Establishing a process to reduce, recycle and reuse the waste electrolyte from fluorine generation

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DECLARATION

I, Elna Fourie, declare that this dissertation, submitted to the University of the Witwatersrand, is my own, unaided work. It has not been presented before for any degree or examination to any other University.

Fourie

Elna Fourie

Signed on the fourth day of May 2005

ABSTRACT

Waste electrolyte from fluorine cells is a major waste problem for the fluorine chemical industry. Processes have to be developed to reduce, recycle and re-use the spent electrolyte that has up to now been stockpiled. This dissertation is a compilation of the research work that has been done to derive a process to treat waste electrolyte for re-use.

Different conversion processes were investigated to develop a Waste Management plan for the fluorine generating facility in respect of the electrolyte.

Gravity settling, centrifuging, filtration, the addition of KF.HF to the to the electrolyte to decrease the HF concentration in the electrolyte and consequently decrease the solubility of Fe, Cu and Ni and addition of NaOH to the electrolyte to convert soluble Fe to the insoluble triple salt were tested.

Gravity settling and centrifuging were shown to produce the best solution. However, significant sedimentation of the insoluble metal impurities in the electrolyte is timeously. The implementation of sedimentation as an industrial separation process to purify waste electrolyte of excess metal impurities is therefore impractical. The results indicated that sparging molten electrolyte with N_2 gas to remove HF (thus precipitating soluble Fe, Cu and Ni, and removing moisture to reduce corrosion of metal components), followed by sediment centrifuging, appears to be a practical basis for an industrial waste electrolyte treatment process.

During an assessment carried out by the Economics Trends Research Group (ETRG) (3) at the University of Cape Town a strong argument was made for the need to direct companies in South Africa to address environmental concerns with high priority. In South Africa there is very little awareness of the concept of Clean Technology. Not only must the level of contamination be reduced before waste is released into the environment, but natural resources like water must be conserved, and energy consumption must be reduced.

Public concern over degradation of the environment can no longer be ignored.

Globally, the chemical industries are considered to be the main culprits in the degradation of the environment. The assessment carried out by the ETRG showed that the chemical industries are classed among the top 5 generators of toxic and hazardous waste in every country. The metallurgical sector (mining) is in most cases classed as the top waste generator.

Development and implementation of technologies that are more efficient are not a matter of choice any more. Each new facility that is developed should meet the challenge of generating as little waste as possible.

Unfortunately, many old industries and facilities did not focus on increasing efficiency and minimising waste. These old facilities experience a challenge now to develop technology to make them part of this Cleaner Production and Technology era.

Cleaner Production implies generating less effluent or waste and recycling waste to be used as raw material in the same or another facility. Cleaner Production also concentrates on the increase of efficiency but this is often limited by the chemical properties of substances. This research was based on the ideas for implementation of Cleaner Production in the fluorine generation facility at Necsa.

Waste reduction almost always implies investment in equipment and development of new technologies. However there is ample evidence to show that the cost of rehabilitation of contaminated environment is exceedingly high in comparison with the precautionary steps taken to prevent contamination.

Waste/Effluent Management have become new buzz words in the industrial environment.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Necsa, for the opportunity to further my studies in this way.

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- My husband Dawid and my son Shemuel; also for their understanding during the long period of my research.

I am most grateful to my Creator, because through Him, all things are possible.

Success is sweet
and
sweeter if long delayed
and gotten
through many struggles

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GLOSSARY

For the purpose of this document, the following terms shall have the meanings given.

Analysis	:	A method for determining and evaluating the detailed performance of a process.
Anhydrous hydrogen fluoride	:	Hydrofluoric acid 99.95% pure, with a moisture content less than 400 ppm.
Anode	:	The positive electrode of an electrolytic cell.
Cathode	:	The negative electrode of an electrolytic cell.
Clean production	:	The adoption of industrial processes directed at reducing the consumption of natural resources, eliminating the generation of waste materials, and ensuring that products are environmentally compatible throughout their lifecycles.
Clean technology	:	Fundamentally technology which improves the thermodynamic efficiency of production processes and substitutes less hazardous processes for harmful ones.
Effective	:	Producing a definite or desired result.
Electrolyte	:	A solution that conducts an electric current by means of ions contained in the solution. For the sake of this study it is a highly water-soluble fluoride mixture consisting of potassium fluoride and hydrogen fluoride (KF.nHF).
Facility	:	Buildings, containers or equipment in which a process is conducted.
Process Safety	:	A discipline that focuses on the prevention of explosions, accidental chemical releases or the unsafe handling of hazardous chemical substances.
Process	:	The activity involving any chemicals, including their use, manufacturing, transportation, and storage, or the combination of such activities.
Safety	:	The expectation that a process will not lead to a state in which any human life or the environment is adversely affected.

Storage : The holding of waste in a facility that provides for its containment, with the intention of retrieval.

Waste : Material in gaseous, liquid or solid form and in concentrations or chemical forms that do not permit economic recovery and that are designated for disposal.

Waste management : All activities that relate to waste, such as generation, handling, transport, storage and disposal.

ABBREVIATIONS

AHF - Anhydrous hydrogen fluoride
F_2 - Fluorine
HF - Hydrofluoric acid
HSE - Health, Safety, and Environmental
KF.2HF - Fluorine cell electrolyte (Potassium bifluoride)
KF.HF - Potassium bifluoride
PTFE - Polytetrafluoroethylene
SS - Stainless steel
TPA - Tonnes per annum
UF_4 - Uranium tetrafluoride
UF_6 - Uranium hexafluoride
XDA - X-ray diffraction analysis

CHAPTER ONE

1 INTRODUCTION

1.1 Background to the fluorine chemical industry at Necsa

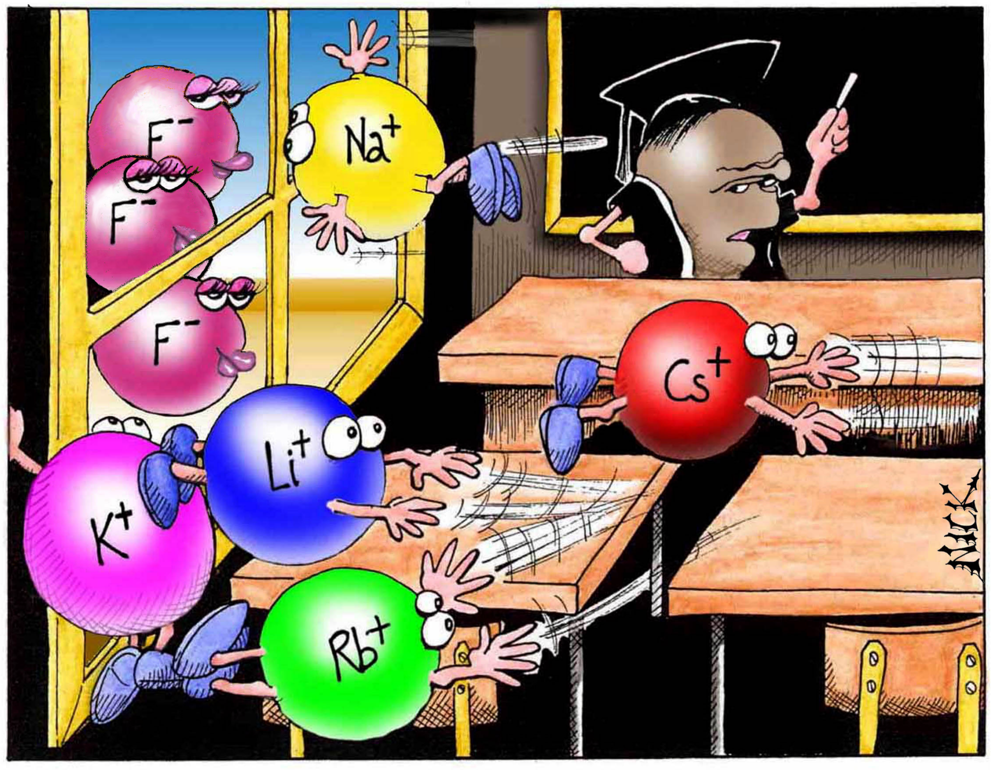
Necsa is situated at Pelindaba in the North West Province approximately 1280m above sea level. It is a beautiful area, with a view over the Magalies Mountains and the Hartbeespoort Dam.

Fig 1.1: Necsa

The South African nuclear programme started as early as 1948 and focussed on research and development in the nuclear field. Until World War 2, there was no commercial production of elemental fluorine. Nuclear bomb projects and nuclear energy applications made it necessary to produce large quantities of fluorine since this was required for the manufacturing of uranium hexafluoride, a volatile compound of uranium used in the gas diffusion process for enriching the uranium i.r.o its U^{235} isotope. In the early 70s a conversion plant was erected at Pelindaba to produce uranium hexafluoride (UF_6). The generation of fluorine (F_2) through the electrolysis of potassium bifluoride formed part of the uranium enrichment project launched by the government. The enriched uranium was used as fuel in the generation of nuclear power at Koeberg, near Cape Town, and in the generation of radioactive isotopes for industrial and medical diagnostics at Pelindaba in the Safari 1 reactor. The uranium conversion project was stopped in the early 90's, but Necsa continued to generate fluorine for other commercial applications. Typical applications of fluorine are the manufacture of fluoro-chemicals, surface fluorinated polyfins, semiconductor chamber cleaning, etching, laser gas mixture production etc. The use of fluorine gas increased phenomenally, but unfortunately that also implied that the generation of waste electrolyte increased. Today the amount of waste electrolyte generated (and that still expected to be generated in the coming years) has become a serious problem.

1.2 Fluorine

Fluorine is a member of the Group 7 elements known as the halogen group. It is the most electronegative and reactive of all elements, and reacts with practically all organic and inorganic substances. Fig 1 "demonstrates" the reactivity of fluorine. Finely divided metals, glass, ceramics, carbon, and even water burn in fluorine with a bright flame. It even forms compounds with noble gases such as xenon, radon, and krypton.



"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive..?"

Fig 1.2: Fluorine, the most reactive element

Cartoon included by kind permission of Nick Kim

Table 1A in Appendix A indicates the properties of fluorine

The unique properties of fluorine have been exploited, and several plants using fluorine gas as main raw material are currently in operation at Necsa. Table 1.1 below shows the different products manufactured using fluorine as raw/feed material. Necsa's first application of fluorine other than in the nuclear field was the surface fluorination of polymers.

Product	Formula
Inorganic fluorides:	
Compressed Fluorine and fluorine/nitrogen mixtures	F_2/N_2
Surface fluorination of polymers	
Sulphur Hexafluoride	SF_6
Chlorine Trifluoride	ClF_3
Tungsten Hexafluoride	WF_6
Nitrogen Trifluoride	NF_3
Xenon Difluoride	XeF_2
Organic fluorides:	
Octafluorocyclobutane	$c\text{-}C_4F_8$
Carbon Tetrafluoride	CF_4
Perfluoroheptane	C_7F_{16}

Table 1.1: Products manufactured, using F_2 as one of the raw/feed materials

The semi-conductor industry is totally dependent on fluorine since all the deposition, etching and chamber cleaning processes used in the "fabs" of components are inorganic and organic fluorides. The organic fluoride industry is expanding enormously as more and more environmental friendly "clean" products are developed to replace existing refrigerants, adhesives, surface modification substances etc.

The manufacturing of fluorine gas is a very hazardous process but this has been mastered at the Necsa site over the past 30 years. Necsa makes South Africa one of the few producers of fluorine gas in the international market. Fluorine is available commercially in cylinders pressurised up to 2 800 kPa(g). Fluorine is corrosive, and so are most of the soluble fluorides. It is difficult to store as it reacts with most materials. Carbon steel, nickel, stainless steel and Monel metal containers can be used if conditioned before initial use. The conditioning process is known as passivation. Passivation implies the formation of a stable metal-fluoride layer on the surface of the containers.

1.3 Fluorine generation

Fluorine is generated by means of electrolytic splitting (electrolysis) of a hot molten mixture of hydrogen fluoride and potassium bifluoride. The electrolyte (KF.2HF) is very corrosive. The fluorine cells are manufactured from mild steel, lined with a corrosion resistant metal layer on the inside. The cells are equipped with a lid on which the anodes and cathodes are mounted and connected with bus bars to a supply of direct current provided by rectifiers. Anodes are manufactured from carbon and the cathodes from mild steel.

When a current is applied to the cell, HF is electrolysed to release F_2 at the anode and H_2 at the cathode. A potential difference of 2.87 Volts is required to dissociate HF into F_2 and H_2. The rate of F_2 and H_2 formation in the cell is a function of the current applied. Due to the electrical design of the rectifiers, the actual current of each of the compartments within a cell unit may differ.

The F_2 and H_2 flow from the compartments via pipes to common F_2 and H_2 manifolds. During the generation of F_2, the HF content of the electrolyte is depleted. The HF concentration is maintained at 40.8% ± 0.3% (m/m) by continuous addition of Anhydrous Hydrofluoric Acid (AHF).

The optimum operating temperature of the F_2 cells is 85ºC and even if a cell is not in operation, the electrolyte must be kept at approximately 85°C to prevent solidification. The temperature in the cells is controlled with a closed circuit hot water heating and cold water cooling system. Hot or cold water is fed to the cell through Monel coils, situated between the cell compartments.

The H_2 manifolds from all the cells are connected to a common header. The H_2 is contaminated with electrolyte carryover and HF vapour, and is therefore scrubbed with KOH to remove the impurities before being released to the atmosphere via a stack.

Electrolyte is carried over with the F_2. The F_2 also contains a substantial amount of HF vapour. The crude F_2 is purified by removing the electrolyte carryover and HF vapour in consecutive separation processes. The purified F_2 is compressed with special diaphragm compressors.

The compressed fluorine gas is piped via a header to the different facilities on the Necsa site or via compressed gas cylinders to other customers. Reasonably safe handling techniques for fluorine are now available and one can even transport liquid fluorine although it is not recommended.

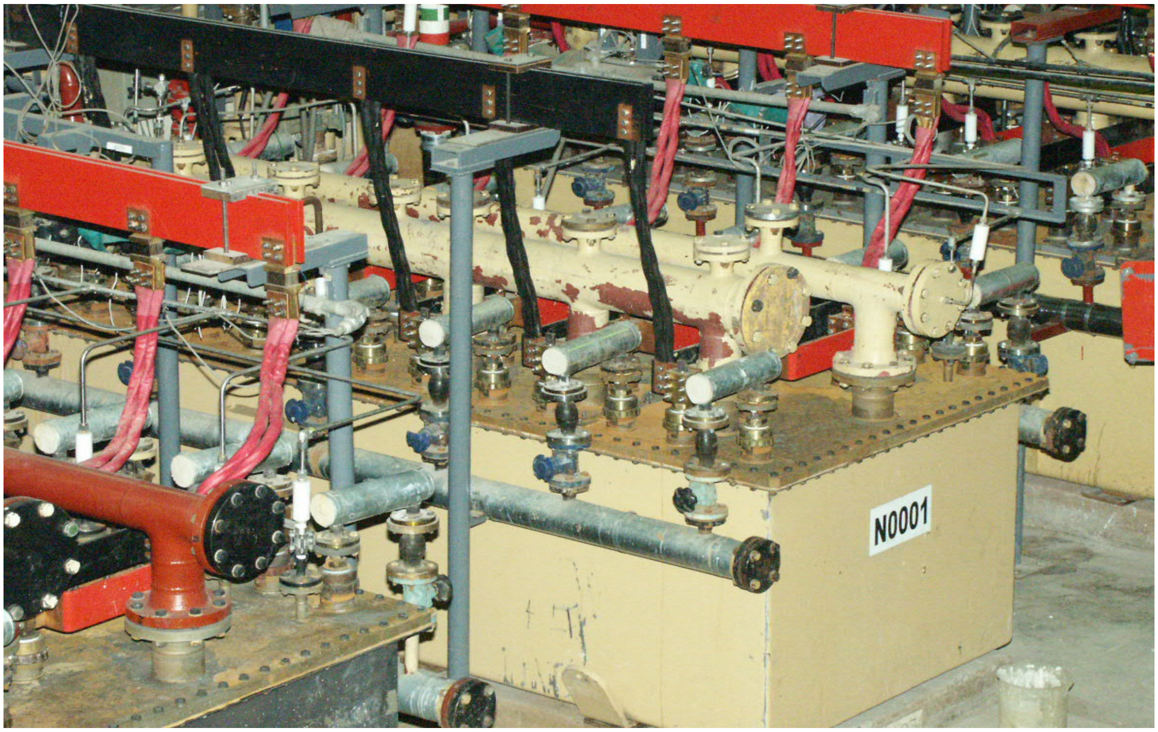


Fig 1.3: Fluorine cell

As the cells are connected to an external power source, a cell and all components connected to it are electrically insulated from the ground to prevent a path for stray currents. Stray currents cause galvanic corrosion inside the cells and lead to the premature failure of components such as the water coils.

1.4 Fluorine cell electrolyte (KF.nHF)

The first electrolysis baths for generating F_2 used pure HF, but the yield was very low. KF.HF was added as an agent to increase the electrical conductivity of the HF. A molten mixture of KF.HF and HF is currently still in use in the electrolysis process in industrial generation of F_2.

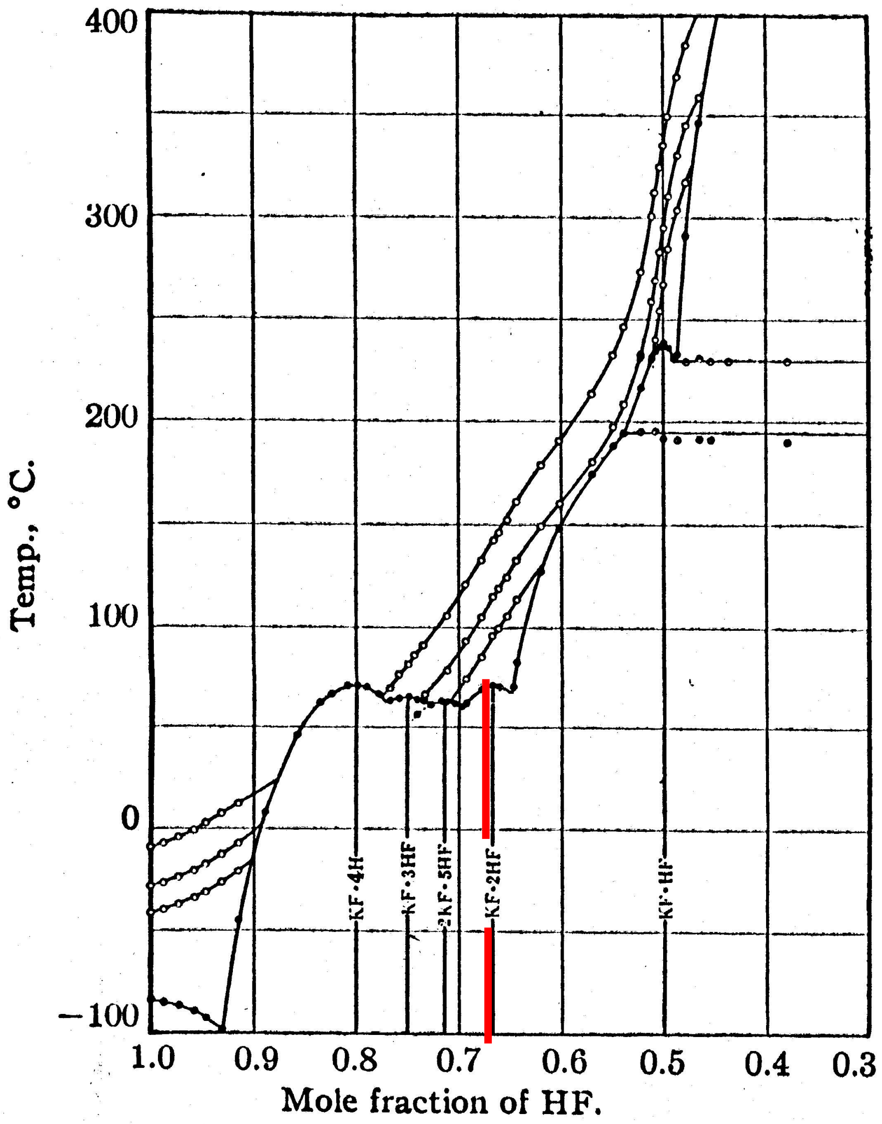
Dry KF.HF in a crystalline form (fine powder) is poured into a make-up vessel and heated with steam while adding additional HF to make a KF.2HF solution referred to further on in this document as electrolyte. The electrolyte make-up vessel is shown below.

Fig 1.4: Electrolyte make-up vessel

The molecular ratio of HF:KF used in industrial F_2 cells is 2:1 (HF 40.8 %(m/m)); with a melting point of 71.7 °C.

1.4.1 Partial pressure of HF over KF.nHF

As early as 1934 Cady(1,20) did a phase study of the system KF/HF and measured the partial pressure of HF over the KF.nHF system, and its variation with temperature. Cady's data is of great importance to the rational design and operation of F_2 cells.



—The system potassium fluoride–hydrogen fluoride: ●, freezing point; ⊖, eutectic point; ◑, transition point; ○, vapor pressure. The highest vapor pressure curve is for a pressure of 25 cm., the middle for 10 cm. and the lowest for 5 cm. of mercury.

Fig 1.5: Melting point/composition diagram for the KF.nHF system (Fig 2, p1432,Cady(20))

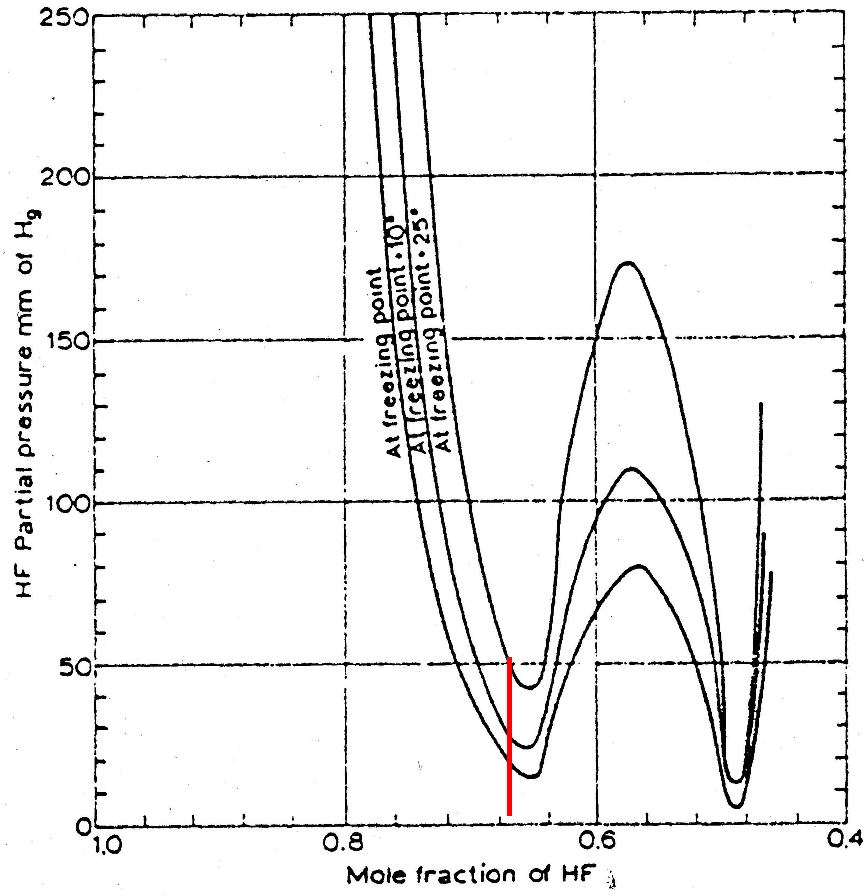


Fig 1.6: Partial pressure of hydrogen fluoride over KF.nHF system: Temperatures near the melting point. (from Fig 3(1))

From figure 1.5 it is clear that an electrolyte with approximate composition KF.2HF has the lowest possible HF partial pressure associated with a convenient and practical operating temperature. The HF concentration in the H_2 usually corresponds to the HF partial pressure over the electrolyte at the temperature and composition existing in the main bulk of electrolyte.

In the case of F_2 in view of a high anodic over voltage the anode surface may be appreciably hotter than the bulk of the electrolyte, especially if most of the F_2 is not discharged in free bubbles. Cady's vapour pressure figures were statistically analysed by Baines and Davies(2) who derived a partial pressure equation from HF as a function of temperature and HF composition:

$$LogP_{HF} = 2.0733 - 4244/T + 0.2975C_{HF} + 47.94(C_{HF}/T) - 0.003785C_{HF}^{2} \ldots.1$$

where:

P is the HF partial pressure in mm Hg
T is the absolute temperature in K
C is the HF concentration in weight %

Fig 1.7 indicates that it is advantageous to operate the F_2 cell at low HF concentrations and low temperatures, to minimize HF losses. From Fig 1.7 it can be seen that an increase of HF concentration from 38% at 80℃ to 41% at 110℃ results in an eight fold increase in HF losses. Low HF concentrations in the electrolyte are associated with a decrease in electrode conductivity hence an increase in the working voltage of the cell. The optimum HF concentration is the mixture KF.2HF.

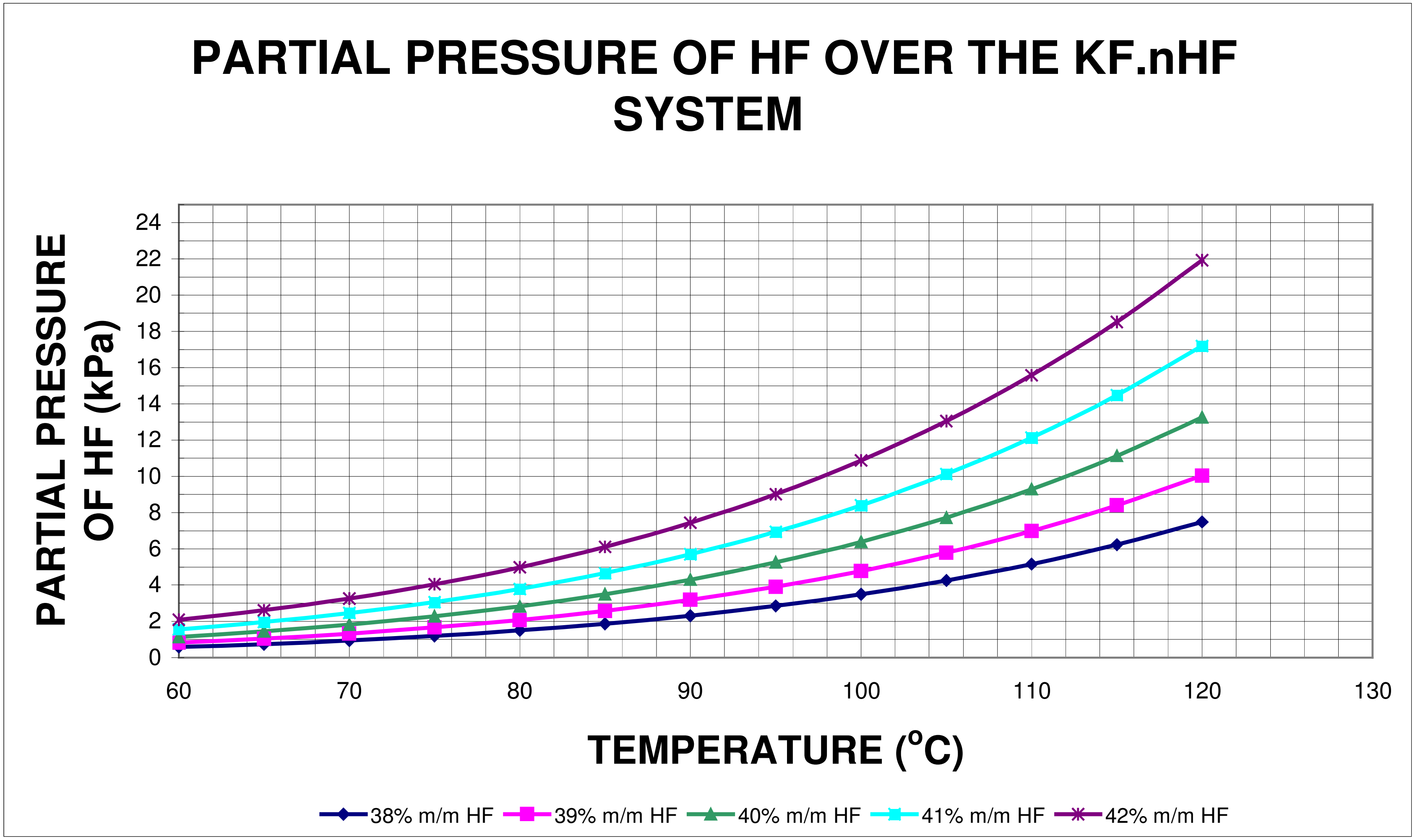


Fig 1.7: Partial pressures of HF over KF.nHF calculated with equation 1

1.4.2 Electrical conductivity (1)

Fig 1A in Appendix A shows the electrical conductivity of the electrolyte as a function of HF concentration and temperature. In order to achieve electrical conduction in the cell KF.HF is added to HF as mentioned in 1.5.1. It is indicated in Fig 1A that an increase in temperature and HF concentration results in an increase in electrical conductivity.

1.4.3 Density(1)

The density of KF.nHF is influenced by temperature as well as HF concentration. The easiest way to prevent high HF concentrations in the cell is by ensuring that the cell is operated at the correct temperature of 85ºC. The addition of HF is automatically controlled through the level indication of the electrolyte. Temperature increase in the cell causes a decrease in electrolyte density thus an increase in electrolyte volume and hence influences the proper addition of HF due to false level indication. The effect of this scenario is that the HF concentration in the electrolyte is less than the optimum 40.8%.

This may cause:

- an increase in the cell voltage;
- a decrease in electrical efficiency;
- an even higher rise in the electrolyte temperature.

Figure 2A in Appendix A illustrates the effect of temperature and HF concentration on the density of electrolyte (HF concentration curves from 40.1% to 41.3% is extrapolated data).

1.4.4 Surface tension(1)

Fig 3A in Appendix A is the surface tension of the electrolyte as a function of HF concentration at 80 and 90 ℃. Fig 3A indicates a linear relationship between surface tension and composition corresponding to a decrease of about 2.5 dyne/cm for each 1% increase in HF concentration. The temperature coefficient appears to be about 0.1dyne/℃. Water up to 3% has only a small effect on the surface tension of mixtures containing 38.5 to 52.1% of HF.

The addition of 2% of lithium fluoride to mixtures containing 39 to 51% of HF and about 1% of water at 80℃ produced small and erratic changes in surface tension (2.5 to 7 dyne/cm). LiF is used in commercial cells as an addition to the electrolyte to promote electrolyte surface tension.

1.4.5 Corrosion in KF.nHF

Electrochemical corrosion due to the applied potential difference over the cell causes corrosion of cell components. Electrochemical corrosion mainly affects the screens and the skirt. The components are subjected to bipolar corrosion where the sides facing the anode act as a cathode and the sides facing the cathode act as an anode.

Erosion corrosion due to the movement of electrolyte causes corrosion mainly on the anode holder bar.

Chemical corrosion due to the corrosiveness of the electrolyte causes corrosion of all cell components in contact with the molten electrolyte and the HF vapour. The corrosiveness of the electrolyte increases as the HF concentration increases.

Figure 4A in Appendix A indicates the Fe concentration as a function of the HF concentration in the electrolyte. The corrosion rate of electrolyte with an HF concentration below 42% is approximately a 10th to a 15th in comparison with a HF concentrations above 42%.

The composition of the electrolyte tends to change with the operational age of a cell because of the precipitation sludge and the solution of metal salts (metal double salts like K_2FeF_5, K_2FeF_6, $KCuF_3$ etc.).

1.4.6 KF.HF specification

The KF.HF specification to the supplier is stated in table 2A in Appendix A.

1.4.7 Hydrogen fluoride (HF)

Hydrogen fluoride is a colourless, corrosive gas or liquid that is made up of a hydrogen atom and a fluorine atom. HF fumes strongly when exposed to air and it dissolves readily in water. HF is a very corrosive and toxic chemical and when personal exposure occurs, it can lead to severe health risks and if not treated correctly HF exposure can be fatal. Nevertheless the HF industry has a very good safety record.

When HF is dissolved in water it is called hydrofluoric acid. Table 3A in Appendix A contains the physical properties of HF. Commercially, hydrogen fluoride is the most important fluorine compound used for the generation of fluorine. A well known application of HF is the etching of glass. Another large use is in the manufacture of fluorocarbons, which are used as refrigerants, solvents, and aerosols.

The used HF in the fluorine cells is manufactured at the Necsa site. The HF plant was built in the early 70s. Moisture and other impurities are removed through distillation, resulting in a > 99% pure product known as anhydrous hydrogen fluoride (AHF). HF used for the feed to cells, i.e. electrolyte make-up, should conform to the specification as indicated in Table 4A in Appendix A.

1.4.8 Electrolyte analysis

The electrolyte is analysed at various stages in its lifetime. The following analyses of electrolyte are done:

1.4.8.1 New electrolyte make up

Once the KF.HF has been poured into the electrolyte make-up vessel additional hydrogen fluoride is added. The mixture is heated to approximately 100℃ and stirred for a time. The newly made electrolyte is then analysed before being transferred to the cell. The new electrolyte is analysed for HF, LiF and Li. LiF is added as a wetting agent for the electrodes

1.4.8.2 Cell conditioning

The electrolyte is very hygroscopic. Water contamination in the newly made up or used electrolyte must be removed to acceptable levels, i.e. less than 500 ppm. The moisture influences the conversion process, (oxi-hydro fluorine bondings occur between the fluorine gas and water that forms a layer on the surface of the anodes and decreases the effective contact area between the electrolyte and the anodes) and accelerate the corrosion in the cell.

A preliminary electrolysis (running the cell at very low current) to electrolyse the water is performed to reduce the water concentration to levels below 500 ppm. Water is electrolysed during this period to form O_2 on the anode and H_2 on the cathode.

1.4.8.3 Normal cell operation

Level measurement alone is not sufficient to control the HF concentration in the cells. The precipitation of the metal salts, the effect of temperature and HF concentration on the density of the electrolyte, and the loss of electrolyte due to carry over of electrolyte in the gas stream all have an influence on the HF concentration of the cell. It is therefore necessary to analyse the electrolyte on a monthly basis to determine the HF concentration.

1.4.8.4 Ad hoc electrolyte analysis

Ad hoc samples are taken from the electrolyte only if quality problems are being experienced with a particular cell.

CHAPTER TWO

2 HEALTH, SAFETY AND ENVIRONMENT

2.1 The Necsa Health, Safety, and Environmental Policy

Necsa is fully aware of the need to avoid causing environmental damage, especially to its beautiful surroundings at Pelindaba, and has embraced the concepts of cleaner technology, recycling, and waste reduction.

Fig 2.1: View over the Hartbeespoort Dam and Magalies Mountains

The Necsa health, safety and environmental policy (6), which incorporates these concepts, was declared some years ago. To date however, no full-scale project has been launched to recover, recycle or reduce the waste electrolyte.

Necsa management and employees are committed to managing the environmental effects of their nuclear, chemical and related activities so as to ensure sustainable development, and to protecting their health and safety, and that of the public, by implementing this policy.

Necsa will

- **continually improve health, safety and environmental (HSE) performance by:**
  - setting performance objectives and targets
  - regularly reviewing performance
  - promoting awareness and motivation, training, commitment and involvement of staff
  - actively reducing the number of HSE related incidents and public concerns
  - identifying and removing barriers to safe behaviour
  - providing the necessary resources to achieve the above goals
- **comply with relevant HSE legislation, national and international standards and other requirements by:**
  - **continuing to manage, reduce, prevent and control wastes, effluents and emissions for nuclear, chemical and other activities**
  - keeping the exposure of personnel and the public as low as reasonably achievable (ALARA)
  - monitoring workplace and environmental impacts
  - conducting internal and external audits
  - **maintaining product stewardship (i.e. taking responsibility for full life-cycle of products)**
- **integrate HSE aspects into business and other activities by:**
  - establishing and documenting an integrated management system, which ensures sustainable development for all HSE aspects
  - utilising the Behavioural Based Safety Process to create and maintain a positive safety culture
  - including HSE aspects in the strategic choices of new business areas
  - conducting risk and HSE assessments prior to establishing new facilities or modifying existing ones
  - providing relevant emergency planning and services
  - **practising recycling, reprocessing and re-use of materials**
  - promoting conservation of energy, water and other resources
- **promote open communication on HSE aspects with stakeholders by:**
  - disclosing all HSE related incidents and information at regular community forum meetings
  - interacting timeously with authorities and the public regarding new facilities
    promoting HSE awareness among staff, contractors, suppliers, lessees, clients and the community.

2.2 Environmental impact of fluorine and fluorides

Although fluorides occur naturally in the earth's crust where they are found in rocks, coal, clay, and soil, the manufacturing of inorganic and organic fluoride compounds has a definite negative and irreversible impact on the environment if not managed correctly.

The most general fluoride compounds found naturally in the earth's crust are calcium fluoride (CaF_2) and sodium aluminium hexafluoride (Na_2AlF_6). Fluorine cannot be destroyed in the environment; it can only change its form.

Most fluoride compounds are very toxic, the toxicity depending on the solubility of the compound in water. The more soluble, the higher the availability of the fluorine ion. Potassium fluoroborate and potassium hexafluoro phosphate are very stable and pose no threat to the environment.

There are other fluoride compounds that are very stable but have a great global warming effect. The problem is that fluoride can easily be released into the air in wind-blown soil. Fluorides that are attached to very small particles may stay in the air for many days. The fluorides released into air are washed out of the air by rain and eventually fall onto land or into water streams.

Naturally, fluorides occur in very small amounts in the air. Typical levels measured in areas around cities are less than 1 microgram of fluoride per cubic meter ($\mu g/m^3$) of air. The amount of fluoride that one breathes in a day is much less than one consumes in food and water.

Natural levels of fluoride in surface water are about 0.2 parts of fluoride per million parts of water (ppm). Levels of fluoride in well water generally range from 0.02 to 1.5 ppm.

The concentration of fluoride in soil is usually between 200 and 300 ppm. However, levels may be higher in areas with fluoride-containing mineral deposits. Higher levels may also occur where phosphate fertilizers are used, where coal-fired power plants or fluoride-releasing industries are located, or near hazardous waste sites.

Necsa monitors on a continual basis for fluorides in its environment. The chemical facilities with potential to release fluorides to the atmosphere monitor their ventilation stacks continuously. Each chemical facility has an air, water and soil permit and has to comply with the conditions of the permits.

The biggest natural source of fluorides released to the air is volcanic eruption. Fluorides released into the atmosphere from volcanoes, power plants, and other high temperature processes are usually hydrogen fluoride gas. Hydrogen fluoride gas is absorbed by rain and fog to form aqueous hydrofluoric acid, and reaches the ground again in that form.

In water, fluorides associate with various elements present in the water. In freshwater streams, fluorides occur mainly as aluminium fluoride bonds. In seawater, fluorides bond mainly with calcium and magnesium.

When fluoride-containing waste is dumped on soil, the fluorides are strongly retained by the soil. Different associations with soil components are formed that are not easily decomposed again. Leaching removes only a small amount of the fluoride from soil. Fluoride may be taken up from soil by plants, and accumulate in them, or soil fluoride may be deposited as dust on the upper parts of plants.

The amount of fluoride taken up by plants depends on the type of plant, the nature of the soil, and the amount and form of fluoride in the soil. Fluoride has been detected in tea plant leaves and some seafood. At Necsa studies were done in the 80s already to determine the impact of fluoride on the environment[18]. It was found that fluoride accumulates on the outside layer of the plant leaves and influences the respiration and photosynthesis of the cells. This can lead to the death of the contaminated plants.

Animals that eat fluoride-containing plants may accumulate fluoride. The direct effect on animals of accumulated fluoride is from the fluoride accumulated in the bones or shell of the animals rather than in edible meat.

From the above paragraphs it should be clear why waste electrolyte, containing so much fluoride that can easily be dissolved in water, is a major source of concern. The possible impact of electrolyte on the environment was one of the reasons why the waste electrolyte was kept under Necsa's control since the start of fluorine generation.

The relatively easy choice of having all the waste electrolyte removed by a waste contractor is not an option that will be easily considered by Necsa. Analytical methods used to determine the levels of fluoride in the electrolyte do not determine the specific form of fluoride present. Some forms of fluoride may be insoluble or so tightly attached to particles or embedded in minerals that they are not taken up by plants or animals and some forms are completely soluble. The fluorides need to be treated first. Should a waste contractor remove the waste it will just be stored in an H:H area for future generations to deal with. Moving the problem from one facility to the other will not give a solution to the problem. Necsa has accepted stewardship for this waste and will try to minimise it.

2.3 Health impact of fluorine and fluorine related products

2.3.1 Fluorine

Fluorine is a pale yellow gas with a pungent, irritating odour. For detail information on the reactivity, toxicity, first aid and personal protection of fluorine see attached Material Safety Data Sheet (MSDS) in Appendix B section 1.

2.3.2 Hydrogen Fluoride

Hydrogen fluoride is a clear, colourless, fuming corrosive liquid or gas with a strong, irritating odour. For detail information on the reactivity, toxicity, first aid and personal protection of hydrogen fluoride see attached Material Safety Data Sheet (MSDS) in Appendix B section 2.

CHAPTER THREE

3 PROBLEM STATEMENT:

There is already more than 110 tons of waste electrolyte (KF.2HF) on the NECSA site contaminated with metal impurities. The expected waste generation per annum is more than 30 tons.

3.1 Impurities in the electrolyte

The impurities of importance in the electrolyte of the Necsa fluorine cells are:

- Metal impurities
- Moisture
- Other impurities

During the operational life of a F_2 cell the process wetted cell components are corroded and eroded.

Corrosion is from the molten cell electrolyte as well as the HF vapour in the vapour space above the electrolyte surface. Erosion is mainly from the H_2 and F_2 gas bubble movement as well as the induced movement of the electrolyte in the cell. The metal components in the cell are the mild steel cathodes, Monel liner, lid and screens and the copper anode holder bars.

