- Meteorological tendencies;
- The suitability of existing emergency procedures for the risks identified
- Any requirements laid down in terms of the Environment Conservation Act, 1989 (Act No. 73 of 1989); and
- Any organizational measures that may be required.

The required site emergency plan needs to be readily available and should be explained to all employees. Regular testing of the plan should also be done and recorded. Any incidents that would lead to the use of the emergency procedure should be reported to the local authorities. Near misses should be recorded in a register for inspection purposes.
The law also stipulates that the HF supplier is required to be available on a 24 hour basis to provide advice in case of emergencies. Details of the regulations can be found in the OHS Act, 1993 (Department of labour, 2001).

5.2.2 Hazardous chemical substances (HCS) regulations

Employees are required by law to train personnel due to work with hazardous substances about the dangers of the proposed work with the help of a health and safety committee. The training should be done before commencement of the work and in intervals. The topics to be covered include:

- The contents and scope of the OHS regulations;
- The potential source of exposure and risks to health caused by exposure;
- The potential detrimental effect of exposure on reproductive ability;
- The measures to be taken by the employers to protect an employee against any risk from exposure;
- The precautions to be taken by an employee to protect himself or herself against the health risks associated with the exposure, including the wearing and use of protective clothing and respiratory protective equipment;

- The necessity, correct use, maintenance and potential of safety equipment, facilities and engineering control measures provided;
- The necessity of personal air sampling and medical surveillance;
- The importance of good housekeeping at the workplace and personal hygiene;
- The safe working procedures regarding the use, handling, storage and labeling of the HCS at the workplace; and
- Procedures to be followed in the event of spillages, leakages or any similar emergency situation which could take place by accident (department of labour, 1995).

An assessment regarding any means by which employees could be exposed to the HCS needs to be conducted. Monitoring systems need to be put in place for monitoring the HCS with the presence of an authorised inspector. Any environment where the exposure limit is exceeded or anticipated to be exceeded should be a respirator zone and all employees are required by law to wear the recommended respirators at all times. The recommended occupational exposure limit for HF gas is 3ppm (Department of labour, 1995). Occupational guidelines for HF gas for the EU and countries UK and US can be seen in Table 8. The different levels stipulated in the table are based on different laws and regulations of each country or institute.

Table 8: Occupational guidelines for HF gas

Country /Institution	**Level (ppm)**	**Level ($\mu g/m^{-3}$)**	**Averaging period**
European Union (EU) (European Union)	-	2500	8 hr Time Weighted Average (TWA)
	1	830	Short Term Exposure Limit (STEL)
United Kingdom (UK) (HSE, 2002)	2	2500	15 min
	1.8	1500	8 hr TWA
Unites states of America (US) (NIOSH (1995), OHSA)	6	5000	15 min ceiling
	3	2500	8 hr TWA
	3	2500	10 hr TWA

Techniques for monitoring the employees for any symptoms of exposure need to be available at the onsite clinic. Evaluations of workers to be exposed to the HCS needs to be done before or within 14 days of the commencement of the work. Any people classified unfit to work should not be permitted to work. Records of monitoring of exposure limits and medical surveillance records need to be updated regularly.

5.3 National Road Traffic Act (NRTA)

Transportation of dangerous goods presents a risk, from loading, transportation and offloading of the substances. This has led to the formulation of a dangerous goods regulation in the NRTA. Chapter eight of the NRTA highlights the responsibilities of the HCS supplier, which includes an environmental impact assessment (EIA) of the route taken to transport the hazardous chemical and applying for transportation licence. According to DWAF, the transport requirements include:

- The packaging/containerisation of the hazardous substance
- Labelling of containers
- Vehicle requirements and licensing thereof
- Driver training, licensing and responsibilities
- Loading of the vehicle and securing of the load
- Placarding of the vehicle and transport documentation (department of transport, 2003)

The term “dangerous goods and substances” includes hazardous waste.
Inclusive to chapter VIII of the act, are the codes of practice from South African National Standards (SANS) which have guidelines regarding transportation of dangerous goods and incorporate the following SANS codes:

- 0228: Identification and classification of dangerous goods and substances – provides information pertaining to the substance.
- 0229: Packaging of dangerous goods for rail and transportation – provides information on the recommended packaging for goods as well as testing of those packages and correct labelling and marking.
- 0233: Intermediate bulk containers for dangerous substances – requirements for intermediate bulk containers and suitability of container and substance permitted for transportation.

- 0230: Inspection Requirements for road vehicles – statutory inspection requirements for vehicles transporting classified dangerous goods, including requirements by in-house and outside agencies.
- 0231: Operational Requirements for road vehicles – operational rules and procedures including responsibilities of the operator of the vehicle. Specifies drivers qualifications and duties.
- 0232-1: Emergency information System for Road Transportation – placarding requirements for vehicles.
- 0233–3: Emergency information System: Emergency action Codes – emergency response guides to be used in case of an incident (Department of transport, 2002a).

A decision regarding the frequency of acid deliveries will have to be made. The waste will be placed in designated containers and a waste removal company will have to be notified to collect once the containers become full. Although AR is not responsible for the transportation of the acid or waste, the company has the responsibility of knowing whether the supplier complies with the national road traffic act when delivering the acid. This includes ensuring that:

- The correct and visible danger warning signs are posted on the transporting vehicle
- A transport emergency card (TREMCARD) as well as a dangerous goods declaration accompanies the vehicle
- A route plan identifying the highways, main roads, etc which will be used for delivery
- A waste certificate in case of transporting hazardous waste (Department of transport, 2002b)

Some examples of the placards can be seen in Figure 1



Figure 1: Examples of placarding for transporting of a single substance and for waste

5.4 Environmental management

Chapter 7 of the National Environmental Management Act, 1998 stipulates the responsibilities of employers involved in activities which have or are most likely to negatively impact the environment. Potential impacts of the ongoing activities should be assessed. The employees also need to be properly briefed about the environmental dangers the products might cause, as well as the procedures to follow when working with such hazards to minimise the risks (DEAT, 1998).

Emphasis should be placed on putting measures in place to contain or prevent the movement of pollutants from the environment. A contingency plan needs to be put in place in case of accidental release to the environment.

Employers should ensure that working conditions are safe for employees and thorough training should be provided to ensure safety in the work place. Employees are entitled to refusal to work if there are unsafe working conditions.

5.5 Environmental conservation

The waste information regulations of 2004 states that the generator of hazardous waste exceeding 20 kg needs to apply to the relevant department in the province before the commencement of the waste generation (DEAT, 2003). The process mass balance needs to be consulted to calculate the amount of waste, both solid and liquid, which will be generated.

Apart from ensuring proper waste disposal, proper bunding of the acid as well as process fluids needs to be put in place to prevent HF from entering the drains and polluting public waters. HF is moderately to highly toxic to aquatic life and terrestrial plants, therefore proper steps have to be taken to prevent contamination of the environment.

Practical implementations of the legislation need to be put in place with regards to the operation of the pilot plant. The relevant considerations are discussed in the sections to follow.

5.6 Transportation and offloading

According to the HF Industry Practice Institute (HFIPI), concentrations of 60% HF or less can be transported and stored in intermediate bulk containers (IBC's). Depending on the volumes of HF which will be required, bulk storage facilities might be required to avoid frequent deliveries of the acid. This will reduce the risk of accidental release on the road when delivering, as well as minimizing excessive handling of the acid when transferring to the required venues.

The HFIPI also states that acids over 450L are no longer considered as intermediate bulk volumes, but should rather be stored in bulk storage facilities. The sections which will require HF should be placed within close proximity to minimise pipe lines required for the transfer of the acid.

Although HF needs to be heavily regulated due its nature, the South African government is also looking at the possibility of increasing HF production in the country as there is anticipation of increase in demand. A feasibility study to build a 30 000 t/y to 50 000 t/y hydrogen fluoride (HF) production facility began at the end of 2005, which was funded by members of a consortium consisting of government and private, local and international sponsors (Anon, 2005). South African Nuclear Energy Corporation plant (Necsa), which is the only HF supplier in South Africa, was built and sized for the South African refrigerant and nuclear-fuel market. As a result of this, Necsa was unable to compete globally because it could not take advantage of economies of scale. It is anticipated that about 60 percent of the plant's production will be used in South Africa's aluminium, stainless-steel, and petrochemical and future refrigeration industries, and the rest exported as high-value speciality and performance fluorochemicals. If the titanium pilot plant is successful, this will also increase the HF requirements as acid in the region of 720 l/day are required for a 7 kg/hr solids throughput.

6 HANDLING

Proper handling of the acid is crucial as accidental release could lead to contamination of waterways and severe burns for people who may come into contact with the acid. In order to ensure safe handling of the acid, the following points need to be considered:

- Control measures
- Engineering controls
- Personal protective equipment
- Storage and transport
- Labelling
- Health assessments
- Education and training

6.1 Control measures

Steps should be taken to minimise exposure to hydrofluoric acid as far as workable in areas where there is a likelihood of worker exposure. A thorough examination of work practices is essential, which should be done in the form of a work risk assessments. 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;
- Isolation
- Engineering controls;
- Administrative controls; and
- Use of personal protective equipment.
- Hazard communication

As can be seen in the list above, all the necessary controls should be put in place such that PPE will be the last resort as a control measure.

6.1.1 Elimination

Elimination is the removal of a chemical from a process and should be the first option considered when minimising risks to health. In situations where it is not feasible or practical to eliminate the use of a chemical, substitution should be considered. Substitution includes replacing with a less hazardous substance or the same substance in a less hazardous form. It is possible in some processes to eliminate or substitute HF with other chemicals as illustrated in the following points:

- An alternative method was devised for testing of cement in a laboratory;
- A different acid combination used on difficult-to-clean glassware in a laboratory;
- In Australia, production of “pearl” light globes by etching glass with HF/bifluorides has been replaced by an electrostatic powder coating process;
- An alternative 2-step chemical treatment used to remove matrix from industrial diamonds, prior to recycling;
- A formulation using alkali and hot water is being trialled for graffiti removal;
- Alkali solution for the cleaning of some shipping containers;
- Nitric-acid based alternative, which works more slowly, instead of a HF-based aluminium cleaner;
- Phosphoric acid to remove rust from boats;
- Surfactant-based formulation in automated cleaning of trucks, although this is likely to be less effective;
- Regular cleaning schedule of food-processing machine, to avoid build-up that would require HF to remove;
- Use of HF in cleaning reduced by restricting to certain types of vehicle; and
- Blast cleaning techniques are reported to have replaced chemical etching of glass in many cases. Carbon dioxide (dry ice) blasting technique has been reported as an alternative in the removal of graffiti. In general mechanical cleaning processes instead of chemical ones may be suitable for some metal cleaning operations e.g. Maintenance of equipment (NICNAS, 2001).