3.1.1 Metal impurities

The metal impurities present in the spent electrolyte are Fe, Li, Cu, Cr, Na, Ni and Pb.

The products from the different corrosion and erosion processes are therefore:

- Solid metal particles;
- Dissolved metals as soluble fluorides.

Under normal operational conditions the electrolyte in the cells is replaced because of the high metal content in it. The high metal concentration in the electrolyte affects the lifetime and efficiency of the fluorine cells due to stray electric currents between the suspended metals in the electrolyte and the fluorine cell anodes that lead to galvanic corrosion, increase the viscosity of the melt (thereby making temperature control very difficult) and reduce current efficiency.

Heavy metal contamination such as Pb, although being analysed for in the KF.HF, is not applicable to the Necsa F_2 cells because of the absence of any Pb or other heavy metal in the cell components. LiF is added to the electrolyte as a wetting agent.

3.1.2 The metal impurities of importance in the Necsa fluorine cells are Fe, Cu and Ni.

3.1.2.1 Iron(Fe)

The solubility of the heavy metals with respect to the electrolyte is only a few hundred parts per million, however it was found that Fe could dissolve in the electrolyte to concentration up to 4%(m/m) or 40 000 ppm (8). Fe contamination is mainly caused by the corrosion of the cathodes manufactured from mild steel. The specified Fe concentration in the KF.HF is less than 200 ppm. Most of the problems experienced from metal impurities are Fe related (see paragraph 3.1.1). High dissolved Fe concentrations have the same effect on the viscosity as the Fe particles.

3.1.2.2 Copper (Cu)

Copper contamination is caused by the corrosion of the copper anode holders. Dissolved Cu as copper fluorides has no significant effect on the performance of the cell. However high concentrations of solid Cu particles in suspension may have an adverse effect on the performance of the fluorine cells.

Most of the depleted electrolytes, after being left to settle, have a dark “red” and “purple” sediment at the bottom of the waste containers.

Fig 3.1: Dark “red” and “purple” precipitate

X-ray diffraction analysis (XDA) indicated that the dark “red” and “purple” sediment consisted of the compound $KCuF_3$ and electrolyte. No other crystalline compounds, except electrolyte, were detectable with XDA. Literature references(7) further confirmed with wet chemical quantitative analysis that the sediment was $KCuF_3$, with electrolyte. However the reported colours of this compound are that of light colours, e.g. white, (9) light blue(10) or pale violet (11). The red colour must therefore be from the presence of another compound. The only other reported compounds with a red colour found in F_2 cells, are Ni (IV) compounds(8), but due to the instability of the (+4) oxidation state, Ni(IV) is quickly reduced upon exposure to the atmosphere. No colour change was observed on exposing the red precipitate, ruling out the possibility of a Ni(IV) compound.

A subsequent sample taken from a precipitate on top of the anode holder bar (also called the hanger or bus-bar and above the liquid electrolyte level) was identified by both element analysis and X-ray diffraction to be pure $KCuF_3$ - see Table 3.1 and Fig 3.2. This sample had two layers, a light pink and a light brown layer of a low density. Since this sample was free of electrolyte, a logical conclusion is that this compound is insoluble in electrolyte and is most probably the foam on top of the electrolyte. If this conclusion is correct, this compound should also be present in blockages of the gas manifolds.

	Percentage of the element found in the sample		**Percentage of the element in**
Element	Pink sample	Brown sample	$KCuF_3$
K	25.4	26.7	24.5
Cu	38.7	37.2	39.8
Fe	35.7	34.7	35.7
Si	1.22	1.26	0
Total	101.0	99.9	100.0

Table 3.1: Chemical analysis of precipitate found on top of Cu anode holder bar

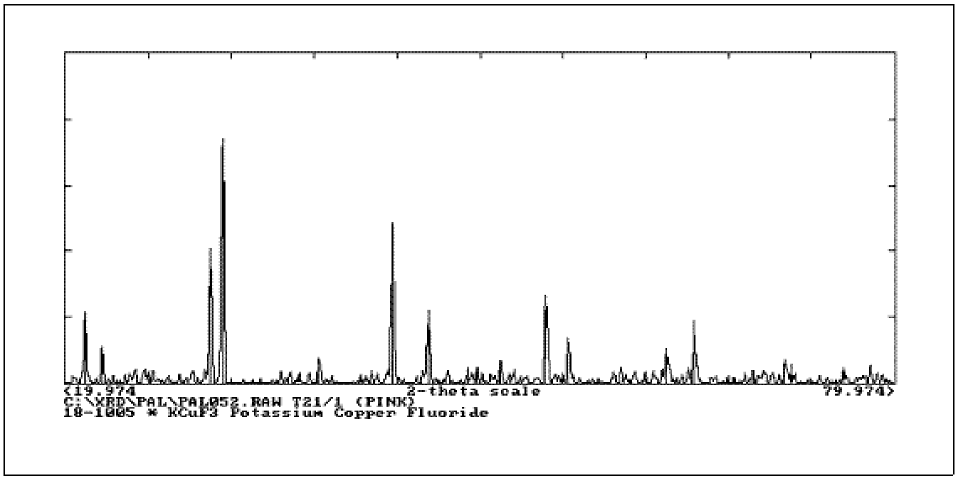


Fig 3.2: X-ray diffraction pattern of pink compound found on Cu anode holder

The finding that Cu is the main metallic element present in the compounds in the sludge, is supported by the visual observation of the extent of the corrosion and erosion of the Cu anode holder bars. Since the corrosion of copper is slower than that of nickel in molten KF·2HF,(12) and since more Ni containing components than Cu containing components are wetted by the electrolyte in Necsa cells, one would expect Ni to be the major metallic component in the sludge. The fact that this is not the case, is a further indication that erosion, and not corrosion, is the major mechanism for Cu dissolution.

3.1.2.3 Nickel (Ni)

Ni contamination in the F_2 cell is the product from the corrosion and erosion of the cell Monel liner, the Monel screens and the skirts. The solubility of Ni in the electrolyte is of the order 100 ppm. High Ni concentrations in the electrolyte are not desirable due high concentrations of Ni particulates causing the effects as discussed in 3.1. Low concentrations of dissolved Ni and Ni particulates are beneficial to the cell operation. Nickel salts in the electrolyte are very effective in reducing the anode/electrolyte contact angle provided that the Ni is in suspension (particles) and in a higher valency state (K_2NiF_6) (1). Water concentration > 0.1% makes it impossible to oxidize the Ni to a higher valency state. The effects of water and Ni are interdependent and effective wetting of the anode can only be achieved with a low water content in the electrolyte.

3.2 Moisture impurities

The electrolyte is very hydroscopic due to the nature of the KF.HF. Water contamination in the used electrolyte must be removed to acceptable levels due to negative impact on cell performance:

3.2.1 Corrosion of metal components

High moisture concentrations in the electrolyte accelerate the corrosion rates of metal components and associated metal contamination of the electrolyte. Corrosion of metal components shortens the life of a cell with the implication of increased production costs.

3.2.2 Induced anode polarization effect

It was discovered if the electrolyte contains less then 0.02% moisture, the F_2 forms a graphite intercalation component (GIC) on the anode surface. GIC having a composition of $C_xF(HF)_y$ is well wetted by the electrolyte. The addition of LiF promotes the formation of GIC, but only if the moisture content is less than 0.02% otherwise the LiF reacts with the water and is unavailable for GIC formation. Too high a moisture concentration in the electrolyte has the effect of a poor wettable CF_2 layer forming on the anode being the main reason for the anode effect.

The LiF is added to the electrolyte to a concentration > 900 ppm (solubility of LiF in KF.2HF at 100℃) to ensure LiF in suspension. The Necsa spec is 0.6% LiF in the electrolyte.

3.2.3 Unwanted gas contamination

Gaseous impurities such as O_2 and OF_2 are formed with the possible formation of CO, CO_2 and CF_4.

3.2.4 Explosion hazard

The oxy-fluoride OF_2 is unstable and can decompose with an explosion.

3.3 Other impurities

It is necessary for the sulphate concentration of the electrolyte to be reasonable low; 2% caused some attack of the anode while 5% resulted in complete disintegration (1) .

Although the carbon anodes in the cell also erode, the carbon contamination in the electrolyte is normally very low.

3.4 Storage of waste electrolyte

The storage of the waste electrolyte is very expensive due to the corrosive and toxic nature of the salt. The depleted or waste electrolyte at Necsa has up to now been contained in specially designed containers. The storage area is inside a building, and the area is bunded to reduce the risk in the event of a release into storm water drains resulting in water contamination. The total amount of waste electrolyte is currently estimated to be more than 110 tons.

Fig 3.3: Solidified electrolyte inside container

Fig 3.4: Storage area inside a building

CHAPTER FOUR

4 LITERATURE REVIEW ON ELECTROLYTE PURIFICATION

4.1 Necsa lab scale sedimentation tests

During 2003 the first set of analyses was done at Necsa on electrolyte obtained from a specific fluorine cell. The cell was operated for 130.6 weeks and was 8985.36 hours in operation. The electrolyte was directly poured into a container at 70℃. The container with electrolyte was put into an oven and left overnight at 70℃. The electrolyte solidified at that temperature and the oven was set at 80℃. The difference in the top and bottom of the electrolyte was clearly visible after being left for a while to melt. Once all the electrolyte was melted again, it was shaken thoroughly to have a homogeneous mixture again. The mixture was sampled and some of the electrolyte was poured into smaller containers to perform the sedimentation tests. The smaller containers were left for different periods of time allowing the metal particulate impurities to settle. Samples were taken at different time intervals and different levels in the sample containers. The time intervals, sample level and test results are indicated in the tables below. The same test was repeated at 85℃ and at 90℃. There was very little change in results with change of temperature from 80 to 90 ℃. Results of the tests done at 80℃ are indicated in Table 4.1. The results obtained in the tests done at 85 and 90 ℃ are indicated in Appendix C. Table 1C and Fig 1C, 2C and 3 C indicate detailed results and graphs of the sedimentation tests performed at 85℃, and Table 2C indicates results of tests performed at 90 ℃.

	Metals	Li (ppm)	Cu (ppm)	Fe (ppm)	Ni (ppm)
Sample number	Sample position from top of container (mm)	Samples taken after 6 hours			
1	18	916	24	3	47
2	55		25	9	44
3	93		24	3	44
4	131		25	3	45
5	170		25	1	49
6	211	869	57	5	69
		Samples taken after 12 hours			
1	18	871	24	5	45
2	55		23	3	57
3	93		24	2	51
4	131		24	4	44
5	170		24	5	46
6	211	839	39	9	57
		Samples taken after 24 hours			
1	18	883	21	3	43
2	55		22	3	43
3	93		21	3	42
4	131		21	3	43
5	170		22	5	45
6	211	846	36	4	57
		Samples taken after 48 hours			
1	18	895	20	11	38
2	55		20	11	39
3	93		18	13	46
4	131		20	11	40
5	170		14	9	36
6	211	753	25	33	55
		Samples taken after 96 hours			
1	18	845	15	3	34
2	55		17	4	37
3	93		15	4	35
4	131		16	4	36
5	170		18	5	43
6	211	1276	23	21	63

Table 4.1: Tests performed at 80°C

4.2 Patents

Little is published with regard to the purification of the electrolyte (KF.nHF). Except for the US patent [(14)], no information could be found on the purification of the electrolyte contaminated with particulates. The only information found on the purification of the electrolyte is patents with regard to the removal of soluble contaminants.

4.2.1 US Patent 2422907 of June 24 1947(14)

This patent describes the treatment of F_2 cell electrolyte with sodium fluoride of sodium bifluoride to precipitate the soluble Fe. The patent describes the mechanism of the reaction of KF with FeF_3 to form a triple salt $NaF.2KF.FeF_3$ (K_2NaFeF_6) which is insoluble in the electrolyte . The patent emphasizes that only the stoichiometric amount of Na salt shall be added (1 atom Na for every 1 atom Fe).

It is also mentioned in the patent that a cleaner interface line of separation was seen between the settled particles and the supernatant solution. This was in contrast to the untreated samples after settling where the interface was not clear.

The resulting precipitate probably carries down other finely divided particles.

It was also found that the yield of finely divided particles depended on the settling time. The patent also mentioned that if the sodium salt is added to the molten electrolyte, the sodium salt tends to become lumpy. This problem is solved by mixing of the Na salt with 2 to 3 times its mass of molten electrolyte to obtain a uniform slurry.

It was found that after a settling times of 16 hours the yield was 60%, after 40 hours 75%, and after 312 hours 86%.

The patent describes 6 examples of the treatment of KF.nHF with a Na salt. In example 1 of the patent KF.2HF contained 4.3% Fe, 2.3% Ni and 0.6% Cu. The molten sample also contained a visible amount of suspended particles. The electrolyte was allowed to settle, 255 g of the settled electrolyte containing 4.2 % of Fe was mixed with 11.9 g of $NaHF_2$ until the $NaHF_2$ was properly dispersed and allowed to settle for 22 hours. The residual suspension was washed with water and filtered. Analysis of the clear supernatant liquid and the filter cake indicated the following:

Component	Clear liquid	Filter cake
Fe	0.28%	17.6%
Ni	0.14%	
Cu	0.14%	
K		33%
Na		8.7%

Table 4.2: US Patent 2422907 test results

4.2.2 Japanese patent 56-179621 of 20 May 1983(15)

This patent claims the purification of a KF.nHF melt (electrolyte) by decreasing the HF concentration to a level of less than 38% (m/m). When the HF concentration is reduced to about 38% the dissolved Fe precipitates as an insoluble $KFeF_4$ salt. The melt should be at a temperature less than 75℃ which is the melting point of an electrolyte with an HF concentration of 38% (m/m). The patent states that when the Fe concentrations is less than 1% it becomes difficult to control the HF concentration and the electrodes frequently disintegrate in a short time. Lowering the HF concentration in the KF.nHF melt (electrolyte) was achieved as follows:

- By the addition of KF or KF.HF (potassium bifluoride).
- By bubbling a dry inert gas such as N_2, He or Ar through the electrolyte to strip the HF.
- By reducing the pressure to sub atmospheric levels above the molten electrolyte to remove the HF, or by a combination of stripping with a dry inert gas while simultaneously reducing the pressure (applying a vacuum to the system).

The patent cited 2 examples to explain their invention. In the first example different quantities of KF was added to KF.2HF melt containing 3,10 % (m/m) Fe and 104 ppm Ni to represent different HF concentrations. The solutions were stirred while at 100 to 130℃, and left to stand for 20 hours before the supernatant solution was analysed. Over the HF concentration range from

40,8 % (m/m) to 34 %(m/m) the Fe concentration was reduced from 3.1 % (m/m) to 0.008 % (m/m) while the soluble concentration dropped from 104 ppm to 20 ppm.

In the second example different quantities of nitrogen gas were blown through KF.2HF melt at 110 to 130 °C to obtain different HF concentrations. After standing for 20 hours the supernatant was analysed. Over the HF concentration range from 41.8% (m/m) to 34.2% (m/m) the Fe concentration was reduced from 2.95 % (m/m) to 0.010% (m/m) while the soluble Ni concentration dropped from 107 ppm to 22 ppm.

The electrolyte samples used to perform these tests were not obtained from industrial F_2 cells but were made up in a laboratory. The effect of other contaminants in the electrolyte is therefore not clear. It is also not clear how dry the samples were and what the effect of moisture in the electrolyte could have on the test.

4.2.3 Japanese patent abstract JP 59-247939 of June 1986(16)

This patent claims the purification of F_2 cell electrolyte KF.nHF through the addition of a sodium (Na) compound to precipitate some of the dissolved Fe. The patent states that the Fe can dissolve in the electrolyte in large quantities up to 4% (m/m) and that it is not advisable to operate a F_2 cell with Fe concentrations exceeding 0.5% (m/m) since severe electrode damage occurs at Fe concentrations exceeding 0.5 % (m/m). NaF, NaOH or Na_2SiF_6 is added to the molten electrolyte at a temperature higher than the melting point of the KF.nHF (>75°C).

The amount of Na salt to be added should be equivalent to the stoichiometric quantity to produce the insoluble triple salt K_2NaFeF_6. Excess Na salts will dissolve in the electrolyte and may render the electrolyte unsuitable for F_2 electrolysis. The patent also claims a process for continuous removal of the precipitated Fe. The patent claims that the addition of Na salt also precipitates some of the dissolved Cu and Ni. Two experimental examples were included to illustrate the claims:

In the first example different quantities of NaF were added to 1 kg of a KF.2HF sample containing 0.33% (m/m) Fe. The solutions were stirred, left to stand at 100℃ for 5 hours and the supernatant solution analysed. The test results are indicated in Table 4.3

Amount of NaF added. NaF/KF.2HF	Fe concentration before adding NaF (ppm)	Fe concentration after adding NaF (ppm)	Na concentration after adding NaF (ppm)	Sampling temperature ℃
0.0 wt %	3300	-	-	100
0.1 wt %	3300	1754	50	100
0.5 wt %	3300	625	50	100
0.5 wt %	3300	13	110	100
1.0 wt %	3300	5	1650	100

Table 4.3: Result of example 1 of JP 59-247939

In the second example 0.0011g of NaOH was added to a similar sample as example 1 at 85℃ the solution was stirred for 30 minutes, left to stand for 5 hours and the supernatant solution was analysed.

Amount of NaOH added.	Fe concentration before adding NaOH	Fe concentration after adding NaOH	Na concentration after adding NaOH	Sampling temperature
0.0011 g	3300 ppm	35 ppm	10 ppm	85℃

Table 4.4: Result of example 2 of JP 59-247939

As in the previous patent the electrolyte samples used to perform these tests were not obtained from industrial F_2 cells but were made up in a laboratory. Therefore also in this patent the effect of other contaminants in the electrolyte is not clear. It is also not clear how dry the samples were and what the effect of moisture in the electrolyte could have on the test.

4.2.4 European Patent EP 0608087A2 of 17 January 1994 (17)

(Also US Patent 5840266 of 24 November 1998)

This patent claims the dehydration of a wet KF.nHF ($2.2 \leq n \leq 1.8$) mixture or F_2 cell electrolyte by a method of passing an inert gas (N_2 in this case) through the molten electrolyte at temperatures ranging from 80 to 100 °C for a period of time.

The patent also claims that the process of bubbling N_2 gas through a KF.nHF mixture can be applied as a method to purify HF. The patent claims that HF concentrations containing up to 60 % (m/m) of what can be treated in this way, stripping large amounts of H_2O without the loss of substantial amounts of HF. The patent indicated that their results suggested that the partial vapour pressure of the H_2O above the aqueous HF solution is much greater than that of HF and that H_2O as the more volatile component may be removed preferentially from the mixture.

The results of HF concentration change with time appears to describe a linear relationship (0.3%/h) while the H_2O loss with respect to time is non linear. The results of several experiments were presented as examples indicating that the water content of the mixture can be reduced from 10% to 1.5% (m/m) with a reduction in HF concentration from 40.8 to 39.2% over a period of 9 hours.

In another experiment a KF.nHF mixture containing 5.8% (m/m) H_2O was sparged with N2 for 10 hours after which the H_2O concentration was 0.05% (m/m) and the HF concentration in the KF.nHF 35.8% (m/m).

CHAPTER FIVE

5 SCOPE:

This research is primarily focussed on the development of a process to remove solid metal particles in the crude Necsa waste fluorine cell electrolyte to acceptable levels. The secondary focus is to investigate technologies to reduce the soluble metal concentration, especially the soluble Fe content, to below the specified levels of 200 ppm (m/m). In the secondary focus, novel technologies will be investigated with the primary method to reduce the soluble Fe to acceptable levels.

The scope of the document is the following:

5.1 Investigation of existing technologies to remove metal impurities:

5.1.1 Removal of solid metal impurities by means of:

- sedimentation; and
- filtration.

5.2 Investigation of novel technologies:

5.2.1 Centrifuging to remove solid metal impurities.

5.2.2 Decrease of the solubility of metallic impurities by reducing the HF concentration (by adding KF, or by stripping the HF with an inert gas), followed by filtration.

5.2.3 Addition of NaF or NaOH to precipitate soluble metal impurities as insoluble triple salts.

5.3 Moisture removal investigation:

5.3.1 Stripping of the moisture in the electrolyte with an inert gas.

5.4 Experimental strategy.

The strategy with the different experiments is the following:

5.4.1 Experimental confirmation of the sedimentation tests done by Necsa using waste electrolyte with a very high concentration of metal impurities.

5.4.2 Filtration tests on waste electrolyte with different concentrations of metal impurities.

5.4.3 Filtration tests on waste electrolyte treated by lowering the HF concentration in the electrolyte by means of :

- Dry N2 gas sparging;
- Addition of KF.HF.

5.4.4 Filtration tests on waste electrolyte treated with NaOH to form an insoluble triple salt K_2NaFeF_6.

5.4.5 Centrifuging tests on waste electrolyte with different concentrations of metal impurities.

5.4.6 Centrifuging tests on waste electrolyte treated by lowering the HF concentration in the electrolyte by means of :

- Dry N2 gas sparging;
- Addition of KF.HF.

5.4.7 Centrifuging tests on waste electrolyte treated with NaOH to form an insoluble triple salt K_2NaFeF_6.

5.4.8 Moisture removal through stripping with an inert gas followed by:

- Filtration; and
- Centrifuging.

5.5 Implementation

5.5.1 Process synthesis from interpretation of experimental results – Block flow diagram.

5.5.2 Mass and energy balance – Process flow diagram.

5.5.3 Economic evaluation of process.

CHAPTER SIX

6 TEST FACILITY

6.1 Safety

Due to the presence of HF the research studies were done under the prescribed safety standards applicable for working in an HF environment.
A Preliminary Risk Assessment was performed during which exposure to HF gas and diluted HF liquid were identified as the main concerns. An area justification was done identifying an area close to the fluorine generation facilities as the most suitable place. It implied that certain services could be shared such as scrubber extraction, steam, building ventilation, compressed nitrogen, instrument and breathing air, and electricity. Sharing the ventilation implied that should there be any emissions, these will be measured by the already installed instrumentation of the fluorine generation facility to serve as the record required by the air pollution permit. It was also cost effective to share the utilities and other services.

The test facility was built as far as reasonably possible according to the Necsa specifications for HF. The layout of equipment was done in such a way as to minimize the risks of being exposed. Personal protective equipment was used during the tests as a secondary line of defense should any emissions occur.

Fig 6.1 indicates the PPE used during the test runs. A full air suit with fresh air supply was worn during the sampling of the molten electrolyte and at any point in time where exposure to the molten electrolyte was possible.

Because of the nature of the samples being a solid salt at room temperature the risk of handling is much lower than the molten salt handled during the test runs. The handling of samples required the wearing of chemical resistant gloves, a long sleeve over coat and safety glasses. Fig 6.2 indicates the PPE used during the runs.

Fig 6.1: PPE used during test runs

Fig 6.2: PPE used during sample analysis

6.2 Description of test facility

(See Fig 6.6: Process flow diagram of test facility)

6.2.1 Equipment description

The test facility comprises the following:

Item	Description
Melt vessel MV-01	1350 mm long, 102.26 mm inside diameter stainless steel electrolyte melt vessel equipped with a mild steel steam jacket. The vessel is equipped with removable top and bottom flanges. Vessel volume 11.1 litres.
Filter housing FS-01	520 mm long, 108.2 mm inside diameter stainless steel filter housing equipped with 880 W electrical clamp-on heater.
Filter housing FS-02	520 mm long, 108.2 mm inside diameter stainless steel filter housing equipped with 880 W electrical clamp-on heater.
Monel filter F-01	20 micron Monel candle filter, inside diameter 65 mm, 460 mm long.
PTFE filter F-02	3 micron sintered PTFE candle filter, inside diameter 60 mm, 465 mm long.
Dry scrubber S-01	490 mm long, 90 mm diameter stainless steel dry scrubber filled with 3.5 kg of dry limestone pellets. Scrubber volume is 3.1 litres.
Rotameter FI-01	Nitrogen gas rotameter with a flow range of 0 to 172 l/min @ 230 kPa(a)
Pressure indicator PI-01	Melt vessel pressure indicator with a pressure range of 0 to 800 kPa
Temperature indicator TI-01	Melt vessel temperature indicator
Temperature indicator controller TIC-01	Monel filter housing clamp-on heater temperature controller
Temperature indicator controller TIC-02	PTFE filter housing clamp-on heater temperature controller
Piping	½" and 3/8" Stainless steel tubing with "Swagelock" fittings.
Valves	½" ball valves and 3/8" needle valves
Heating tape	60 Watt electrical self limiting trace heating on vessels and piping where possible.
Insulation	Hot thermal insulation on all vessels and piping where possible.

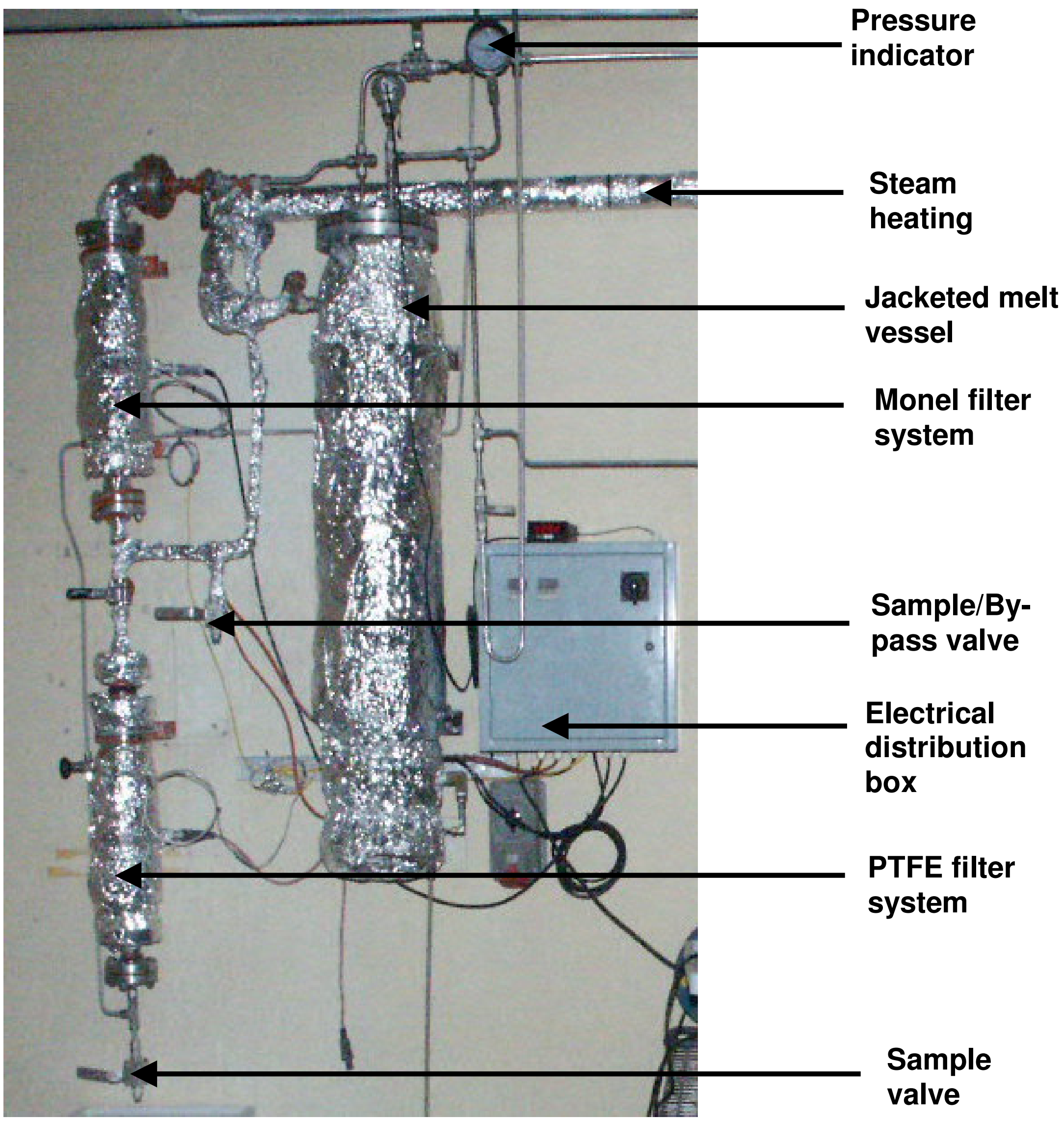


Fig 6.3: Test facility

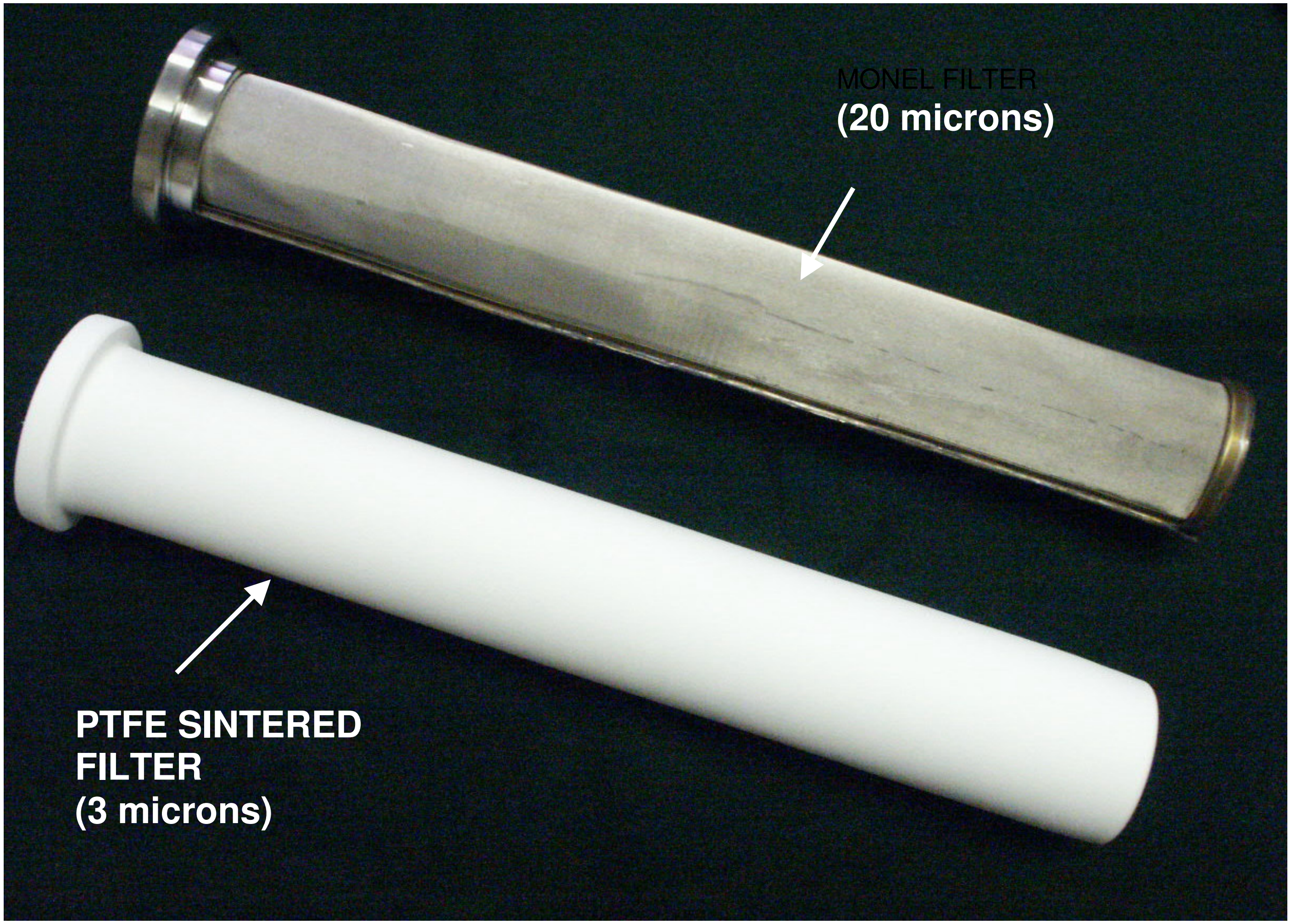


Fig 6.4: Monel and Teflon Filters

6.2.2 Test facility interfaces

Figure 6.5 indicates the systems that interface with the test facility.

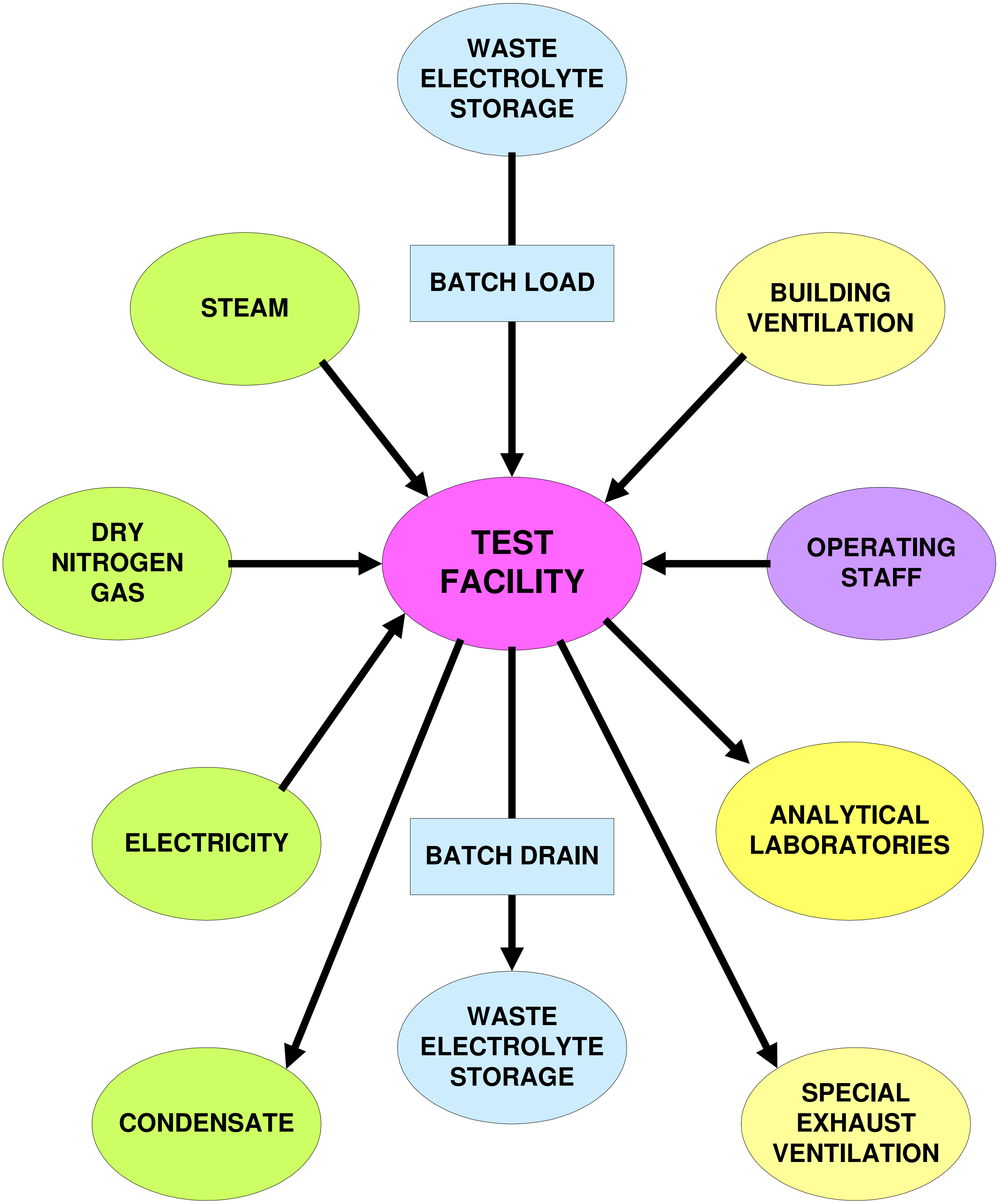


Fig 6.5: Interface diagram of test facility

6.2.3 Process description

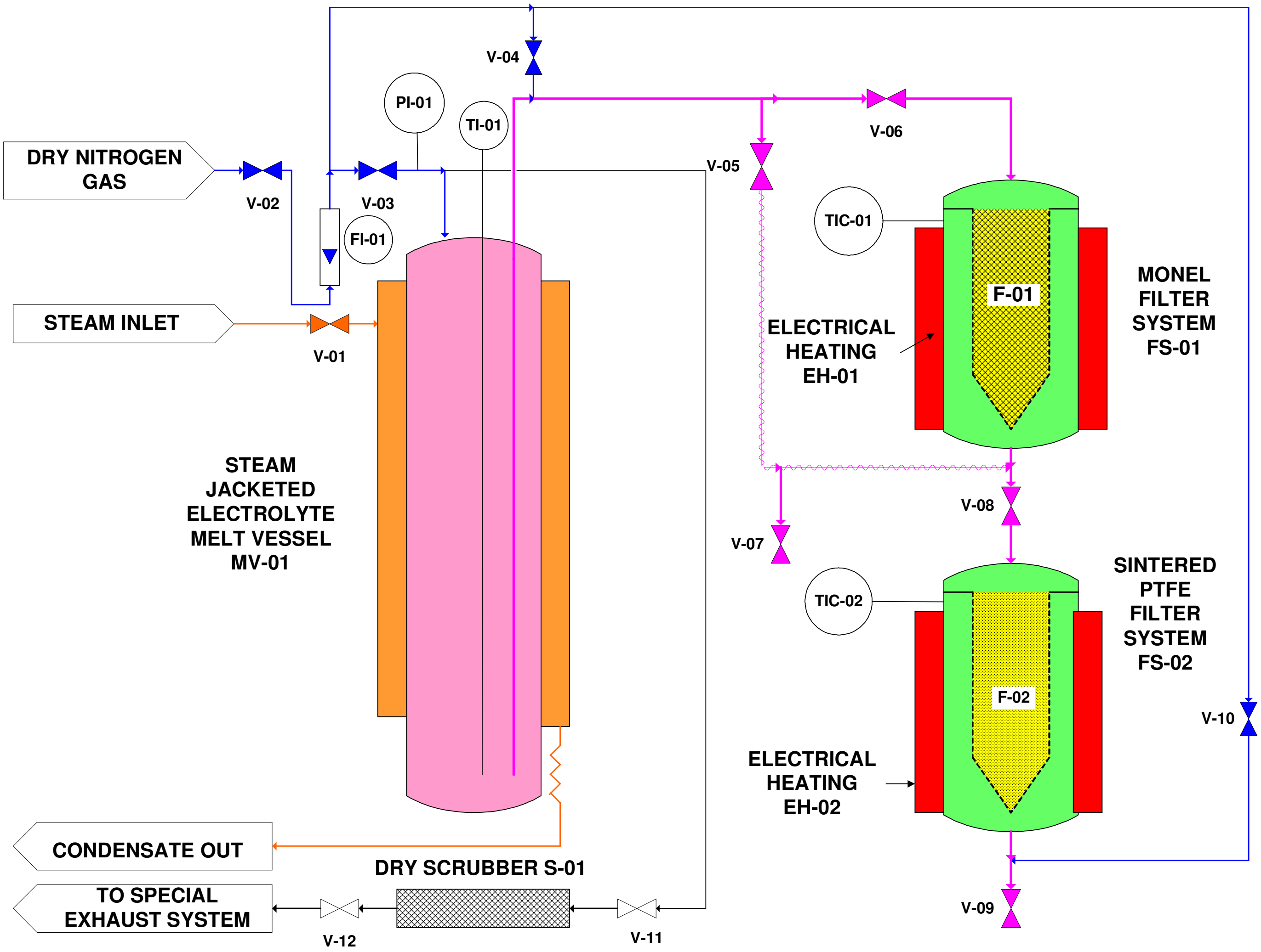


Fig 6.6: Process flow diagram of test facility

Between 7 and 7.5 kg of waste electrolyte was loaded from the top into the melt vessel. The vessel was heated via the jacket with steam at 135℃. The filter housings were heated with clamp-on electrical heater with a temperature controlled at 95℃. The trace heating was controlled at 95℃ via the clamp-on heater temperature controllers. Once the molten electrolyte in the melt vessel reached a temperature of more than 100℃ the melt vessel was pressurized with nitrogen gas to a pressure of 200kPa(g). The molten salt to be used as a batch reference sample was sampled before introducing it to the filter systems. Samples were taken after the Monel filter as well as after the PTFE filter.

The electrolyte samples were allowed to thaw before being sent to be analyzed.

During experiments done on the stripping of the HF and moisture removal, nitrogen gas was bubbled through the molten salt via the reactor dip tube. The stripped HF and moisture were trapped in the dry limestone scrubber.

During most of the centrifuge tests the molten electrolyte was taken from the melt vessel via the by-pass valve and did not flow through the filter systems. These samples were centrifuged while the electrolyte was still in a molten form.

The molten electrolyte used in the sedimentation test was obtained from the melt vessel through the same route used for the centrifuge tests.

6.3 Commissioning

Cold commissioning comprised:

- Leak testing to test the integrity of the connection and equipment.
- Simulation run with nitrogen gas to test calibration of the instrumentation.
- Identification of possible exposure scenarios before the introduction of the first electrolyte to the test facility.
- Selection of personal protective equipment suitable for the handling of HF.

6.4 Operation

(See Fig 6.6: Process flow diagram of test facility)

6.4.1 Filtration tests: Untreated electrolyte

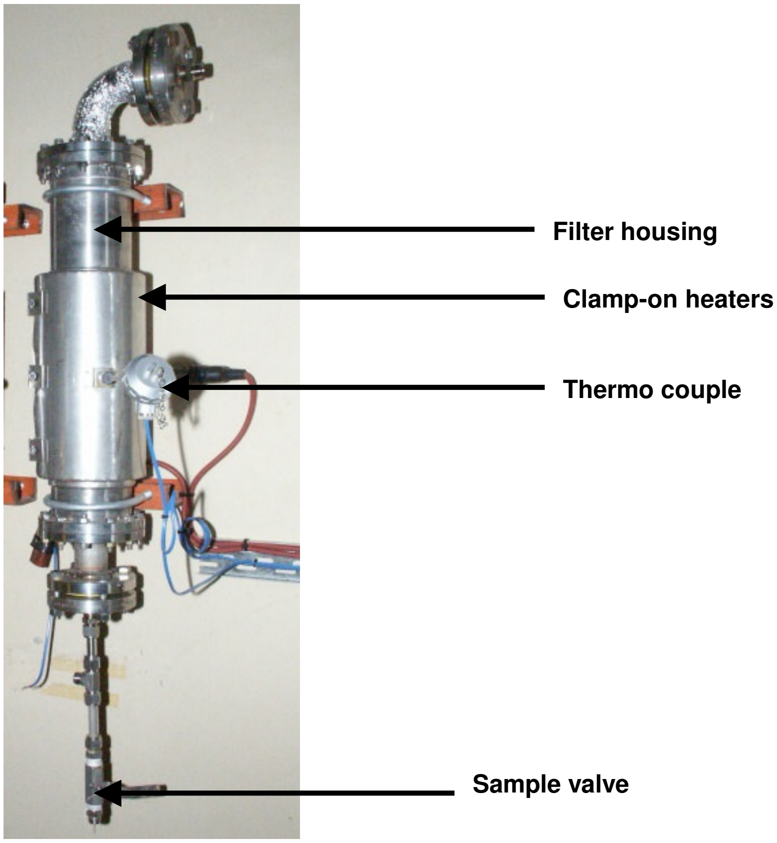


Fig 6.7: Filter system

Electrolyte was obtained from the stored solidified batches. The electrolyte stored had been drained into the storage containers from the fluorine cells and allowed to cool down. During the cooling down process sedimentation of the impurities had taken place. This sedimentation was clearly visible in some of the waste containers. Even if the electrolyte from one cell were to be used for all the tests, the electrolyte would not be homogeneous throughout all the runs. To ensure that the whole spectrum of waste electrolyte would be covered during this research very “dirty” (visually observed) and “not so dirty” electrolyte was used for the tests. As indicated previously the sediment was clearly visible on the bottom of some of the containers and some electrolyte was visibly dirty throughout.

7 to 7.5 kg of solidified electrolyte was crushed, the top flange of the jacketed melt vessel MV-01 was removed and the electrolyte was introduced into the vessel. The top flange was fitted and tightened. A leak test was performed to ensure that the flange was leak tight.

It was ensured that all the valves on the test facility were in a closed position.

Steam was introduced into the melt vessel jacket by slowly opening valve V-01 on the steam inlet to the jacket. The clamp-on electrical heaters EH-01 on the Monel filter system and EH-02 on the PTFE filter system were switched on and the temperature controllers were set at 95℃. The electrical tracing was switched on automatically with the clamp-on electrical heaters.

The electrolyte was allowed to heat for approximately two hours before the run. The temperature varied between 116 and 132℃ as indicated by TI-01 on the Melt vessel. Nitrogen was introduced into the reactor through the dip tube by opening valves V-02 and V-04, to ensure that the dip tube was not blocked and to determine if all the electrolyte was melted. The dip tube was about 20 mm from the bottom of the reactor.

The reactor was pressurized to 200 kPa(g) as indicated on PI-0, by opening valves V-02 and V-03 on the nitrogen supply line. Once the desired pressure was reached the nitrogen valves V-02 and V-03 were closed. Valve V-05 was opened to transfer the electrolyte via the tubing into the filter by-pass line. A reference sample was taken by slowly opening valve V-07. It was necessary to heat some of the piping and valves that were not traced as well as the top and bottom of the filter housings with a hot air blower to enhance the flow of the molten electrolyte through the system.

Valve V-05 and V-07 were closed and V-06 opened to allow electrolyte to flow into the Monel filter system FS-01. Valve V-07 was opened to take a electrolyte sample from the Monel filter. Once the desired sample had been taken valve V-07 was closed.

Valve V-08 was opened to allow the molten electrolyte in the Monel filter system to enter the PTFE filter system. It was necessary for intense hot air blower intervention to ensure that the electrolyte passed through the PTFE filter system. Valve V-09 was opened to take a sample of the electrolyte through the PTFE filter system.

The samples were captured in poly-ethylene sample bottles specially prepared to minimize moisture and other possible contamination. The sample bottles were rinsed with steam and left for a couple of hours in an oven at 60℃ to dry.

Once the sample through the PTFE filter system had been taken the system was emptied into a waste electrolyte container. The heating on the system was sustained for another 15 minutes while purging the system with nitrogen to prevent contamination between different batches. After the nitrogen purging had been completed al the valves were closed and the electrical supply to the test facility was isolated until the next run. The Monel and PTFE filter cartridges were changed after each set of tests.

6.4.2 Filtration tests: KF.HF addition

The amounts of electrolyte and KF.HF needed to make up a 7.5 kg electrolyte batch of a specific HF concentration are indicated in Table 6.1. Table 1D in Appendix D is the calculation of the KF.HF required to make up a batch of electrolyte with a specific HF concentration.

HF concentration % (m/m)	**40.8**	**39.5**	**39**	**38.5**	**38**
Mass of KF.HF (kg)	0	0.63	0.88	1.12	1.37
Mass of waste electrolyte (kg)	7.5	6.87	6.62	6.38	6.13
Total mass of batch (kg)	7.5	7.5	7.5	7.5	7.5

Table 6.1: KF.HF required to obtain defined HF concentrations.

For each of the electrolyte batches at different HF concentrations the operational procedure was similar to that described in 6.4.1 for untreated electrolyte. Measurements of the HF concentration of the reference sample as well as the other samples were done to verify the HF concentrations.

6.4.3 Filtration tests: Stripping with inert gas

The dry scrubber S-01 was filled with limestone and valve V-11 and V-12 closed. The required limestone mass was calculated as indicated in Table 4D in Appendix D.

Fig 6.8: Limestone scrubber

The operating procedure described in 6.4.1 was followed up to the point where the electrolyte was allowed to heat for approximately two hours.

Valves V-02, V-04, V-11 and V-12 were opened to allow dry nitrogen gas to bubble through the electrolyte. The flow indicated on the rotameter FI-01 was set at 10% at a melt vessel MV-01 pressure of 120 kPa(g) (PI-01) by adjusting valves V-04 and V-11. The 10 % rotameter setting is equivalent to a nitrogen flow rate of 17 l/min, which is the calculated value to strip the HF in the electrolyte from a concentration of 41.5 % to 39% in an hour. The calculation of required nitrogen flow through the dip tube is indicated in Table 2D in Appendix D.

Fig. 6.9: Rotameter float position

After purging the electrolyte with nitrogen for an hour the reactor was pressurised to 200 kPa(g) by closing valve V-11. Once the desired pressure had been reached the nitrogen valves V-02 and V-03 was closed. Valve V-05 was opened to transfer the electrolyte via the tubing into the filter by-pass line. A reference sample was taken by slowly opening valve V-07. It was necessary to heat some of the piping and valves that were not traced as well as the top and bottom of the filter housings with a hot air blower to enhance the flow of the molten electrolyte through the system.

Valves V-05 and V-07 were closed and V-06 opened to allow electrolyte to flow into the Monel filter system FS-01. Valve V-07 was opened to take an electrolyte sample from the Monel filter. Once the desired sample had been taken valve V-07 was closed.

Valve V-08 was opened to allow the molten electrolyte in the Monel filter system to enter the PTFE filter system. It was necessary for intense hot air blower intervention to ensure that the electrolyte passed through the PTFE filter system. Valve V-09 was opened to take a sample of the electrolyte through the PTFE filter system. The HF concentrations of each of the samples were determined before the samples were sent for metal analysis.

The samples were captured in polyethylene sample bottles specially prepared to minimize moisture and other possible contamination. The sample bottles were rinsed with steam and left for a couple of hours in an oven at 60℃ to dry.

Once the sample through the PTFE filter system had been taken the system was emptied into a waste electrolyte container. The heating on the system was sustained for another 15 minutes while purging the system with nitrogen to prevent contamination between different batches. After the nitrogen purging had been completed all the valves were closed and the electrical supply to the test facility was isolated until the next run.

6.4.4 Filtration tests: Addition of NaOH

One gram of NaOH was added to the crushed electrolyte after loading the electrolyte into the reactor. The one gram of NaOH added is the stoichiometric requirements for converting the soluble Fe concentration of 200 ppm to the insoluble triple salt. For the calculation see Table 5D in Appendix D.

The top flange was fitted and tightened. A leak test was performed to ensure that the flange was leak tight.

It was ensured that all the valves on the test facility were in a closed position.

Steam was introduced into the melt vessel jacket by slowly opening valve V-01 on the steam inlet to the jacket. The clamp-on electrical heaters EH-01 on the Monel filter system and EH-02 on the PTFE filter system were switched on and the temperature controllers were set at 95℃. The electrical tracing was switched on automatically with the clamp-on electrical heaters.

The electrolyte was allowed to heat for approximately two hours before the run started. The temperature varied between 116 and 132°C as indicated by TI-01 on the melt vessel. The electrolyte in the melt vessel was stirred for 15 minutes by bubbling dry nitrogen gas through the molten electrolyte via the dip tube. Nitrogen was introduced into the reactor though the dip tube by opening valves V-02 and V-04. Valves V-11 and V-12 were opened to the dry scrubber. The flow indicated on the rotameter FI-01 was set at 10% by adjusting valves V-04 and V-11.

After 15 minutes of stirring the electrolyte with nitrogen the reactor was pressurized to 200 kPa(g) by closing valves V-11. Once the desired pressure had been reached the nitrogen valves V-02 and V-03 were closed. Valve V-05 was opened to transfer the electrolyte via the tubing into the filter by-pass line. A reference sample was taken by slowly opening valve V-07. It was necessary to heat some of the piping and valves not traced as well as the top and bottom of the filter housings with a hot air blower to enhance the flow of the molten electrolyte through the system.

Valves V-05 and V-07 were closed and V-06 opened to allow electrolyte to flow into the Monel filter system FS-01. Valve V-07 was opened to take a electrolyte sample from the Monel filter. Once the desired sample had been taken valve V-07 was closed.

Valve V-08 was opened to allow the molten electrolyte in the Monel filter system to enter the PTFE filter system. It was necessary for intense hot air blower intervention to ensure that the electrolyte passes through the PTFE filter system. Valve V-09 was opened to take a sample of the electrolyte through the PTFE filter system. The HF concentrations of each of the samples were determined before the samples were sent for metal analysis.

The samples were captured in polyethylene sample containers specially prepared to minimize moisture and other possible contamination. The sample bottles were rinsed with steam and left for a couple of hours in an oven at 60°C to dry.

Once the sample through the PTFE filter system had been taken the system was emptied into a waste electrolyte container. The heating on the system had been sustained for another 15 minutes while purging the system with nitrogen to prevent contamination between different batches. After the nitrogen purging was completed all the valves were closed and the electrical supply to the test facility was isolated until the next run.

6.4.5 Centrifuging tests: Untreated electrolyte

The operating procedure described in 6.4.1 was followed up to the point where the electrolyte was allowed to heat for approximately two hours. The temperature varied between 116 and 132°C as indicated by TI-01 on the melt vessel. Nitrogen was introduced into the reactor through the dip tube by opening valves V-02 and V-04, to ensure that the dip tube was not blocked and to determine if all of the electrolyte was melted. The reactor was pressurized to 200 kPa(g) as indicated on PI-01.

Once the desired pressure had been reached the nitrogen valves V-02 and V-04 were closed. Valve V-05 was opened to transfer the electrolyte via the tubing into the filter by-pass line. A sample was taken by slowly opening valve V-07.

This sample was poured into four centrifuge tubes all have equal volumes to ensure that the centrifuge is balanced. The four tubes were placed into the centrifuge and rotated for approximately 10 minutes at approximately 10 000 rpm. The four tubes were kept in an oven at 60 °C before the molten electrolyte was poured into the tubes to ensure that the electrolyte remained in the molten state long enough to complete the spinning sequence. The rest of the electrolyte sample was prepared and kept as a pre-centrifuge reference sample to be analysed for HF and the metals.

Fig 6.10: Centrifuge used during tests

After 10 minutes the four tubes were removed and the supernatant electrolyte at the top of the tubes was removed and prepared in sample containers for analysis. The visible sediment at the bottom of the tubes was also removed and prepared in different sample containers for analysis.

6.4.6 Centrifuging tests – KF.HF addition

The operating procedure described in 6.4.2 was followed up to the point where the electrolyte reference sample was taken. The reference sample was large enough to be centrifuged.

Equal quantities of the sample were poured into 4 tubes to ensure that all four have equal volumes. The four tubes were placed in the centrifuge and rotated for approximately 10 minutes. The 4 empty tubes were kept in a oven at 60 °C before the molten electrolyte was poured into the tubes to ensure that the electrolyte stayed in the molten state long enough to complete the spinning time. The rest of the electrolyte sample was prepared and kept as reference sample to be analysed.

After 10 minutes the four tubes were removed and the supernatant electrolyte at the top of the tubes was removed and prepared in sample containers for analysis. The visible sediment at the bottoms of the tubes were also removed and prepared in different sample containers for analysis.

6.4.7 Centrifuging tests: Stripping with inert gas

The operating procedure described in 6.4.1 was followed to the point where the electrolyte was allowed to heat for approximately two hours.
The dry-scrubber S-01 was filled with new limestone to ensure proper scrubbing during the entire run.

Valves V-02, V-04, V-11 and V-12 were opened to allow dry nitrogen gas to bubble through the electrolyte. The flow indicated on the rotameter FI-01 was set at 10%, at a melt vessel MV-01 pressure of 120 kPa(g) (PI-01), by adjusting valves V-04 and V-11. The 10 % rotameter setting is equivalent to a nitrogen flow rate of 17 l/min.
After 30 minutes of stripping, valve V-11 was closed and the pressure in MV-01 was allowed to rise to 200kPa. Once the desired pressure on PI-01 had been reached the nitrogen was isolated by closing valves V-04 and V-02.

A reference sample was taken by opening valve V-05 and then slowly opening valve V-07. The reference sample was large enough to be used in the 4 tubes of the centrifuge. This sample was poured into four tubes with all four having exact volumes. The 4 tubes were placed into the centrifuge and rotated for approximately 10 minutes. The 4 empty tubes were kept in an oven at 60 °C before the molten electrolyte was poured into the tubes to ensure that the electrolyte remained in the molten state long enough to complete the spinning phase. The rest of the electrolyte sample was prepared and kept as pre-centrifuged reference sample to be analysed for HF and the metals. The HF concentrations of all the samples was determined.
Valves V-05 and V-07 were closed, and the pressure on melt vessel MV-01 was released to atmospheric pressure by opening valve V-11 through the dry scrubber. Nitrogen was introduced to the melt vessel again to continue the

stripping process. This was done in exactly the same way as described previously for nitrogen stripping under filtration tests.

6.4.8 Centrifuging tests: Addition of NaOH

The operating procedure described in 6.4.1 was followed to the point where the electrolyte was allowed to heat for approximately two hours. These tests were carried out at exactly the same time as the filter test with the addition of NaOH was conducted. When the reference sample for the filter test was taken the sample was large enough to pour some molten electrolyte into the centrifuge tubes to be centrifuged in the same manner as prescribed in 6.4.5. The same principle was applied when the samples for the Monel and PTFE filter systems were taken. Out of each of these samples some of the molten electrolyte was poured into the centrifuge tubes and centrifuged according to procedures described in 6.4.5.

6.4.9 Sedimentation

The operating procedure described in 6.4.1 was followed to the point where the electrolyte was allowed to heat for approximately two hours. A reference sample of the batch was taken as described in 6.4.1 and directly after that molten electrolyte was poured through the same valves into a special measuring cylinder shown in Fig: 6.11.

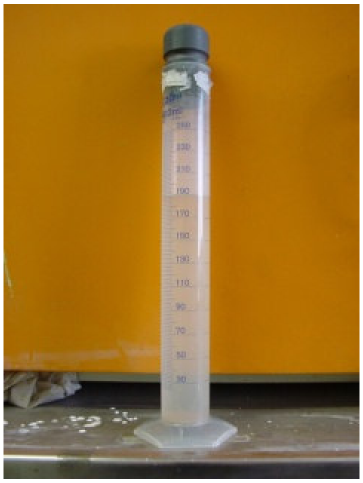


Fig 6.11: Sedimentation test container

Fig 6.12: Lab sedimentation test oven

The container was closed and the electrolyte allowed to solidify to ensure safe transport to the laboratory where the sedimentation test could be conducted. The electrolyte in the container was put into the laboratory oven and allowed to melt for more than a day. Early the next morning the cylinder with molten electrolyte was shaken properly and allowed to stand for 6 hours before being sampled. The cylinder was taken out of the oven and four different samples were taken at different distances from the top of the cylinder. These samples were prepared and sent for analysis.

6.4.10 Moisture tests

The operating procedure described in 6.4.7 was followed and every time after the reference sample was taken an additional sample was taken in a separate container and prepared for analysis of the moisture content. Due to their hygroscopic nature of KF.2HF, these samples were analysed for moisture as soon as possible after being taken and prepared. The metal impurities and HF concentration of the samples were determined after determination of the moisture content.

6.5 Analytical methodology

The determination of Fe, Cu, and Ni was done with an atomic absorption spectrophotometer (AA-30) using hollow cathode tubes for Fe, Cu and Ni.

A standard iron, copper and nickel solution was used to calibrate the AA.

2 grams ($\pm$ 0.1mg) of electrolyte was weighed in a polythene beaker. (No glass equipment can be used due to the presence of HF). The weighed electrolyte was dissolved in distilled water and 4 ml of concentrated nitric acid was added to ensure that al the metal particles were dissolved. It is unlikely that the triple salt K_2NaFeF_6 precipitate will dissolve in the aqueous HNO_3.

The solution was then diluted and injected into the AA. The concentration of each element was determined by using the standard AA techniques. The concentration of each element was determined in µg/ml.

The upper limit of the AA is 20 000 µg/ml and the lower detection limit is 2 ppm.

Fig 6.13: Atomic absorption spectrophotometer (AA-30)

Moisture was determine through Karl Fisher method.

A specific mass of the electrolyte sample is weighed off. (Mass should be approximately 10g)
This electrolyte is then dissolved in 100ml of pyridine, shaken and allowed to stand for 30 minutes .
A blank pyridine sample (10ml) is measured with the Karl Fisher instrument to determine a background value for the moisture in the blank pyridine.
10ml of the pyridine extract is then titrated with the Karl Fisher instrument. The Karl Fisher reagent will absorb the moisture in the solution and a value will be titrated according to the amount of moisture absorbed. The background value of the blank pyridine sample will be subtracted from the total value and the moisture value in the electrolyte will be calculated using a formula in accordance with the reaction.

6.6 Waste Handling

A decontamination procedure was written as part of the emergency procedure should any exposure to emissions of electrolyte or HF occur.

Any waste produced during the test runs was stored in the original containers from which the electrolyte used in the test was taken.

Any HF released from any test was scrubbed in a limestone scrubber. The scrubber was designed to have a capacity sufficient for the test runs. The building special exhaust and scrubber systems would only be used for emergency situations should any occur.

CHAPTER SEVEN

7 RESULTS AND DISCUSSIONS

7.1 Sedimentation

Necsa conducted sedimentation tests on the electrolyte as described in Chapter 4 paragraph 4.1. These tests were however done with electrolyte with low concentrations of Fe, Cu and Ni.

It was decided to repeat the sedimentation test with waste electrolyte with high concentrations (> 20 000 ppm) of Fe, Cu and Ni at a temperature of 85°C.

Figures 7.1, 7.2 and 7.3 are graphical representations of the Fe, Cu and Ni concentrations in the supernatant molten electrolyte at 0 hours and 6 hours.

7.1.1 Fig 7.1: Fe concentration

The Fe concentration in the supernatant electrolyte decreased from more than 20 000 ppm to less than 1745 ppm in 6 hours.

7.1.2 Fig 7.2: Cu concentration

The Cu concentration in the supernatant electrolyte decreased from more than 20 000 ppm to less than 3378 ppm in 6 hours.

7.1.3 Fig 7.3: Ni concentration

The Ni concentration in the supernatant electrolyte decreased from more than 20 000 ppm to less than 1491 ppm in 6 hours.

Although the Fe concentration decreased considerably during the 6 hours, it is unlikely that the concentration will decrease to less than 200 ppm in a reasonable time.

Sedimentation, as a means of removal of the solid Fe, Cu and Ni in the waste electrolyte, was not investigated any further because of the long time needed for sedimentation of these solids; thus making the implementation thereof on a industrial scale impractical. A US patent (14) claimed yields of 75% after 40 hours and 86% after 312 hours.

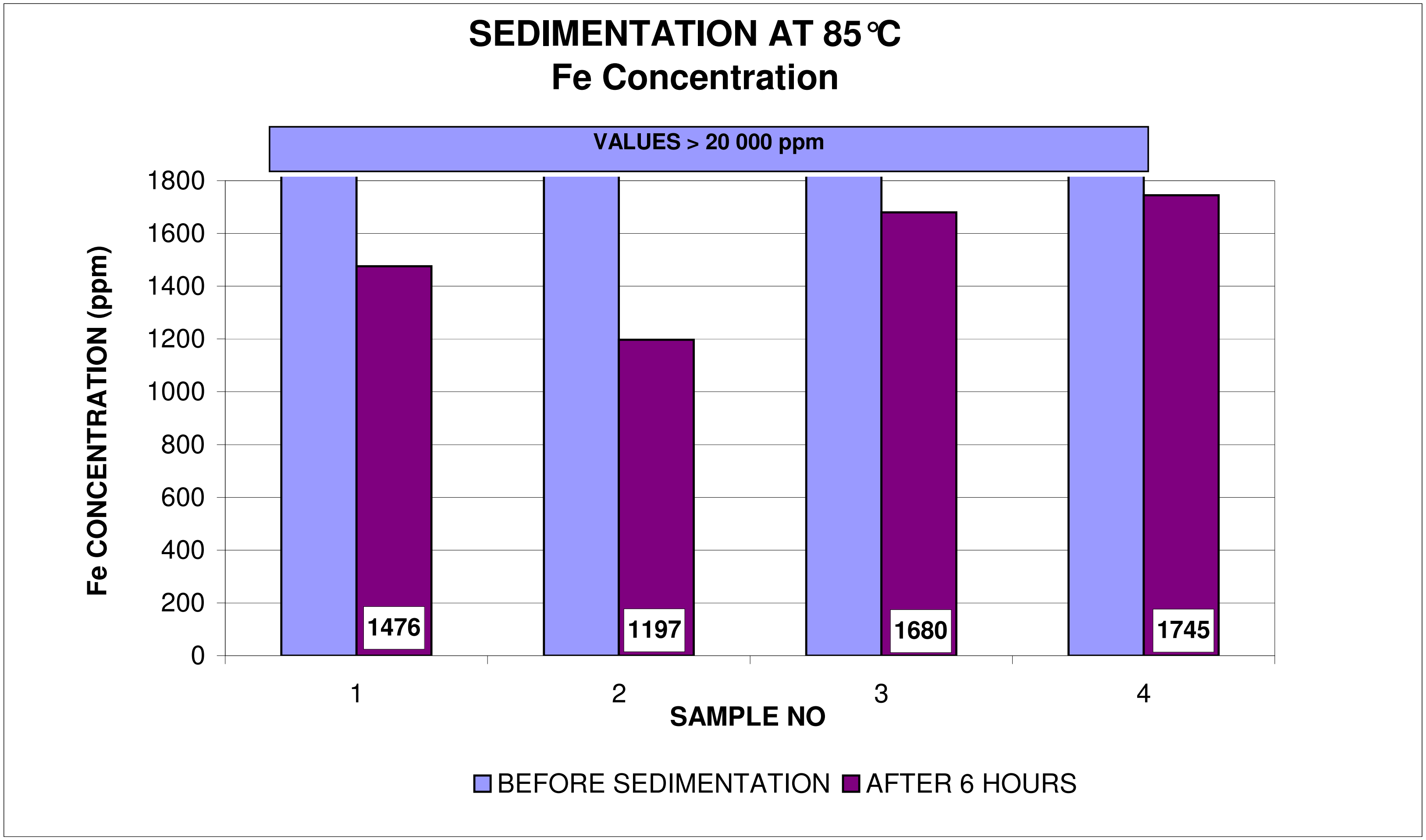


Fig 7.1: Fe concentration in the supernatant electrolyte after sedimentation.

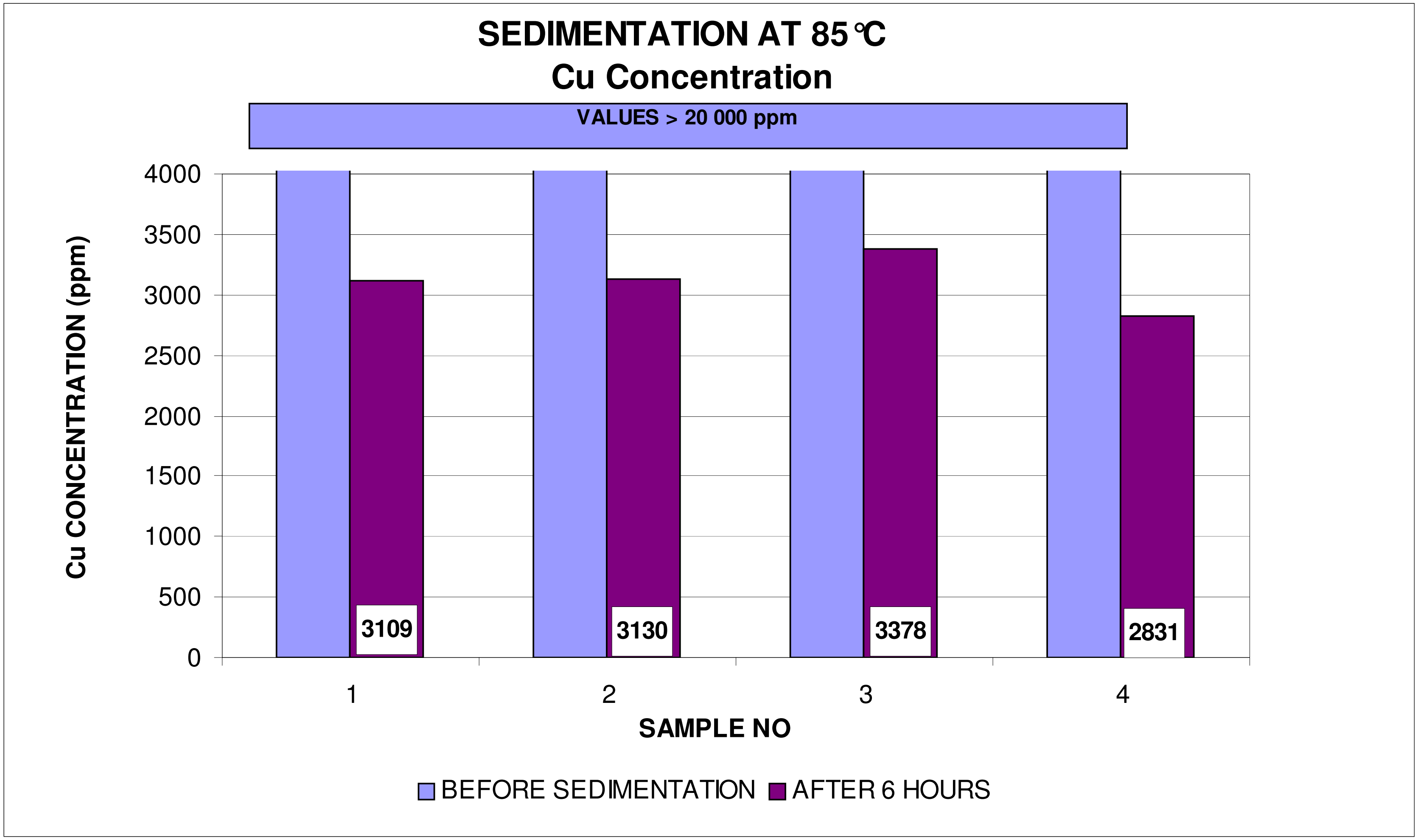


Fig 7.2: Cu concentration in the supernatant electrolyte after sedimentation.

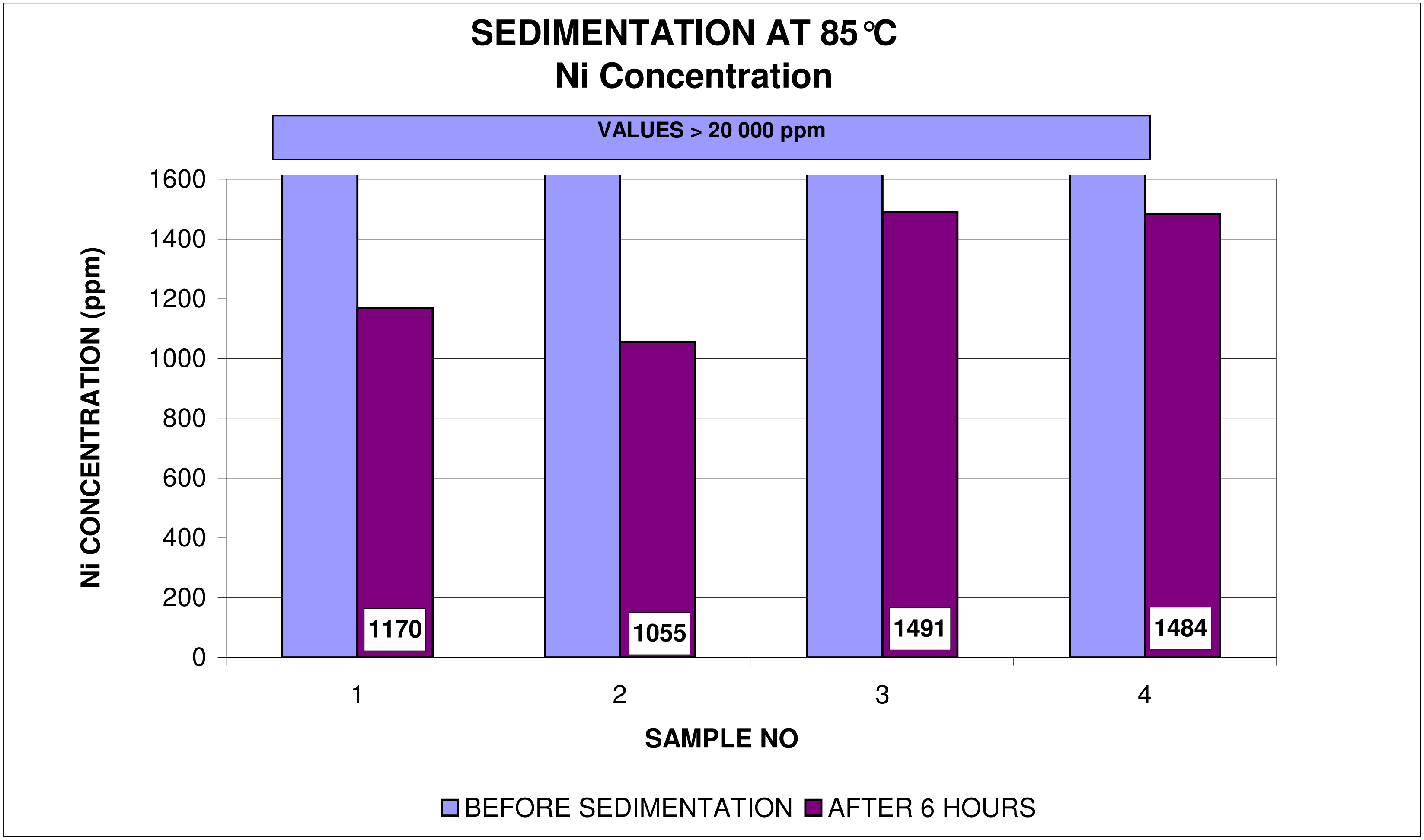


Fig 7.3: Ni concentration in the supernatant electrolyte after sedimentation.

7.2 Filtration: Untreated electrolyte

Fig 7.4, 7.5, and 7.6 are the graphical representation of the total Fe, Cu and Ni concentration, respectively, in the filtered electrolyte of 6 electrolyte batches.

7.2.1 Overall observation

The concentration of the total Fe, Cu and Ni in the electrolyte filtrate was expected to be lower than that of the unfiltered sample. Figs 7.4, 7.5 and 7.6 however indicated the contrary: In all six the batches, the total Fe, Cu and Ni concentrations increased after filtration.

As there was no explanation for these results, it was decided to open the Monel and PTFE filter housings and to remove and inspect the filters. Fig 7.7 is the removed Monel filter. The filter was coated with a fine copper powder. Similar occurrences have been experienced in the Necsa chemical plants on equipment exposed to dilute hydrofluoric acid.

Anhydrous hydrogen fluoride is not corrosive towards mild steel, stainless steel and Monel which are all suitable to be used in an AHF environment without any serious acid attack on the metals. However hydrofluoric acid with even low concentrations of moisture is very corrosive especially at elevated temperatures. Except for Monel and copper under certain conditions, the stainless steels and mild steel are not suitable materials to be used in an HF environment.

The explanation for the increase in total concentration of Fe, Cu and Ni during filtration of the molten electrolyte is:

- The vapour pressure of H_2O above moist molten electrolyte is higher than that of the HF(17). The vapour from the molten electrolyte consisting of dilute HF and N_2 comes in contact with filter elements and filter housing prior to the molten electrolyte. A typical HF concentration in the vapour of moist electrolyte with an HF concentration of 42% at

120 °C is more than 10 %. (See calculation in table 1E and fig 1E in appendix E)

- The diluted HF at elevated temperatures dissolves the Ni from the Monel alloy thus exposing the alloy matrix as fine Cu and to a lessen extent the Ni particles – the visual Cu appearance on the Monel filter.
- The material of construction on the filter housings is stainless steel. The diluted HF dissolves some of the Fe but also releases some of the Fe from the stainless alloy as fine Fe particles.
- The pore size of both the Monel filter and to some extent that of the PTFE filter is larger than the size of most of the metal particles resulting from the metal corrosion, so that the particles are not filtered effectively and therefore with the dissolved Fe, Cu and Ni contribute to the increase in the metal concentration after filtration.

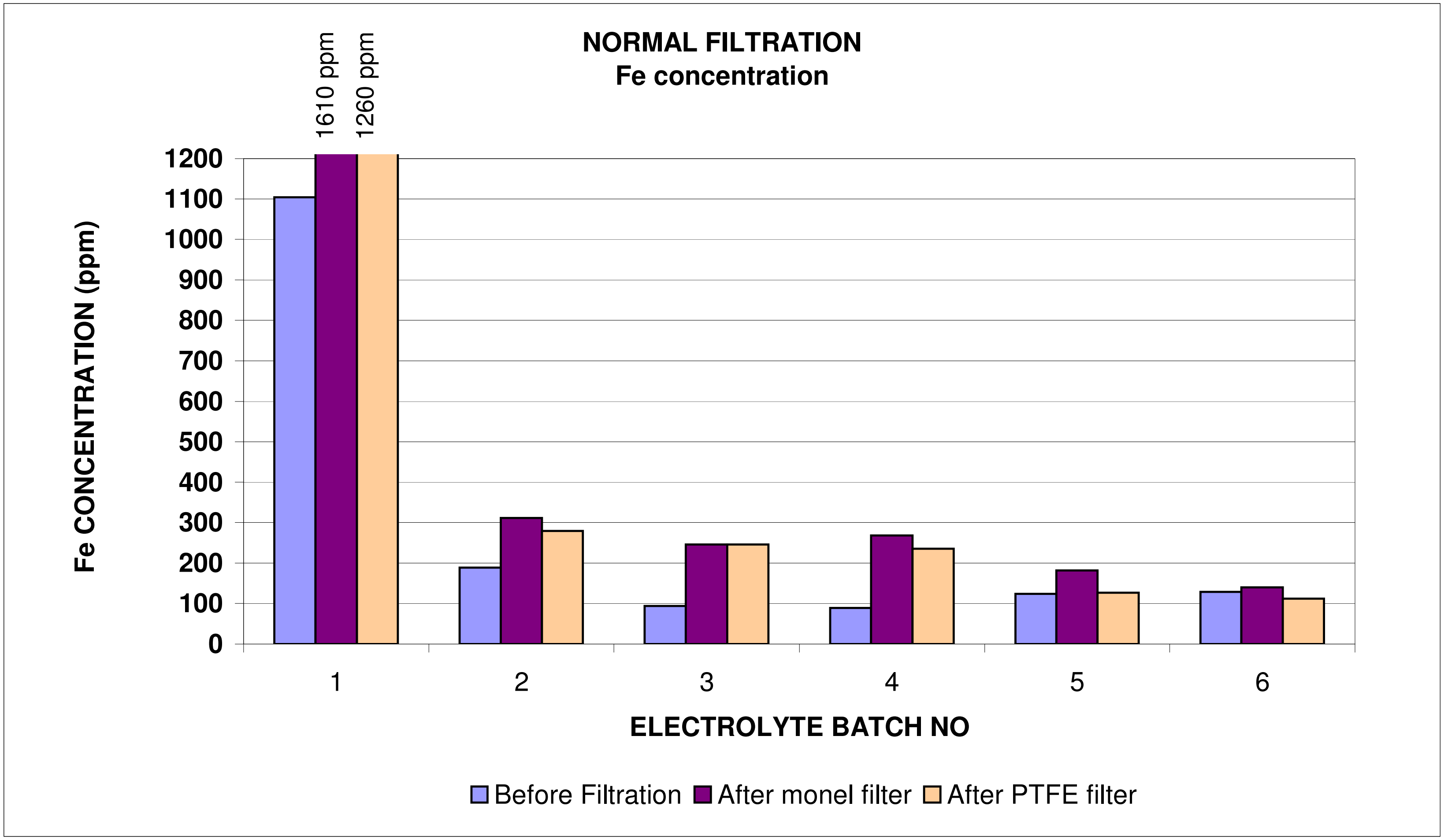


Fig 7.4: Total Fe concentrations before and after filtration

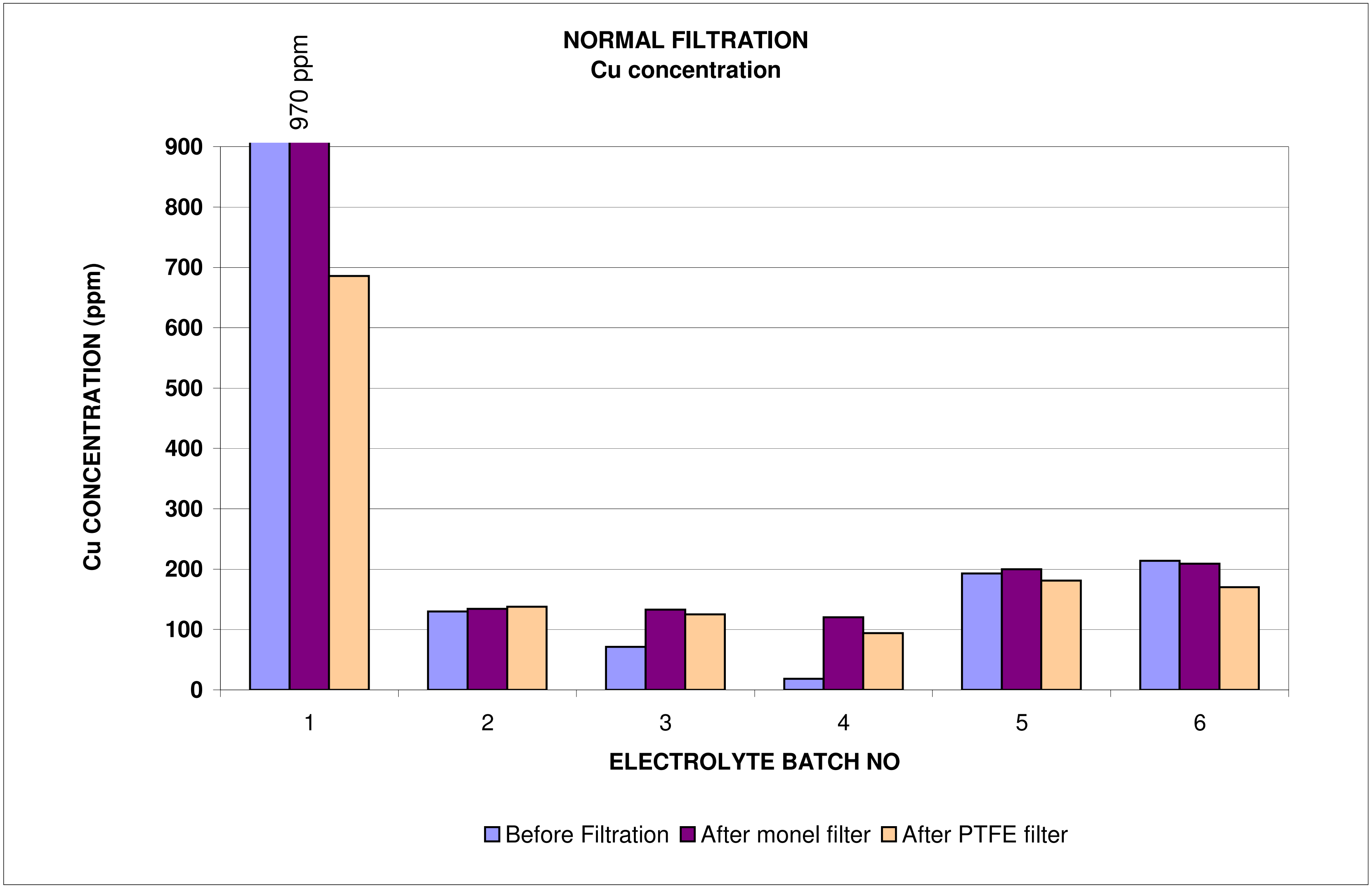


Fig 7.5: Total Cu concentrations before and after filtration

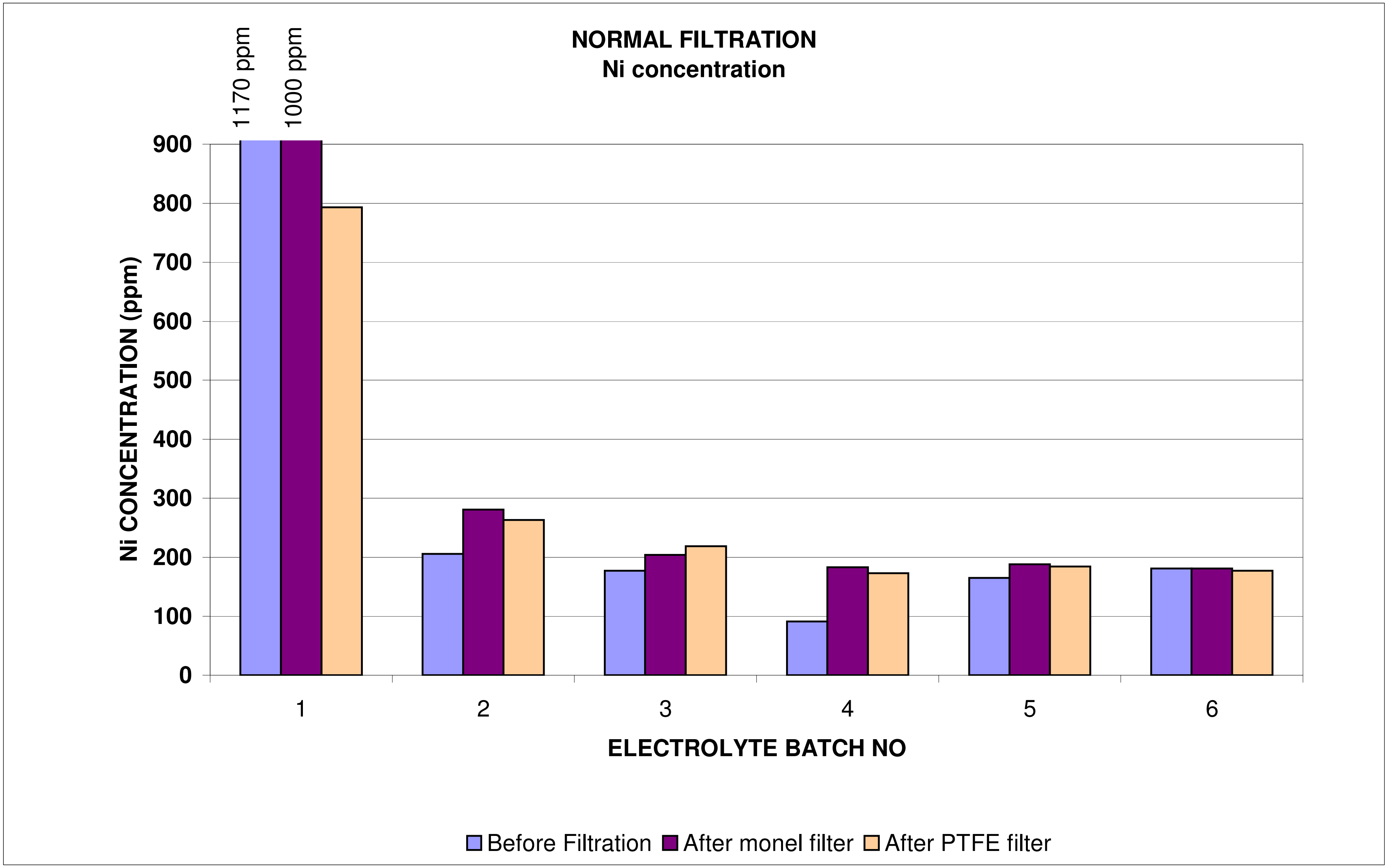


Fig 7.6: Total Ni concentrations before and after filtration

Fig 7.7: Corrosion clearly visible on Monel filter

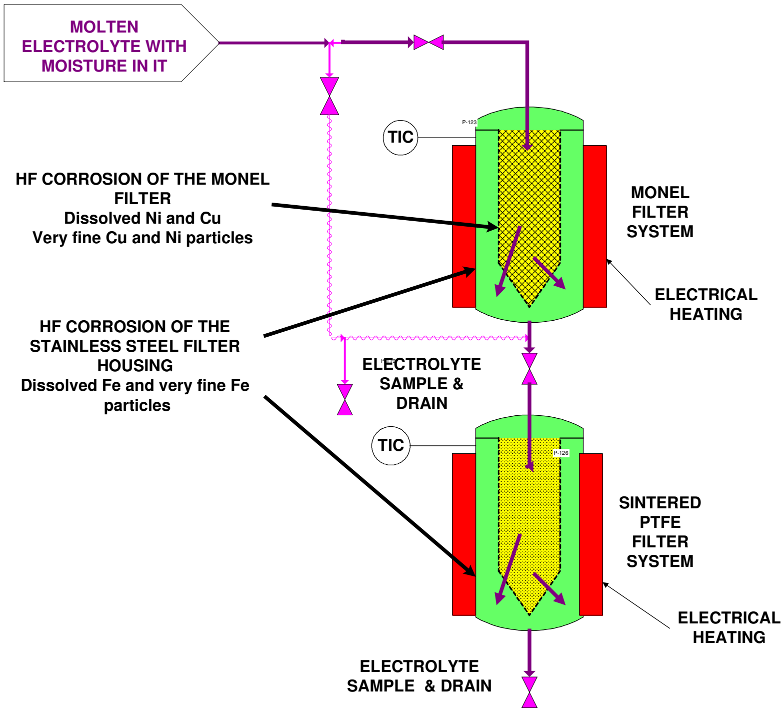


Fig 7.8: Flow diagram indicating sources of corrosion

7.3 Filtration: Fe concentration

7.3.1 Fig 7.4: Untreated electrolyte

Batches 1 to 5 indicate an increase in the total Fe concentration as discussed. The Fe concentration after the Monel and PTFE filters remains unchanged in batch 3. Batches 1, 2, 4, 5 and 6 indicate that the PTFE filter removes some of the fine Fe particles. Batch 5 indicates that the Fe concentration before and after filtration is identical.