In the case of the pilot plant, the entire process is based on the use of HF and thus replacement would not be an option as it may involve sacrifices in product performance. Other control measures would thus have to be considered.

6.1.2 Isolation

Isolation is a control measure used to separate employees, as far as practicable, from the chemical hazard. This can be achieved by distance or enclosure. In many uses of HF it is not

practicable to separate it from workers. However, isolation may ensure that workers are not unnecessarily in the vicinity of HF. Examples of strategies used are:

- All parts of the process where the product stream may contain HF fenced off and access strictly controlled;
- Remote control operations at alkylation plants;
- Formulating area is roped off when the area is in use;
- Work area located away from busy sections in a laboratory. Similarly, a metal dip tank operation was isolated in one corner of a factory area, away from forklift paths and other processes to improve safety. Several formulators mix products containing HF in an area separate to the main plant;
- Fume cupboard pull-up screens provided a barrier in a laboratory;
- Separation of the formulation area from the packing area by barrier screens and,
- Barriers or markers used to restrict entry during use in public areas, during graffiti removal and anti-slip floor treatment (NICNAS, 2001).
- A polycarbonate screen with glove compartments is an example of isolation, which can be used in the pilot plant to separate the workers from the process, particularly when taking samples.

6.1.3 Engineering controls

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

The need for engineering controls differs from industry to industry because the uses, quantities and concentrations used for HF are so variable. Anhydrous (100%) HF is handled in closed systems in all alkylation plants and in surface treatment of plastics. Almost all users of aqueous HF were reported to use open or partially closed processes. Varied engineering controls were reported for anhydrous HF in alkylation, as part of the complex overall control systems used in the petroleum refining process (NICNAS, 2001). These measures include flushing provisions to remove all HF from piping, special sampling vessels, isolation equipment, some of which is controlled remotely, special weighing and pumping equipment, HF-detecting paint, spray water systems and visible and audible alarm systems.

Another important control system is the use of ventilation, which will be vital in the pilot plant due to process conditions. 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 qualified people. 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 effective in the control of health hazards as is the use of ventilated process enclosures or local exhaust ventilation. The general ventilation systems may however be useful to control minor emissions of contaminants of low toxicity. Attention should be given to fan selection and to the placement of air extractors and fresh air supply openings when designing a mechanical ventilation system where emissions occur. 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, such as 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 (NOHSC, 1989).

6.1.4 Administrative controls

Administrative controls involve the use of procedures which provide safety guidelines for the process involved. This includes safe working procedures which workers need to adhere to ensure safety in the work area. Safe work practices may aid in the control of risks from hazardous substances. For HF these may be quite varied, as it is handled in both anhydrous and aqueous forms, at concentrations ranging from 100% to < 1%, in both large and small quantities and is used in a wide range of industry sectors and applications.

In a study conducted by NICNAS, 2001, it was noted that some specific safe working practices adopted for HF were:

- Special warning signs or labels in work area or at entrance to area,

- Specifying that HF is in use. Some suppliers provide special labels;
- Use of bottles with internal lip in neck to avoid airlocks, so that liquid will pour out smoothly, rather than in bursts;
- Use of written procedures;
- Summaries of MSDS and/or procedures posted at workstation;
- Restricted access to area where HF is used, through signs or barriers;
- Area kept very clean;
- Only skilled workers such as qualified chemist or experienced employee allowed to handle HF;
- HF ordered from supplier just before use, avoiding storage at site;
- Deliveries of HF not accepted unless drums and pallet in good condition;
- Acid tanks covered when not in use;
- Presence of at least one other person when HF is being used. It has been recommended that workers should not work alone with HF of > 10% concentration;
- Scrupulous attention to washing down all equipment and surfaces that have been in contact with HF, in order to avoid future accidental contact with the material.
- Gravity feed systems used by several formulators for filling containers from a mixing tank, in order to avoid pumping the product;
- Unused HF returned to the supplier when use ceased; and,
- Good design and correct choice of packaging to assist users with safety.

Personal protective equipment

Personal protection of the individual should mainly be required as a supplement to other preventative actions. It should not be regarded as a substitute for other control measures and must only be used in conjunction with substitution and elimination measures. The selection of appropriate PPE is important, and involves individual fitting for the workers as well as worker training in their correct use and maintenance. PPE 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 HF. Details of the required PPE can be found in chapter 7. 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 and invasive operations.

Storage and transport

Areas where hydrogen fluoride in aqueous or gaseous forms is stored should be provided with efficient ventilation. HF vapour monitors, extraction fume hoods/air vents with scrubbing capabilities should also be available in the storage venue as there could be an accumulation of HF vapours if there is no ventilation. In enclosed storage areas, hydrofluoric acid vapour may cause serious corrosion of sprinkler systems.

The acid should be stored close to ground level, on corrosion resistant surfaces, and in well-marked areas so it cannot be confused with other acids like hydrochloric acid. Controlled access to the storage area should be available to ensure that no unauthorised people have access to the acid.

Precautions should be put in place to ensure that there are no external sources of fire, corrosive material, vehicles and any other material that can affect the facility. Should complete separation from the abovementioned materials be unavoidable, protective measures should be provided and maintained.

Secondary containment must be provided in case of accidental releases. Consideration should be given to possible arrangements to accomplish rapid removal of acid from the pilot plant area in case of extreme emergencies. Additional empty tanks should be available together with appropriate piping for rapid transfer of acid if necessary. Work areas should also be placed on top of corrosion resistant surfaces, with additional bunding to minimise the effect of any spillages.

The storage tanks and reactor vessels must be checked for leaks before transferal of HF into any of the respective containers. 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 South Africa national Standards (SANS) for the Transport of Dangerous Goods by Road and Rail.

Storage tank considerations

If Intermediary Bulk Containers (BC's) will be used for HF storage, the following points will have to be considered for the tank:

- IBC are not intended to be pressure vessels, therefore, venting is important to prevent the IBC from collapsing as liquid is removed for top loading IBC's.
- The tank vent piping cross sectional area should be at least twice that of the liquid inlet line(s).
- The vent line should be directed to a fume scrubbing system of adequate capacity to minimize back pressure being exerted on the plastic tank.
- The maximum pressure on the tank at any time should not exceed six inches of water.
- It is recommended that all liquid transfers from the tank be made by way of an eductor (extractor) (or dip) line through properly supported and flanged connections located on top of the tank.
- For connections that will be below the liquid level at the bottom or sides, flanged-type fittings rather than bulkhead fittings should be employed. For tanks equipped with all top mounted connections, additional spill protection may be provided by installing the plastic tank inside a secondary containment tank with a liquid level detection device located between the inner and outer tanks.
- The secondary containment tank should be employed in addition to other barrier requirements of the site. For transfer of liquid to and from the tank, it is recommended that a pump be utilized rather than differential air pressure.
- The tank must be equipped with appropriate liquid level detection devices. Visual inspections for indication of vertical stress cracks should be completed (Berg, 2005b).

The equipment selection for the operation of the plant should be such that minimal man handling will be required. The following considerations should be considered when choosing the equipment:

- Sealed equipment such as a self-priming siphon or pump when transferring hydrofluoric acid should be used. Some literature states that pumps without seals such as canned motor or magnetic drive pumps require no seal maintenance and are thus better suited. These are not applicable for the scale of the operation but can be used for large scale. If peristaltic pumps are used, it is important to chose the correct pipe diameter as failure to do so could lead to tearing of the tubing
- Tanks/containers of hydrofluoric acid and reactors must have fitted lids or caps
- Valves should always be installed with stems in an upright vertical or a horizontal position to minimize possible contact with seal leakage.

Utilities

There are a number of utilities that will be required in the pilot plant, depending on the control philosophy that will be implemented. The list of utilities is necessary for safe operation of the storage facility and the pilot plant:

- Electrical power
- HF fume scrubbing capability
- Service water
- Potable water, (for safety showers/eye wash)
- Drainage to a containment area or water treatment facility
- Plant compressed air
- Instrument air, for any automated systems
- Breathing air
- Nitrogen
- Steam if necessary
- Adequate lighting

Safety shower and eye wash facilities should be located close to the off loading area and within close proximity of the storage tanks and work area. An alarm should also be installed in the safety showers in order to notify staff of any accident that might have happened. Regular testing and maintenance is also necessary.

6.1.5 Hazard communication

There are various methods which can be used to communicate hazards associated with HF. Some of these methods are discussed in the following subsections.

Labeling

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 have a pictorial warning in addition to written information for easy detection.

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 HF 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. The primary safety considerations that need to be made for the purpose of the plant design include PPE, first aid and emergency procedure and decontamination areas. All procedures need to be thoroughly discussed with the workers before the operation of the plant can begin. A list of guidelines for safe working in the pilot plant must be provided for in a safe working practices procedure. The list must cover considerations regarding HF handling, with respect to storage, pumping and decontamination. Guidelines for PPE care, as well as safety considerations for people working with HF are also included.

The importance of the proper use of all safeguards against exposure to themselves and their fellow workers should be stressed. 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. The following information should be made available for all workers:

- Written operating procedures identifying plant policies on emergency response actions;
- Comprehensive employee and contractor training programs to promote consistently safe work-practices;
- Scheduled maintenance programs to ensure equipment reliability - includes equipment testing and inspection;
- Safety reviews prior to startup of the processes.

The operation of HF monitors also need to be explained to workers to assist them in knowing when HF gas is at an unsafe level

Case studies involving HF incidents can be used to make workers aware of safety involving HF with the aim of:

Explaining the physical, chemical and toxicological properties of HF;

Applying the principles of hazard identification, risk assessment and control to the case study; and,

Identifying the significant faults that led to the accident in the case study and emphasize the importance of the hierarchy of controls in preventing further accidents.

MSDS

Material Safety Data Sheets (MSDS) are the primary source of information for workers involved in the handling of chemical substances.

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. The pilot plant campaign will run for three months, therefore annual training will not be required, however, this should be borne in mind for the future. MSDS should be obtained from the hydrogen fluoride suppliers and made available to the workforce. All recommendations should be carefully followed. Relevant legislation should be explained and enforced (NOHSC, 1989).

7 REQUIRED PPE

The protective equipment that should be worn for protection against HF needs to be impervious. This includes gloves, boots, apron/protective suit, and a face shield with safety glasses. A respirator is also necessary to filter out HF fumes. The PPE should be neoprene or butyl rubber based. These materials are sufficiently HF resistant if cared for properly.

Different levels of protection are required depending on the prevailing situation. The same PPE will therefore not be worn for emergencies and normal operation. The subsections below highlight the level of protection depending on the activity involved.

A decision with regards to which workstations will be considered high risk zones needs to be made based on risk assessments that will be done for the plant. Although the HF will only be used in certain sections of the plant, there is always a possibility of HF traces and fumes carrying throughout the plant. However, with the appropriate safety installations such as the air vents and proper ventilation, high risk PPE can be limited to areas requiring HF. Such considerations will determine the level of protection required for each section of the plant. The amount of gas respiratory equipment required will have bearing on the design of the plant, including plant layout and the compressed air required for the protective suits.