Because of the dissimilarity of the Fe concentrations of the 5 batches, due to the overwhelming effect of the corrosion in the filter systems, it is not possible to reach any sensible and useful conclusions from the filtration results. Only batch 6 indicates that the filter system removes the particulate Fe to a level below the Fe concentration of the pre-filtered electrolyte. This is however one batch out of the six and the filter efficiency* is only 13.2%.

7.3.2 Fig 7.9: KF.HF addition.

As expected, the samples with a HF concentration of 39.5%(m/m) and 38.6%(m/m) indicate a significant reduction of the total Fe concentration after the Monel filter. The electrolyte sample with 38.1% HF however indicates a gradual increase in the Fe concentration with the flow of electrolyte through the filter system.

The Fe concentration in all three samples undergoes a sharp increase after the PTFE filter. Dissolved Fe corrosion products from the filter systems may be the reason for the high total Fe concentration after the PTFE filter.

Corrosion of the filter system by moist HF vapour and moist molten electrolyte is so great that it is impossible to draw any conclusions about advantages of the addition of KF.HF to the molten electrolyte to lower the HF concentration in the electrolyte and thus to precipitate some of the soluble Fe.

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* Defined as:
Filter efficiency = (Concentration before filtration – Concentration after filtration) / (Concentration before filtration)

7.4 Filtration: Cu concentration

7.4.1 Fig 7.5: Untreated electrolyte

Batches 2, 3 and 4 indicate an increase in the total Cu concentration as discussed. In batch 2 the Cu concentration after the Monel and PTFE filters is the same. Batches 1, 3, 4, 5 and 6 indicate that the PTFE filter removes some of the fine Cu particles. Batch 2 indicates that the Cu concentration before and after filtration is similar while batches 1, 5 and 6 indicate that the Cu is filtered to a concentration level below that of the initial pre-filtered sample.

Except for batch 1 with a filter efficiency of 52% the differences are however small and in most of the batches insignificant and not of any practical use.

7.4.2 Fig 7.10: KF.HF addition.

The samples with a HF concentration of 39.5%(m/m) and 38.6%(m/m) indicate a significant reduction of the total Cu concentration after the Monel filter as expected. The electrolyte sample with 38.1% HF however indicates a gradual increase in the Cu concentration with the flow of electrolyte through the filter system.

The Cu concentration in all three samples undergoes a sharp increase after the PTFE filter. As in the case of the Fe, dissolved Cu corrosion products from the filter systems may be the reason for the high total Cu concentration after the PTFE filter.

Corrosion of the filter system by moist HF vapour and moist molten electrolyte is so great that it is impossible to draw any conclusions about the advantages of the addition of KF.HF to the molten electrolyte to decrease the HF concentration in the electrolyte and thus to precipitate some of the soluble Cu.

7.5 Filtration: Ni concentration

7.5.1 Fig 7.6: Untreated electrolyte

Batches 2 to 5 indicate an increase in the total Ni concentration as discussed. Batches 1,4,5 and 6 indicate that the PTFE filter removes some of the fine Ni particles. Batch 6 indicates that the Ni concentration before and after filtration is nearly the same while batches 1 and 6 indicate that the Ni is filtered to a concentration level below the initial pre-filtered sample. Except for batch 1 with a filter efficiency of 32 the differences are however small and in most of the batches insignificant and not of any practical use.

7.5.2 Fig 7.11: KF.HF addition.

The samples with an HF concentration of 39.5%(m/m) and 38.6%(m/m) indicate a significant reduction of the total Ni concentration after the Monel filter as expected. The electrolyte sample with 38.1% HF however indicates a gradual increase in the Ni concentration with the flow of electrolyte through the filter system similar to the Fe and Cu concentrations as discussed before..

The Ni concentration in all three samples undergoes a sharp increase after the PTFE filter. Dissolved Ni corrosion products from the filter systems may be the reason for the high total Ni concentration after the PTFE filter.

Corrosion of the filter system by moist HF vapour and moist molten electrolyte is so great that it is impossible to draw any sensible conclusions about the advantages of the addition of KF.HF to the molten electrolyte to decrease the HF concentration in the electrolyte and thus to precipitate some of the soluble Ni.

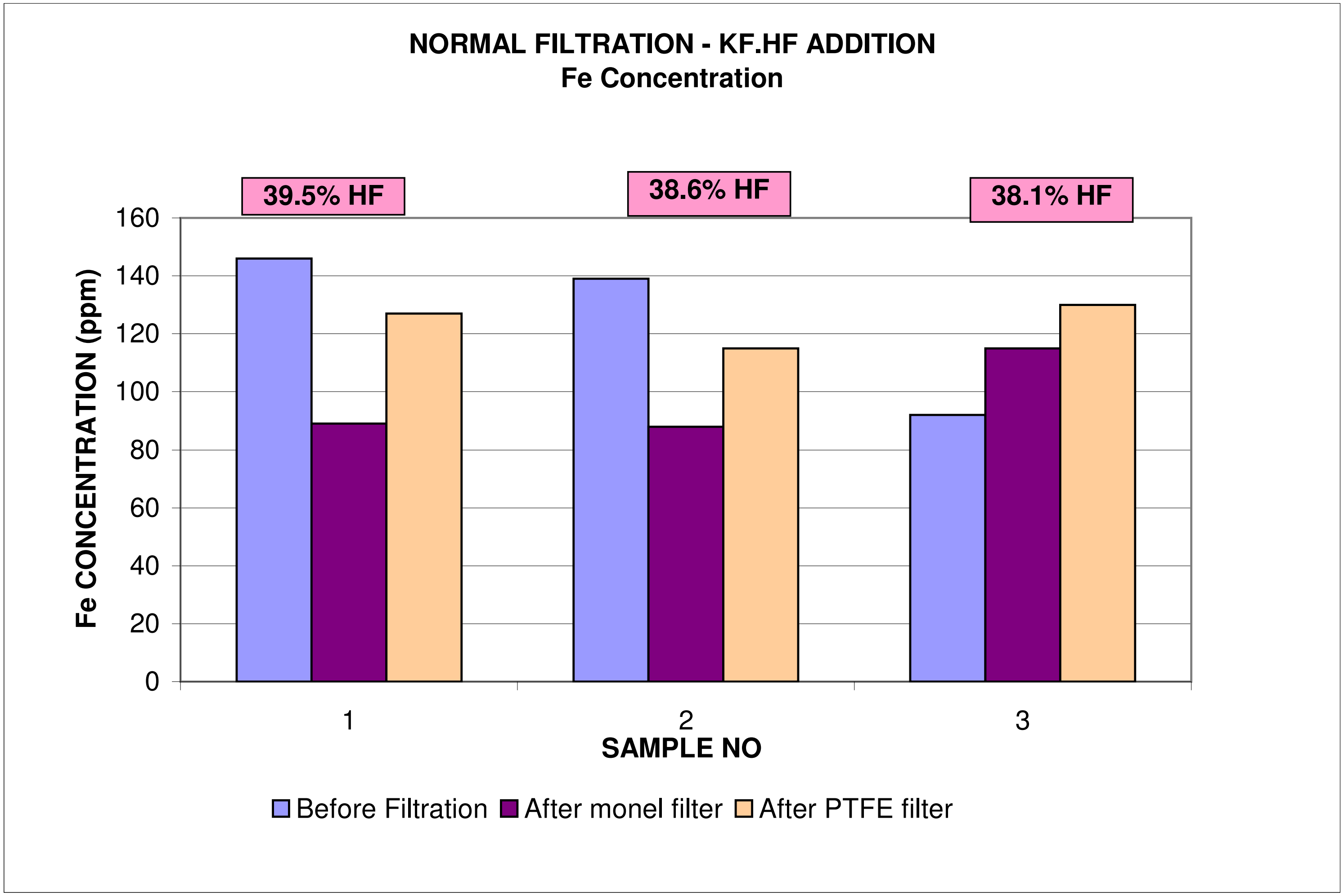


Fig 7.9: Total Fe concentration in the electrolyte after the addition of KF.HF

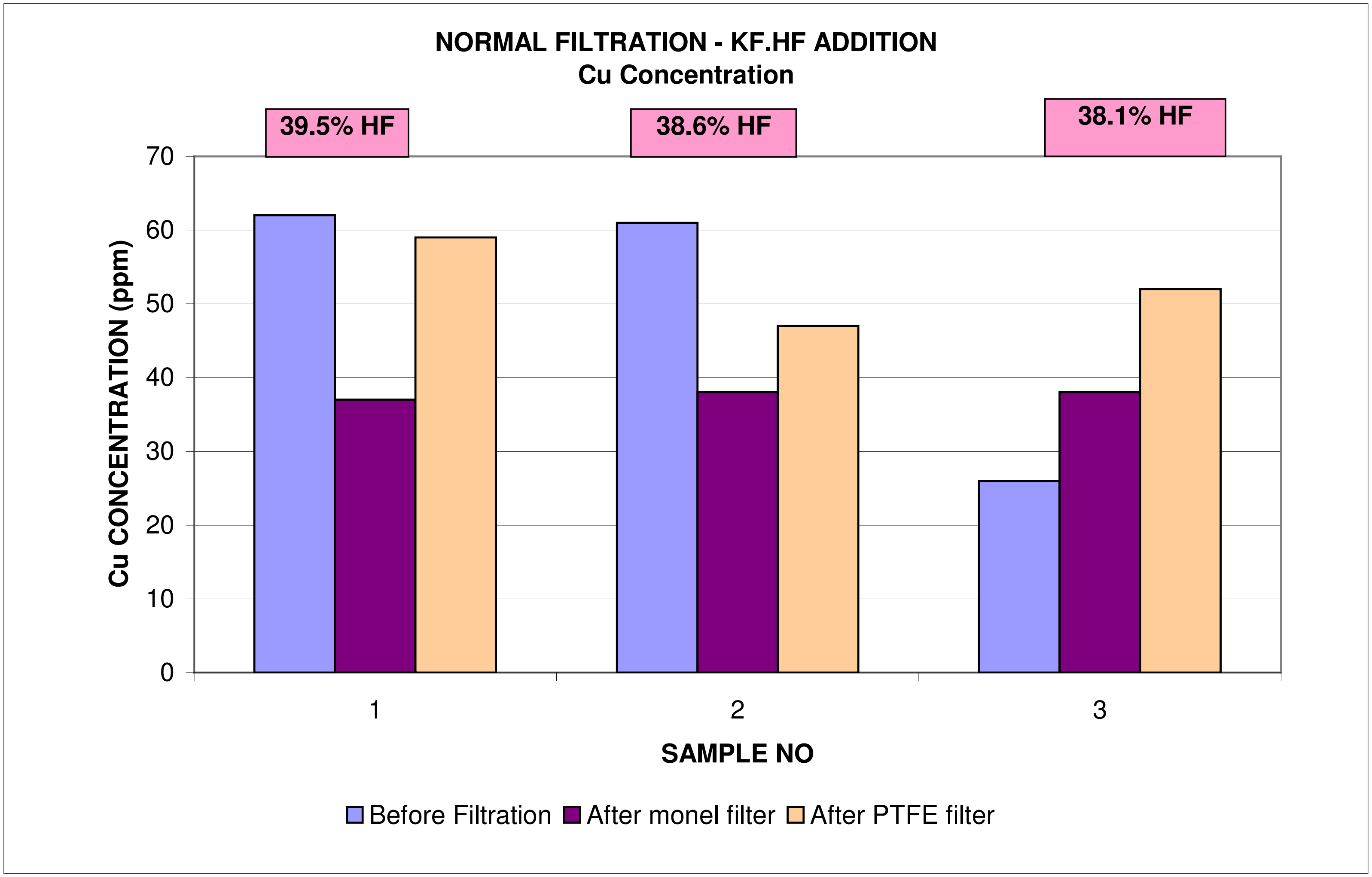


Fig 7.10: Total Cu concentration in the electrolyte after the addition of KF.HF

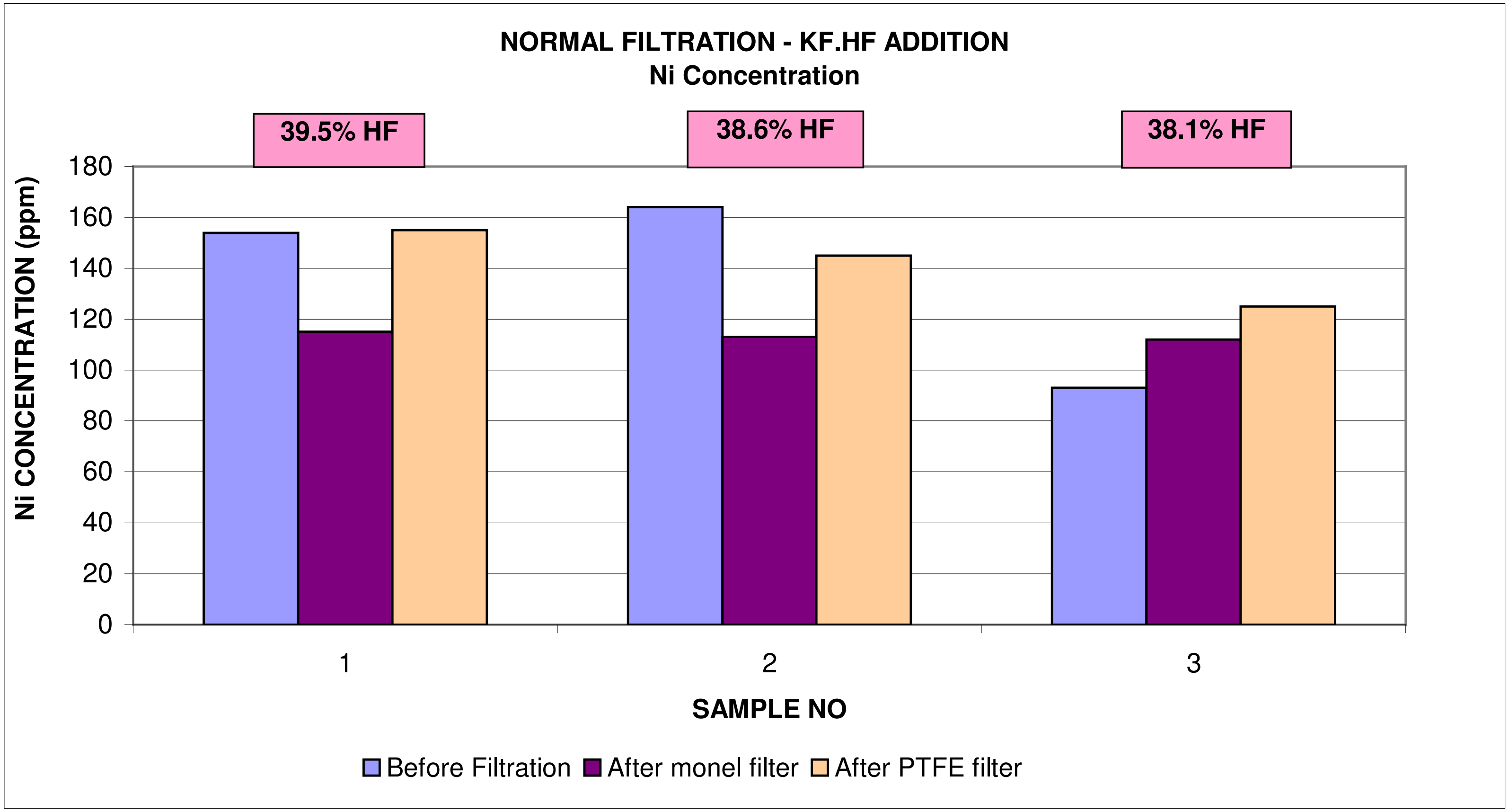


Fig 7.11: Total Ni concentration in the electrolyte after the addition of KF.HF

7.6 Filtration: Stripping with dry nitrogen

Fig 7.12 indicates the total Fe, Cu and Ni concentrations in the molten filtered electrolyte after stripping of the molten electrolyte to decrease the HF concentration from 42% to 40.5%.

7.6.1 Fe concentration

Although the Fe concentration increased due to corrosion in the Monel filter system the PTFE filter decreased the Fe concentration to such an extent that a filter efficiency of 68% is obtained. The total Fe concentration after filtration is 192 ppm which is less than the specified maximum concentration in clean electrolyte of 200 ppm.

7.6.2 Cu concentration

Although the Monel filter systems corroded as indicated by the high value of the Cu concentration after filtration with the Monel filter, the ratio is less than in the case of the untreated electrolyte. The PTFE filter removed a substantial quantity of the Cu particles. The total Cu concentration decreased from 266 ppm to 179 ppm, a reduction of (266-179)/266 = 33% of total Cu. The filter efficiency is 33% based on the total Cu.

7.6.3 Ni concentration

The Ni concentration is reduced through filtration with an efficiency of 16% total Ni.

The Ni concentration after filtration is still relatively high in comparison to literature values (16) of ~100 ppm, but this is probably due to the addition of particulate and dissolved Ni to the molten electrolyte during corrosion in the filter system.

The results as represented in Fig 7.12 indicated that the stripping of the HF in the molten electrolyte with an inert gas, in this case nitrogen gas, to reduce the HF concentration in the electrolyte, not only precipitates soluble Fe, Cu and Ni but also reduces the moisture level in the electrolyte with the effect of less corrosion of the filter systems.

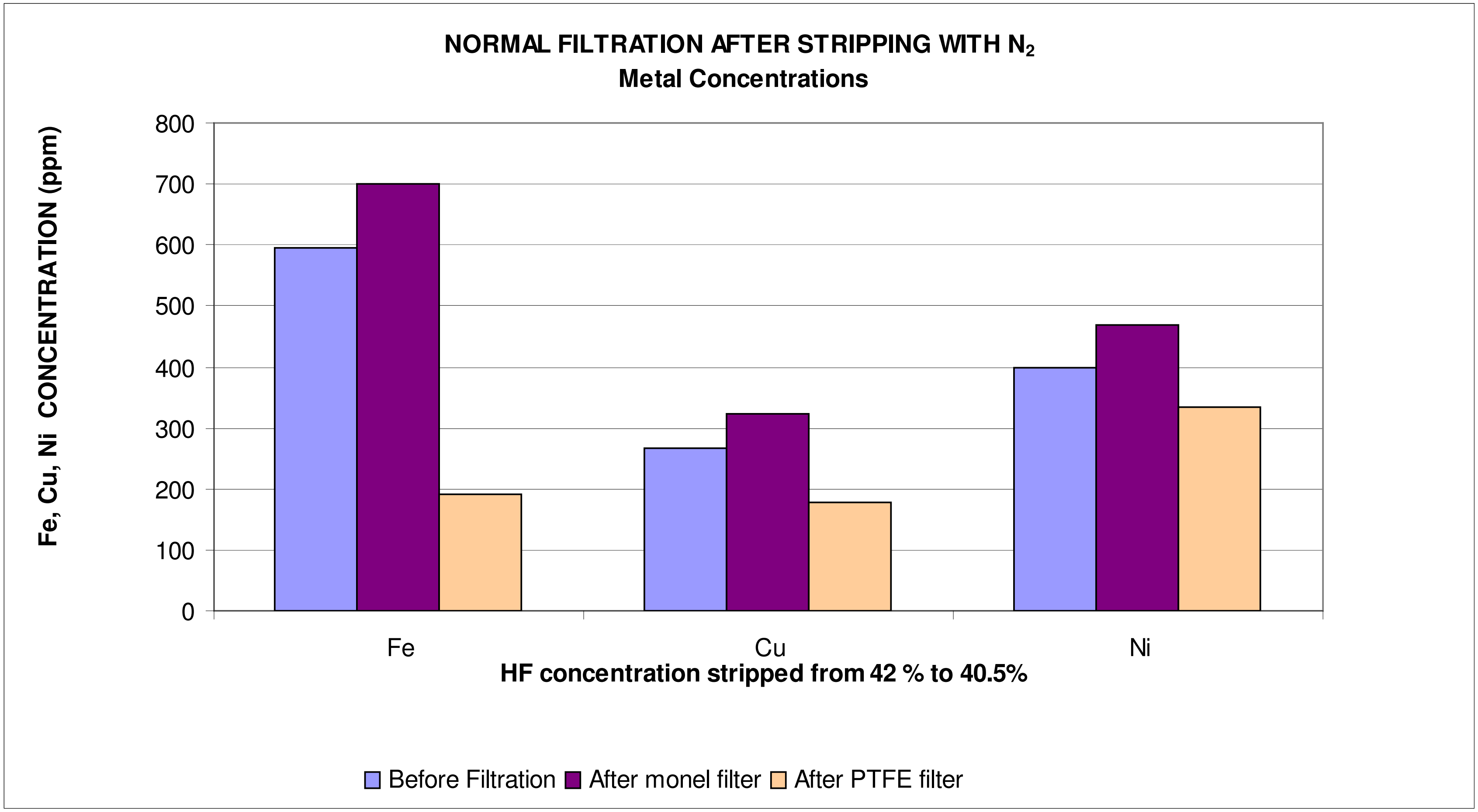


Fig 7.12: Metal removal results from filtration after stripping with an inert gas

7.7 Filtration: Addition of NaOH

Fig 7.13 indicates the effect of the addition of a stoichiometric quantity of NaOH to the molten electrolyte.

7.7.1 Fe concentration

During the addition of NaOH to the molten electrolyte an insoluble triple salt K_2NaFeF_6 is formed(16). This salt is insoluble in the aqueous HNO_3 solution used to dissolve the metals before analysis on the AA spectrophotometer. Comparison of the untreated reference sample with the treated unfiltered sample indicates a slight decrease in the total Fe concentration. The addition of Fe due to corrosion of the filter systems is so extensive that although the PTFE filter removes some of the Fe particles, the total Fe concentration after filtration is still higher than the Fe concentration of the unfiltered sample.

7.7.2 Cu concentration

Although the Cu concentration of the treated unfiltered electrolyte samples is less than the untreated electrolyte reference sample, the addition of Cu to the electrolyte due to corrosion in the filter systems (especially the Monel filter) is so overwhelming that the Cu concentration in the electrolyte after filtration is substantially higher than in the pre-filtered electrolyte.

7.7.3 Ni concentration

The Ni concentration in the treated electrolyte sample is lower than the Ni concentration in the untreated electrolyte. As in the case of the Fe and Cu the effect of the addition of soluble and particulate Ni because of corrosion of the filter systems is such that the Ni concentration in the filtered sample is much higher than the Ni in the pre-filtered electrolyte.

Because of the corrosion of the filter systems the effect of filtration to remove solid metal particles and the precipitated triple salt from the electrolyte treated with NaOH is not clear. Comparison of the metal concentrations of the different reference samples with the treated electrolyte samples prior to filtration however indicates that the addition of NaOH did precipitate some of the soluble metal fluorides.

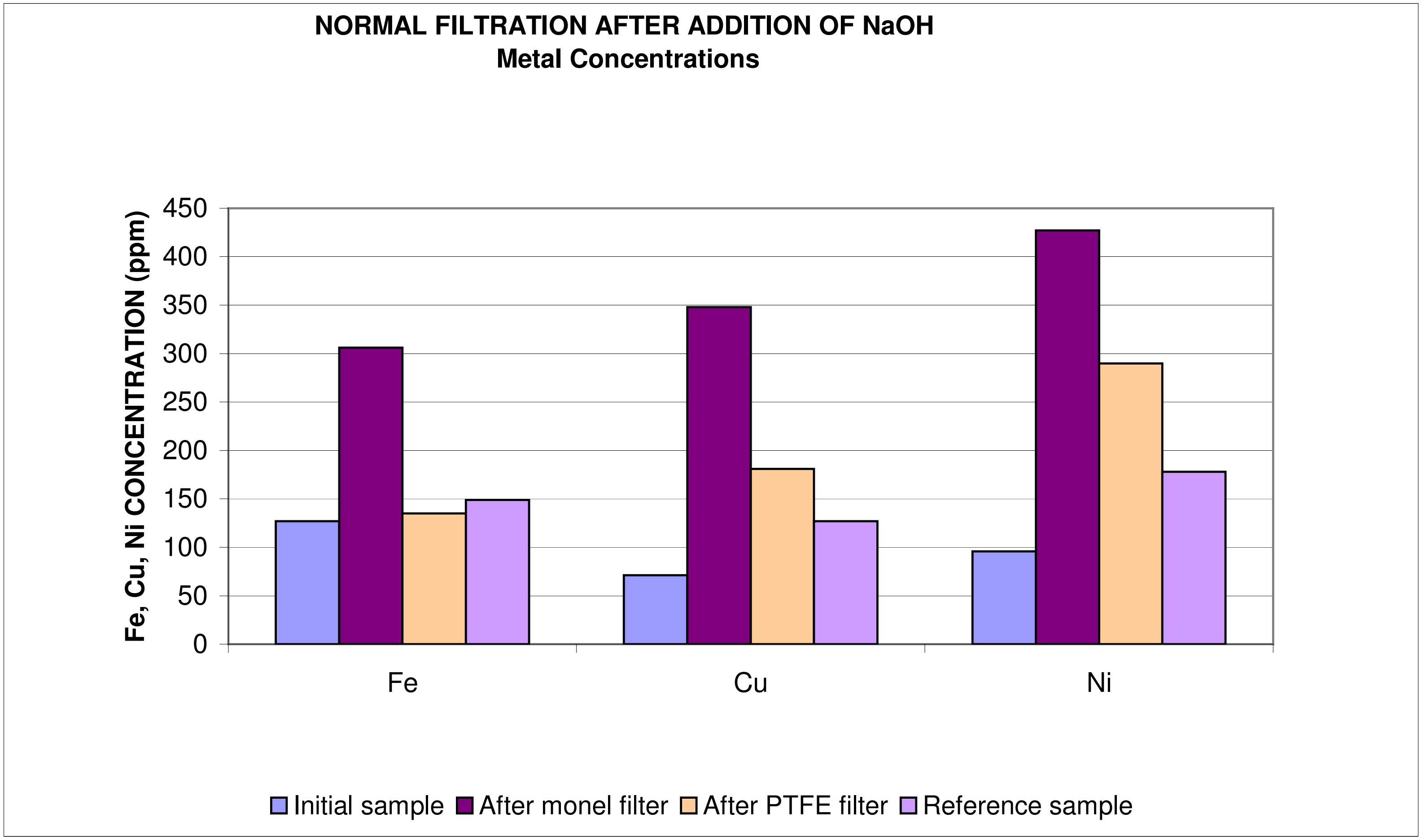


Fig 7.13: Metal removal results from filtration after the addition of NaOH

7.8 Filtration: Comparison of filter efficiencies

7.8.1 The Monel filter system

Fig 7.14 is a graphical representation of the filter efficiencies for the Monel filter system.

7.8.2 The Monel and PTFE filter systems

Fig 7.15 is a similar representation of the filter efficiencies of the Monel and PTFE filter systems. In the figures the efficiency is calculated as:

Filter efficiency = (Concentration before filtration – Concentration after filtration) / (Concentration before filtration)

A positive efficiency indicates a nett removal of Fe, Cu or Ni particles from the molten electrolyte. A negative efficiency indicates the generation of solid and soluble Fe, Cu and Ni in the filter systems.

7.8.3 Total metal concentrations in the electrolyte after the Monel and PTFE filter systems.

Fig 7.16 indicates that only the stripping of the HF from the electrolyte with N_2 gas and the addition of KF.HF to the electrolyte (to decrease the HF concentration in the electrolyte with the effect of precipitating soluble metal fluorides) have positive efficiencies.

The larger efficiency stems from the stripping with dry N_2 gas. The N_2 gas not only removes the HF from the molten electrolyte, but also removes a substantial amount of water from the electrolyte with the implication that apart from the precipitation of the metals to an extent, the corrosion of the filters and filter housings is less.

The addition of KF.HF decreases the HF concentration in the electrolyte and to a lesser extent the moisture content of the electrolyte. The indicated concentration values are however not as significant as the concentration values from the stripping with N_2 gas.

The figures also indicate the overwhelming extent of the corrosion of the filter systems. Most of the efficiencies are negative and some with an efficiency of more than 100%. Fig 7.16 indicates that the processes with a positive efficiency also reduce the Fe concentration in the electrolyte, after filtration, to less than 200 ppm.

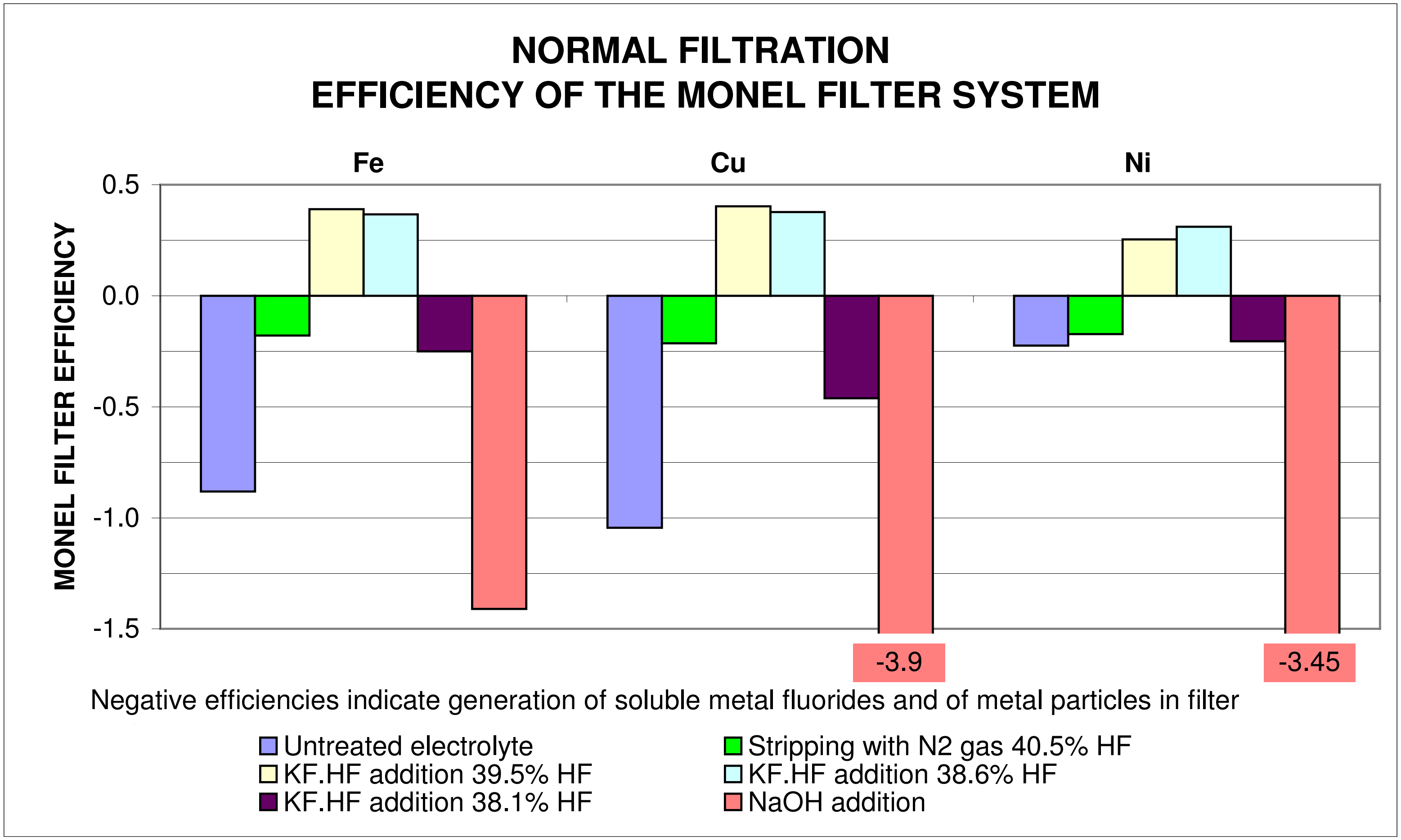


Fig 7.14: Efficiency of the Monel filter system

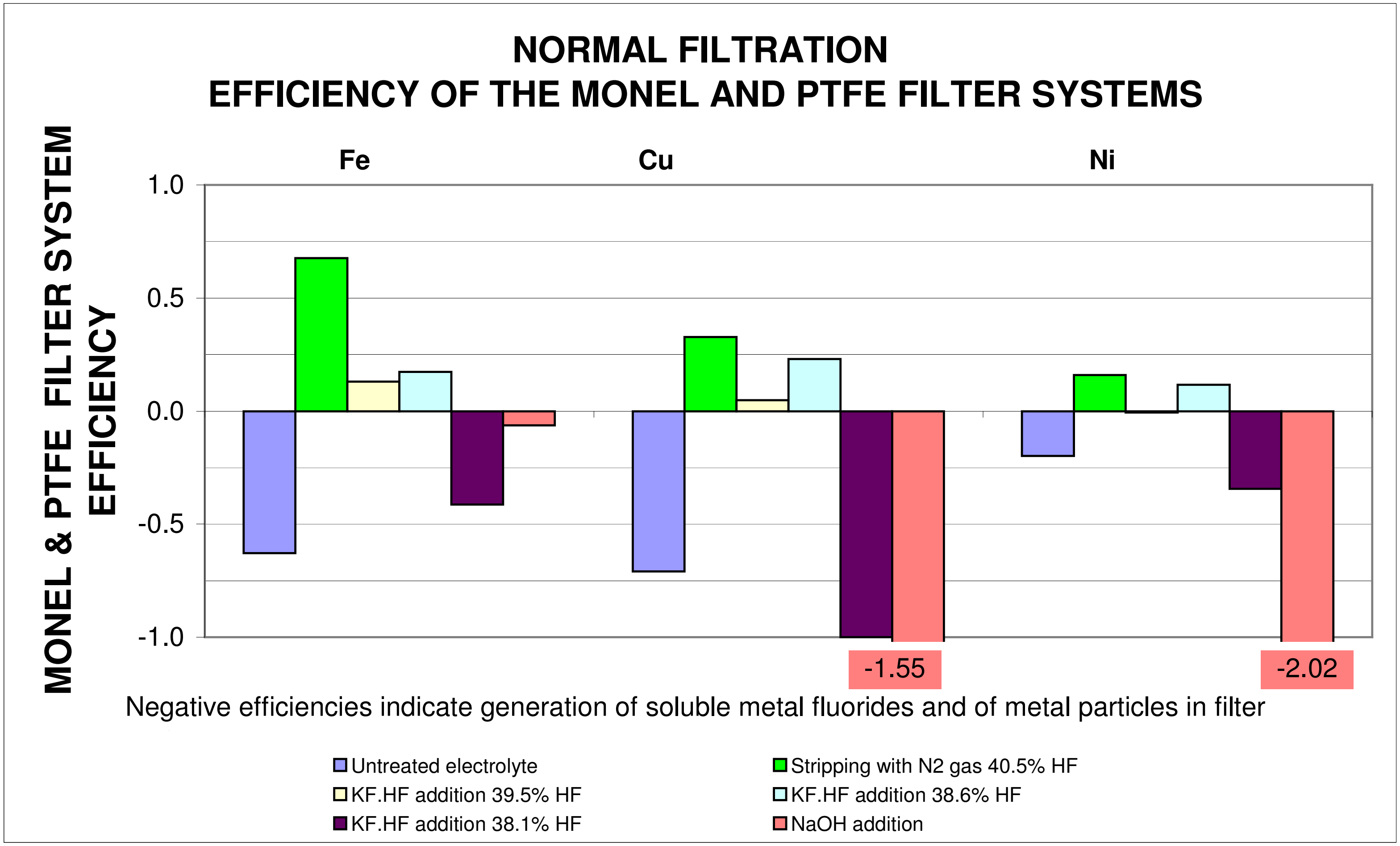


Fig 7.15: Efficiency of the Monel and PTFE filter systems

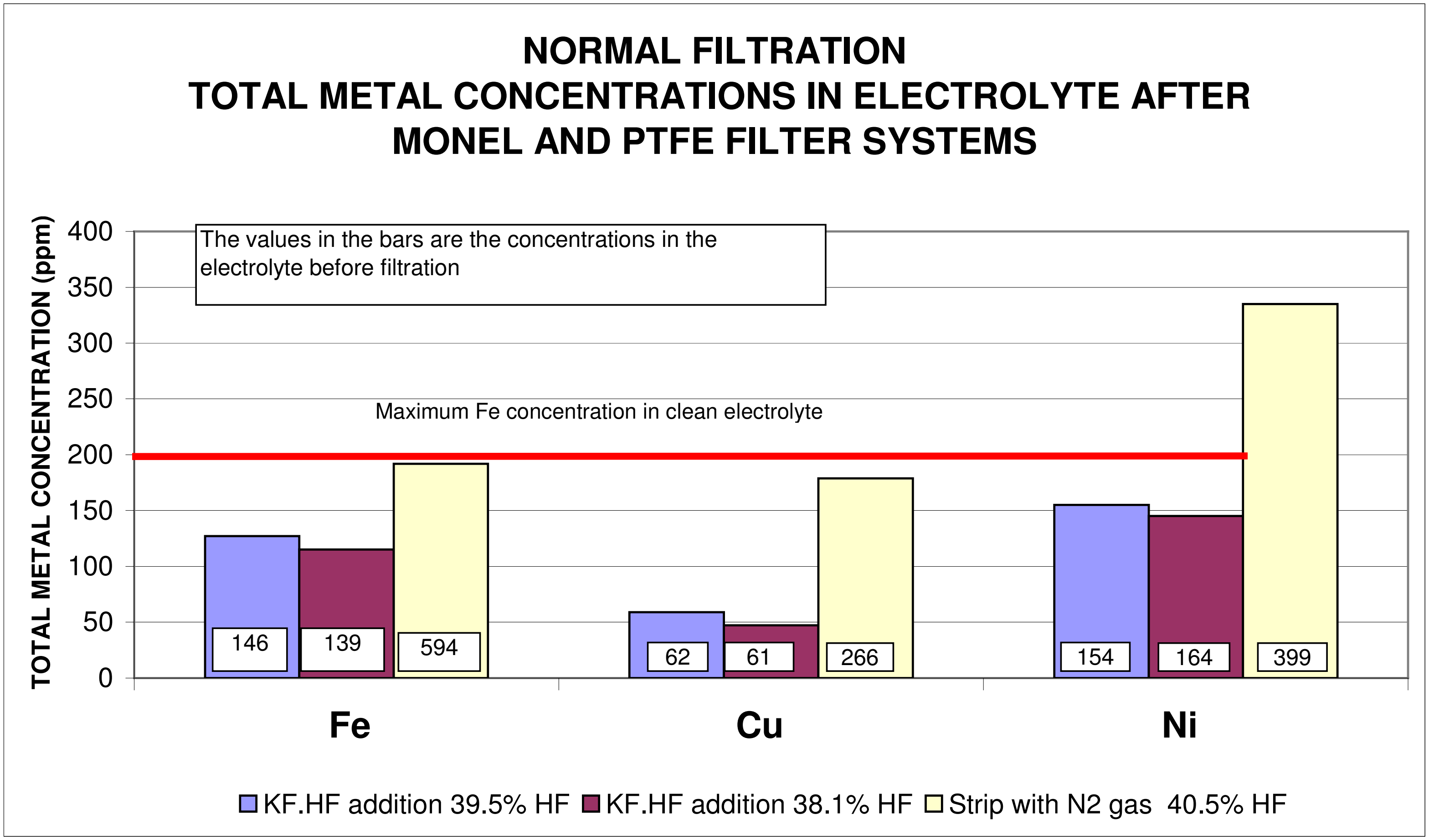


Fig 7.16: Metal concentrations in electrolyte after the filter systems

7.9 Centrifuging: Untreated electrolyte

The centrifuging efficiency is defined as :

Centrifuging efficiency = ((Concentration before centrifuging) – (Concentration after centrifuging))/(Concentration before centrifuging)

Samples from a batch of molten electrolyte with a low total concentration of metals and one with a high total concentration of metals were centrifuged and analysed for total Fe, Cu and Ni concentrations.