Neoprene has been identified as being fairly resistant to HF as well as impervious and should thus be used for PPE. The recommended level of protection which is required may depend on the allocated sections which workers are restricted to in the plant. It should also be noted that if different PPE is allocated based on which section a worker is confined to, other workers not working in the high risk sections have a higher risk of exposure should an emergency occur.
The different levels of PPE as specified by Working Group Storage, Transport and Safety committee (WGSTS, 2001) are discussed it the subsequent sections

7.1 Emergency response PPE (level 1)

This PPE is mandatory for emergency cases and for areas which are identified to have a high probability to HF exposure. The PPE 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. The list below specifies the required PPE:

- Fully encompassing HF resistant/ gas proof suit (EN 943-2).
- Suitable gloves either built in or completely sealed at the wrists (EN 488)
- Self contained breathing apparatus (BA) Set (EN 132 : 1990 Annex A)
- Standard hard hat worn inside the suit (EN 397).
- HF resistant Wellington-type boot (EN 467: 1995) with steel toe and shank worn inside outer leg seal.

Two of these suits will be available in case of emergencies. Proper care should be applied to storage of this equipment. Pictures of level 1 PPE can be seen in Figure 2

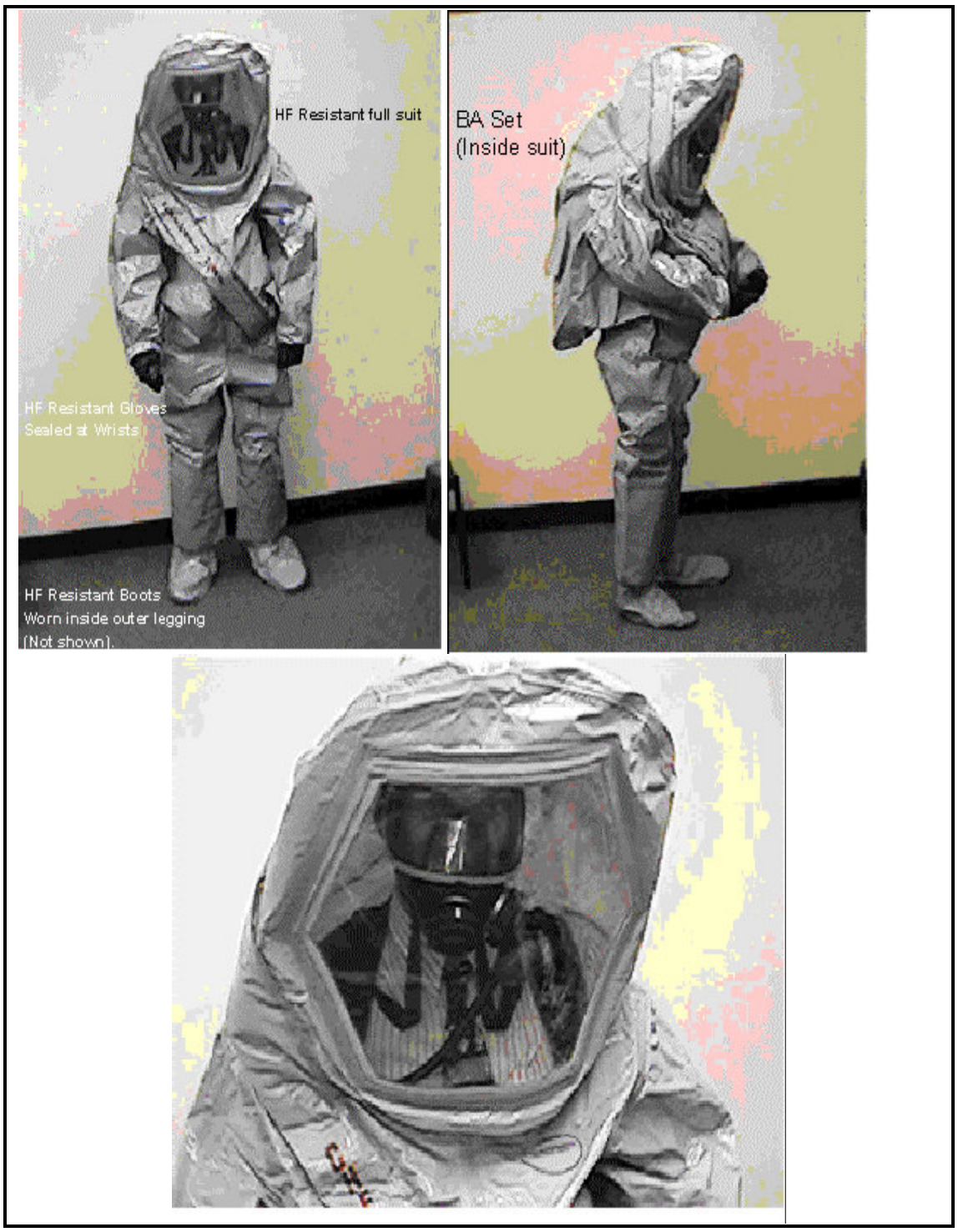


Figure 2: Front and side views of emergency response PPE

7.2 Increased Risk PPE (level 2)

This PPE 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. The design of this PPE is also such that HF cannot penetrate the suit. The required PPE is as follows:

- Air-fed HF resistant jacket with high waist trousers (EN 467:1995) sealed at safety boots and gloves with integral, air fed hood (Visor to EN 146; air fed hood to EN 270, or
- Fully encompassing HF resistant one piece suit (Visor to EN 146; prEN 943-2).
- Standard hard hat worn inside the jacket (EN 397).
- HF resistant gloves (inner and outer gloves) (EN 374-3).
- Air line (resistant to HF attack) providing suitable supply of breathing air (EN 132 : 1990 Annex A; EN 270 : 1994; EN 137)
- HF resistant Wellington-type boots (EN 467 : 1995) or over-boots with steel toe and shank. Boots permanently attached to a one-piece, gas tight suit may also be worn.

Figure 3 illustrates level 2 PPE.



Figure 3: Increased risk PPE

7.3 Routine operational PPE (level 3)

Level 3 personal protective equipment is used for routine operational tasks involving non-invasive interactions with process equipment. It is designed to give a greater degree of protection against incidental contact with process fluids for individuals working in the HF handling area. This PPE should be used for operations which involve interaction with the process but which are NOT expected to cause a release of process fluids. Level 3 PPE can be seen in Figure 4. The personal protective equipment is defined as:

- Standard hard hat (EN 397) with HF resistant nape and face shield. Shield MUST be in the down position when within the HF handling area.
- Chemical goggles (EN 166-345-B). MUST be worn under shield when within the plant boundaries.
- HF resistant gloves (EN 374-3).
- HF resistant jacket (EN 467 : 1995) with sleeves sealed at gloves.

- HF resistant high waist trousers (EN 467:1995) sealed at Wellington-type boots.
- HF resistant Wellington-type boots (EN 467 : 1995) or overboots with steel toe and shank.



Figure 4: Routine operational PPE

7.4 Standard PPE (level 4)

This PPE is only worn where the risk assessment specifies that there will be no contact with HF containing equipment (see Figure 5). This PPE can be worn by personnel working in sections which do not have HF as part of the feed streams.

- Standard hard hat (EN 397).
- Safety spectacles with side shields or chemical goggles (EN 166-345-B).
- HF resistant Wellington-type boots (EN 467: 1995) over-boots or safety shoes with steel toe.

- HF resistant gloves (EN 374-3).
- Escape air packs or suitable filtration systems should also be readily available to enable an escape in the unlikely event of a leak.
- The blue nitrile gloves should be worn underneath the HF resistant gloves (green gloves)



Figure 5: Standard PPE

7.5 PPE CARE

All personal protective equipment used on the plant should be assumed to be contaminated with HF and treated with appropriate care. Decontamination of used personal protective equipment should be done at designated venues. Initial decontamination should take place immediately on leaving the area, for example, by use of a shower. Care should also be exercised during the removal of all personal protective equipment.

In cases where the PPE needs to be shared, complete decontamination by neutralisation should be available for use by the operating teams. Personal hygiene must also be practiced. The following steps should be taken to test the integrity of the PPE prior to re-use within the HF facility:

- Gloves should be tested before each trip onto the plant by inflating with air and submerging in a water bath, suits may 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.
- 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.
- Decontamination water must be temporarily stored in the hazardous waste containers before being removed by Wastetech

7.6 PPE decontamination

PPE care requires a designated trained person to ensure proper care of PPE as it is expensive. Because some of the PPE will be shared to cost cutting measures, the following steps need to be followed in order to ensure proper PPE care:

- A decontamination tank with sodium bicarbonate solution at pH 9 should be used for initial neutralization of PPE exposed to HF
- From the first tank, rinsing is done in the second tank with water
- The PPE is then left to dry for the next shift
- A schematic diagramme of the proposed plant layout to accommodate PPE decontamination can be seen in Figure 6.

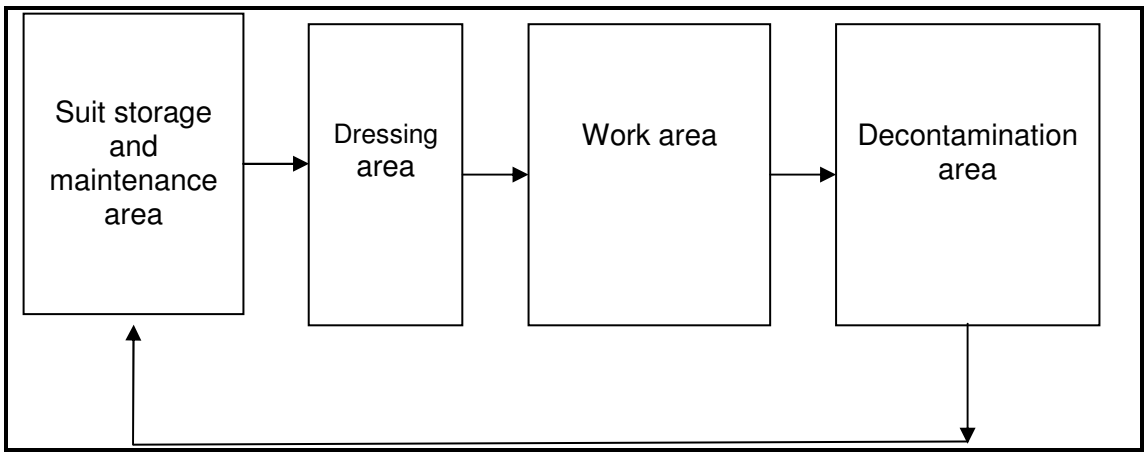


Figure 6: Schematic diagram of plant layout to accommodate a PPE decontamination bay (Provided by Respirex PPE supplier)

8 MATERIAL OF CONSTRUCTION

HF attacks many different materials, therefore choosing of correct material of construction for HF is a challenging but important task. Most materials are not resistant to HF. They are either corroded by the acid, or in terms of plastics, the material strength weakens when exposed to HF. As a result of this, the best material are those that either have low corrosion rates, or low breakthrough times. This chapter describes the different material compatibility with HF.

Reactions with HF, particularly for the pilot plant chemistry, are exothermic, resulting in temperatures exceeding 90^{o}C. Materials used for this section therefore need to be compatible to HF at high temperatures.

8.1 Metallic alloys

Metal alloys are generally not recommended for HF use as they may exhibit high corrosion rates and environmental cracking. There are however some alloys such as nickel based alloy 400 which has a low corrosion rate (<10 mm/yr) for a wide range of concentrations. The temperature range is however not sufficiently wide for this particular work (up to 60^{0}C) and the alloy may be subject to stress corrosion cracking (SCC). It was reported that SCC can occur in the vapour space when a surface is exposed to moist HF contaminated with oxygen (Howells et al., 2005). This low corrosion rate is applicable in air free liquid under 60℃. Nickel based Alloy 600 is reported to be resistant to dilute aqueous HF at ambient temperatures. It has also been used in valves and other equipment in place of Alloy 400 to avoid possible SCC. Figure 7 shows an iso-corrosion chart for 0.51mm/yr data in hydrofluoric acid for various nickel alloys.

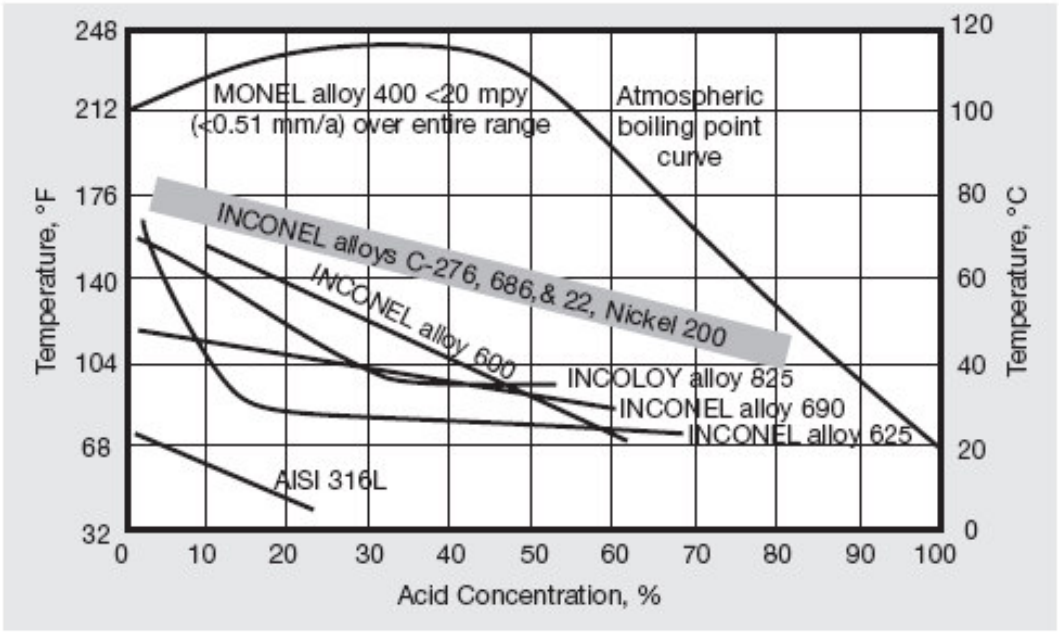


Figure 7: A summary iso-corrosion chart for 0.51 mm/yr data in hydrofluoric acid (special metals).

Precious metals including gold, silver and platinum are resistant to various concentrations of aqueous HF even up to boiling point. It would however not be feasible to use precious metals as materials of construction. Contrary to this, test work that was performed by Osborne et al., 2002 showed that gold-plated alloy 400 experienced one of the highest corrosion rates, when dipped in a 33% HF solution, for the alloys they were testing. The alloys which were tested together with their composition can be found in Table 9.

Table 9: Approximate chemical composition of selected alloys for test work performed by Osborne et al, 2002

Alloy	**Composition (wt %)**
Monel 400	67 Ni–31.5 Cu–1.2 Fe
Inconel 600	76 Ni–15.5 Cr–8 Fe
Hastelloy C - 276	57 Ni–16 Cr–16 Mo–4 W
Stainless steel 316	12 Ni–17 Cr–2.5 Mo–1-2 Mn–65 Fe

Source: R. B. Rebak, J. R. Dillman, P. Crook, and C. V. V. Shawber, "Corrosion Behavior of Nickel Alloys in Wet Hydrofluoric Acid," *Mater. Corros.* **52**, 289-297 (2001).

The gold-plated coupons had an average corrosion rate of 23 mm/yr over the first 7 days, and one coupon had lost most of its plating by day 4. It was claimed that Alloy C-276 outperformed all other alloys, with an average corrosion rate of 5 mm/yr, and appeared intact and virtually unaffected by the testing (Osborne et al., 2002). The presence of air has however been claimed to cause fairly high corrosion rates in hot aqueous acid for alloy C-276.

Carbon steel can be used for HF concentrations higher that 70% HF at temperatures below 38^0C, exhibiting a corrosion rate of 2 – 30 mm/yr. Carbon steel has an unusual characteristic that corrosion increases rapidly below 70% HF achieving a maximum at about 30%. Below 30%, the corrosion rate declines but is still quite aggressive even at very low concentrations. Figure 8 shows corrosion rates for carbon steel in HF at 21 – 38^0C (Aiken, 2001).

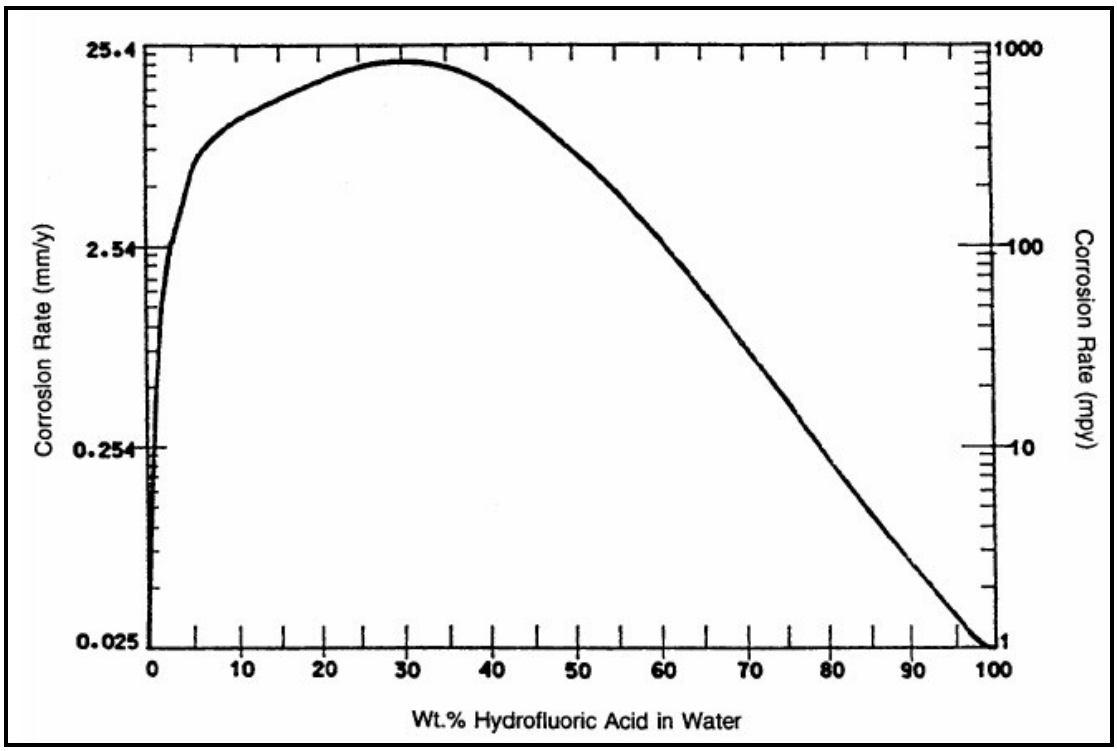


Figure 8: HF corrosion data for carbon steel

In general the 300 series stainless steels are not useful for aqueous HF because they exhibit much higher corrosion rates than carbon steel. Type 304 has poor resistance to any significant concentration while type 316 has some resistance to dilute (maximum of 10%) aqueous HF at ambient temperatures. Type 316 may be subject to pitting and stress cracking; therefore, it is not recommended (Howells et al., 2005). In corrosion tests performed by Osborne et al, 2002 in Oak Ridge laboratory, in 33% HF showed that SS-316 coupons showed the highest corrosion rate for the tested alloys. Stainless steel was found to settle out at approximately 550 mm/yr by the fourth week of testing. Over the course of the test, these coupons lost an average of 60% of their weight, leaving them with very little mass below the level of the liquid. A photograph of the before and after picture on the sample can be seen in Figure 9



Figure 9: Condition of stainless steel before and after testing. Photograph sourced from Osborne et al., 2002.

8.2 Non metallic materials

Watson-Marlow-Bredel has three different materials compatible to HF that are used for flexible tubing. These are marprene and neoprene which can be used for cold HF and flourel which can be used for hot solutions only up to 80^0C (WMB, 2007). The disadvantage with flourel however, is that it has been reported to have a short life of about 250hrs from practical experience.

High density polyethylene, polypropylene and PVC materials are also fairly resistant to weak hydrofluoric acid solutions up to 50% HF concentrations. These can thus be used for storage and for reactor vessels but normal temperature limitations must be followed. It has been reported that PVC deteriorates at a faster rate than the other plastics, therefore, use of this material should be avoided (Grunenburg, 2007).

Aqueous HF is resisted by certain fluoroplastics including PTFE (polytetrafluoro-ethylene), PFA (perfluorinated alkoxy tetrafluoroethylene), FEP (tetrafluoroethylene hexafluoro-propylene copolymer), CTFE (chlorotrifluoro-ethylene), ECTFE (ethylene chlorotrifluoro-ethylene copolymer), ETFE (ethylene tetrafluoroethylene) and PVDF (polyvinylidene fluoride).

Fluoropolymers can be used as loose or bonded liners in vessels and piping systems. Loose liners can be used in any concentration of aqueous HF at temperatures up to 150℃ in some services (Howells et al, 2005). Loose liners require vent holes in the pipe and vessel walls to prevent permeated hydrogen fluoride gas from creating pressure against the vessel or pipe which might collapse the liner. Structural damage to the liner sheet can occur due to permeating HF and temperature/pressure cycles. Fluoropolymers can also be used as coatings e.g. teflon/halar coatings and are adequately resistant to HF and other chemicals. Although these coatings are HF resistant, it is important to ensure that they are applied properly as pinholes could provide pathways for penetration of acids.