7.9.1 Fig 7.21: Fe concentration

The 4 centrifuged samples from batch 1 have almost equal values for the Fe concentration analysed in each tube, This batch had a low concentration of total Fe when started.

The Fe concentration of the 4 centrifuged samples from batch 2 varies, This batch had a high concentration of total Fe initially when started.

The Fe concentration of the centrifuged samples in batch 2 is however in the same concentration range as the Fe concentration of the centrifuged samples of Batch 1, an indication that batch 2 contains more solid Fe particles. These particles vary in size and the very small and fine particles may take longer to sedimentate under the centrifugal force, thus the scatter in the Fe concentration of the 4 samples of batch 2.

The average centrifuging efficiency for batch 1 and 2 are 57% and 99,6 % respectively.

The average Fe concentration of the 8 centrifuged samples is 51 ppm which is well below the maximum specification of 200 ppm for fresh electrolyte

7.9.2 Fig 7.22: Cu concentration

The average centrifuging efficiency of the 4 samples of batch 1 is 20% while the average centrifuging efficiency of the 4 samples from batch 2 is 99.2%.

Batch 1 with the low total Cu concentration contains a high concentration of soluble Cu fluorides relative to batch 2 that seems to be high in Cu particle concentration. The slight scatter in Cu concentrations of the centrifuged samples can be because of deviations in the method of sampling, the analytical procedures, and the centrifuging time. The average Cu concentration of the 8 centrifuged samples of batch 1 and 2 is 168 ppm.

7.9.3 Fig 7.23: Ni concentration

The Ni concentrations of the 4 samples of batch 1 are higher than the Ni concentration of the samples prior to centrifuging. However the centrifuging efficiency is –7%. This small difference in the Ni concentration of the electrolyte before and after centrifuging may be because of variations in the sampling technique and the analytical procedure. The Ni concentration of the electrolyte before and after centrifuging can be assumed to be the same. This assumption implies that all of the Ni present in Batch 1 is soluble Ni fluorides. The average centrifuging efficiency of the 4 electrolyte samples of batch 2 is 99.3%, an indication that most of the Ni is present as Ni particles. As in the case of the Fe the difference in Ni concentrations of the 4 samples of batch 2 after centrifuging may be attributed to the presence of a substantial quantity of very small Ni particles. The average Ni concentration of the 8 centrifuged samples is 163 ppm.

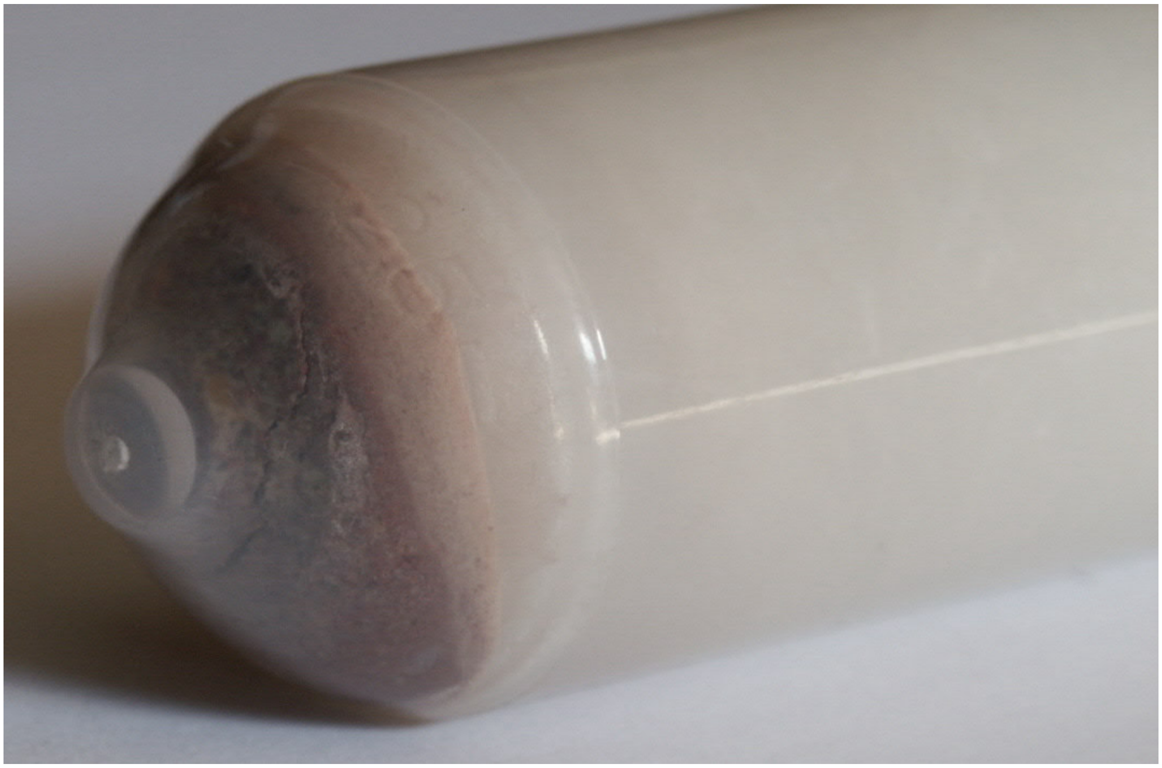


Fig 7.17: Electrolyte samples after centrifuging

Fig 7.18: Visible metal sediment after centrifuging

The metal sediment as well as the purified electrolyte is clearly visible in the centrifuge tubes

Fig 7.19: Electrolyte with high concentration of metal impurities

Fig 7.20: Supernatant electrolyte after centrifuging

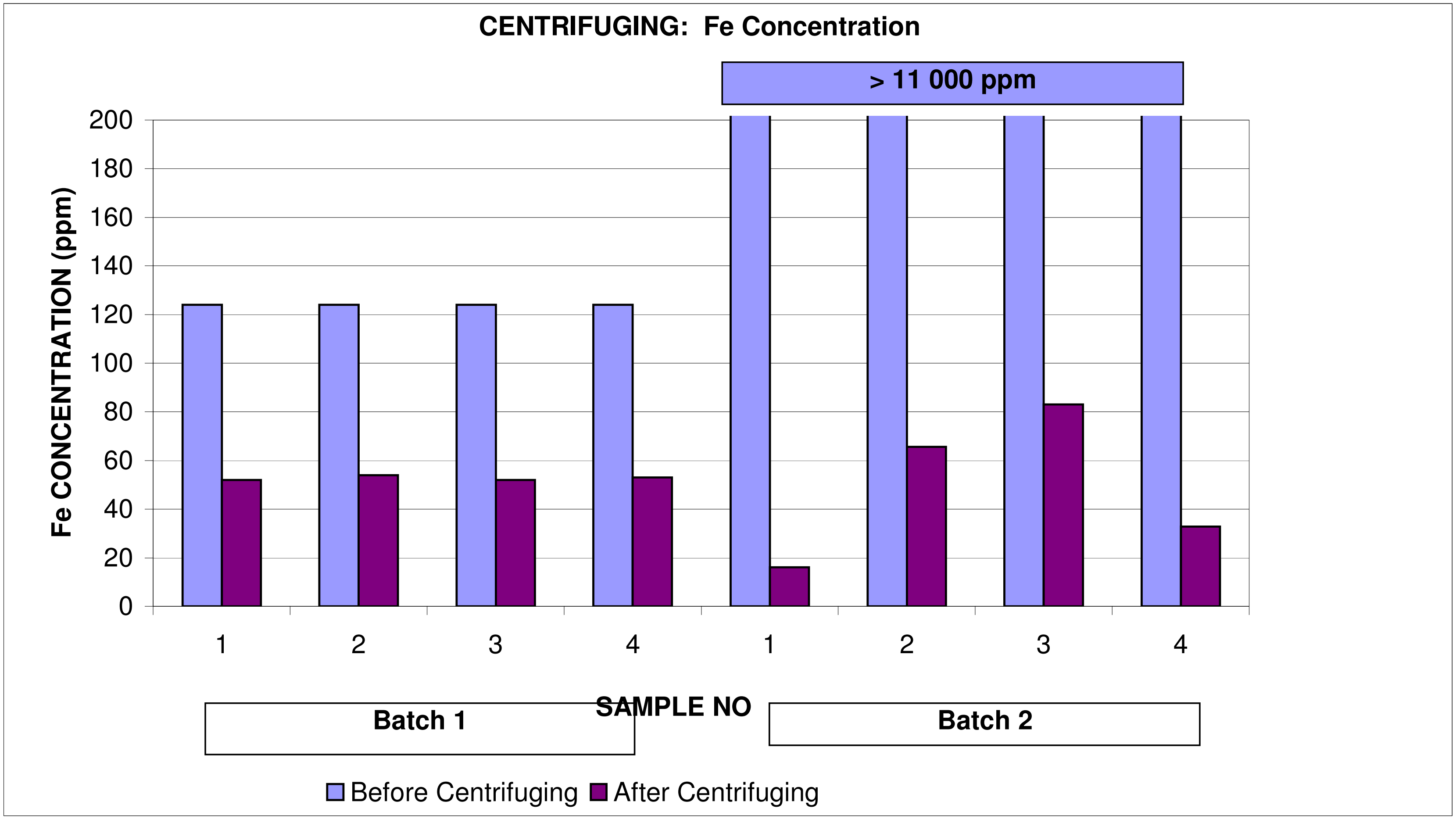


Fig 7.21: Centrifuging: Fe results

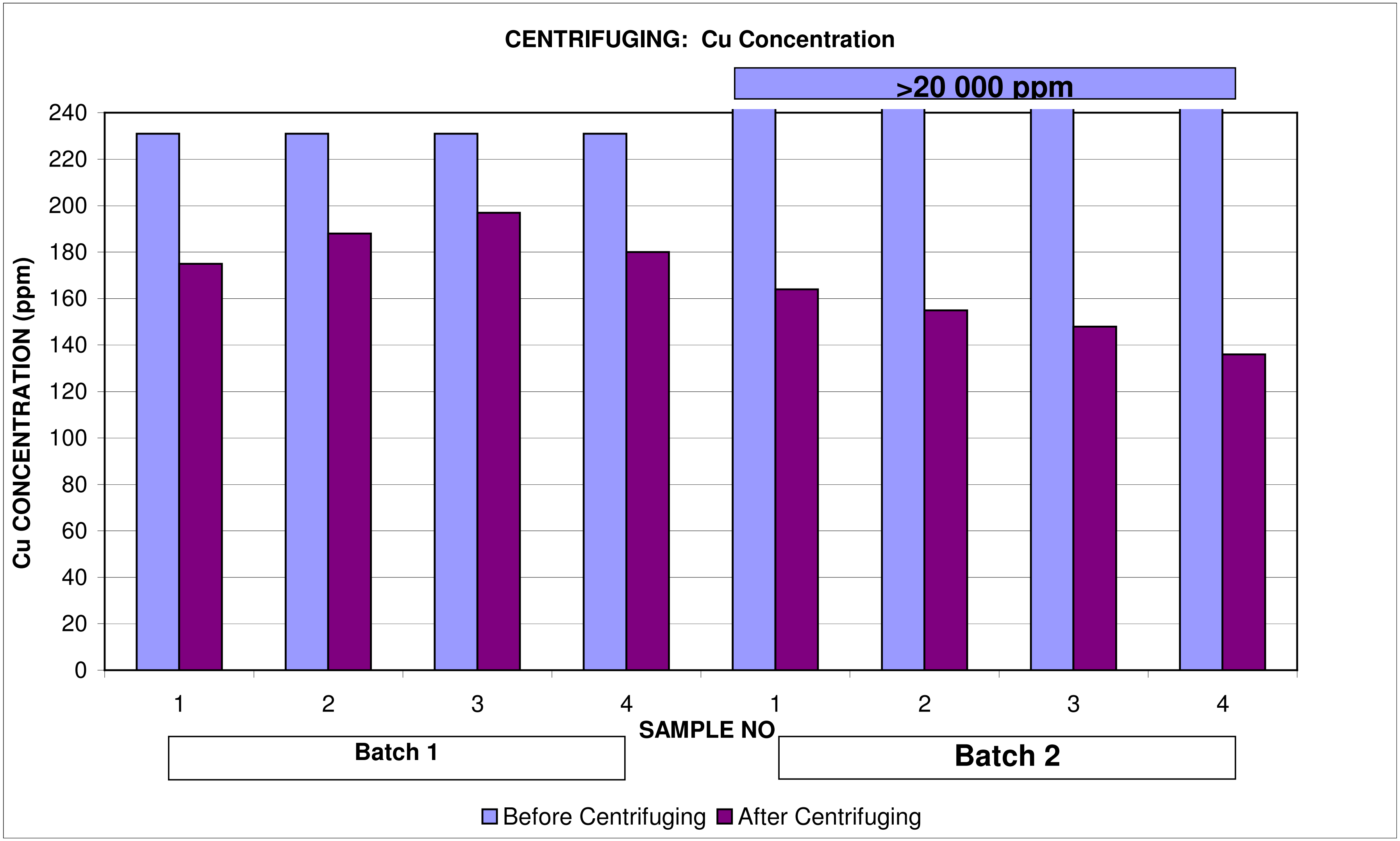


Fig 7.22: Centrifuging: Cu results

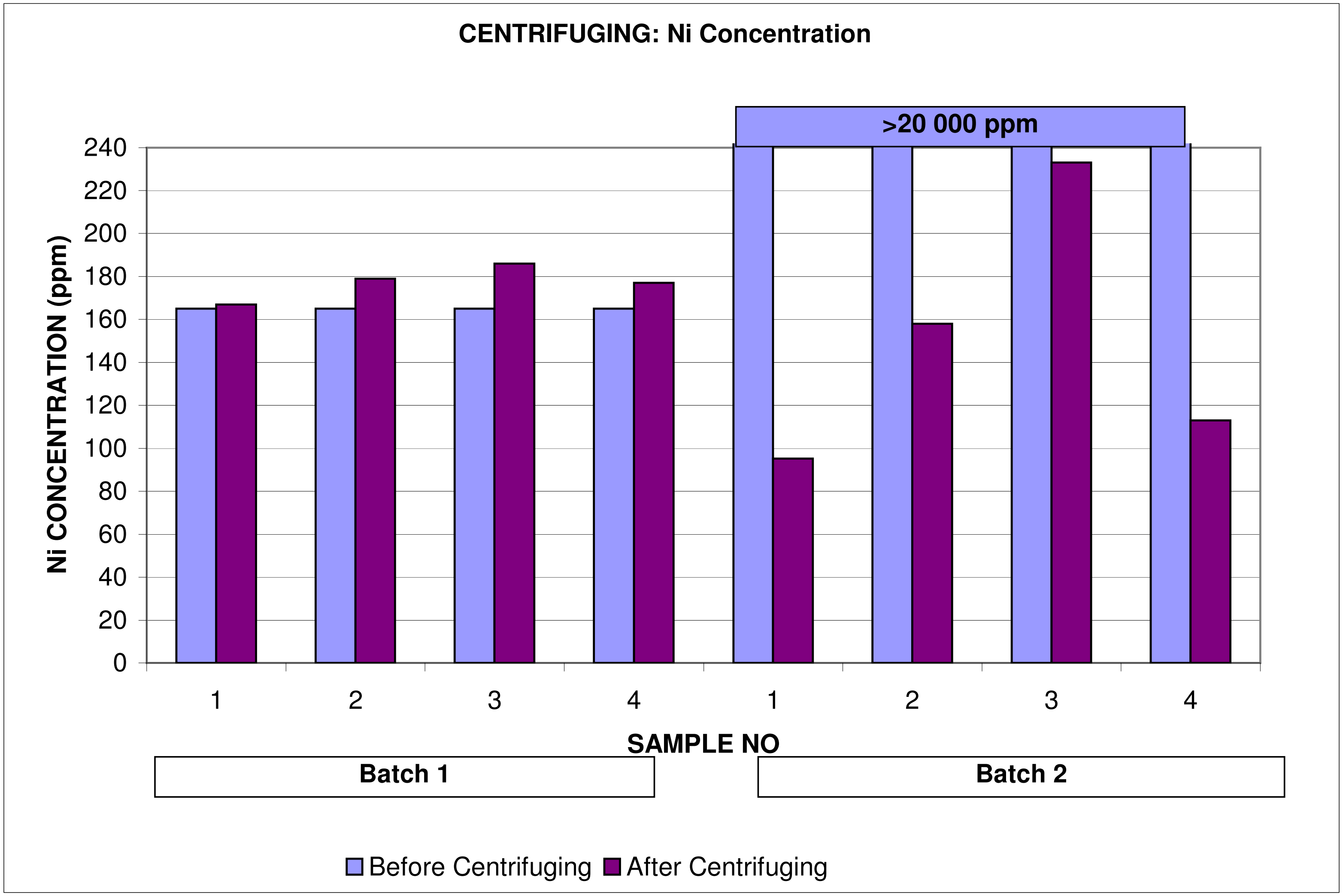


Fig 7.23: Centrifuging: Ni results

7.10 Centrifuging: Addition of KF.HF

According to Japanese patents (14, 15) KF.HF can be added to the molten electrolyte to lower the HF concentration in the electrolyte. At low HF concentrations in the electrolyte the solubility of the soluble metal fluorides decrease and some of the metals precipitate as insoluble fluorides.

A calculated quantity of KF.HF was added to the electrolyte to decrease the HF concentration in the molten electrolyte from 41.1% to 39.1%.

7.10.1 Fe concentration

Fig 7.24 indicates the effect of the decrease in HF concentration in the molten electrolyte on the Fe concentration. The average centrifuging efficiency of the 4 samples centrifuged is 99.61%. The maximum total Fe concentration in the molten electrolyte after centrifuging is 85.4 ppm which is well below the specified maximum Fe concentration of 200 ppm in freshly made-up electrolyte.

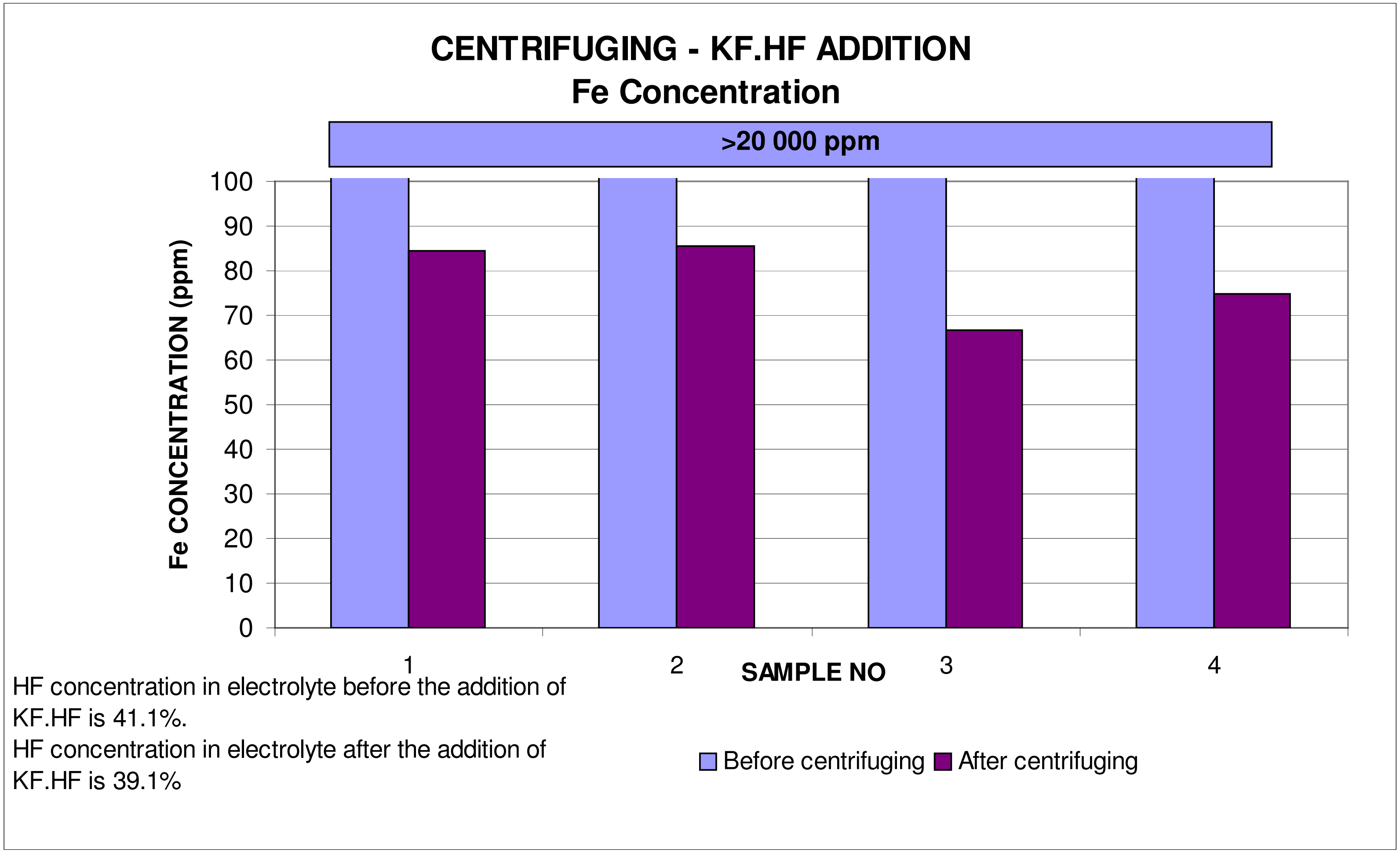
7.10.2 Cu concentration

Fig 7.25 indicates the decrease in the Cu concentration in the molten electrolyte after centrifuging at a lower HF concentration of the electrolyte. The average centrifuging efficiency of the 4 molten electrolyte samples centrifuged is 99.25%.

The maximum total Cu concentration in the molten electrolyte after centrifuging is 164 ppm.

7.10.3 Ni concentration

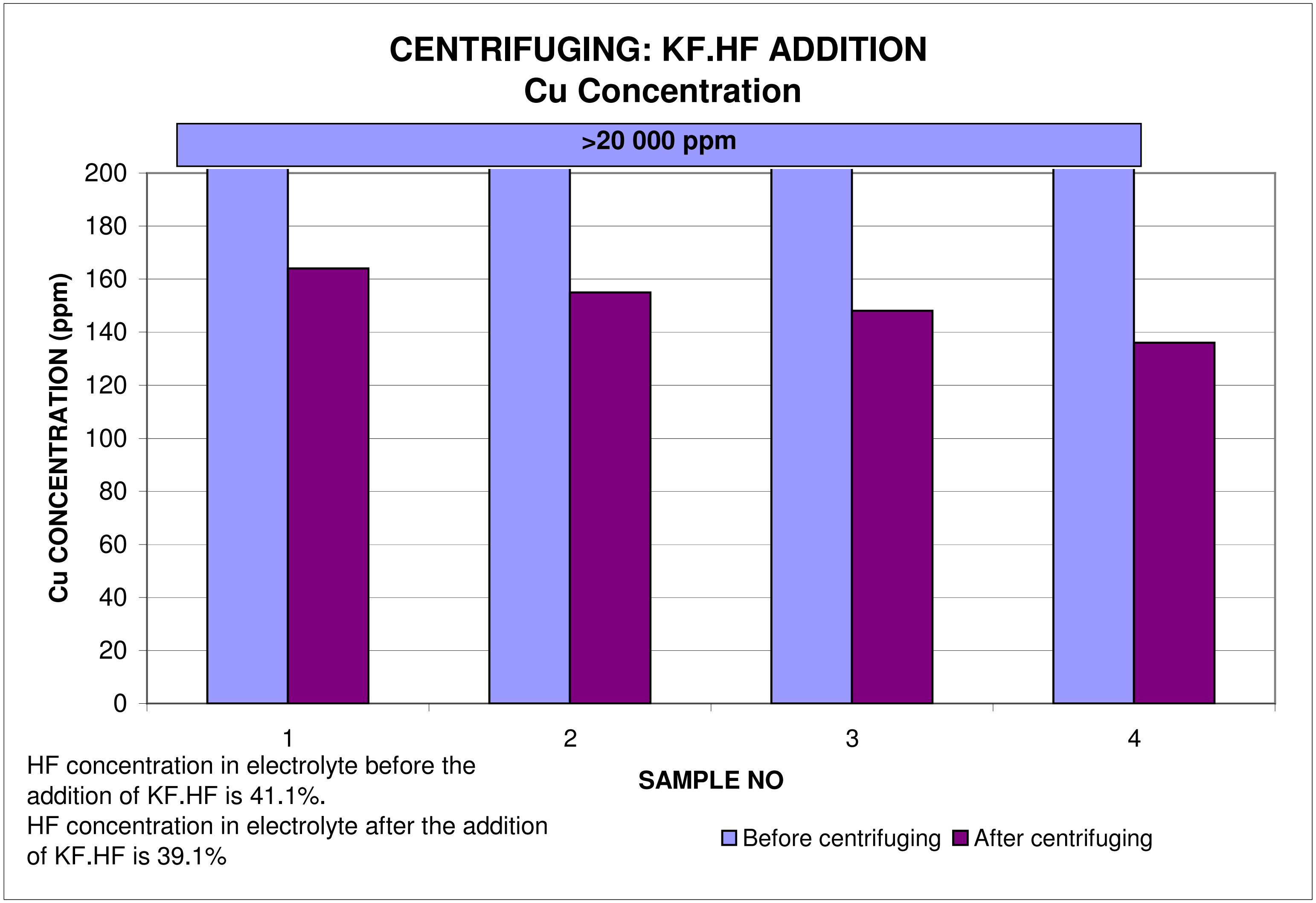
After centrifuging the Ni concentration in the electrolyte decreased from more than 20 000 ppm to a maximum of 188 ppm as indicated in Fig 7.26. The average centrifuging efficiency the 4 molten electrolyte samples centrifuged is 99.17%.



HF concentration in electrolyte before the addition of KF.HF is 41.1%.

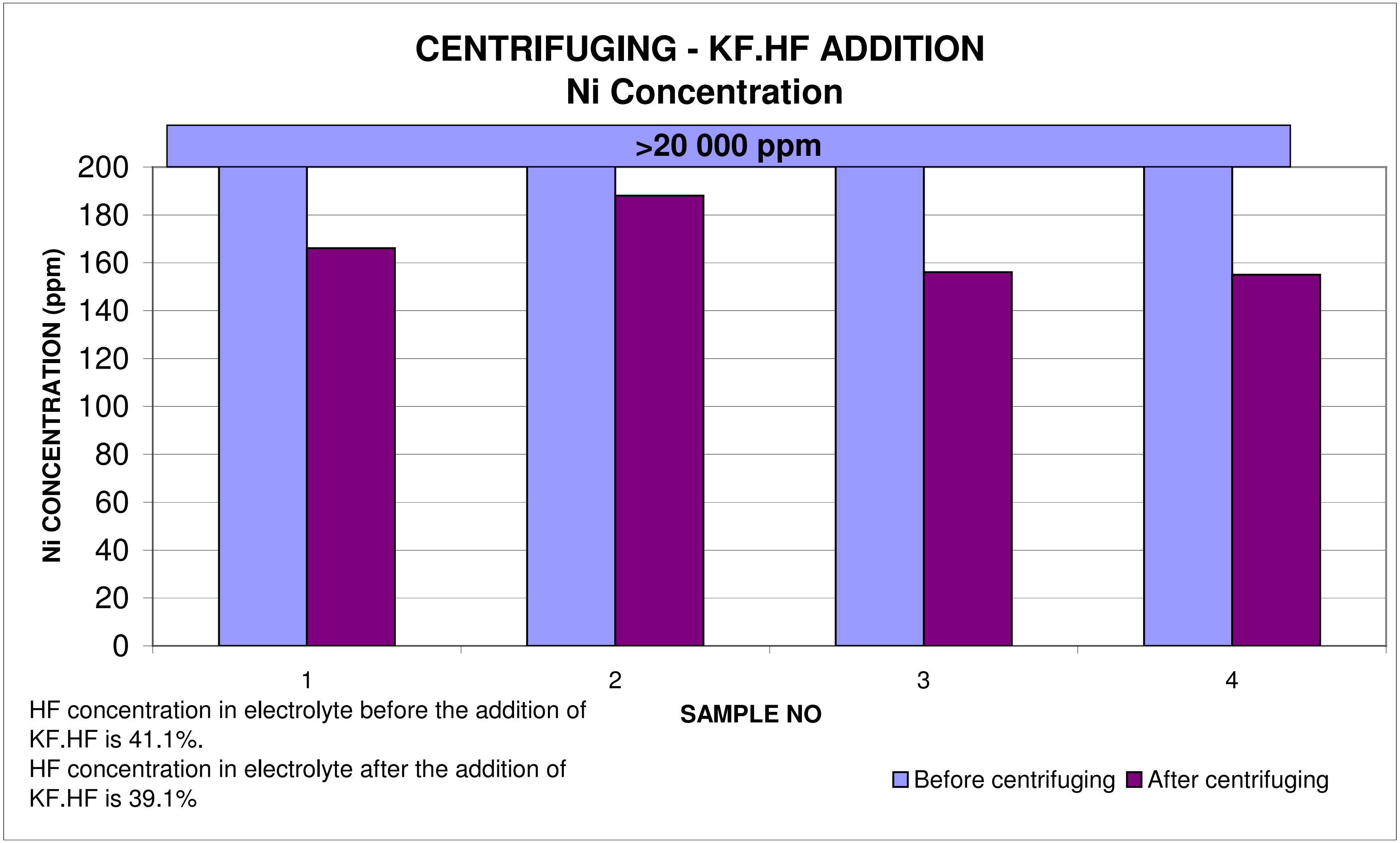
HF concentration in electrolyte after the addition of KF.HF is 39.1%

Fig 7.24: Centrifuging after addition of KF.HF: Fe concentration



HF concentration in electrolyte before the addition of KF.HF is 41.1%.
HF concentration in electrolyte after the addition of KF.HF is 39.1%

Fig 7.25: Centrifuging after addition of KF.HF: Cu concentration



HF concentration in electrolyte before the addition of KF.HF is 41.1%.
HF concentration in electrolyte after the addition of KF.HF is 39.1%

Fig 7.26: Centrifuging after addition of KF.HF: Ni concentration

7.10.4 Comparison of centrifuging after the KF.HF addition, with the centrifuging of untreated electrolyte

The batches of electrolyte treated with KF.HF were high in metal concentrations (more than 20 000 ppm of Fe, Cu and Ni). Batch 2 of the untreated electrolyte had a similar metal concentration level.

Fe centrifuging efficiency

Fig 7.27 indicates the Fe centrifuging efficiency of the untreated molten electrolyte, compared with the molten electrolyte treated with KF.HF to decrease the HF concentration of the electrolyte. It is not clear from the 4 samples if there is any difference between the efficiencies of the untreated and KF.HF treated electrolyte, the average efficiencies are almost the same.

Cu centrifuging efficiency

Fig 7.28 indicates that the centrifuging efficiency of the untreated electrolyte and electrolyte where different quantities of KF.HF have been added are identical.

Ni centrifuging efficiency

Fig 7.29 indicates that the Ni centrifuging efficiencies of the electrolyte with KF.HF added are slightly lower than the centrifuging efficiencies of the untreated electrolyte.

Conclusion

Comparison of the centrifuging efficiencies of untreated electrolyte and electrolyte with KF.HF addition to decrease the HF concentration indicates that the efficiencies are very similar and that the effect of the decrease of the HF concentration in the electrolyte by the addition of KF.HF is not apparent.

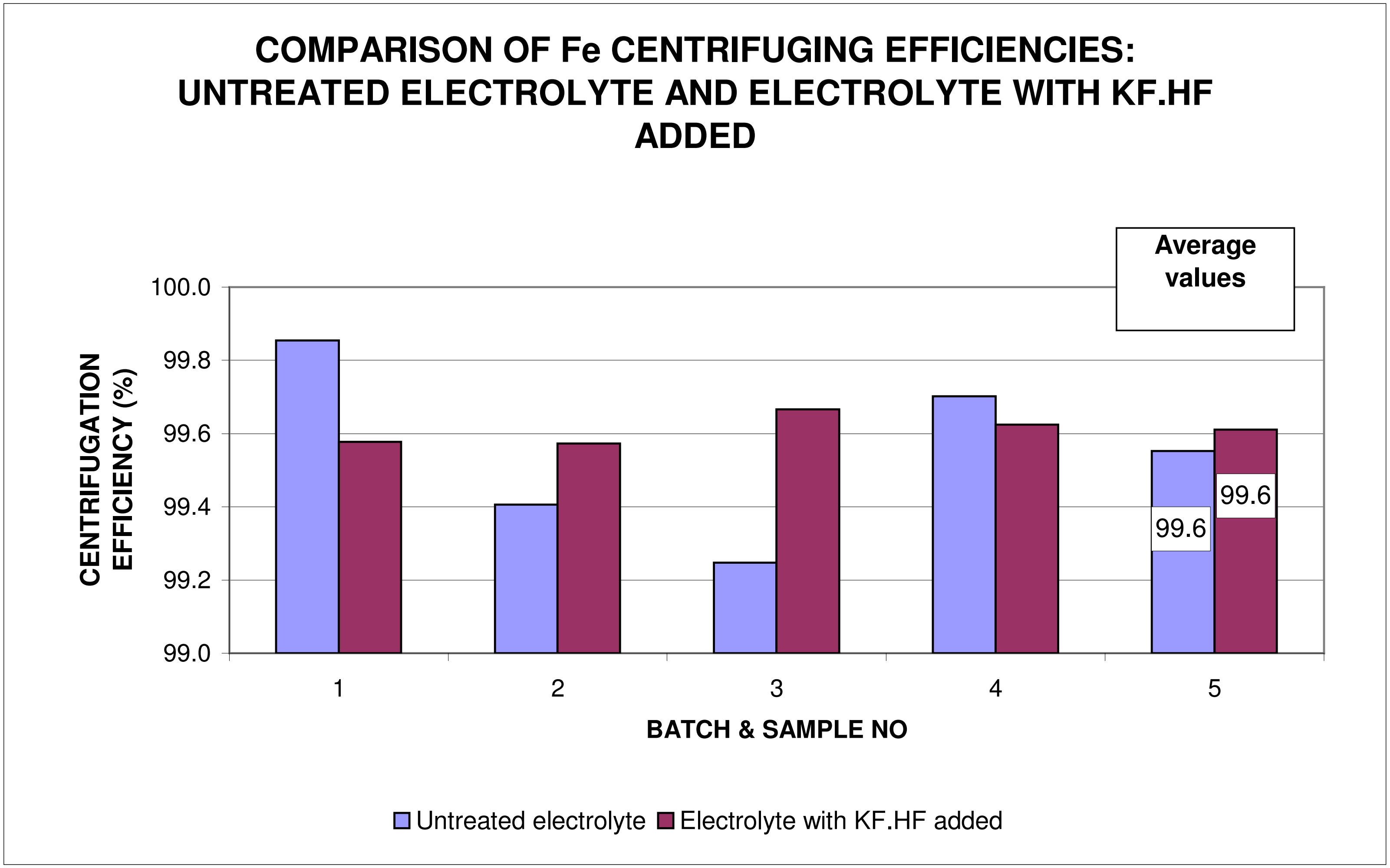


Fig 7.27: Comparison of Fe centrifuging efficiencies

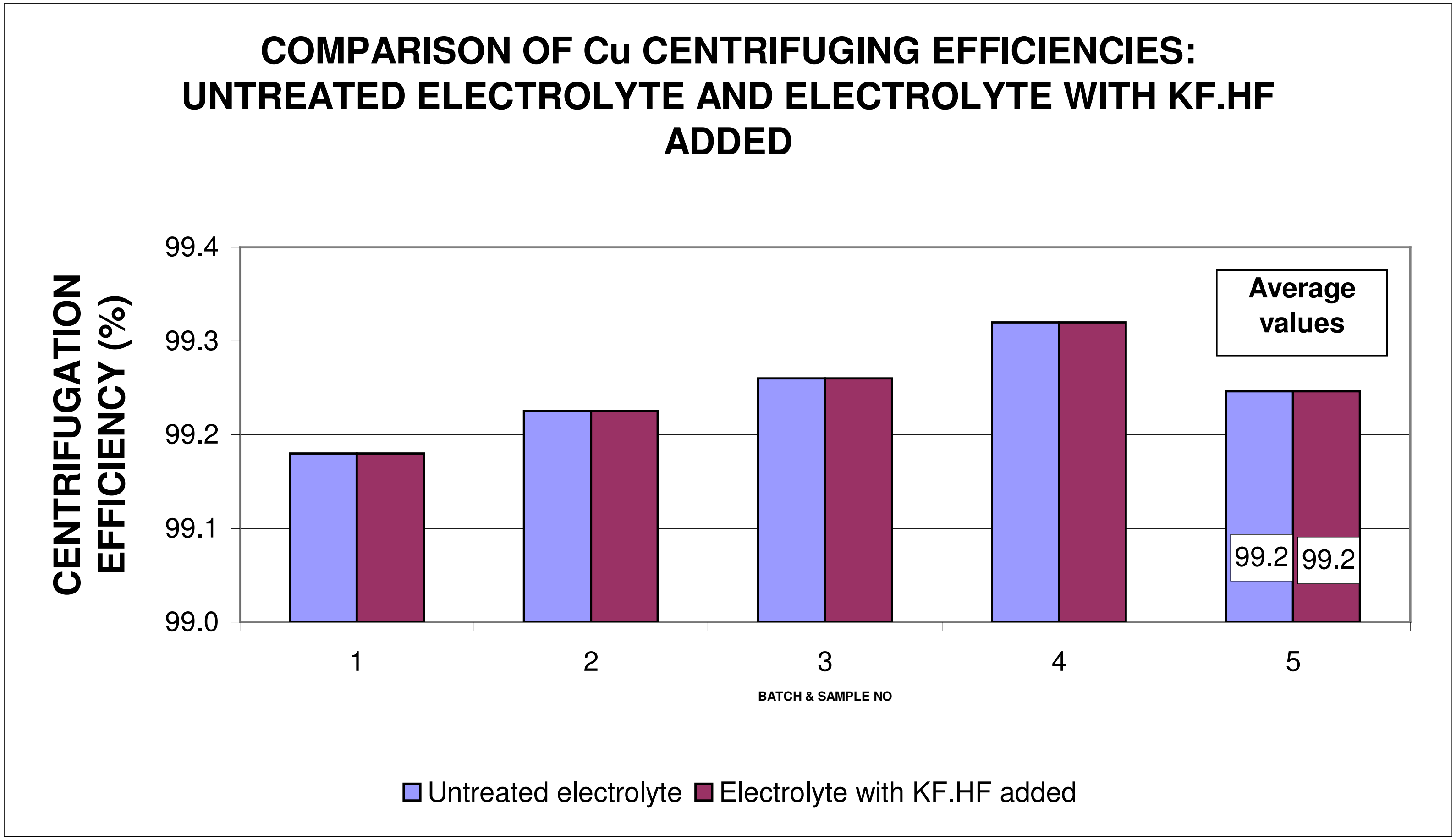


Fig 7.28: Comparison of Cu centrifuging efficiencies

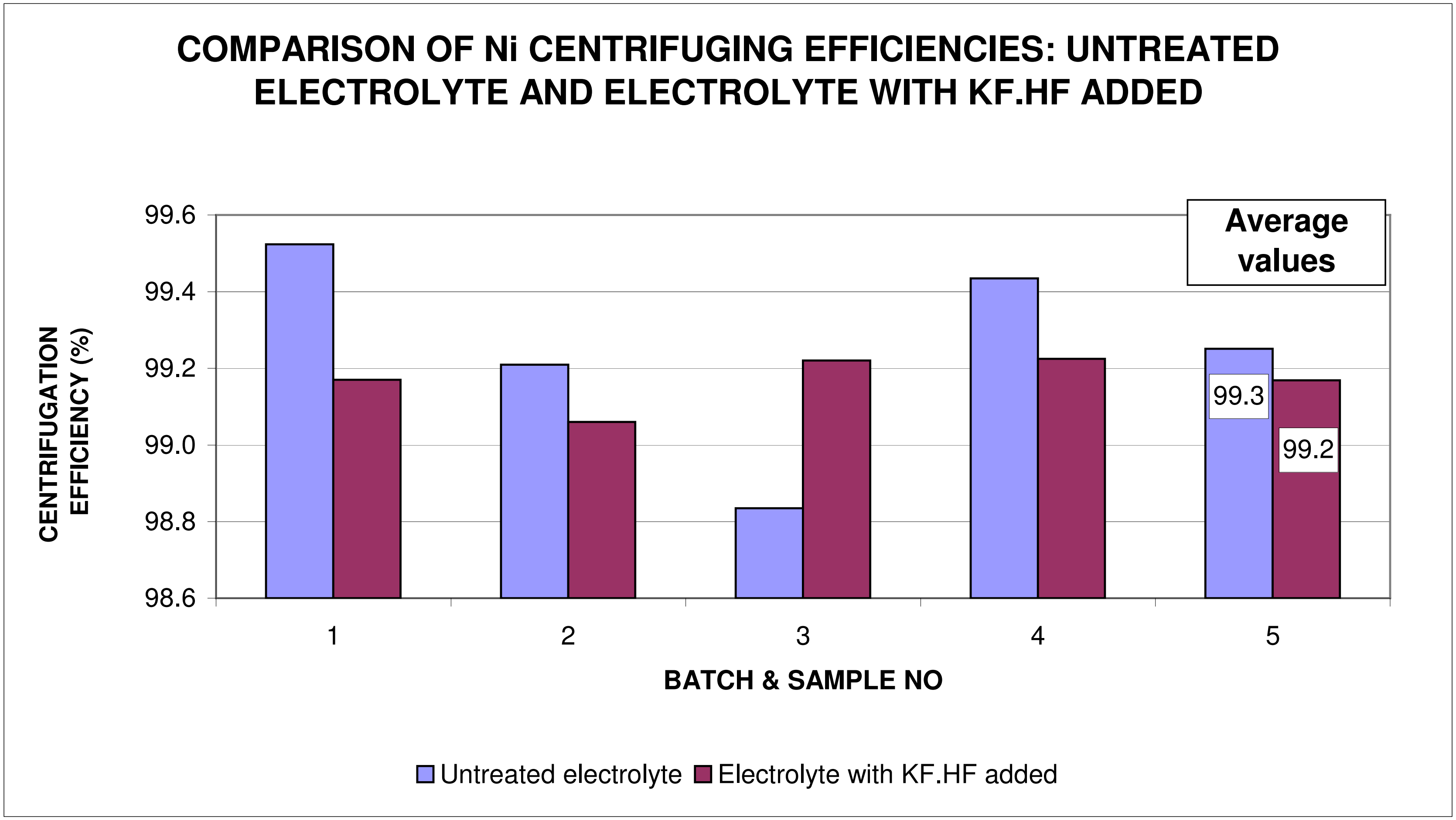


Fig 7.29: Comparison of Ni centrifuging efficiencies

7.11 Centrifuging: Stripping of the HF with dry N_2 gas

A Japanese patent (15) claimed that one of the methods to reduce the solubility of soluble Fe fluorides is to decrease the HF concentration in the molten electrolyte by sparging the electrolyte with an inert gas to strip the HF from the molten electrolyte.