Graphite can also be used for HF service up to 80%, at least to atmospheric boiling point, where it is impregnated with fluoroplastic and no additional resin. Graphite impregnated with phenolic resin is useful for HF service up to 60%, at least to its atmospheric boiling point (Howells et al, 2005).

8.3 Recommendations for storage vessels

Storage of the acid is inevitable in most cases where this acid is used in processes. It is therefore important to ensure that proper design parameters are adhered to when designing these vessels. Howells et al., 2006 outlines certain design considerations for this purpose.

- **Shell** - ASME SA516-55 through 70 (Inclusion shape controlled).
- **Heads** - ASME SA-516 grade 70 (Inclusion shape controlled) hot formed heads are preferred. If heads are cold formed, they must be stress relieved. If heads are spun, center hole plug weld must be inspected by 100% radiography.
- **Nozzles** - SA-106 grade B, except bottom nozzles to be forged SA-105 long weld neck flange. For bottom nozzle, - long weld neck (5/8" wall thickness for the typical 2" size) is recommended for all bottom nozzles to provide sufficient corrosion allowance. Thin nozzles will corrode and leak before the corrosion allowance of the vessel is utilized.
- **Corrosion Allowance** - < 40 mm/yr is recommended, bearing in mind the material thickness.
- **Radiography** - Fully radiograph all butt welds.
- **Heat Treatment** - Stress relief at 621℃ minimum is recommended.
- Structural Shapes and Plates - ASME SA-36

- **Paint** - A white heavy-duty corrosion resistant paint is recommended for exterior tanks to reduce temperature in direct sun light. This is especially important for rubber lined tanks.

The supplier will provide HF at a concentration of 20%, and therefore IBC's can be used to store the acid, provided the storage tank considerations highlighted in section 6.1.4 are adhered to.

9 OPERATING CONSIDERATIONS

Although the plant could be designed in a manner which minimises exposure to hazardous chemicals, failure to consider operability of the plant could lead to the same accidents which must be avoided. It is therefore important to look at the major factors which influence safe operation of the plant. These include sampling, maintenance and because of the nature of the process fluids, equipment decontamination.

9.1 Sampling

Due to the nature of the samples that will be taken in the plant, there should be minimal human interaction. A high frequency of sampling is expected considering that there will be a need to collect as much information as possible when running a pilot plant. Another point is that actions involving process intervention can lead to many spillages and process fluids exposure and therefore safety measures need to be put in place.

The pipe systems for areas of sampling should be such that the risk of spillages is minimised when drawing samples. A sampling procedure, with clear instructions for sampling, will be made available to workers to help minimise exposure to HF containing slurries. A full sampling schedule needs to be made available to the employees to help in identifying all the sampling points.

Samples which are taken need to be representative of the process and therefore a sampling procedure should be developed such that sampling will not disturb the system when drawing samples and flushing sampling pipe lines. There are two options for sampling, namely automatic and manual. Automatic samplers are ideal as they minimize the need for workers to come into contact with process streams. They are however expensive and would not be feasible for pilot plant scale. Figure 10 provides an illustration of an online automatic sampler.

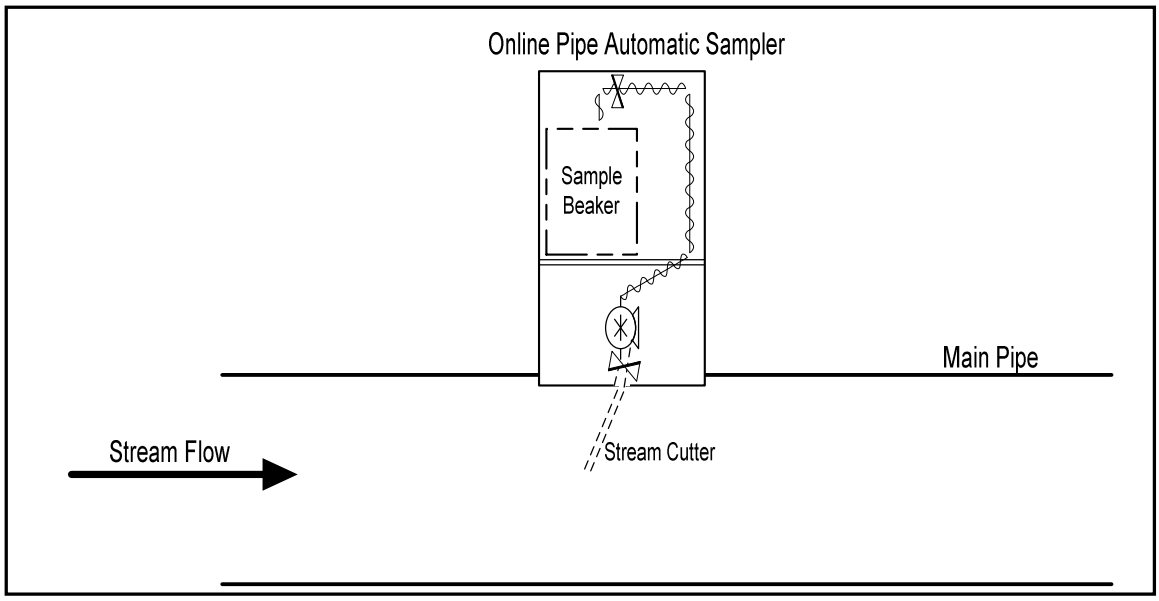


Figure 10: Schematic of an online automatic sampler

Figure 11 illustrates a manual sampler where the valve needs to be manually opened whenever a sample needs to be taken. Manual samplers will have to be used as there are cost constraints. The pipelines which will be used will also be of small diameters (< 10mm) and therefore sampling equipment needs to be as simple as possible. The following need to be considered to ensure proper working of the sampler:

- The valve should be as close to the main line as possible and the flange should not be placed directly below the main line. This is to ensure that less solids settle at the draw off point, thus minimising flushing requirements before sampling
- The valve needs to be easy to open but should allow different opening positions to control the amount of sample drawn at a time
- Where possible, samples need to be taken from tanks via a dip tube arrangement

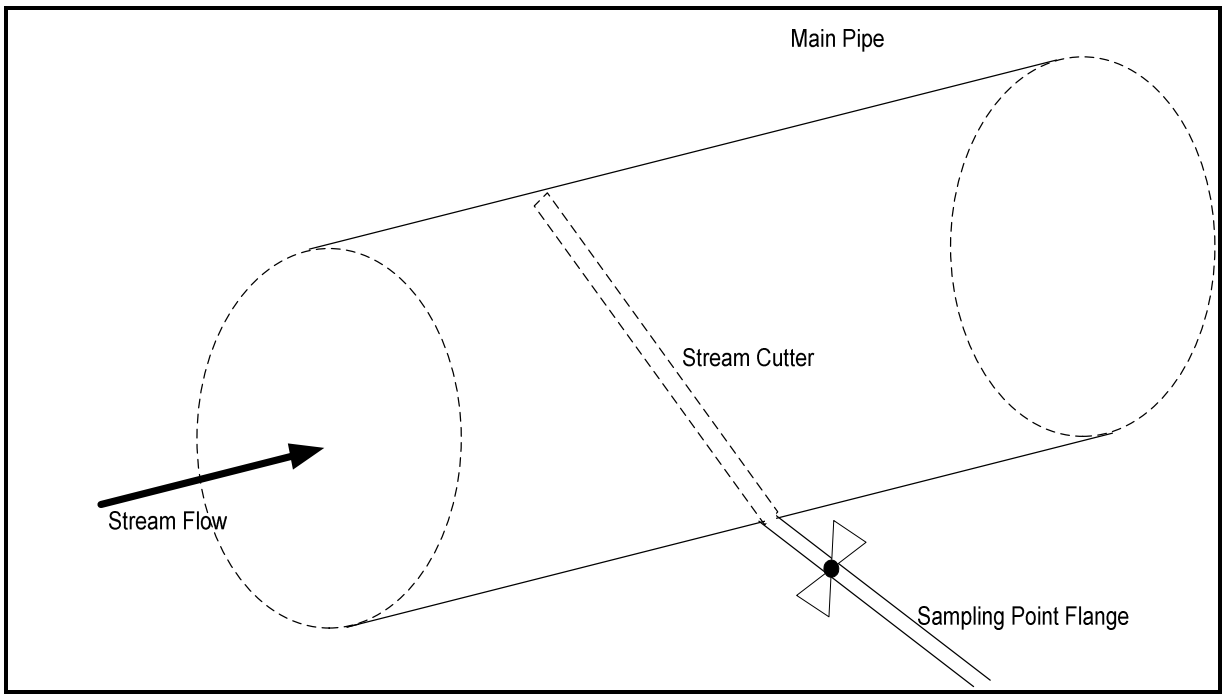


Figure 11: Flange type manual sampling point

It has been suggested by Grunennburg (2007) that all sampling points if not the entire rig should be placed behind a polycarbonate screen with glove boxes/compartments to minimise contact with process fumes and solutions. Flushing of the sampling line also needs to be considered for any pipe blockages which could occur.

9.2 Maintenance

The design of the experimental rig needs to be done such that sufficient maintenance can be easily done, bearing in mind the bulky PPE that could be worn by the maintenance team. Any elevated platforms and tank tops which may be in the plant should be equipped with standard pitch stairways rather than vertical barrel-back ladders. This is to enable employees wearing protective clothing, which may include self-contained breathing apparatus, to safely and easily gain access. All portions of the HF storage and handling system should be readily accessible since future routine inspection of all parts of the storage system will be an ongoing requirement.

Sufficient clearance between vessels, piping and pumps should be provided to allow for emergency escape routes. Special consideration should be given to future lifting needs since lifting over equipment containing HF is not recommended. If lifting over such equipment is unavoidable, the HF equipment should be emptied.

9.3 Equipment decontamination

Where equipment is small enough immersion into sodium bicarbonate or lime solution is recommended for decontamination, with water flushing afterwards. Larger parts could be cleaned with sodium bicarbonate or lime spray and then water flushing.

Caution needs to be taken when handling equipment which was possibly contaminated with HF. Aqueous HF reacts with metals to form metal fluorides and hydrogen. These fluoride scales can cause burns if handled, even if they appear dry. Packing, gaskets and pump seals absorb HF making them hard to decontaminate. Aqueous HF droplets may form on such materials even after washing as HF diffuses into the surface and parts of equipment. This means that although the equipment could be tested as HF free, they may not be safe later. Litmus paper can be made available for all workers to test the pH of all liquids in the plant as low pH could mean that the liquid contains HF.

As a general safety procedure no equipment should leave the plant area, particularly if equipment has not been decontaminated.

10 HF EMERGENCIES

Emergency preparedness is of utmost importance when dealing with dangerous chemicals. It is therefore important to have procedures in place to ensure that prompt reaction to emergencies is experienced. The different types of emergencies pertaining to HF will be discussed in this chapter together with reaction plans.

10.1 First aid

Every person who will be involved in the pilot plant should have HF first aid training. The supplier of the acid must provide free training on the handling of HF and all involved staff need to attend the training. In addition to the training, there should be a designated area where all the procedures including material safety date sheets will be readily accessible for all workers. Calcium gluconate gel should be available for the personal use of each worker. This will assist in avoiding delays in treatment when necessary, as well as possible misplacement of the gel. Safety showers and eyewashes must also be within close proximity of the work area.

Rehearsed procedures for first aid, arranging further medical treatment, and minimisation of further harm to workers or the public are also necessary for the optimal handling of accidents.

10.2 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. In cases where hydrofluoric acid is exposed to fire, but there are no spillages, the following procedure must be followed (NOHSC, 1989):

- 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.

10.3 Spillage handling

Proper secondary containment must be put in place for the acid storage containers. The spillage kit, including neutralising chemicals and absorbent material should be placed as close to the storage tanks as possible, as well as at a designated area which will be easily accessible to all the workers. This is to ensure that any leaks or spillages will be confined to one area and that there will be no overflow into the municipal drainage system. All operators need to be thoroughly trained in spillage handling.

In addition to the emergency equipment and chemicals provided, the designated professional emergency response team (EnviroServ) needs to be contacted. The HF supplier can also be contacted and should be available 24 hours a day for telephonic consultation, as per legal requirement. Contact numbers for both groups should be available at a designated location. The procedure for handling spillages is as follows:

10.3.1 Small spills

- Copious quantities of water (at least 10 times the volume of the spill) can be put onto the spill extremely quickly.
- Where this is not possible, **SLOWLY** absorb the spill in lime. This will reduce the reaction rate and reduce gas evolution. The resultant slurry can then be safely disposed of. Other neutralising agents which can be used are KOH, NaOH and $NaHCO_3$. It is however important to use dilute alkalis to avoid a generation of heat, which results in HF gas emissions
- Spill kits can also be used to contain and absorb any chemical spillages, including all process solutions.

10.3.2 Large spills

Water must not be used for large spills as this could result in the generation of heat, resulting in the release of toxic gases. Again, the spill kit, including absorbent socks should be used to confine the spill to one area. The spill should be soaked with lime, which both stops the flow of the spill and neutralises the acid.

PAM, a high molecular weight, low particle size, solid Polyacrylamide was used as part of spillage treatment (Necsa, 2006). The production of this chemical has however ceased (Valkenburgh, 2007). This product could be sprayed onto any spill of HF and was highly effective in reducing fumes. When sprayed onto a spill, a cover which reduces fumes was formed, with the resultant product being a solid gel. This gel could easily be placed in containers for effluent disposal. The disadvantage with the formed solid gel was that it was extremely slippery.

Sand was also recommended for containing spillages in some HF MSDS's. This however is very unsafe as HF reacts with, amongst other elements, the silica in the sand, resulting in very toxic fluorosilicate fumes.

Figure 12: Alkaline materials for neutralisation of HF (Honeywell)

ALKALINE MATERIAL	COMMON NAMES	FORM AVAILABLE	HAZARDS + REACTION	LB. / LB. 100% HF	SALT PROPERTIES
SODIUM HYDROXIDE (NaOH)	CAUSTIC SODA	100% SOLID BEADS or FLAKE <50 % SOLUTION	DOT Class 8 (Corrosive) Very High Heat of Dilution & Neutralization*	4.00 lb. / lb. 100% HF	Sodium Fluoride (NaF) DOT Class 6 (Poison) Sol. in Water = 4.0%
POTASSIUM HYDROXIDE (KOH)	CAUSTIC POTASH	85% SOLID BEADS or FLAKE <45 % SOLUTION	DOT Class 8 (Corrosive) Very High Heat of Dilution & Neutralization*	6.23 lb. / lb. 100% HF	Potassium Fluoride (KF) DOT Class 6 (Poison) Sol. in Water >40%
SODIUM CARBONATE (Na_2CO_3)	SODA ASH	DRY POWDER	Rapid Evolution of Carbon Dioxide Gas (CO_2)	2.85 lb. / lb. 100% HF	Sodium Fluoride (NaF) DOT Class 6 (Poison) Sol. in Water = 4.0%
SODIUM BICARBONATE ($NaHCO_3$)	BICARB BAKING SODA	DRY POWDER	Rapid Evolution of Carbon Dioxide Gas (CO_2)	4.20 lb. / lb. 100% HF	Sodium Fluoride (NaF) DOT Class 6 (Poison) Sol. in Water = 4.0%
CALCIUM CARBONATE ($CaCO_3$)	LIMESTONE	PEBBLES	Slow Reaction Slow Evolution of Carbon Dioxide Gas (CO_2) Pebble Surface Can Become Passivated	2.69 lb. / lb. 100% HF	Calcium Fluoride (CaF_2) Non-hazardous Sol. In Water = 0.004%
CALCIUM OXIDE (CaO)	QUICKLIME	DRY POWDER	DOT Class 8 (Corrosive) Very High Heat of Hydration & Neutralization*	1.46 lb. / lb. 100% HF	Calcium Fluoride (CaF_2) Non-hazardous Sol. In Water = 0.004%
CALCIUM HYDROXIDE [$Ca(OH)_2$]	HYDRATED LIME	DRY POWDER SLURRY IN WATER	High Heat of Neutralization* Slippery When Wet	2.01 lb. / lb. 100% HF	Calcium Fluoride (CaF_2) Non-hazardous Sol. In Water = 0.004%

Figure 12: Alkaline materials for neutralisation of HF (Honeywell)

10.3.3 Disposal

The Environmental Conservation Act (ECA), (1998) stipulates that all “HCS waste which can cause exposure, should be disposed of only on sites specifically designated for this purpose in such a manner that it does not cause a hazard inside or outside the site concerned” (DEAT, 2003). The ECA also states that any contract agreement between the company and the hazardous waste removal contractor needs to specify that the outsourced company agrees to comply with the environmental conservation regulations (DEAT, 2003).

Enviro-Serv, Waste tech division (EnviroServ, 2007) is a qualified waste disposal company in South Africa and can be used for such work. Arrangements must be made with the waste removal department regarding collection of both waste solutions and solid residue, including used PPE. Enviro-Serv supplies skips and containers for the collection and removal of waste. These should be placed far from other process chemicals and clearly marked. Caution needs to be taken to ensure that the waste does not mix with any incompatible materials.

10.3.4 Emergencies

According to the health and safety act, in the hazardous installation regulations, emergency planning is defined as “a plan in writing which, on the basis of identified potential incidents at the installation, together with their consequences, describes how such incidents and their consequences should be dealt with on-site and off-site” (Government gazette, 2001). In addition to that, the plan should include (Berg et al., 2005a):

- The need for and sources of off-site emergency response equipment and personal protective equipment suitable for HF exposure.
- The need for off-site emergency response personnel who are trained in handling HF emergencies.
- The need for and location of emergency medical treatment specific to HF exposure.
- The mechanism for notifying the surrounding community and communicating a response appropriate to the situation; for example, evacuation or shelter in place.
- Availability of temporary safe havens for operators and other facility personnel.
- Consequences of potential HF release.
- Possible contamination of runoff water.
- Emergency repair methods.

An on-site emergency team, which will be the first line of response, should be elected for each shift. It is best to provide emergency training for all shift workers for each shift instead of having a few designated people. This will prove useful in case some individuals are unable to respond to the emergencies as they themselves could need help. The emergency team should be trained to respond to emergencies in the plant while waiting for the professional emergency response team which will be called. A designated area should be provided for keeping the emergency PPE.

Escape routes should also be clearly marked and identified to all the workers to assist orderly evacuation in case of emergencies.

NECSA, the acid supplier, must be available to provide advice telephonically in case of emergencies. The second line of response, EnviroServ, must be called in to assist the onsite emergency response team and ensuring that spillages are contained and cleaned up. Prior arrangement must be made and a brief description of the hazardous chemical (HF) as well as risk assessment documentation will have to be submitted to the emergency response team to assist them for adequate preparation.

Should there be any casualties, an ambulance should be called in or a designated person in the plant should take the casualty for medical treatment. It is however not recommended to transport a contaminated person using a private vehicle as the vehicle itself could be contaminated, spreading the contamination to every other person using the vehicle. Depending on the severity of HF contact, the exposed individual will have to be hospitalised. The emergency response system is summarised in Figure 13

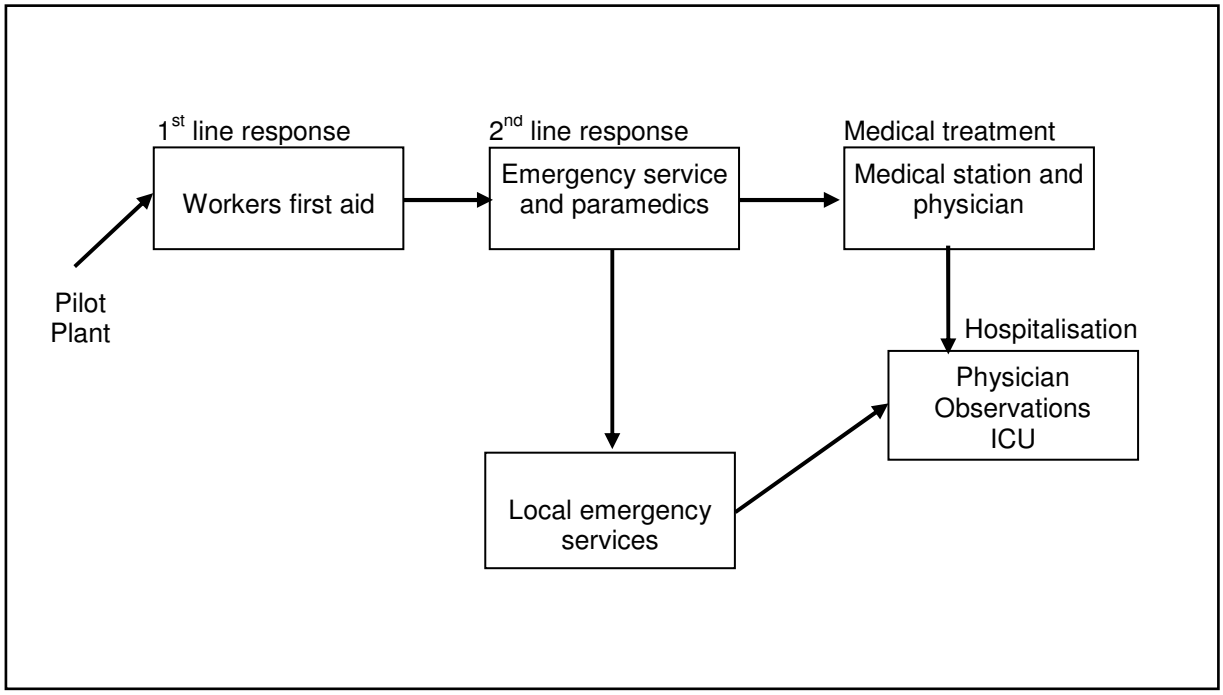


Figure 13: Emergency response system

10.3.5 Safety equipment

The HF supplier has suggested that wherever there is any risk of contact with HF action deluge type showers should be available. These should be platform activated. The plant layout should be such that pathways to the safety showers and eyebaths are clear at all times. A picture illustrating the suggested type of safety equipment can be found in Figure 14. Eye baths should be easy to open and available at all hazard spots. These equipments should not be more that 10 seconds from work stations. It is suggested that safety equipment should be within15 metres of the areas requiring HF (Necsa, 2006).