A molten electrolyte batch was purged with N_2 gas at 17 l/min for 1.5 hours. Samples were taken every 30 minutes, centrifuged and analysed for total Fe, Cu and Ni.

7.11.1 Fe concentration

Figure 7.30 indicates the total Fe concentration of the electrolyte after centrifuging at different HF concentrations in the electrolyte. Although the effect of the decreasing HF concentration in the electrolyte on the solubility of the Fe is not clear, the effect of the centrifuging itself is indicated clearly. The total Fe concentration is decreased from 149 ppm to a maximum of 41 ppm. This is well below the specified maximum concentration of freshly made-up electrolyte of 200 ppm.

7.11.2 Cu concentration

Fig 7.31 indicates that although the Cu concentration of centrifuged electrolyte at different HF concentrations is similar, centrifuging decreased the total Cu in the electrolyte from 127 ppm to a maximum of 60 ppm.

7.11.3 Ni concentration

The Ni concentration follows the same trend as the Fe and Cu as indicated in Fig 7.32. The Ni concentration is decreased from 178 ppm to a maximum of 95 ppm.

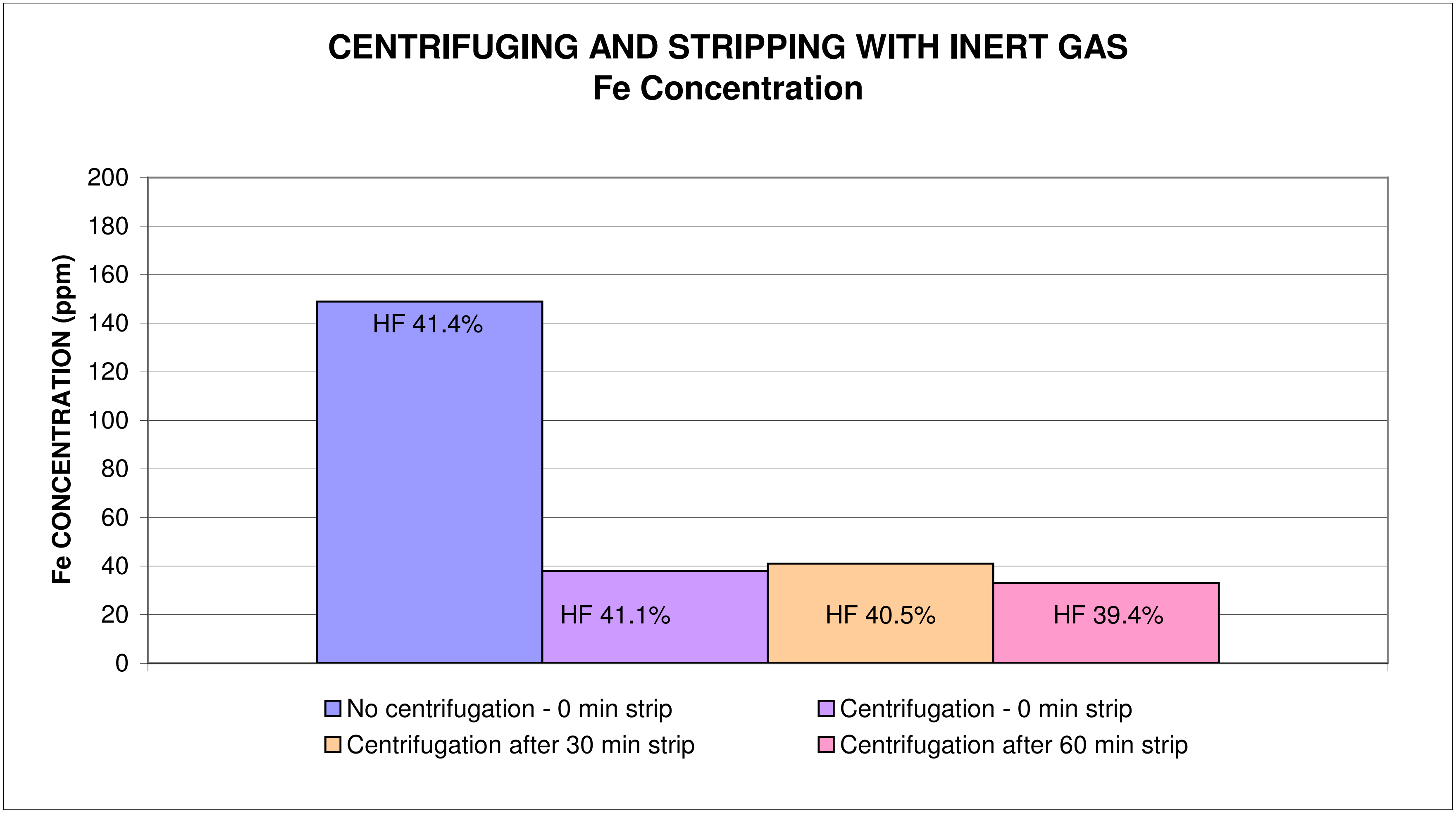


Fig 7.30: Centrifuging after stripping with N_2 gas: Total Fe concentration

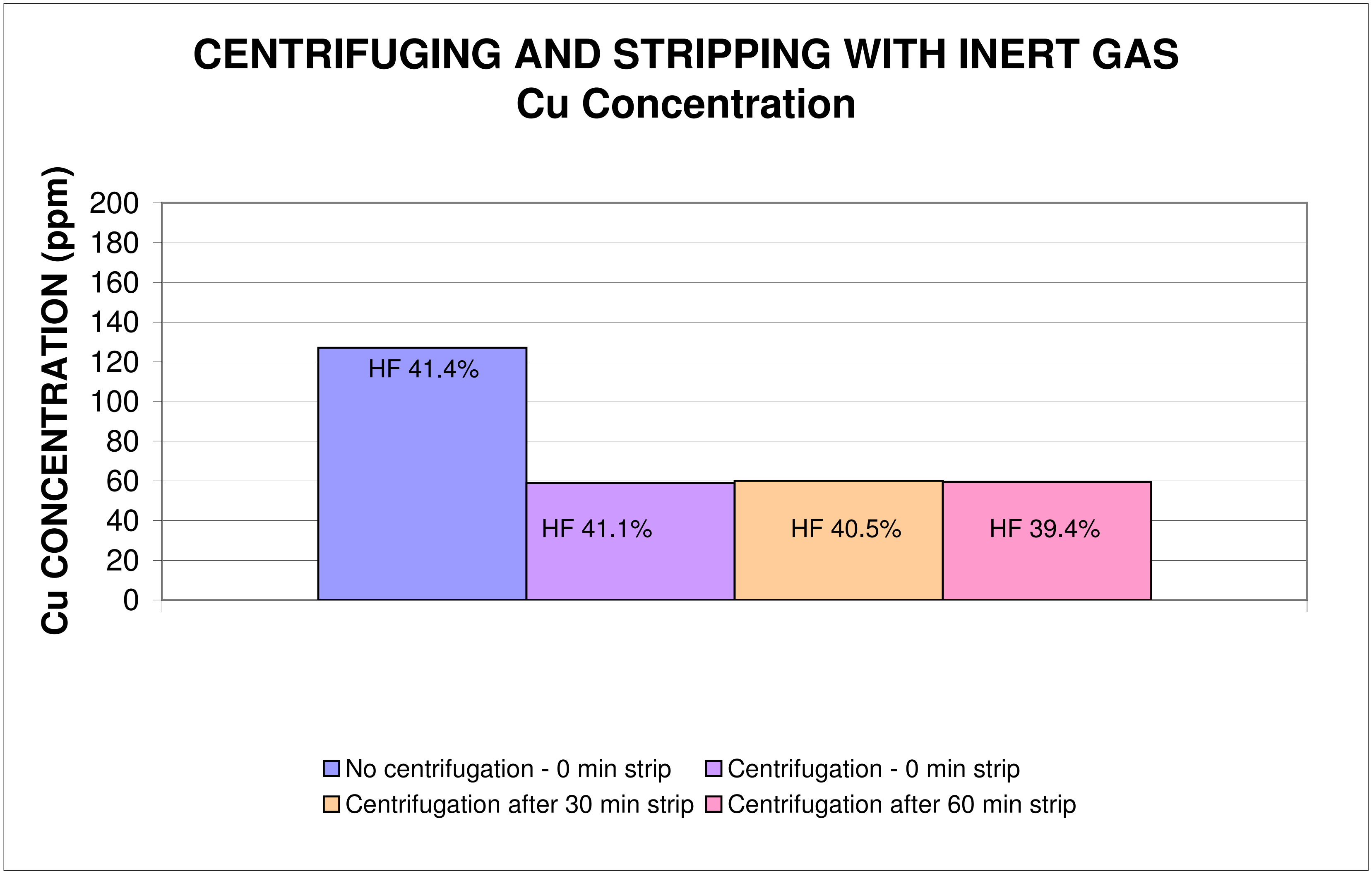


Fig 7.31: Centrifuging after stripping with N_2 gas: Total Cu concentration

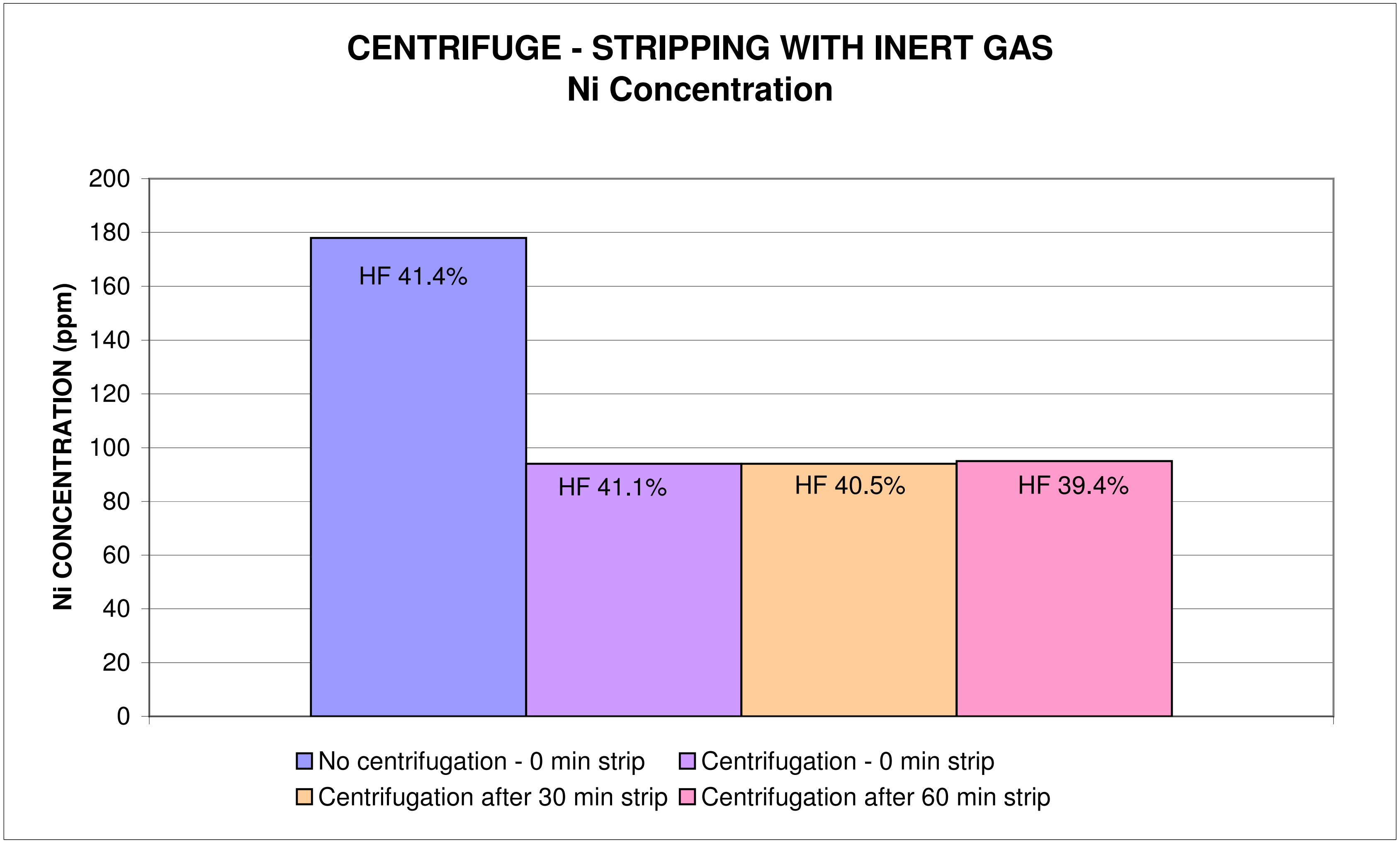


Fig 7.32: Total Ni concentration – Centrifuging after stripping with N_2 gas.

7.11.4 Centrifuging: Comparison of the metal concentrations of untreated centrifuging electrolyte with electrolyte stripped with N_2 gas.

Batch 1 of the untreated electrolyte and the batch stripped with N_2 gas are both waste electrolyte with low initial electrolyte metal concentrations.

	Fe	Cu	Ni
Batch 1 untreated electrolyte	124	231	165
Batch stripped with N_2 gas	149	127	178

Fe concentrations:

Fig 7.33 indicates the effect of the stripping of the HF from the electrolyte compared to untreated electrolyte after centrifuging. The average Fe concentration of Batch 1 untreated electrolyte decreased from 124 ppm to 52.8 ppm after centrifuging. The Fe concentration of the batch stripped with N_2 gas decreased from 149 ppm to an average of 37.3 ppm after centrifuging.

Cu concentration:

Fig 7.34 indicates the effect of the stripping of the HF from the electrolyte compared to untreated electrolyte after centrifuging. The average Cu concentration of Batch 1 untreated electrolyte decreased from 231 ppm to 185 ppm after centrifuging. The Cu concentration of the batch stripped with N_2 gas decreased from 127 ppm to an average of 59.5 ppm after centrifuging.

Ni concentration:

Fig 7.35 indicates the effect of the stripping of the HF from the electrolyte compared to untreated electrolyte after centrifuging. The average total Ni concentration of Batch 1 untreated electrolyte decreased from 165 ppm to 177.3ppm after centrifuging. The Ni concentration of the batch stripped with N_2 gas decreased from 178 ppm to an average of 94.3 ppm after centrifuging.

7.11.5 Centrifuging: Electrolyte yield.

The volumetric yield, as measured from the visual indication on the centrifuge tubes, is more than 90 %.

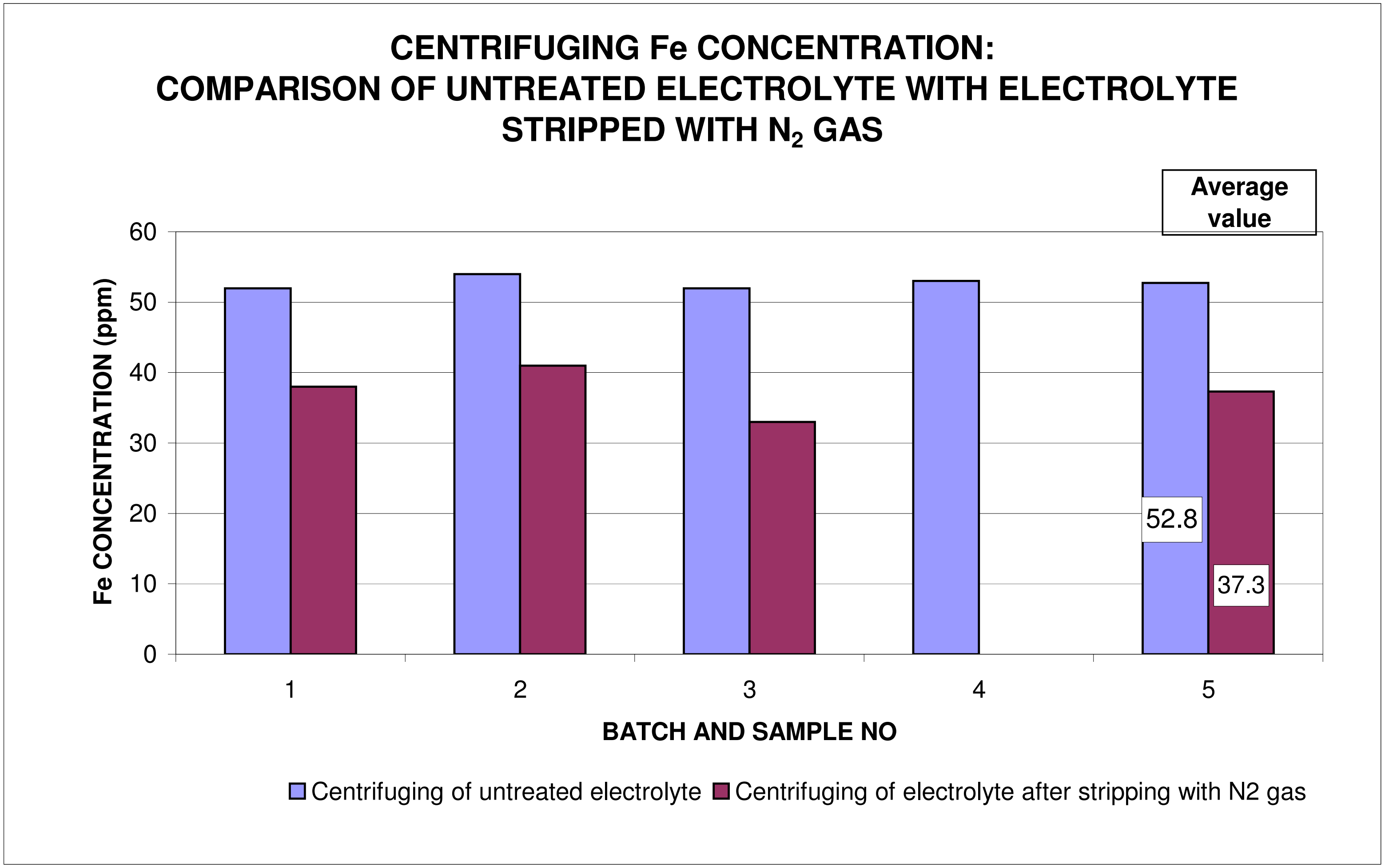


Fig 7.33: Centrifuging: Comparison of Fe concentration of untreated electrolyte with electrolyte stripped with N_2 gas.

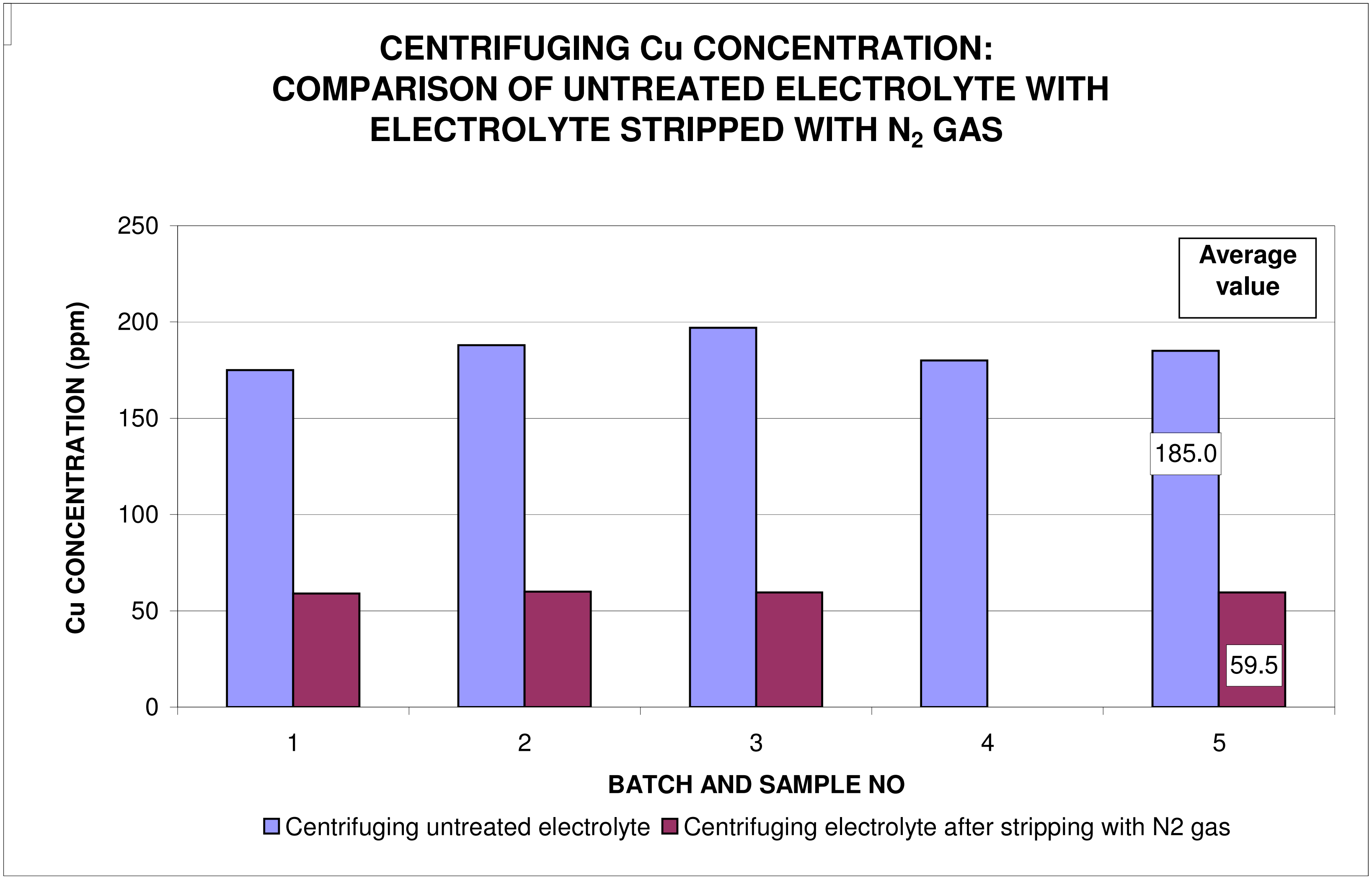


Fig 7.34: Centrifuging: Comparison of Cu concentration of untreated electrolyte with electrolyte stripped with N_2 gas

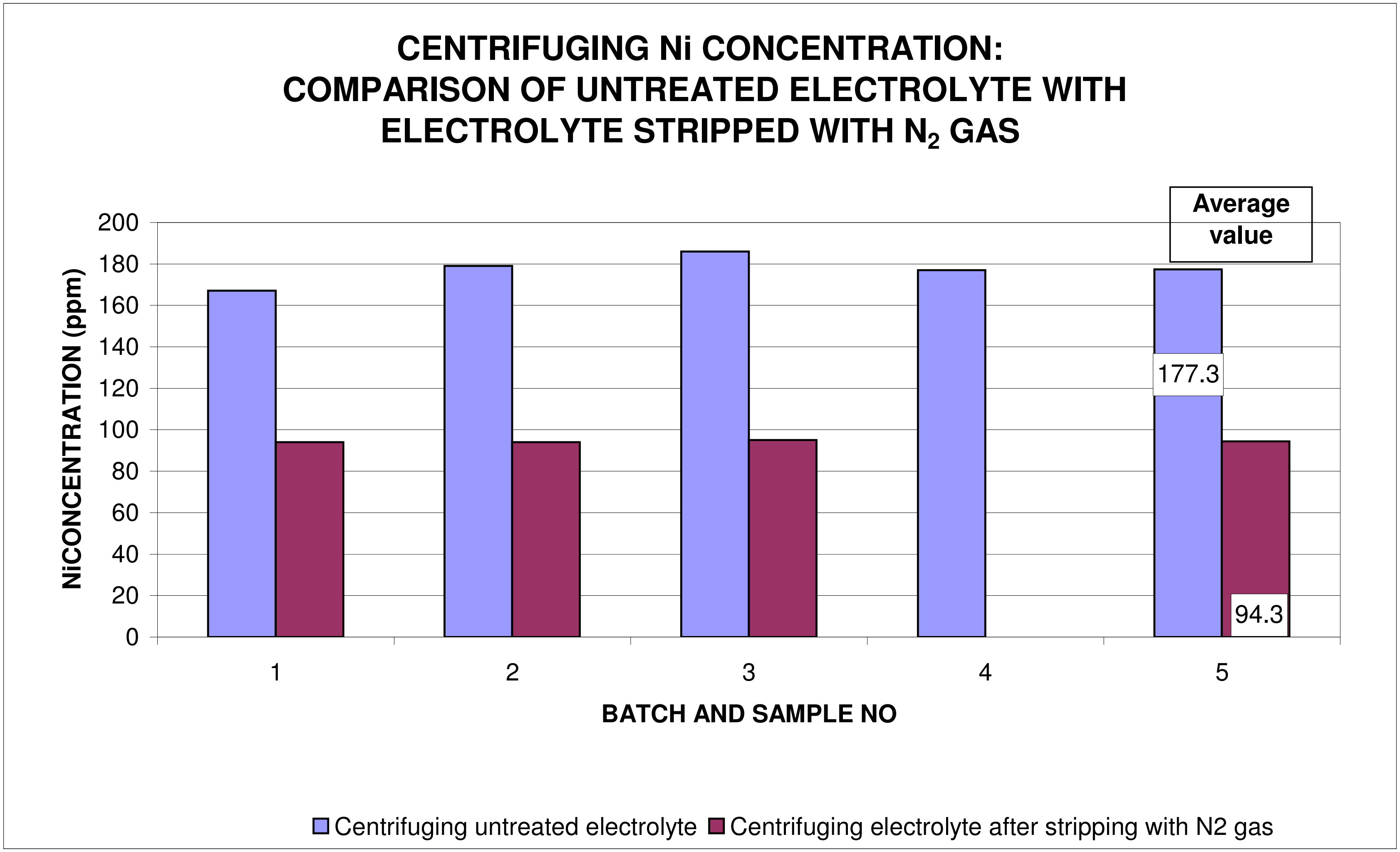


Fig 7.35: Centrifuging: Comparison of Ni concentration of untreated electrolyte with electrolyte stripped with N_2 gas

7.12 Centrifuging: Addition of NaOH

A Japanese patent extract (16) claims that if the stoichiometric quantity of Na in the form of NaOH or NaF is added to molten electrolyte, the soluble FeF_3 is converted into an insoluble triple salt K_2NaFeF_6. A combined test run with filtration and centrifuging was done and the centrifuging results are indicated in Fig 7.36.

Keeping in mind that the K_2NaFeF_6 is not soluble in the aqueous HNO_3 used to treat the samples prior to the AA analysis, fig 7.36 indicates that after the addition of NaOH there is a decrease in Fe, Cu and Ni concentrations before centrifuging. The patent (16) refers to Fe in particular but fig 7.36 indicates that the effect of the formation of triple salts is greater with the Cu and the greatest with the Ni.

Fe concentration

Centrifuging of the Na treated electrolyte removed a large quantity of Fe particles present in the electrolyte as indicated by the decrease in total Fe concentration. The Fe concentration decreased from 149 ppm to 62 ppm.

Cu concentration

The Cu concentration decreased to a lesser extent than the Fe, thus indicating fewer Cu particles present in the molten electrolyte. The Cu concentration decreased from 127 ppm to 71 ppm.

Ni concentration

The Ni concentration after the addition of NaOH did not decrease after centrifuging, which is an indication that no Ni particles were present in the samples and that all the Ni is in solution as soluble Ni fluorides. The Ni concentration of the untreated electrolyte however decreased from 178 ppm to 96 ppm after the addition of NaOH.

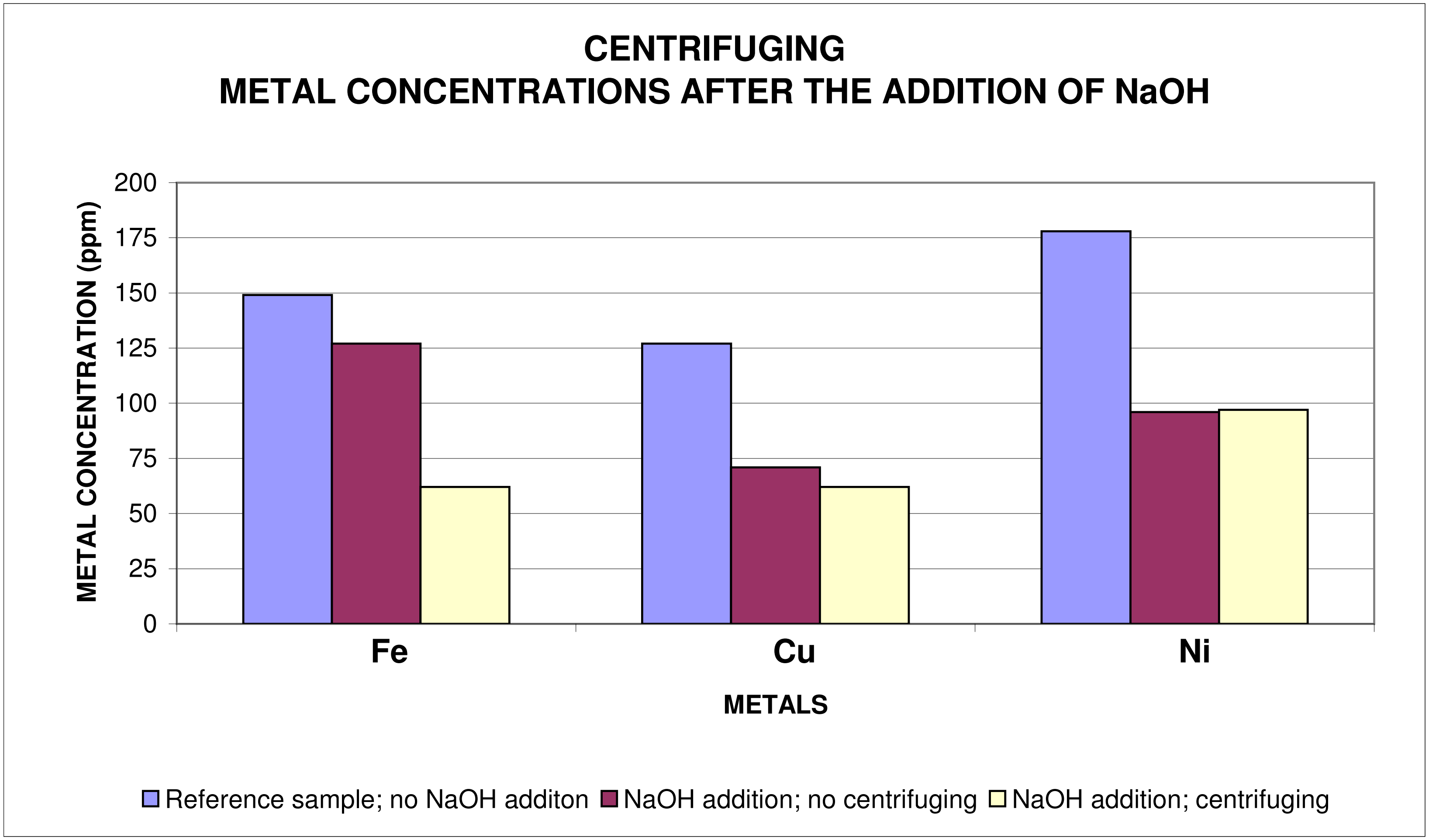


Fig 7.36: Metal concentrations after the addition of NaOH to the electrolyte

7.13 The effect of corrosion of the filter systems

A combined test run was performed during the addition of the NaOH to the molten electrolyte. The purpose of the experiments were to determine the variation in soluble and insoluble metal concentrations through the filter system. During this test the follow operations were done in sequence:

- A reference sample of the electrolyte with no NaOH added was analysed for total Fe, Cu, and Ni.
- NaOH was added to the calculated stoichiometic quantity of Fe and after the electrolyte was stirred with N_2 gas another 2 samples were taken. One sample was analysed while the second sample was centrifuged and the supernatant liquid analysed .
- The NaOH treated molten electrolyte was filtered through the Monel filter system and one sample was analysed, and a second sample centrifuged before the supernatant of the centrifuged sample was analysed.
- The molten electrolyte was filtered through the Monel and PTFE filter systems, one sample was analysed, and a second sample was centrifuged and the supernatant electrolyte analysed.

Fig 7.37 indicates the results of the different NaOH tests.

Fe concentration

As discussed before in paragraph 7.12, there is a clear decrease in the Fe concentration in the NaOH treated electrolyte after centrifuging. After the Monel filter the total Fe concentration indicates a large increase, due to corrosion of the stainless steel filter housing. The centrifugal sample after filtration through the Monel filter is an indication of the soluble and very fine Fe if compared with the sample that was only filtered.

Filtering of the electrolyte with the PTFE filter indicates no decrease in Fe concentration. However centrifuging of the Monel and PTFE filtered sample indicates a total Fe concentration similar to the centrifuged sample before filtration. The overall conclusion is that the Fe generated in the filter systems is particles of Fe.

Cu concentration

The same trend as for the Fe is indicated in fig 7.37 for the Cu concentration. The increase in Cu concentration after the Monel filter is larger than that of the Fe. It is to be expected that the total Cu concentration will increase, because of the corrosion of the Monel filter.

The decrease of the Cu concentration in the electrolyte after centrifuging compared to the total Cu concentration after the Monel filter is greater than the similar decrease in the case of the Fe concentration.

The indication is that the increase in the total Cu concentration after the Monel filter is mainly Cu particles due to the dissolving of the Ni in the Monel alloy.

There is an increase in the Cu concentration after the PTFE filter, indicating that very fine Cu particles are released from the outside of the Monel filter element.

Fig 7.37 also indicates that the centrifuged sample after the PTFE filter has a nearly identical total Cu concentration to that of the centrifuged sample before filtration.

As in the case of the Fe, the indication is that the Cu generated in the filter systems due to corrosion, is Cu particles.

Ni

The Ni concentration follows the same trend as the Fe and Cu, except that the Ni concentration after the Monel and PTFE filters is larger than the similar Fe and Cu concentrations. The centrifuged Ni concentrations after the Monel and PTFE filters are higher than the corresponding Fe and Cu concentrations, indicating that a large portion of the generated Ni, because of the filter corrosion, is soluble Ni fluorides and very fine Ni particles.

The concentration of the centrifugal sample after the PTFE filter system is larger than the Ni concentration of the centrifuged sample before filtration which also indicates the generation of very fine particles and soluble Ni fluoride in the filter systems.

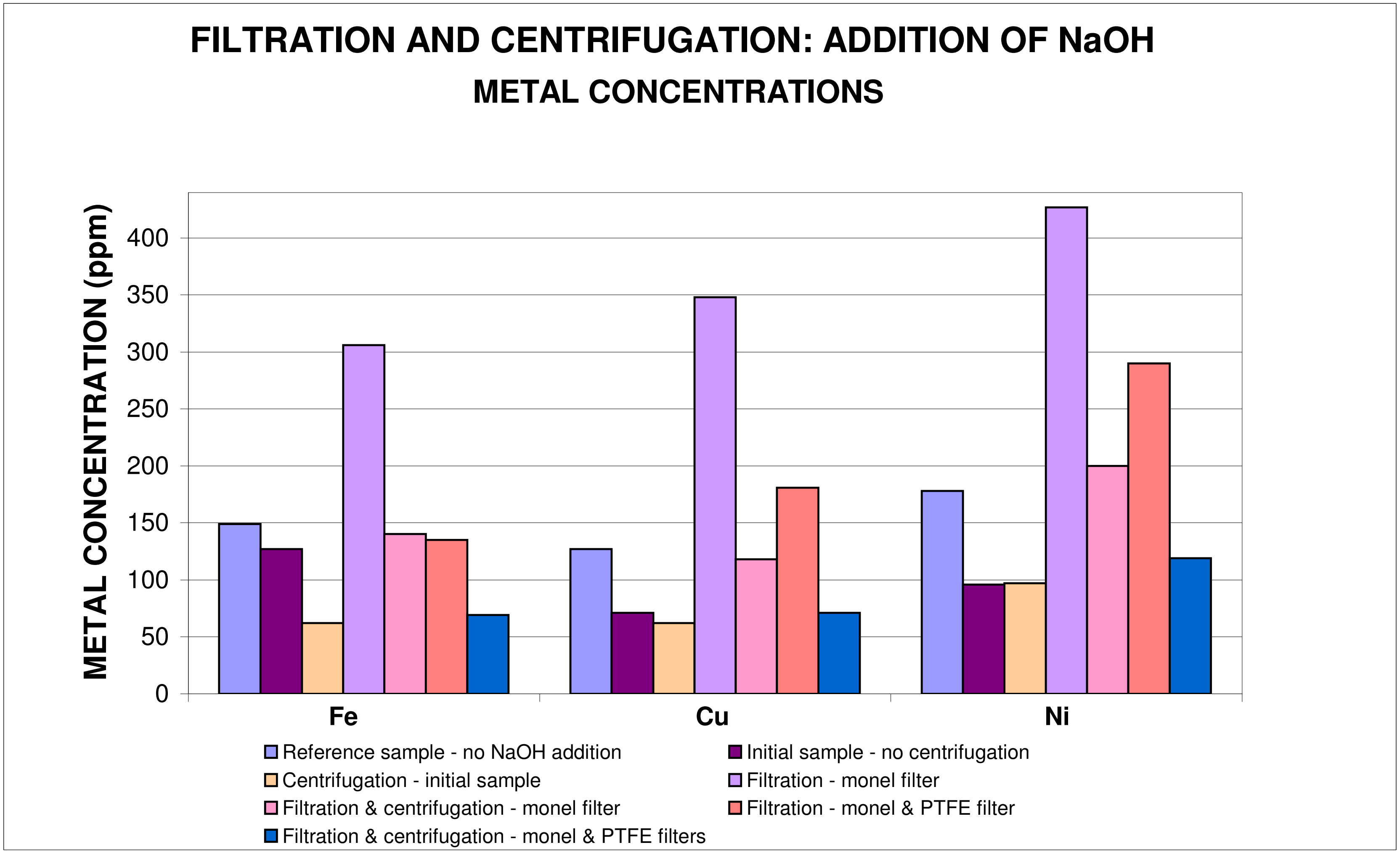


Fig 7.37: Metal concentrations of electrolyte treated with NaOH after filtration and centrifuging.

7.14 Moisture removal

The molten electrolyte was stripped with N_2 gas, for periods of time indicated in the procedure for the operation of the test facility (see section 6.4.10)

The purpose of this experiment was to determine the effect of the moisture content on the soluble and insoluble metal concentrations through the filter system.

Fig 7.38 indicates the decrease of the moisture content of the molten electrolyte as well as the decrease in the HF concentration. In a period of 60 minutes the moisture content of the molten electrolyte decreases from 1794 ppm to 807 ppm.

To demonstrate the hygroscopic nature of the electrolyte, the original moisture content analysed samples were exposed to the atmosphere for a short while and analysed again for moisture content.

Fig 7.39 indicates the increase .in the moisture content of the samples.

The moisture content increased from 1108 ppm to 1656 ppm in the sample stripped with N_2 gas for 30 minutes and from 807 ppm to 1242 ppm in the sample stripped with N_2 gas for 60 minutes.

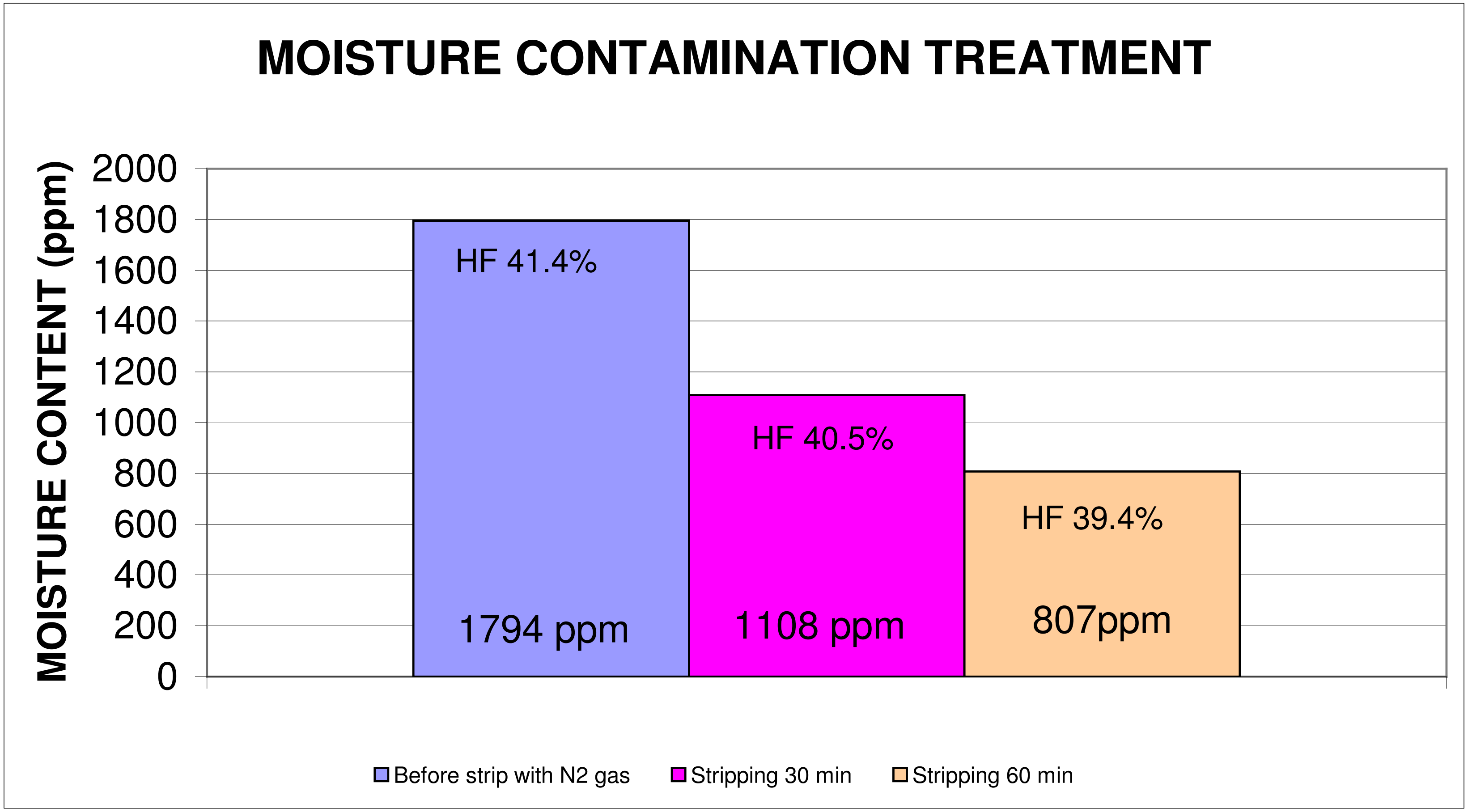


Fig 7.38: Moisture removal results

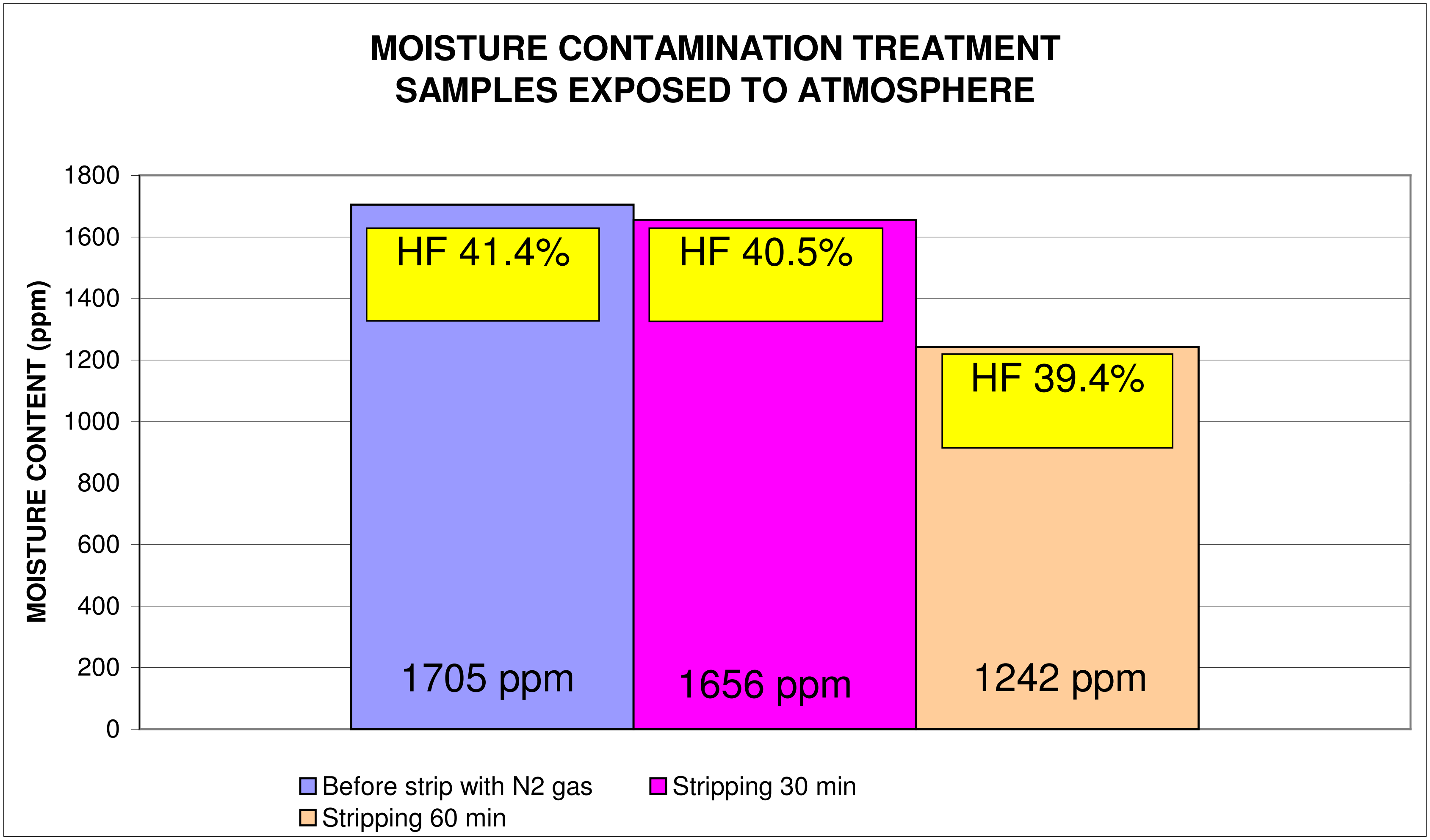


Fig 7.39: Increase in moisture concentration in electrolyte exposed to the atmosphere.

CHAPTER EIGHT

8 CONCLUSIONS

8.1 Sedimentation

Significant sedimentation of the insoluble metal impurities in the electrolyte is only possible after a settling time of more than 6 hours. This makes the implementation of sedimentation as an industrial separation process to purify waste electrolyte of excess metal impurities of Fe, Cu and Ni impractical. An 86 % yield is only possible after 312 hours (14).

8.2 Filtration

Although the filtration results were all overwhelmed by the effect of the corrosion of the filter systems, valuable information was gathered from the results. The only 2 treatment results that indicated positive filtration efficiencies were the results where the molten electrolyte was sparged with N2 gas and the addition of KF.HF, both having the effect of reducing the HF concentration of the electrolyte.

Decreasing of the HF concentration also decreases the moisture level in the electrolyte and the vapour in equilibrium with the molten electrolyte.

Consequently the conclusion is that decreasing of the HF and thus moisture content of the electrolyte is essential in an industrial application since the construction material of the equipment operating at elevated temperatures for treating the electrolyte can only be Monel.

The filtration results of the novel technologies, namely KF.HF addition, stripping with N_2, and addition of Na, did not show the benefit of these technologies claimed in the patents, mainly because of the effect of corrosion of the filter systems.

The filtration results also indicated that the filter systems tested do not remove the Fe, Cu and Ni particles to the acceptable concentration levels. Even the PTFE filter does not filter out the very fine particulates. The implication of these results is that filter media that would effectively remove the Fe, Cu and Ni particles would be expensive with regard to capital investment and operating cost.

The filters have a substantial pressure drop and would create an additional waste problem if they needed to be cleaned with aqueous HNO_3 or discarded.

Another disadvantage is that if the filters are not heated evenly, blockages tend to occur frequently.

8.3 Centrifuging

All the results indicated that sediment centrifugation is the most effective separation process to consider for the separation of Fe, Cu and Ni from the electrolyte and the consequent purification of the electrolyte.

The results of the addition of KF.HF to the electrolyte to decrease the HF concentration in the electrolyte and consequently decrease the solubility of the Fe, Cu and Ni in the electrolyte were not as effective as claimed in the patents (14,15) .

The results of the addition of NaOH to the electrolyte to convert soluble Fe to the insoluble triple salt, support the patent claim (16). The effect of the treatment was however more significant with the Cu and Ni.

As expected after analyzing the results from the filtration tests, the stripping of the electrolyte with dry N_2 gas indicates a distinct decrease in the concentration of Fe, Cu and Ni. Volumetric yields of more than 90% were obtained after centrifuging times of less than 10 minutes.

8.4 Moisture removal

The results of the test to remove moisture from the molten electrolyte by stripping the electrolyte with dry N2 gas, indicate a distinct decrease in the moisture content of the electrolyte with time.

These results support the improvement noticed when the same principle was applied to reduce the HF concentration in the electrolyte in order to precipitate soluble Fe, Cu and Ni.

To summarize: The results indicated that sparging molten electrolyte with N_2 gas to remove HF (thus precipitating soluble Fe, Cu and Ni, and removing moisture to reduce corrosion of metal components), followed by sediment centrifuging, appears to be a practical basis for an industrial waste electrolyte treatment process.

8.5 Confirmation of experimental results

Since the proposed process is based on limited experimental work within the scope of the dissertation, it is recommended that the basis for the process namely the stripping of the HF and moisture to precipitate soluble metal fluorides, and the efficiency of the centrifuging, be confirmed with more laboratory scale experiments.

CHAPTER NINE

9 PROCESS SYNTHESIS

9.1 Proposed process to reduce, recycle and re-use the waste electrolyte from the fluorine cells.

Fig 9.1 is a block flow diagram of the recommended process based on the conclusions of chapter 8. The process is a semi-batch process in the sense that a single batch of 400 kg of waste electrolyte is fed into the melt reactor after being removed from the waste containers with hand operated pneumatic jack hammers and fed to the crusher by hand.
As soon as molten electrolyte reaches a temperature of 120℃, it is purged with nitrogen gas for 12 hours to remove moisture and to decrease the HF concentration in the electrolyte, and precipitate soluble metal fluorides of Fe, Cu and Ni.

The stripped HF is vented to a special exhaust system to be reacted in a limestone scrubber.

The molten electrolyte is then continuously fed to a centrifuge where the sediment is separated from the supernatant electrolyte. The electrolyte still mixed with the sediment is drained into waste containers for removal by an approved waste removal contractor.

The molten purified electrolyte is fed into a freezer cooled with water. The molten electrolyte freezes on the cold walls of the freezer vessel and is mechanically scraped off the walls to fall into another crusher.

The crushed electrolyte is stored in plastic bags inside cardboard drums to be recycled to the F_2 cells.

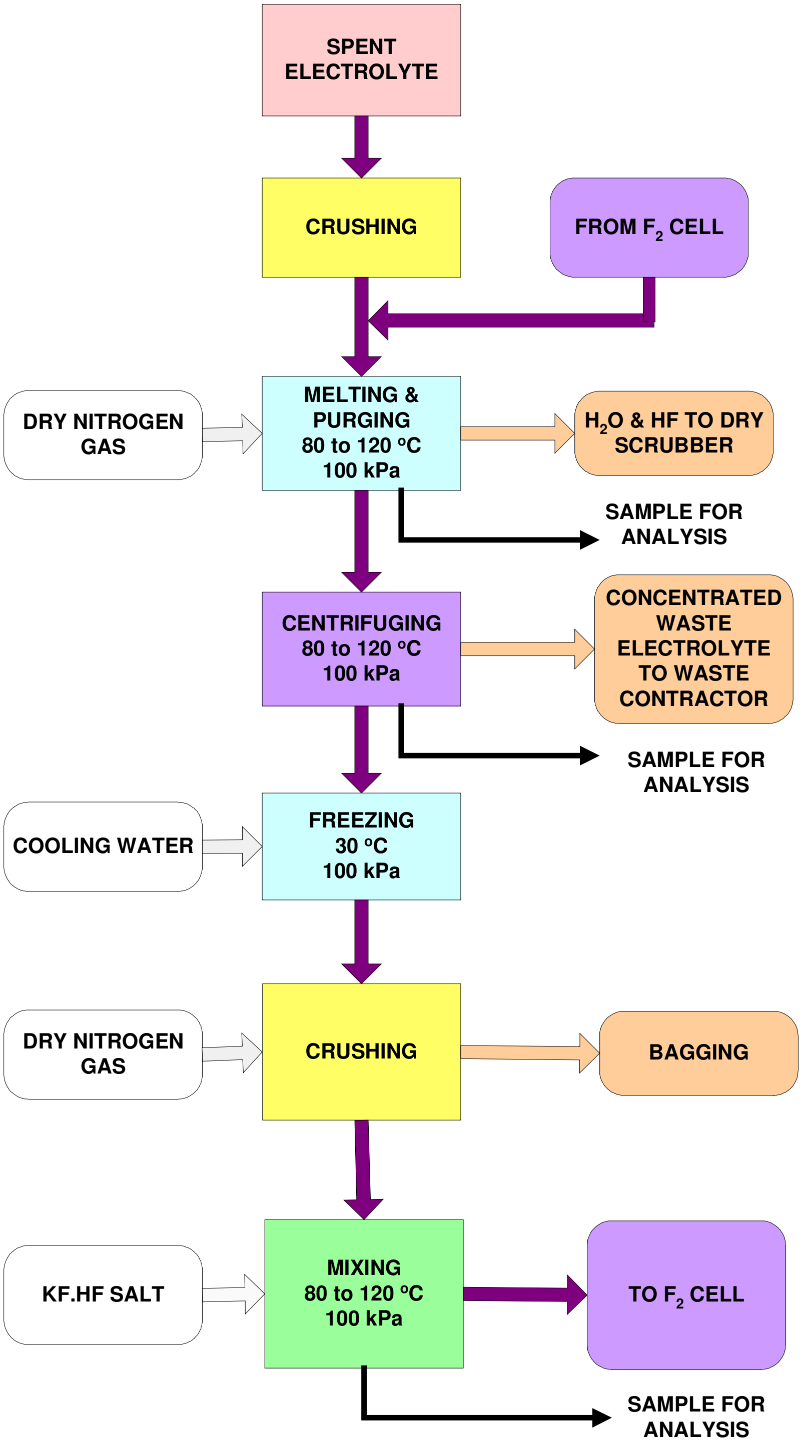


Fig 9.1 Block flow diagram

9.2 Material and energy balance and process flow diagram.

Fig 9.2 is a process flow diagram of the proposed process. The material and energy balance appears in Table 9.1.

The basis for the mass and energy balance and the process flow diagram is the following:

- The design capacity of the plant is 96 tpa. The current waste electrolyte from the F_2 cells is 36 tpa. The extra capacity is to allow for the treatment of 110 tonnes of stored electrolyte, as well as for the future expansion of the F_2 capacity.
- The plant will be operated by operators on a day shift of 8 hours for 5 days a week.
- Stripping of the moisture and HF from the molten electrolyte for 12 hours will be done during the night between the day shifts.
- Samples for analysis will be taken from the melt vessel and supernatant electrolyte stream leaving the centrifuge.
- The purified electrolyte will be bagged and stored for recycle to the F_2 cells.
- The yield is 90% which means that 10% of the treated electrolyte will be discarded as waste.

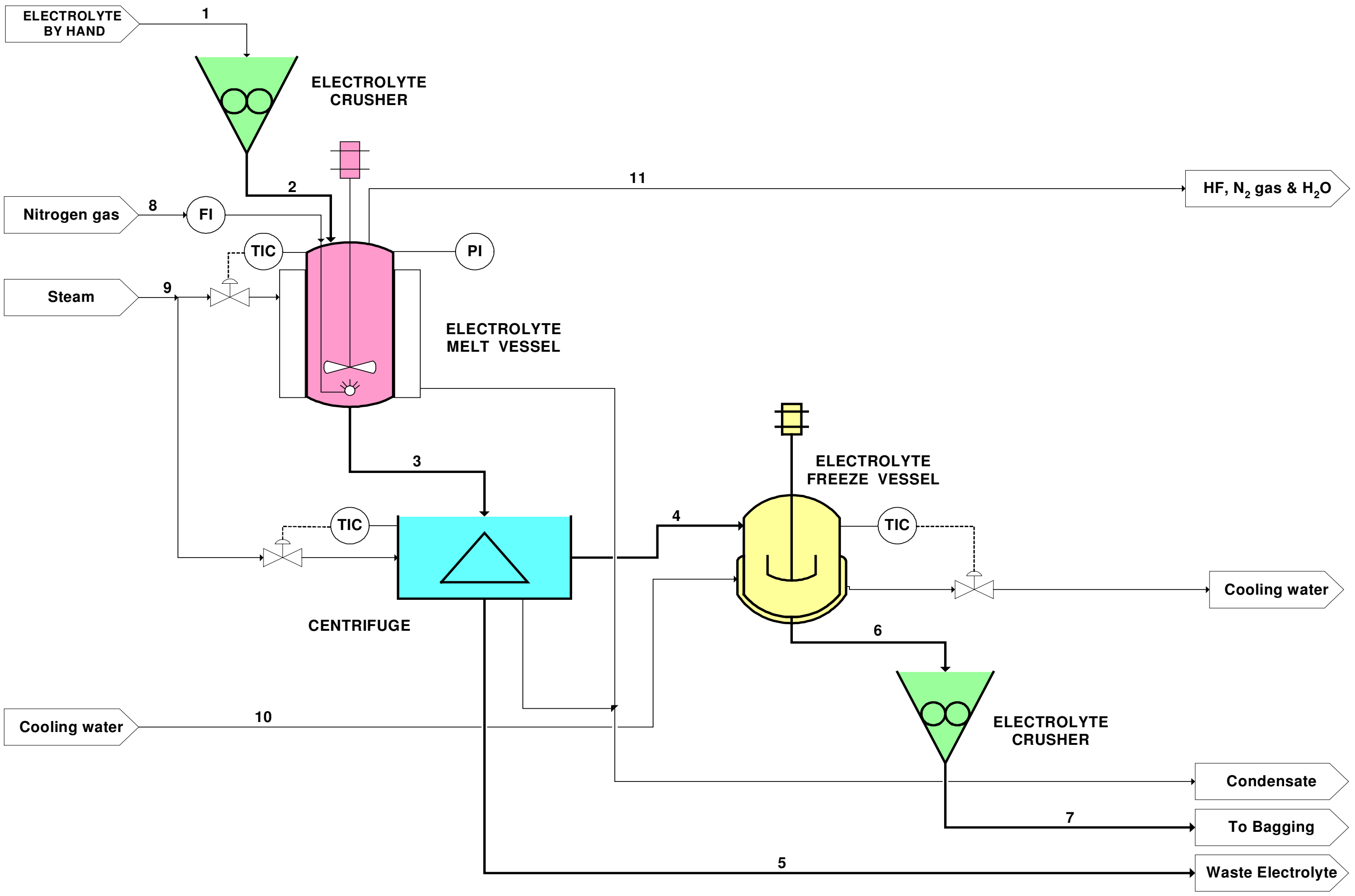


Fig 9.2 Process flow diagram

Plant capacity	tpa	96
	kg/day	400
Operating schedule	hours/day	8
	days/week	5

Stream number		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	
Chemical/ utility		KF.2HF	KF.2HF	KF.1.8HF	KF.1.8HF	KF.1.8HF	KF.1.8HF	KF.1.8HF	N_2 gas	Steam	Cooling water	Stripped HF	Limestone
Phase		solid	solid	liquid	liquid	liquid	solid	solid	gas	gas	liquid	gas	
Mole mass	kg/kmol	98.1	98.1	94.1	94.1	94.1	94.1	94.1	28	18	18	20	
Operating temperature	℃	25	25	120	120	120	40	30	25	135	26	120	
Operating pressure	kPa	88	88	200	100	88	88	88	200	315	600	100	
Batch mass (kg)	kg	400	400									14	
Mass flow (kg/batch)	kg			400	360	40	360	360	191.1	151.2	2064		175
Heat load	kJ									151200	60480		

Table 9.1: Mass and Energy balance summary.

9.3 Economic evaluation

A break-even cost analysis of the waste electrolyte purification plant indicates that for a 96 tpa electrolyte throughput the capital expenditure (capex) is R4,200,000.

The basis for the break-even calculation is (19):

Break-even output = $\frac{Cf}{p-b}$

where C*f* is the fixed cost per year.
b is the variable cost per kg electrolyte output.
p is the price of electrolyte per kg.

Capital Expenditure	R 4 200 000
Life expectancy (= depreciation)	5 years
Loan rate	10%
Cost of electrolyte (p)	R 19.35 / kg

Variable cost (calculated from mass & energy balance):

Variable Cost				
Description:	/ kg electrolyte		Price/Unit:	Cost:
Cooling Water	0.00516	m^3	R 0.30	R 0.00
Steam	0.38	kg	R 1.27	R 0.48
Nitrogen	0.480	kg	R 0.43	R 0.21
Limestone	0.44	kg	R 0.31	R 0.14
Electricity Variable	0.25	kWh	R 0.13	R 0.03
Total Variable Cost: Electrolyte (b)				R 0.86

Table 9.2: Variable cost

The purification plant will use the infrastructure such as buildings, plant management etc. of the existing F_2 generation facility.

The fixed costs per year are:

Description:	BOM:	Price/Unit:	Cost per year
Shift Foreman	0.50	180,000	90,000
Process Controller	2.00	140,000	280,000
Subtotal Direct Labour			370,000
Protective Clothing	1.00	10,000	10,000
Analytical	120.00	180	21,600
Other Operating Cost (Waste removal)	-	17,000	8,500
Subtotal Factory Cost			40,100
Maintenance Labour	0.25	150,000	37,500
Maintenance Materials	1.00	20,000	20,000
Subtotal Repair & Maintenance			57,500
Product Distribution (Containers)	100.00	20	2,000
Depreciation			832,032
Subtotal Production Overheads			834,032
Interest on loan	10 % on capex		420,000
Total fixed cost (C*f*)			1,774,915

Table 9.3: Fixed cost

Market researched indicates the following global fluorine generation capacity. The waste electrolyte estimates generated by these role players in the fluorine generation market were calculated and are indicated below.

Company	Expected F_2 production in t/a	Estimated waste electrolyte generation t/a
Honeywell (USA)	4000	36
Air Products (USA)	5000	225
Solvay (GE +IT)	3000	135
Comurex (FR)	2000	90
BNFL	1500	68
KDK (JP)	1000	45
Central Glass (JP)	1000	45
Asahi Glass (JP)	1500	68
Honghua (China Nuclear)	1200	54
Total	21000	946

Table 9.4: Global F_2 production capacity

The development and implementation of the electrolyte recovery facility is not a economical opportunity to Necsa but is just seen as a opportunity for the implementation of cleaner production however a possible business opportunity exist in the selling of this technology to other generators of fluorine. This will be investigated after the successful implementation and operation of such a facility at Necsa.

9.4 Environmental management

The proposed process implies a reduction in waste electrolyte of 90%. This means that only 10 % of the annual amount of KF.HF used in the fluorine plant will need to be purchased.

HF will be scrubbed with $CaCO_3$ that forms CaF_2, which can be used as landfill. In the future, the recovery of the HF through condensing can be investigated.

CHAPTER TEN

10 REFERENCES

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APPENDIX A

FLUORINE[21]	
Molecular mass	37.996 8
Boiling point @ 101.325 kPa (1 atm)	85.02 K (-188.13℃)
Triple point Temperature Pressure	53.54 K (-219.61℃) 221.3 Pa (1.66 mmHg)
Critical temperature	144.30 K (-128.85℃)
Critical pressure	5 215.2 kPa (51.47 atm)
Critical volume	0.066 2 ℓ/mol (1.742 ℓ/kg)
Critical density	0.574 kg/ℓ
Critical compressibility factor	0.288
Latent Heat of fusion @ 53.54 K (-219.61℃)	510.36 J/mol (121.98 cal/mol)
Refractive index, Liquid, n_D @ 85.02 K (-188.13℃)	1.2
Density: Saturated vapour @ 85.24 K (-187.91℃) & 101.53 kPa Liquid at saturated pressure & 85.02 K (-188.13℃)	 5.63 kg/m^3 1507 kg/m^3
Latent heat of vapourization @ 85.02 K (188.13℃)	166.356 kJ/kg
Viscosity: Gas @ 101.325 kPa and 273.15 K (0℃) Liquid @ 83.2 K (-189.95℃)	 0.0218 cp 0.257 cp
Thermal conductivity: Gas @ 101.325 kPa and 273.15 K (0℃) Gas @ 101.325 kPa and 85.02 K (-188.13℃) Liquid @ 85.02 K (-188.13℃)	 247.63 x 10^{-4} $^{W}/_{m}$ K 71.85 x 10^{-4} $^{W}/_{m}$ K 0.159 $^{W}/_{m}$ K
Heat capacity of gas @ 101.325 kPa and 294.26 K (21.11℃)	Cp = 31.449 kJ/kmol.K

Table 1A: Fluorine properties

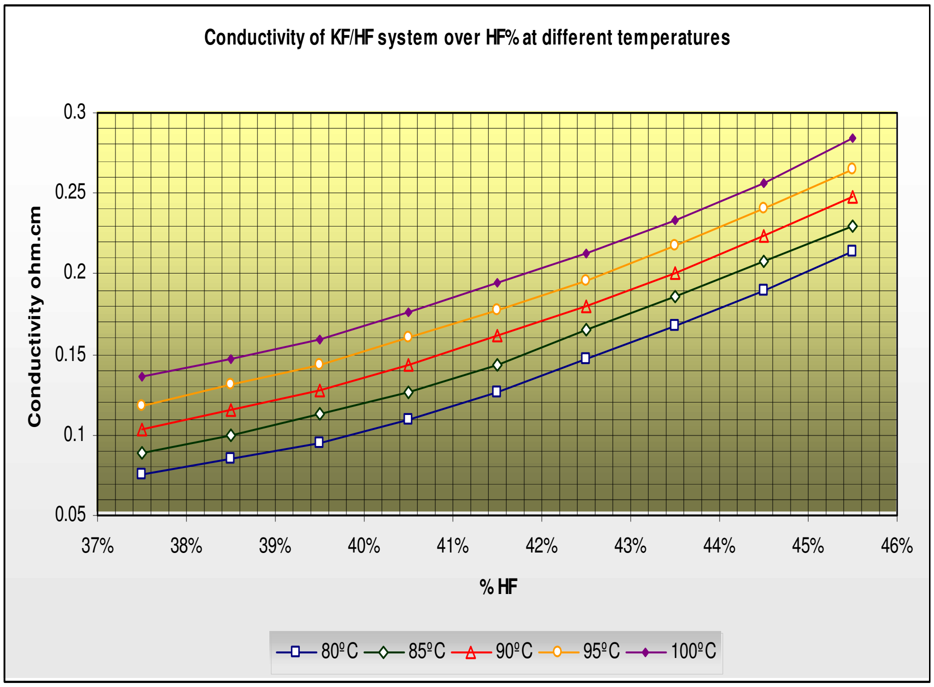

Fig 1A: Electrical conductivity KF/HF as a function of HF concentration and temperature (1)

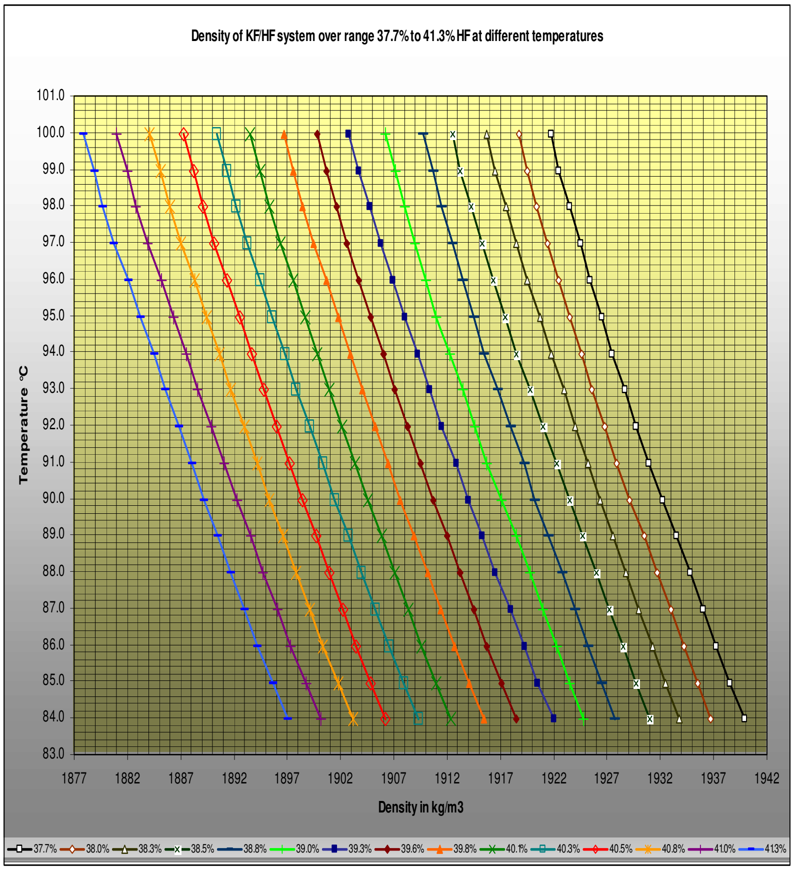

Fig 2A: Density of KF. HF (37.7% to 41.3% HF) at different temperatures(1)

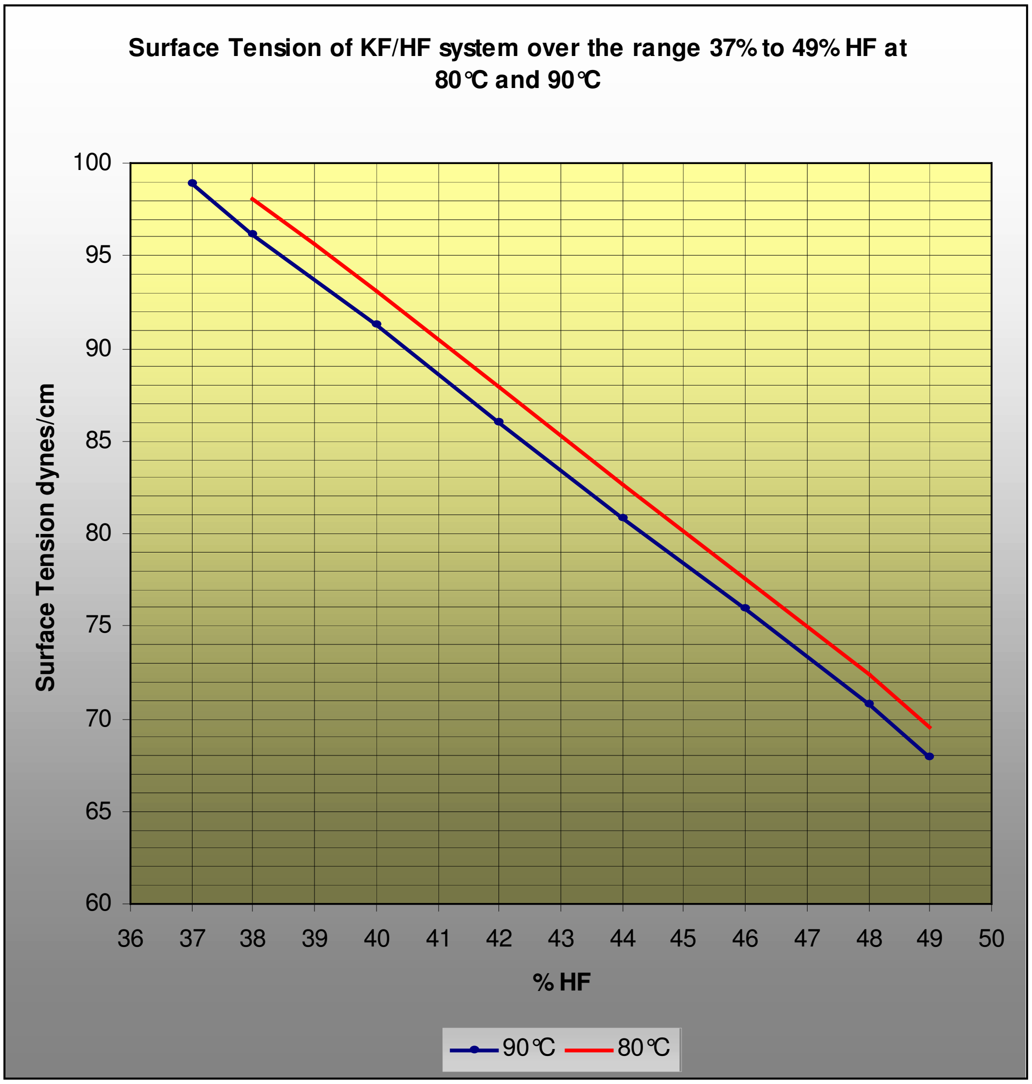

Fig 3A: Surface tension of KF/HF (37% to 49% HF) at 80ºC and 90ºC(1)

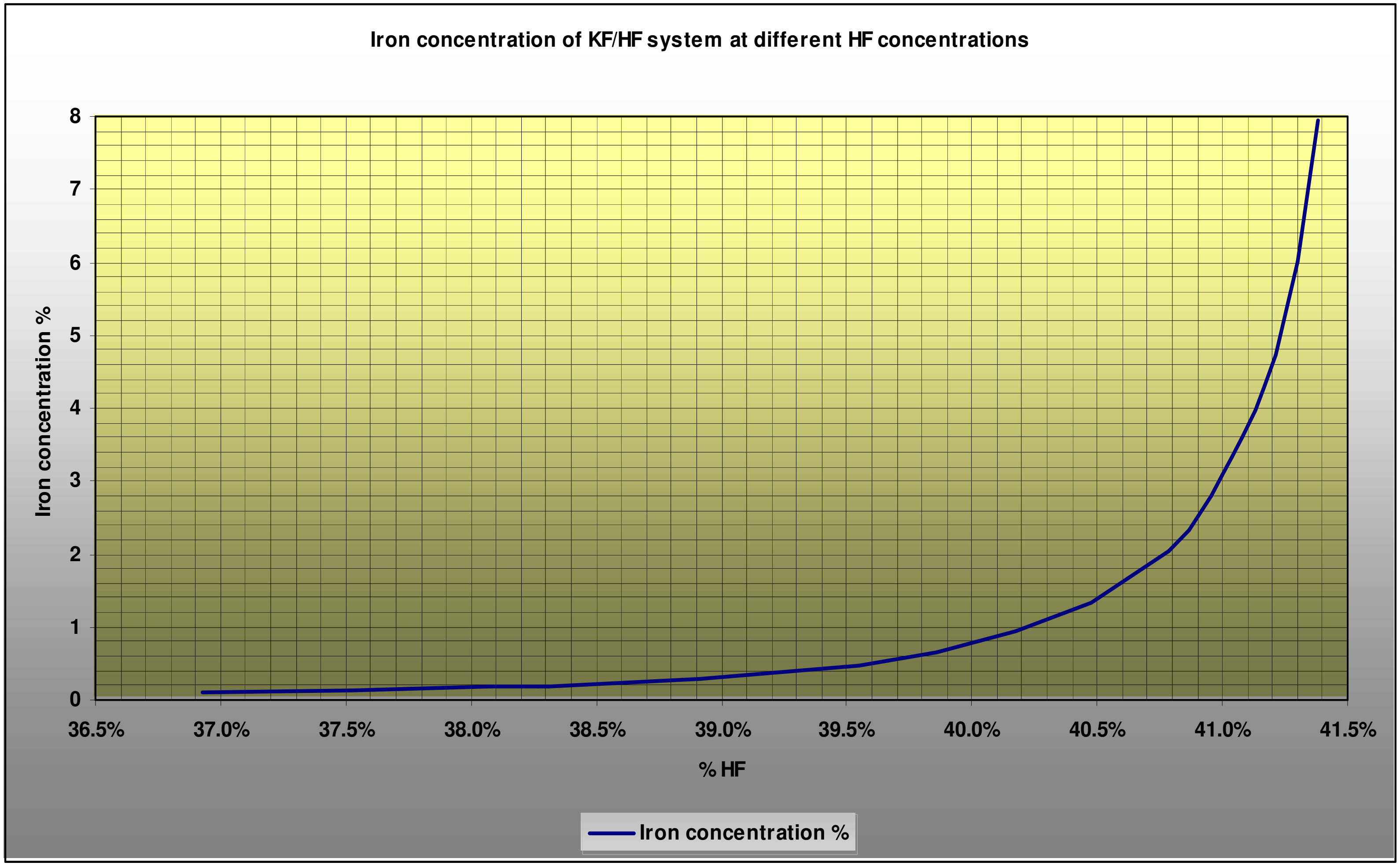

Fig 4A: Iron concentration of KF.HF system at different HF concentrations (1)

Component		Concentration		
KF.HF	>	99.00	%	(m/m)
KCl	<	0.02	%	(m/m)
K_2SiF_6	<	0.50	%	(m/m)
SO_4^{-2}	<	0.01	%	(m/m)
Fe	<	0.02	%	(m/m)
Heavy metals (Pb, As)	<	0.005	%	(m/m)
H_2O	<	0.05	%	(m/m)
Na^+	<	0.50	%	(m/m)

Table 2A: Potassium Bifluoride Specification

HYDROGEN FLUORIDE (21)	
Formula mass (HF)	20.006 4
Molecular mass: Saturated vapour @ 293.15 K (20℃) Saturated vapour @ 373.15 K (100℃)	 74.88 (3.743 moles HF associated) 49.08 (2.453 moles HF associated)
Boiling point @ 101.325 kPa (1 atm)	292.67 K (19.52℃)
Triple point	189.78 K (83.37℃)
Critical temperature	461.15 K (188℃)
Critical pressure	6 485 kPa (64.0 atm)
Critical volume	69 mℓ/0.020 01 kg)
Critical density	0.290 kg/ℓ
Critical compressibility factor	0.12
Latent Heat of fusion @ 189.79 K (-83.36℃)	196.355 kJ/kg (46.93 kcal/kg)
Refractive index, Gas @ 298.15 K (25℃) and 5 893 Å	1.157 4
Density, Gas @ 101.325 kPa (1 atm) @ 298.15 K (25℃)	2.201 kg/m^3
Specific Gravity, Gas @ 101.325 kPa (1 atm) (Air =1) @ 298.15 K (25℃)	1.858
Density, Liquid @ 292.67 K (19.52℃)	0.957 kg/ℓ
Latent heat of vapourization @ 292.67 K (19.52℃)	6 732 J/0.02001 kg

Viscosity, Liquid @ 273.15K (0℃)	0.256 cp
Thermal conductivity, Gas @ 101.325 kPa and 373.8 K (100.65℃)	254.471 x 10^{-4} $^{w}/_{m}$ K
Heat capacity: Vapour @ 101.325 kPa and 373.15 K (100℃) Liquid @ 273.49 K (0℃)	Cp = 29.29, Cv = 57.57, J/kg K 48.702 J/kg K

Table 3A: Hydrogen fluoride properties

HF	≥	**99.95**	%	(m/m)
H_2SiF_6	≤	0.01	%	(m/m)
H_2SO_4	≤	0.02	%	(m/m)
SO_2	≤	0.001	%	(m/m)
H_2O	≤	0.04	%	(m/m)
As	≤	0.001	%	(m/m)

Table 4A: AHF specification for fluorine cells

APPENDIX B

1. PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME:	Fluorine: Compressed
CHEMICAL FORMULA:	F_2
PRODUCT CODE:	

COMPANY NAME:

PELCHEM: The Chemical Division of NECSA
P O Box 582, Pretoria, 0001, South Africa
Tel: 27 12 305-3396 / **Fax**: 27 12 305-3728
E-mail: cheminfo@pelchem.necsa.co.za / **Cell**: +27 83 628 0831
Emergency tel: +27 12 305-3333/4

2. COMPOSITION/INFORMATION ON INGREDIENTS

CONCENTRATION:	100%
SYNONYMS:	Diatomic fluorine, Difluorine
UN No:	1045
CAS-No:	7782-41-4

3. HAZARDS IDENTIFICATIONS

EMERGENCY OVERVIEW

Pale yellow gas with pungent odour. Potentially fatal if inhaled, respiratory tract burns, skin burns, and eye burns. May explode on contact with water. Strong oxidizer. May ignite or explode on contact with combustible materials. Containers may rupture or explode if exposed to heat. May react on contact with water. Releases toxic, corrosive, flammable or explosive gases.