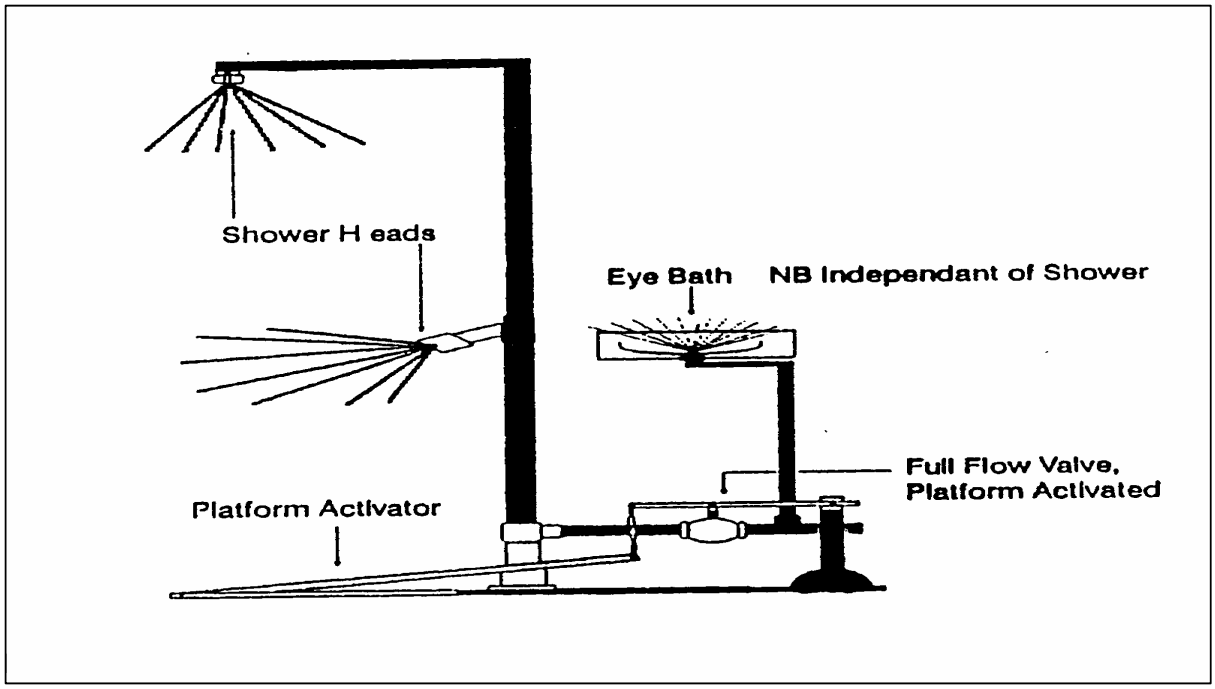


Figure 14: platform activated shower with eyebath

Apart from the materials of constructions which need to be considered, allocation of the following venues needs to be made:

- A decontamination area for PPE or plant equipment/ tool drop station. The decontamination bay should include fresh water for initial and final washing and alkali water for neutralisation purposes
- Plant layout to accommodate the air supply equipment which will be needed for at least the areas which have HF streams entering.
- The two stages requiring HF have to be placed within close proximity of each other in order to avoid numerous pipelines for HF transfer
- A poly carbon screen to be used as a barrier between the rig and people taking samples
- Compressors for air supply (should this option be chosen). PPE suppliers will advise on sizing once the plant layout is available
- Hazardous waste bins location.
- HF storage venue, including adequate bunding/containment as close to the rig as possible
- Drainage system which collects spillages

- Extraction facilities, particularly for areas where there is high risk of HF exposure and the digestion stage where there are off gases
- Emergency evacuation venue

11 CONCLUSION

The use of HF in industry, even in metallurgy, is not a novel idea. HF has been used in many applications including manufacturing of fluorocarbons and other chemicals, aluminium manufacturing, petroleum alkylation, uranium purification and other minor applications.

Although the use of HF is not new, safety considerations must be specific to the work that will be conducted. Therefore, even with the available information on the use of HF, the design and implementation of the safety measures must stem from the risk assessments that must be done for the pilot plant.

Anglo Research must ensure that all safety and legal issues are considered before commencing with the pilot campaign. The discussed acts and regulations provide guidelines for ensuring the protection of workers involved with hazardous chemicals as well as the environment. Most of the safety considerations stem from the stipulated guidelines in the occupational health and safety act. All work procedures must be made available as per hazardous chemical substances regulation.

Both the safety of the workers and the design of the plant were reviewed. Appropriate choices of material of construction, based on the information provided, and the expert advice from HF manufactures needs to be utilised fully to ensure that all relevant aspects of safety are covered.

Although personal protective equipment (PPE) is important, it should be regarded as the last resort with respect to safety, therefore the plant needs to be designed in such a way that even in the absence of adequate PPE, there will be adequate protection of workers.

Every design aspect of the plant must be done in such a way that the environmental and worker exposure to HF is minimised. Once safety of the plant design has been extensively reviewed, the pilot plant can be built. The success of this campaign will be based not only on the achievement of process and product specification, but also on whether it was run without any incidents.

12 REFERENCES

Agency for toxic substance and disease registry (ATSDR) (2006). *Fluorides, Hydrogen Fluoride, and Fluorine*. Department of health and human services U.S.A. Internet: **http://www.atsdr.cdc.gov/toxprofiles/tp11-c5.pdf**. Accessed 08 May 2007.

Aiken, T. (2001). *Materials for Receiving, Handling, and Storing Hydrofluoric Acid*. NACE international Publication 5A171 (2001 Revision).

Anonymous (1999). *Phillips to license new refining technology*. Alexander's Gas and Oil Connections Company News North America. Internet: http://www.gasandoil.com/goc/company/Cnn90415.htm. Accessed 08 May 2007.

Anonymous (2004). *Hydrofluoric Acid Occupational Health and Safety Information*. Internet:http://www.fap.pdx.edu/safety/hydrofluoric_acid/. Accessed 04 April 2007.

Anonymous (2005). *Feasibility study for HF and ATF plant in SA*. Creamer's Mining Weekly.

Anonymous a (2003). Fluorine/ Hydrogen Fluoride. Chemical terrorism. Internet: http://www.bioterrorism.slu.edu/bt/products/ahec_chem/scripts/**Fluorine**.pdf. Accessed 06 May 2007.

Anonymous b (2003). *Management of Exposure to Hydrofluoric Acid (HF).* Oklahoma State University, ESH Lab manual. Internet: http://www.pp.okstate.edu/ehs/hazmat/labman/Appendix-O.htm. Accessed 04 April 2007.

Anonymous, (2006). *Titanium*. Columbia Encyclopedia (6th edition) New York: Columbia University Press. ISBN 0787650153.

Barksdale, J. (1966).*Titanium, its occurrence, chemistry and technology (2nd ed.)*, Ronald Press, New York, NY.

Barksdale, J. (1968). *The Encyclopedia of the Chemical Elements*. Skokie, Illinois: Reinhold Book Corporation, 732-38 "Titanium". LCCCN 68-29938.

Berg, M., Brooks, W., Rodriguez, J., Santay, T. (2005a). *Guideline for the Bulk Storage and Handling 70% Aqueous Hydrofluoric Acid*. Hydrogen Fluoride Industry Practice Institute. Provided by Shelby Jones from American Chemistry.

Berg, M., Sterchic, M., Rommelman, S., Urban E., Santay, T. (2005b). *Guideline for the Bulk Storage and Handling 49% Aqueous Hydrofluoric Acid*. Hydrogen Fluoride Industry Practice Institute. Provided by Shelby Jones from American Chemistry.

Bertolini, J.C., (1992) *Hydrofluoric Acid: A Review of Toxicity*. Journal of Emergency Medicine, Vol. 10 pp 163 – 168.

Biswas, R.K., Habib, M.A.and Dafader, N.C. (1992). *A study on the recovery of titanium from hydrofluoric acid leach solution of ilmenite sand*. Hydrometallurgy, Vol. 28 pp. 119 – 126.

Burd, A. (2004). Hydrofluoric acid—revisited. Burns Vol. 30 pp 720 – 722.

Bureau of land management (1999). *3809 Surface management Regulation: Glossary*. U.S. department of the interior. Internet: http://www.blm.gov/nhp/Commercial/SolidMineral/3809/deis/glossary.html. Accessed 26 July 2007.

Chen, G.Z., Fray, D.J., Farthing, T.W. (2000). *Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride*. Nature, Vol. 407, pp. 361 – 64. DOI:10.1038/35030069. *Abstract*.

Department of Environmental Affairs and Tourism (DEAT) (1998). *National Environmental Management Act (Act no. 107, 1998)*. Government gazette No. 19519.

Department of Environmental affairs and tourism (DEAT) (2003). *Environmental Conservation Act 73 of 1989*. Government Gazette No. R. 518.

Department of health (1992). *Hazardous Substances Act 15 of 1973.* Government Gazette

Department of labour (1995). Occupational Health and Safety Act (ActN o. 85 of 1993): Regulations for hazardous chemical substances. Government Gazette No. 16596.

Department of labour (2001). Occupational Health and Safety Act (ActN o. 85 of 1993): Major hazard installation regulations. Government Gazette No. 22506.

Department of transport (2002a). General info of transportation of dangerous goods industry: Chapter 1: Introduction to the transportation of dangerous goods by road. Internet: http://www.transport.gov.za/library/docs/misc/dgsec1.pdf. Accessed 08 February 2007.

Department of transport (2002b). *General info of transportation of dangerous goods industry: danger warning placcards.* Internet: www.transport.gov.za/library/docs/misc/dgsec2d.pdf. Accessed 08 February 2007.

Department of transport (2003). National Road Traffic Act 93 of 1996: Chapter VIII: Transportation of Dangerous Goods and Substances by Road. Government Gazette No. 20865.

Drosjack, M. (2003.) *Activists push to ban chemical nationwide.* Houston Chronicle Washington Bureau. Internet: http://www.chron.com/disp/story.mpl/business/2157774.html. Accessed 13 April 2007.

Dünser, M.W., Öhlbauer, M., Rieder, J., Zimmermanna, I., Ruatti, H., Anton H. Schwabegger A. H., Bodrogi, F., Huemerb, G.M, Barbara E. Friesenecker B.E., Mayra, A.J., Philipp Lirk, P. (2004). *Critical care management of major hydrofluoric acid burns: a case report, review of the literature, and recommendations for therapy.* Burns Vol. 30 pp. 391–398.

DuPont (2006). *Teflon AF amorphous fluoropolymers*. DuPont Website. Internet: http://www.solutions.dupont.com.au/Teflon_Industrial/en_US/assets/downloads/h75334.pdf. Accessed 13 April 2007.

El-Hazek, N., Lasheen, T.A., El-Sheikh, R., Zaki, S.A. (2007). *Hydrometallurgical criteria for TiO_2 leaching from Rosetta ilmenite by hydrochloric acid*. Hydrometallurgy, Vol. 87 pp. 45–50.

EnviroServ, (2007). *List of products and services*. Internet: http://www.enviroserv.co.za/pages/Content.asp?SectionID=493. Accessed 08 May 2007.

European Union. Internet:

http://ec.europa.eu/employment_social/health_safety/docs/oels_en.pdf. Accessed 17 May 2007.

Grunnenburg, A. (2007). Personal Interview with NECSA process engineer on 9 March 2007.

Habashi, F. (ed.) (1997). *Handbook of Extractive Metallurgy.* Wiley-VCH, Weinham, pp. 1129 – 1180.

Han, K.N., Rubcumintara, T. and Fuerstenau, M.C. (1986). *Leaching behavior of ilmenite with sulphuric acid*. Metallurgical and Materials Transactions **B:** Process Metallurgy, Vol. 18B pp. 325–330.

Hatzifotis, M., Williams, A., Muller, M. and Pegga, S. (2004). *Hydrofluoric acid burns*. Burns, Vol. 30 pp. 156 – 159.

Heard, K., and Delgado, J. (2003). *Oral Decontamination with Calcium or Magnesium Salts Does Not Imporve Survival Following Hydrofluoric Acid Ingestion*. Journal of Clinical Toxicology, Vol. 41(6) pp. 789 – 792.

Honeywell, 2006. *Recommended Medical Treatment for Hydrofluoric Acid Exposure*. Honeywell Hydrofluoric acid. Internet: http://www.honeywell.com/sites/sm/chemicals/hfacid/technical_documents.htm. Accessed 11 April 2007.

Honeywell. *HF neutralisation*. Internet: www.hfacid.com. Accessed 18 May 2007.

Howells, M.E., Jennings, H., Oliveira, F., Wyatt, P. (2005). *Material of Construction Guideline for Hydrofluoric Acid Solution*. Hydrogen Fluoride Industry Practice Institute. Provided by Shelby Jones from American Chemistry.

HSE, 2002. *Occupational Exposure Limits 2002*. HSE Books, Sudbury.

International volcanic health hazard network (IVHHN) (year unspecified). *Hydrogen Fluoride (HF)*. Gas and Aerosol Guidelines, Internet: http://www.esc.cam.ac.uk/ivhhn/guidelines/gas/hf.html. Accessed 17 May 2007.

Kirkpatrick, J.R., Enion, D.S., Burd D.A.R., (1995). *Hydrofluoric acid burns: a review*. Burns, Vol. 19, pp.483– 493.

Krebs, R.E. (2006). *The History and Use of Our Earth's Chemical Elements: A Reference Guide (2nd edition)*. Westport, CT: Greenwood Press. ISBN 0313334382.

Liang, B., Li, C., Zhang, C., Zhang, Y. (2005). *Leaching kinetics of Panzhihua ilmenite in sulphuric acid*. Hydrometallurgy, Vol. 76 pp.173–179.

Mackey, T.S. (1974). *Acid leaching of ilmenite into synthetic rutile*. Industrial & Engineering Chemistry Product Research And Development, Vol. 13, No. 1, pp. 9.

Monhemius, J. (2006). *Section 1: life cycle and process analysis in the mining industry.* Journal of Cleaner Production Vol. 14 pp. 1040-1041.

National Industrial Chemicals Notification and Assessment Scheme (NICNAS) (2001). *Hydrofluoric acid: Priority existing chemical, assessment report no. 19*. Australian Government. ISBN 0 642 70986 6.

National Industrial Chemicals Notification and Assessment Scheme (NICNAS) (2001). *Hydrofluoric acid: Priority existing chemical, assessment report no. 19*. Australian Government. ISBN 0 642 70986 6.

National institute for occupational safety and health (NIOSH) (1995). *Documentation for Immediately Dangerous to Life or Health Concentrations: Hydrogen fluoride (as F)*. Centers for disease control and prevention. Internet: http://www.cdc.gov/niosh/idlh/intridl4.html. Accessed 17 May 2007.

National Occupational Health and Safety Commission (NOHSC) (1989). *Hydrogen fluoride*. Australian government publishing service, Canberra. ISBN 0 644 12820 8.

National Occupational Health and Safety Commission (NOHSC) (1989). *Hydrogen Fluoride*. Australian Government Publishing Service Canberra.

Necsa, (2006). *Hydrogen Fluoride and hydrofluoric acid handling guidelines: Training Module*. Chemical dividion of Necsa: Pelchem (Provided by Eddy Valkenburg, Necsa).

National Pollutant Inventory (NPI) (1999a). *Emission estimation technique manual for phosphate manufacturing*. Canberra, Environment Australia.

National Pollutant Inventory (NPI) (1999b). *Emission estimation technique manual for brick, ceramics and clay product manufacturing*. Canberra, Environment Australia.

National Pollutant Inventory (NPI) (1999c). *Emission estimation technique manual for fossil fuel electric power generation.* Canberra, Environment Australia.

Occupational Health and Safey Administration (OHSA). *Occupational safety and health guideline for hydrogen fluoride*. U.S. departmernt of labour, Internet: http://www.osha.gov/SLTC/healthguidelines/hydrogenfluoride/recognition.html. Accessed 17 May 2007.

Oregon occupational safety & health division (OSHD) (2004). *Programme directive- Hydrofluoric Acid and Hydrogen Fluoride.* Department of consumer & business services, USA. Internet: http://www.cbs.state.or.us/external/osha/pdf/pds/pd-204.pdf. Accessed 11 April 2007.

Osborne, P.E., Icenhour, A.S., Del Cul, G.D. (2002). *Hydrofluoric Acid Corrosion Study of High-Alloy Materials.* Oak Ridge National Laboratory.

Philips Elmet Corporation (PEC) (2003). *Increasing Batch Size in Washing Process Yields Multiple Benefits*. Maine.gov website. Internet: http://www.maine.gov/dep/oia/case/philips3.htm Accessed 15 April 2007.

Rodriguez, M., Quiroga, O. and del C. Ruiz, M. (2007). *Kinetic study of ferrocolumbite dissolution in hydrofluoric acid medium*. Hydrometallurgy Vol. 85 pp. 87–94.

Segal, E.B. (2000). *First Aid for a Unique Acid, HF: A Sequel.* Chemical Health and Safety Vol. 7, issue 1, pp. 19.. Internet: http://www.calgonate.com/enCA/about_hydro.php. Accessed 05 May 2007.

Settle, F. (2005). *Nuclear chemistry – uranium production*. Chemcases.com, Internet: http://www.chemcases.com/nuclear/nc-06.htm. Accessed 08 May 2007.

Shehu, N., Spaziani, E. (1999). *Technical note: Separation of feldspar from quartz using EDTA as modifier*. Minerals Engineering, Vol. 12. No. 11, pp.1393-1397.

Sheridan, R.L., Ryan C.M., Quinby, W.C., Blair, J., Tompkins, R.G., Burke, J.F. (1995) *Emergency management of major hydrofluoric acid exposures*. Burns, Vol. 21 pp.62– 64.

Sievert, W.J. (2002). *Using hydrofluoric safely presentation*. Honeywell website. Internet: http://www.honeywell.com/sites/docs/doc128e30a-f9d1a85207-e0df9bfada07602278603c6cb43673fb.pdf. Accessed 11 May 2007.

Special metals (2006). *Inconel alloy C-276*. Special metals.com, Internet: http://www.specialmetals.com/documents/Inconel%20alloy%20C-276.pdf. Accessed 11 April 2007.

State Environmental Resource Center (SERC) (2004). *Banning cyanide use in mining*. Policy issues package. Internet: http://www.serconline.org/mining/talking.html. Accessed 27 July 2007.

Steel, K.M., Besida, J., O'Donnell, T.A and Wood, D.G. (2001). Production of Ultra Clean Coal Part I—Dissolution behaviour of mineral matter in black coal toward hydrochloric and hydrofluoric acids. Fuel Processing Technology, Vol. 70 pp.171–192.

Strachan, J. (1999). A deadly rinse: The dangers of hydrofluoric acid. *Professional Carwashing & Detailing,* Vol. 23, Issue 1.

Suzuki, R.O. (2005). *Calciothermic reduction of TiO_2 and in situ electrolysis of CaO in the molten $CaCl_2$*. Journal of Physics and Chemistry of Solids Vol. 66, pp. 461-465.

Theodore R. Beck, T.R. (2001). *Electrolytic Production Of Aluminium*. Electrochemistry Encyclopedia. Internet: http://electrochem.cwru.edu/ed/encycl/art-a01-al-prod.htm. Accessed 08 May 2007.

Toxics use reduction institute (TURI) (2000). *Massachusetts chemical fact sheet: Hydrofluoric Acid Fact Sheet*. The Massachusetts Toxics Use Reduction Institute. Internet: http://www.turi.org/content/view/full/557. Accessed 11 April 2007.

Valkenburgh, E. (2007). Personal interview with Commercial Manager: Pelchem on 06 February 2007.

Watson-Marlow-Bredel (WMB) (2007). Tubing selection Guide. Watson-Marlow website, Internet: http://www.watson-marlow.com/watson-marlow/p-tubing.htm. Accessed 08 February 2007.

Working Group Storage, Transport and Safety (WGSTS) (1997). *Physical properties of anhydrous HF and hydrofluoric acid solutions, 2nd edition*. Comité Technique Européen du Fluor, Bruxxelles.

Working Group Storage, Transport and Safety (WGSTS) (2001). *Personal Protective Equipment for Use with HF*. Comité Technique Européen du Fluor, Bruxelles.