4. FIRST AID MEASURES

CARCINOGEN STATUS:

OSHA: N	NTP: N	IARC: N

INHALATION:

Burns, chest pain, bluish skin color, lung congestion, convulsions, and death. Long term exposure may result in tooth discoloration, kidney damage, and liver damage.

When safe to enter area, remove from exposure. Use a bag valve mask or similar device to perform artificial respiration (rescue breathing) if needed. Keep warm and at rest. Get medical attention immediately.

SKIN CONTACT:

Burns. Remove contaminated clothing, jewelry, and shoes immediately. Wash with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). For burns, cover affected area securely with sterile, dry, loose-fitting dressing. Get medical attention.

EYE CONTACT:

Burns. Wash eyes immediately with large amounts of water, occasionally lifting upper and lower lids, until no evidence of chemical remains. Continue irrigating with normal saline until ready to transport to hospital. Cover with sterile bandages. Get medical attention immediately.

INGESTION:

It is unlikely that emergency treatment will be required. Get medical attention, if needed.

NOTE TO PHYSICIAN:

For inhalation, consider oxygen. For skin contact, consider magnesium oxide/water/glycerin paste; calcium gluconate gel.

5. FIRE-FIGHTING MEASURES

FIRE AND EXPLOSION HAZARD:

Negligible fire hazard. Oxidizer. May ignite or explode on contact with combustible materials. Containers may rupture or explode if exposed to heat.

EXTINGUISHING MEDIA:

Water. Do not use dry chemicals, carbon dioxide or halogenated extinguishing agents. Flood large fires with fine water spray.

FIREFIGHTING:

Move container from fire area if it can be done without risk. Cool containers with water spray until well after the fire is out. Stay away from the ends of tanks. For fires in cargo or storage area: If this is impossible then take the following precautions: Keep unnecessary people away, isolate hazard area and deny entry. Let the fire burn. For small fires, contain and let burn.

6. ACCIDENTAL RELEASE MEASURES

ACCIDENTAL SPILL:

Stop leak if possible without personal risk. Avoid contact with combustible materials. Keep unnecessary people away, isolate hazard area and deny entry. Ventilate closed spaces before entering. Notify Local Emergency Center.

7. HANDLING AND STORAGE

Store and handle in accordance with all current regulations and standards. Subject to storage regulations. Protect from physical damage. Keep separated from incompatible substances. Avoid heat, flames, sparks and other sources of ignition.

8. EXPOSURE CONTROLS AND PERSONAL PROTECTION

EXPOSURE LIMITS:

FLUORINE:
OSHA 0.1 ppm (0.2 mg/m3)
TWA 1 ppm (2 mg/m3)
ACGIH TWA 2 ppm (4 mg/m3)
ACGIH STEL 0.1 ppm (0.2 mg/m3)
NIOSH recommended TWA 10hour(s) 0.2 mg/m3 (0.1 ml/m3)

VENTILATION:

Provide local exhaust or process enclosure ventilation system. Ensure compliance with applicable exposure limits.

EYE PROTECTION:

Wear splash resistant safety goggles with a face shield. Provide an emergency eye wash fountain and quick drench shower in the immediate work area.

CLOTHING:

Wear appropriate chemical resistant clothing.

GLOVES:

Wear appropriate chemical resistant gloves.

RESPIRATOR:

The following respirators and maximum use concentrations are drawn from NIOSH and/or OSHA.
1 ppm Any supplied-air respirator.
2.5 ppm Any supplied-air respirator.
5 ppm Any self-contained breathing apparatus with a full-face piece. Any supplied-air respirator with a full-face piece.
25 ppm Any supplied-air respirator with a full face piece that is operated in a pressure-demand or other positive-pressure mode.

Escape - Any air-purifying respirator with a full-face piece and a canister providing protection against this substance. Only non-oxidisable sorbents are allowed (not charcoal). Any appropriate escape-type, self-contained breathing apparatus.

For Unknown Concentrations or Immediately Dangerous to Life or Health - Any supplied-air respirator with full face piece and operated in a pressure-demand or other positive-pressure mode in combination with a separate escape supply. Any self-contained breathing apparatus with a full-face piece.

9. PHYSICAL AND CHEMICAL PROPERTIES

See Table 1A in Appendix A

10. STABILITY AND REACTIVITY

REACTIVITY:

May react with evolution of heat on contact with water. Releases toxic, corrosive, flammable or explosive gases. May explode on contact with water.

CONDITIONS TO AVOID:

Avoid contact with combustible materials. Minimize contact with material.
Avoid inhalation of material or combustion by-products. Keep out of water supplies and sewers.

INCOMPATIBILITIES:

combustible materials, metal oxides, bases, metal salts, peroxides, halogens, halo carbons, acids, metal carbide, metals, oxidizing materials, reducing agents

FLUORINE:

ACETONITRILE + CHLORINE FLUORIDE: May explode at greatly reduced temperatures

ACETYLENE: Violent reaction

ALCOHOLS: Possible ignition on contact

ALDEHYDES: Possible ignition on contact

ALKALI OXIDES: Fire and explosion hazards

ALKANES + OXYGEN: Form explosive peroxides

AMMONIA: Ignition and possible explosion

BORON NITRIDE: Incandescent reaction

CALCIUM DISILICIDE: Ignites on contact

CERAMIC MATERIALS: May ignite

CESIUM HEPTAFLUOROPROPEROXIDE: Possible violent explosion

COMBUSTIBLE MATERIALS: Ignition and possible violent explosion

COVALENT HALIDES: Ignition

CYANOGUANIDINE: Forms explosive products

FLUOROCARBOXYLIC ACIDS + CESIUM FLUORIDE: Possible explosive reaction

1-OR 2-FLUORIMINOPERFLUOROPROPANE: Explosive reaction

GRAPHITE: Possible explosive reaction

HALOCARBONS: Violent or explosive reaction

HALOGENS: Ignites on contact

HEXALITHIUM DISILICIDE: Incandesces when warmed

HYDROCARBONS: Ignites on contact

HYDROGEN: Violent explosive reaction

HYDROGEN HALIDES: Ignites on contact

KETONES: Possible ignition on contact

METAL ACETYLIDES: Ignite on contact

METAL BORIDES: Incandescent reaction

METAL CYANOCOMPLEXES: Incandescent reaction

METAL HYDRIDES: Ignites on contact

METAL IODIDES: Decomposition reaction, with subsequent ignition

METAL OXIDES: Incandescent reaction

METAL SALTS: Ignition and possible formation of explosive products

METALS: Ignites on contact

NITRIC ACID: Explodes on contact

NITROGENOUS BASES: Incandescent reaction

NON-METAL OXIDES: Possible explosion or ignition on contact

NON-METALS: Ignites on contact

ORGANIC ACIDS: Possible ignition

PERCHLORIC ACID + CHLORATES: Form explosive fluorine perchlorate

POLYMERIC MATERIALS: Ignition or possible violent reaction

STAINLESS STEEL: Explosive reaction

SULFIDES: Ignition and possible violent reaction

TEFLON: Possible ignition

TRINITROMETHANE: Possible dangerous reaction

HAZARDOUS DECOMPOSITION:

Thermal decomposition products: halogenated compounds

POLYMERIZATION:

Will not polymerize.

11. TOXICOLOGICAL INFORMATION

IRRITATION DATA:

25 ppm/5 minute(s) eyes-human mild; 140 ppm/30 minute(s) eyes-rat; 467 ppm/5 minute(s) eyes-mouse; 68 ppm/1 hour(s) eyes-dog

TOXICITY DATA:

185 ppm/1 hour(s) inhalation-rat LC50; 150 ppm/1 hour(s) inhalation-mouse LC50; >93 ppm/1 hour(s) inhalation-dog LC; 270 ppm/30 minute(s) inhalation-rabbit LC50; 170 ppm/1 hour(s) inhalation-guinea pig LC50

LOCAL EFFECTS:

Corrosive: inhalation, skin, eye

ACUTE TOXICITY LEVEL:

Highly Toxic: inhalation

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE:

Respiratory disorders

HEALTH EFFECTS:

INHALATION:

ACUTE EXPOSURE:

FLUORINE: When in contact with water, hydrofluoric acid is formed. May be extremely irritating to nose, throat, and respiratory tract. Exposure to 25 ppm for 5 minutes has been reportedto be fatal in man. Momentary exposure to 50 ppm was intolerable to man; 25 ppm was olerated briefly but subjects developed sore throat and chest pain that persisted for 6 hours. Exposure to high levels may cause coughing, choking and chills lasting 1-2 hours after exposure. After an asymptomatic period of 1-2 days, fever, cough, tightness in the chest, rales and cyanosis may indicate pulmonary edema. Flooding amounts may cause asphyxia due to laryngeal and bronchiole spasms and later by bronchiole obstruction. High concentrations may also cause gastroenteric disturbances. These symptoms may progress for 1-2 days and then regress slowly over a period of 10-30 days. Other reported symptoms may include loss of appetite, reduced body weight, muscular weakness, clonic convulsions, and respiratory and cardiac failure. In severe cases, death may occur due to respiratory damage. Animal experimentation resulted in liver and kidney damage. Exposure to 25/m3 caused testicular degeneration in rats.

CHRONIC EXPOSURE:

FLUORINE: Repeated and prolonged exposure to low concentrations of fluorine may cause nosebleeds and sinus trouble. Repeated exposure to more than 6 mg of fluorine per day may result in fluorosis. Symptoms may include weight loss, brittels of bones, anemia, weakness, general ill health, stiffness of the joints and discoloration of the teeth when exposure occurs during tooth formation. Repeated short-term exposures to laboratory animals at levels of 55 to 75 ppm showed no, or very slight effects in the lungs, liver and kidneys.

SKIN CONTACT:

ACUTE EXPOSURE:

FLUORINE: In contact with moisture or water, hydrofluoric acid is formed which may cause severe skin burns and ulceration. Direct exposure can cause severe burns in 0.2 seconds, and an exposure for as long as 0.6 seconds can result in thermal flash burns comparable with those produced by an oxyacetylene flame. May be absorbed through the skin and cause systemic toxicity.

CHRONIC EXPOSURE:

FLUORINE: Repeated and prolonged contact with corrosive substances may result in dermatitis or effects similar to acute exposure.

EYE CONTACT:

ACUTE EXPOSURE:

FLUORINE: In contact with moisture or water, hydrofluoric acid is formed which may cause severe irritation with corneal and conjunctival burns with possible blindness. Contact with low concentration vapors, 5 ppm, may cause irritation.

CHRONIC EXPOSURE:

FLUORINE: Repeated or prolonged contact with corrosive substances may result in conjunctivitis or effects as in acute exposure.

INGESTION:

ACUTE EXPOSURE:

FLUORINE: Ingestion of a gas is unlikely.

CHRONIC EXPOSURE:

FLUORINE: No data available.

11. ECOLOGICAL INFORMATION:

ECOTOXICITY:

PHYTOTOXICITY:

>60000 ug/L 4 week(s) EC50 (Growth) Duckweed (Lemna minor)

12. DISPOSAL CONSIDERATIONS

Dispose in accordance with all applicable regulations.

13. TRANSPORT INFORMATION

UN NO: 1045	**HAZARD CLASS:**	**LABELLING:**
ADR/RID:	**Class:** 2.3; 5.1; 8 **Labels:** Toxic gas **Subrisk:** Oxidizer; Corrosive	**CORRECT TECHNICAL NAME:** Fluorine , compressed, N.O.S
IMDG:	**Class:** 2.3; 5.1; 8 **Labels:** Toxic gas **Subrisk:** Oxidizer; Corrosive	**CORRECT TECHNICAL NAME:** Fluorine , compressed, N.O.S
IATA: Passenger aircraft or railcar: Forbidden Cargo Aircraft only:: Forbidden	**Class:** 2.3; 5.1; 8 **Labels:** Toxic gas **Subrisk:** Oxidizer; Corrosive	**Passenger aircraft or railcar**: Forbidden **Cargo Aircraft only:**: Forbidden

14. REGULATORY INFORMATION

APPLICABLE REGULATIONS:

Refer to country of destination.

SAFETY AND RISK PHRASES:

Refer to country of destination.

15. OTHER INFORMATION

No other information is currently available for this record

16. DISCLAIMER OF EXPRESSED AND IMPLIED WARRANTIES:

Although reasonable care has been taken in the preparation of this document, we extend no warranties and make no representations as to the accuracy or completeness of the information contained herein, and assume no responsibility regarding the suitability of this information for the user's intended purposes or for the consequences of its use. Each individual should make a determination as to the suitability of the information for his or her particular purpose(s).

Table 1B Material Safety Data Sheet FOR F_2

1. PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: Hydrogen Fluoride (Anhydrous)
CHEMICAL FORMULA: HF
COMPANY NAME:
PELCHEM: The Chemical Division of NECSA
P O Box 582, Pretoria, 0001, South Africa
Tel: 27 12 305-3396 / **Fax**: 27 12 305-3728
E-mail: cheminfo@pelchem.necsa.co.za / **Cell**: +27 83 628 0831
Emergency tel: +27 12 305-3333/4

2. COMPOSITION/INFORMATION ON INGREDIENTS

CHEMICAL NAME OF SUBSTANCE: Hydrogen Fluoride (Anhydrous)
SYNONYMS: Hydrofluoride (Anhydrous); HF>99.9%

UN No:	**CAS-No:**
1052	7664-39-3

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

Very toxic by inhalation, in contact with skin and if swallowed. Causes severe burn. Inhalation of vapours in high concentration may cause shortness of breath (lung oedema). Ingestion causes burns of the upper digestive and respiratory tracts. Will penetrate skin and attack underlying tissues and bone. Risk of serious damage to eyes.

4. FIRST AID MEASURES

GENERAL ADVICE:

Remove from exposure, lie down. Show this safety data sheet to the doctor in attendance.

INHALATION:

Remove from exposure, lie down. Consult a physician. Oxygen or artificial respiration is needed. Observe patient for 24 hours for possible delayed symptoms such as delayed pulmonary oedema.

SKIN CONTACT:

Wash off immediately with plenty of water for at least 15 minutes. Take all contaminated clothing off immediately. Consult a physician. The use of calcium gluconate paste may be considered.

EYE CONTACT:

Rinse thoroughly with plenty of water for at least 30 minutes keeping eyes wide open. Consult a physician

INGESTION:

Do not induce vomiting. Administer fluoride-binding substances such as milk. Seek immediate medical attention.

PROTECTION FOR FIRST AIDERS:

Wear suitable protective equipment. Avoid direct contact with contaminated victim or clothing

5. FIRE-FIGHTING MEASURES

SPECIFIC FIRE-FIGHTING HAZARDS:

Reacts violently with water and can splash acid onto personnel.

SPECIFIC METHODS:

Keep any HF containers or tanks adjacent or involved in a fire cool with water spray, if not leaking.

PROTECTION FOR FIRE FIGHTERS:

Wear a self-contained breathing apparatus and full protective flameproof clothing.

6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS:

Ensure adequate ventilation. Use personal protective equipment, complete suit protecting against Hydrogen Fluoride (Anhydrous). Evacuate personnel to safe areas. Keep people away from and upwind of spill/leaks.

ENVIRONMENTAL PRECAUTIONS:

Prevent product from entering drains, environment or natural watercourses. Contaminated ground to be excavated and removed to approved landfill site

METHODS FOR CLEANING UP:

Evaporates: Suppression of fumes with Versicol W25 (Poly Acrylamide). Neutralize residue with calcium hydroxide or slaked lime ($Ca(OH)_2$) and sodium carbonate or soda ash (Na_2CO_3). Completely neutralised residue can be land filled when in compliance with local regulations.

7. HANDLING AND STORAGE

TECHNICAL MEASURE TO PREVENT USER EXPOSURE

Do not breathe vapours or spray mist. Avoid contact with skin and eyes. Wear self-contained breathing apparatus and a protective suit

TECHNICAL MEASURES TO PREVENT FIRE AND EXPLOSION

Check containers regularly for evidence of blistering

SAFE HANDLING PRECAUTIONS

Use only in area provided with appropriate exhaust ventilation.

TECHNICAL STORAGE MEASURES

Mild steel pressure vessels. Manufactured according to ASME 8 or equivalent code. Regular statutory inspections in compliance with local regulations for pressure vessels. Flammable Hydrogen gas can be generated.

STORAGE CONDITIONS

Keep container tightly closed in a dry, cool and well-ventilated area.

INCOMPATIBLE PRODUCTS

Reacts violently with water, strong oxidizing agents – metal (when diluted), concrete, glass & ceramics.

8. EXPOSURE CONTROLS AND PERSONAL PROTECTION

ENGINEERING MEASURES TO REDUCE EXPOSURE:

Ensure adequate ventilation, especially in confined areas. Use compatible materials.

EYE PROTECTION:

Tightly fitting safety goggles and face-shield.

CONTROL PARAMETERS:

OSHA 8Hr TWA 2.5mg/m^3 (3ppm).

STEL 15 min TWA 5mg/m^3 (6ppm).

ACGIH TLV (3ppm). “Ceiling notation”

SKIN AND BODY PROTECTION:

Complete suit with rubber or plastic boots protecting against Hydrogen Fluoride (Anhydrous).

HYGIENE MEASURES:

Avoid contact with skin, eyes and clothing. When using - do not eat, drink or smoke. Contaminated work clothing should not be allowed out of the workplace. Monitor for fluorides (urine samples).

RESPIRATORY PROTECTION:

<25ppm: Wear a positive-pressure supplied air respirator with face shield.

>25ppm: Wear self-contained breathing apparatus and protective suit against Hydrogen Fluoride (Anhydrous).

HAND PROTECTION:

Hydrofluoric acid-resistant and solvent-resistant gloves. Material: rubber, viton, neoprene.

9. PHYSICAL AND CHEMICAL PROPERTIES

See Table 3A in Appendix A

10. STABILITY AND REACTIVITY

CONDITIONS TO AVOID:

None.

STABILITY:

Substance is stable. Hygroscopic - reacts violently with water.

HAZARDOUS DECOMPOSITION PRODUCTS:

Toxic fluoride compounds in certain reactions.

MATERIALS TO AVOID:

Glass, metals, bases and organic materials.

11. TOXICOLOGICAL INFORMATION

ACUTE TOXICITY:

LC50/inhalation/1h/mouse = 456ppm.

LCLO/inhalation/7h/rabbit = 260mg/m^3

CHRONIC TOXICITY:

May cause fluorosis.

LOCAL EFFECTS:

Very toxic by inhalation, in contact with skin and if swallowed.

Risk of serious damage to eyes. Ingestion causes burns of the upper digestive and respiratory tracts. Causes severe burn.

HUMAN EXPERIENCE:

Will penetrate skin and attack underlying tissues, as HF is a calcium “scavenger” binding with calcium in the bloodstream and bones.

OTHER INFORMATION:

No scientific evidence to suggest that HF is related to Carcinogenicity, Mutagenicity and Reproduction toxicity.

12. ECOLOGICAL INFORMATION:

MOBILITY/PERSISTANCE/DEGRADABILITY/BIOACCUMULATION

Unlikely to persist as natural alkalinity will slowly dissipate the acidity.

ECOTOXICITY:

Acute fish toxicity = 60ppm/*/fish/lethal/fresh water (* = time period not specified).

13. DISPOSAL CONSIDERATIONS:

SAFE AND PREFERRED DISPOSAL METHODS:

Contact manufacturer.

CONTAMINATED PACKAGING:

Contact manufacturer.

14. TRANSPORT INFORMATION:

UN NO: 1052

ADR/RID:

Class: 8;6.1	**Labels:** Corrosive; Poison	**Proper shipping name:**
TREM-CARD: 78		Hydrogen Fluoride, Anhydrous
IMDG:		**Proper shipping name:**
Class: 8;6.1	**IMDG-Labels:** Corrosive	Hydrogen Fluoride, Anhydrous
Packaging group: I	**Subrisk:** Poison **EmS:** 8.03	
MFAG: 750		
IATA:		
CLASS: 8;6.1	**CAO-Labels:** Corrosive **Subrisk:** Poison	**Can not be transported by air**

15. REGULATORY INFORMATION

APPLICABLE REGULATIONS:

Refer to country of destination.

SAFETY AND RISK PHRASES:

According to (National equivalent of EC-Dir.67/548), as amended, the product is labelled as follows:

T+ : Very Toxic
C : Corrosive

R26/27/28 : Very toxic by inhalation, in contact with skin and if swallowed.

R35 : Causes severe burns.

S7/9 : Keep container tightly closed and in well ventilated area.

S26 : In case of contact with eyes, rinse immediately with plenty of water and seek medical advise.

S36/37/39 : Wear suitable protective clothing, gloves and eye/face protection.

S45 : In case of an accident or if you feel unwell, seek medical advice immediately (show label where possible).

16. OTHER INFORMATION

RECOMMENDED USE:

Manufacture of chlorofluorocarbons.

Catalyst in the alkylation of petroleum.

Catalyst in the manufacture of detergents.

Production of uranium hexafluoride (UF6) used in the nuclear industry.

Production of fluoride chemicals.

Production of fluorine gas.

REFERENCES:

(CED) Chemical Exchange Directory S.A., Geneva, Switzerland.

Unpublished Reports, AEC of SA Ltd, Pelindaba, South Africa, 1993.

IMDG, SABS 0228, SABS 0229.

Hydrogen Fluoride Handling Guidelines, AECI Chloralkali and Plastics LTD, Sasolburg South Africa, April 1989.

DISCLAIMER OF EXPRESSED AND IMPLIED WARRANTIES:

Although reasonable care has been taken in the preparation of this document, we extend no warranties and make no representations as to the accuracy or completeness of the information contained herein, and assume no responsibility regarding the suitability of this information for the user's intended purposes or for the consequences of its use. Each individual should make a determination as to the suitability of the information for his or her particular purpose(s).

Table 2B: Material Safety Data Sheet FOR HF

APPENDIX C

Metals		Li (ppm)	Cu (ppm)	Fe (ppm)	Ni (ppm)
Sample number	Sample position from top of container (mm)	Samples taken after 6 hours			
1	18	848	28	33	55
2	55		27	32	49
3	93		24	28	47
4	131		28	33	49
5	170		26	30	49
6	211	753	47	49	63
		Samples taken after 12 hours			
1	18	856	24	28	51
2	55		25	30	49
3	93		24	29	48
4	131		23	28	47
5	170		27	30	47
6	211	791	46	52	66
		Samples taken after 24 hours			
1	18	839	23	25	47
2	55		19	22	44
3	93		21	25	46
4	131		21	25	42
5	170		23	26	48
6	211	829	50	68	79
		Samples taken after 48 hours			
1	18	887	19	11	45
2	55		19	12	41
3	93		19	11	42
4	131		19	11	40
5	170		19	11	38
6	211	789	46	68	77
		Samples taken after 96 hours			
1	18	801	18	5	39
2	55		18	5	40
3	93		17	5	37
4	131		17	6	39
5	170		17	7	36
6	211	767	40	44	70

Table 1C: Sedimentation tests performed at 85℃

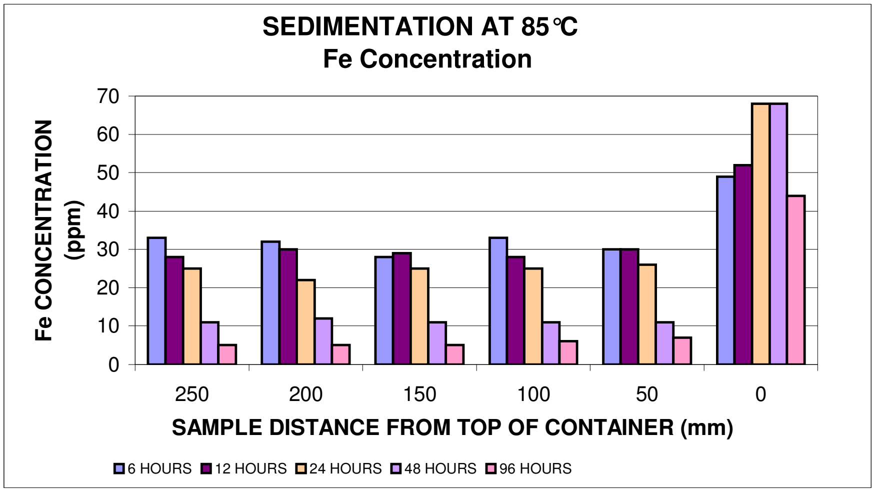

Fig 1C: Total Fe concentration in electrolyte from sedimentation tests

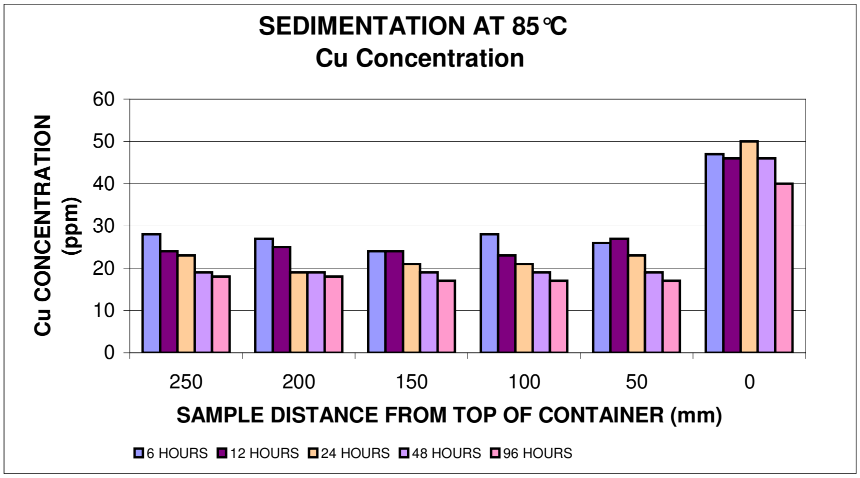

Fig 2C: Total Cu concentration in electrolyte from sedimentation tests

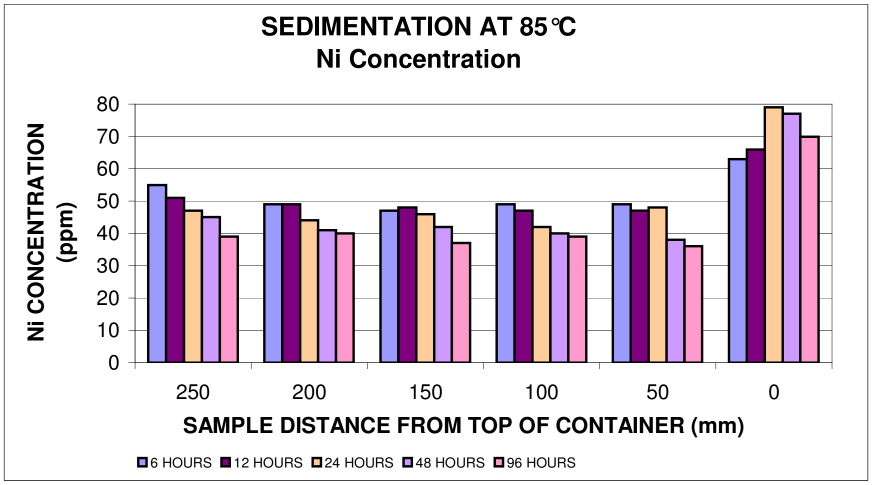

Fig 3C: Total Ni concentration in electrolyte from sedimentation tests

Metals		Li (ppm)	Cu (ppm)	Fe (ppm)	Ni (ppm)
Sample number	Sample position from top of container (mm)	Samples taken after 6 hours			
1	18	1046	30	11	46
2	55		30	14	44
3	93		30	12	46
4	131		31	9	45
5	170		29	9	41
6	211	1094	52	16	66
		Samples taken after 12 hours			
1	18	1068	27	15	47
2	55		28	12	46
3	93		28	14	48
4	131		30	13	52
5	170		27	12	45
6	211	1160	51	37	74
		Samples taken after 24 hours			
1	18	1091	24	3	45
2	55		24	10	42
3	93		24	11	45
4	131		24	9	44
5	170		28	13	48
6	211	1134	53	19	79
		Samples taken after 48 hours			
1	18	1125	21	7	40
2	55		21	7	42
3	93		21	7	42
4	131		21	7	42
5	170		21	10	43
6	211	1127	40	21	63
		Samples taken after 96 hours			
1	18	1199	22	4	44
2	55		20	5	43
3	93		22	20	41
4	131		20	5	41
5	170		21	5	43
6	211	1117	40	27	67

Table 2C: Sedimentation tests performed at 90℃

APPENDIX D

CALCULATION OF KF.HF REQUIRED TO MAKE UP A BATCH OF ELECTROLYTE WITH A SPECIFIC HF CONCENTRATION.		
Mole mass of KF.2HF (waste electrolyte)	98.1	kg/kmol
Mole mass of KF.HF	78.1	kg/kmol
Mole mass of HF	20	kg/kmol
Required HF mass fraction	y	
Total mass of electrolyte	7.5	kg
Mass of KF.HF to be added	x	
Mass fraction of HF in KF.2HF	$\frac{2*20}{98.1} = 0.408$	
Mass fraction of HF in KF.HF	$\frac{2*20}{58.1} = 0.256$	
Required HF mass fraction = [(HF mass fraction)$_{KF.HF}$ *(Mass KF.HF)+(Total mass electrolyte –Mass KF.HF)(HF mass fraction)$_{KF.2HF}$]/Total mass of electrolyte $\therefore\ y = \left[0.256x * \frac{(7.5-x)(0.408)}{7.5}\right]$ Re-arranging to solve x: $x = 7.5 * \frac{(0.408-y)}{(0.408-0.256)}\ \mathrm{kg}$	x = (Total mass electrolyte)* [(HF mass fraction)$_{KF.HF}$ -(HF mass fraction)] / [(HF mass fraction)$_{KF.2HF}$ -(HF mass fraction)$_{KF.HF}$]	

Table 1D: Calculation of KF.HF required

CALCULATION OF N_2 FLOW THROUGH DIP TUBE TO STRIP HF FROM THE MOLTEN ELECTROLYTE		
Input data		
Operating temperature	120	^{o}C
Operating pressure	200	kPa
Time to strip from initial to final HF concentration	1.5	h
Batch mass of electrolyte	7.5	kg
Initial HF concentration in electrolyte	41.32	$\%\ (^{m}/_{m})$
Final HF concentration in electrolyte aim for	38	$\%\ (^{m}/_{m})$
Mole mass of HF	20	kg/kmol
Calculation		
Mass HF stripped = Batch mass [Initial HF con – final HF con]/100	$7.5*(\frac{41.5-38}{100})$ $=0.2625$	kg kg
Vapour density of HF at operating conditions $= \frac{\textbf{(HF mole mass * Pressure)}}{\text{(R * absolute temp)}}$	$\rho_{HF} = (\frac{20*200}{8.316*(273+120)})$ $=1.22 kg/m^3$	
Vapour volume of stripped HF = (Mass of HF stripped) / (Vapour density of HF)	$\frac{0.2625}{1.22}$ $=214.47$	m^3 litre
The vapour volume concentration in the logarithmic average volume calculated from the vapour volume values obtained from Fig 1D in Appendix D at 41% and 38% HF:		
HF vapour volume at 41% HF	17.74	%
HF vapour volume at 38% HF	7.74	%
Log average HF vapour volume	$\frac{17.74-7.74}{\ln(17.74-7.74)}$ $=12.05$	 %

The HF strip rate = Volume of HF stripped /Time to strip	$\frac{214.47}{1.5}*60$ $=2.38 \qquad \ell/\min$
The required N_2 flow rate = (HF strip rate)/(% average HF vapour volume/100)*(1-)/(% average HF vapour volume/100))	$=\frac{2.38}{12.05/100}*(1-\frac{12.05}{100})$ $=17\ell/\min$
The rotameter scale setting is obtained from Fig 2D and Table 3D in Appendix F on the rotameter graph and table	Rotameter setting at 10% to obtain 17 $\ell/\min$

Table 2D: Calculation of N_2 flow required

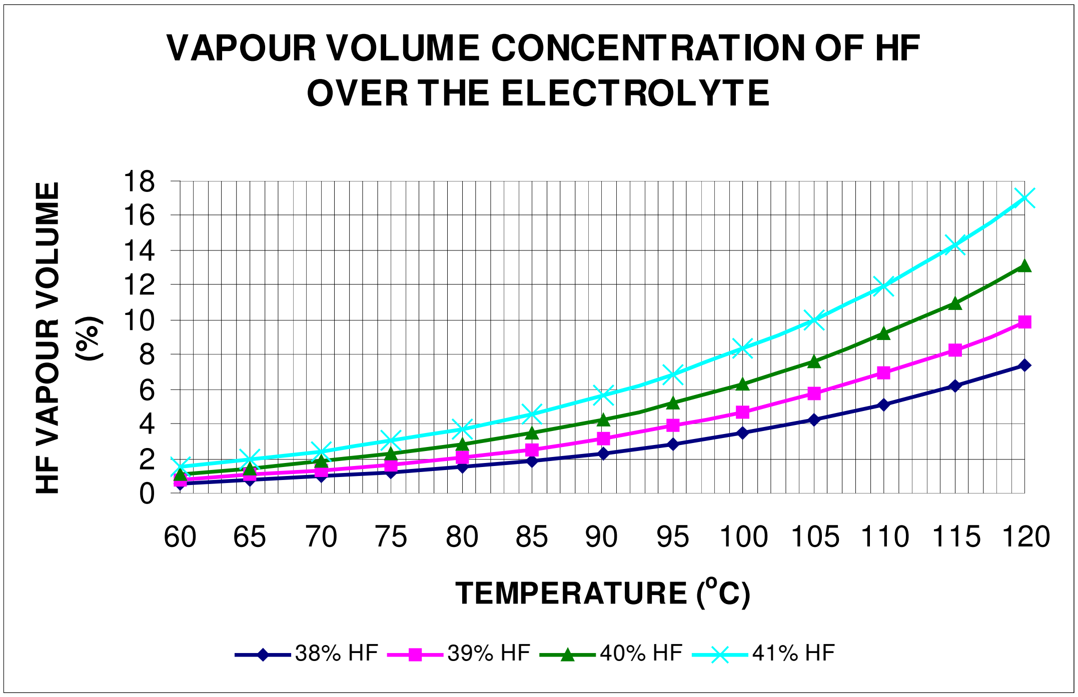

Fig 1D: Vapour volume concentration of HF over KF.nHF

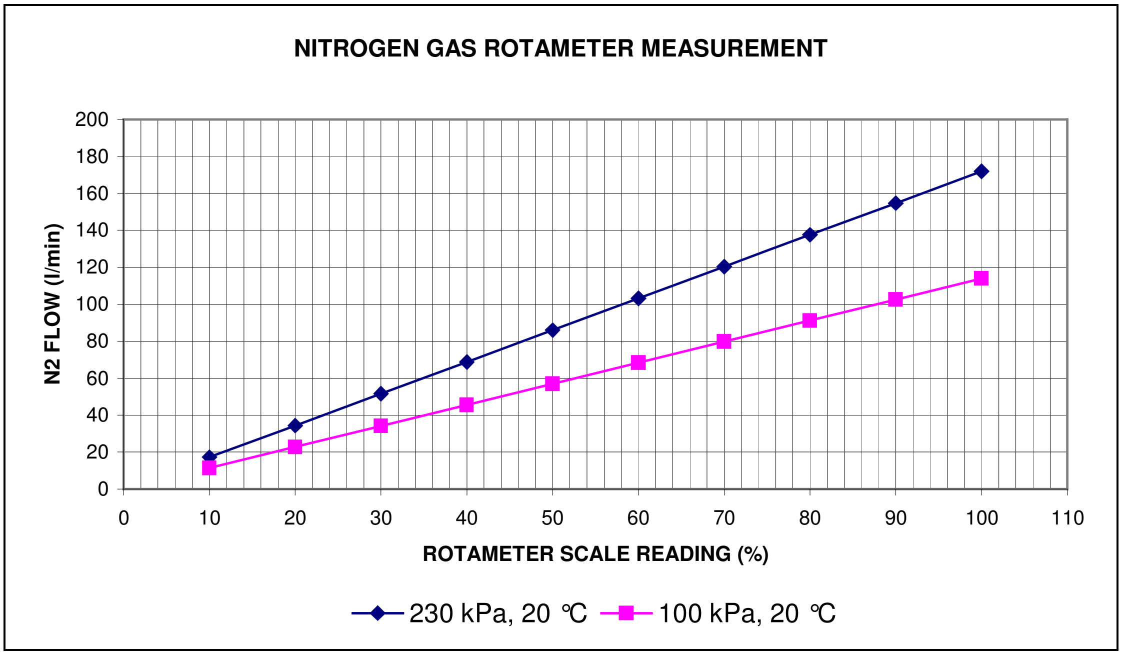

Fig 2D: Rotameter

230 kPa $V_{N2} = 1.720*(\%)$ $R^2 = 1$

100 kPa $V_{N2} = 1.140*(\%)$ $R^2 = 1$ **Not recommended to use**

	FP-1/2-21-G-10/80	
Float	FP-1/2-GNSVT-44	
Gas	Nitrogen	
Temperature	20 °C	
Pressure	230(kPa)	100(kPa)
Float position %	Flow l/min	Flow l/min
100	172	114
90	154.8	102.6
80	137.6	91.2
70	120.4	79.8
60	103.2	68.4
50	86	57
40	68.8	45.6
30	51.6	34.2
20	34.4	22.8
10	17.2	11.4

Table 3D: Rotameter float position

CALCULATION OF THE LIMESTONE REQUIRED IN THE DRY SCRUBBER

The vapour of the HF removed is calculated as 214.47 litre and 0.2625 kg mass. (See calculation of N_2 flow through the dip tube to strip HF from the molten electrolyte)

The mass utilization of the limestone is 20% average because of the insoluble CaF_2 that forms on the surface of the $CaCO_3$ particles thus preventing any HF to react with the inner $CaCO_3$ particle:

$$CaCO_3 + 2HF \Rightarrow CaF_2 + CO_2 + H_2O$$

The mole mass of HF	20	kg/kmol
The mole mass of limestone	100	kg/kmol
The stoichiometric quantity of limestone required = Mass HF stripped/Mole mass HF *2	$=\frac{0.2625}{20*2}$ $=6.56*10^{-3}$ $=0.656$	 kmol kg
Actual quantity of limestone required	$=\frac{0.656}{20}$ $=3.28$	
Bulk density of limestone	1400	kg/m^3
The volume of the limestone required	$\frac{3.28}{1400}*1000$ $=2.3$	litres
The volume of the limestone scrubber	3.1	litres

Table 4D: Calculation on lime stone required

CALCULATION OF NaOH QUANTITIES REQUIRED PER BATCH OF ELECTROLYTE TO PRECIPITATE THE DISSOLVED Fe.		
The NaOH reacts with the soluble Fe in the molten electrolyte to form an insoluble triple salt K_2NaFeF_6		
$2NaOH + KF.2HF \Rightarrow 2NaF + KF + 2H_2O$		
$2NaF + KF + FeF_3 \Rightarrow K_2NaFeF_6$		
The atomic ratio Na:Fe is 1		
Atomic mass of Na	23	g/gmol
Atomic mass of Fe	55.85	g/gmol
Mole mass of NaOH	40	g/gmol
Batch mass of electrolyte	7.5	kg
Dissolved Fe concentration in electrolyte	200 200	ppm mg/kg
Fe mass in a batch of electrolyte	= 7.5*200 = 1.5	g
Moles of Fe in a batch of electrolyte	$\frac{1.5}{55.85}$ $= 0.0269$	gmol
Stoichiometric moles of Na and NaOH required Stoichiometric mass of NaOH required	=0.0269 = 0.0269*40 = 1.1	gmol g

Table 5D: Calculation of NaOH quantities

APPENDIX E

CALCULATION OF HF CONCENTRATION IN THE VAPOUR IN EQUILIBRIUM WITH THE MOLTEN ELECTROLYTE. **(Compilation of Fig 1D)**	
Temperature range	80.3 to 131.2 ℃
Operating pressure	200 kPa
Vapour pressures at temperature of HF above molten electrolyte	From fig 1.7
Vapour pressure of moisture at temperature	From steam tables
Mole fractions	$\frac{\text{Vapour pressures}}{\text{Operating pressure}}$
HF concentration	(Mole fraction HF*mole mass HF)
	(Mole fraction HFx mole mass HF + mole fraction H_2O *mole mass H_2O)
Note The calculated HF concentration is conservative and should be higher, because the H_2O vapour pressure above the electrolyte should in practice be lower than the values taken from the stream tables,	

Table 1E: Calculation of HF concentration in the vapour in equilibrium with the molten electrolyte.

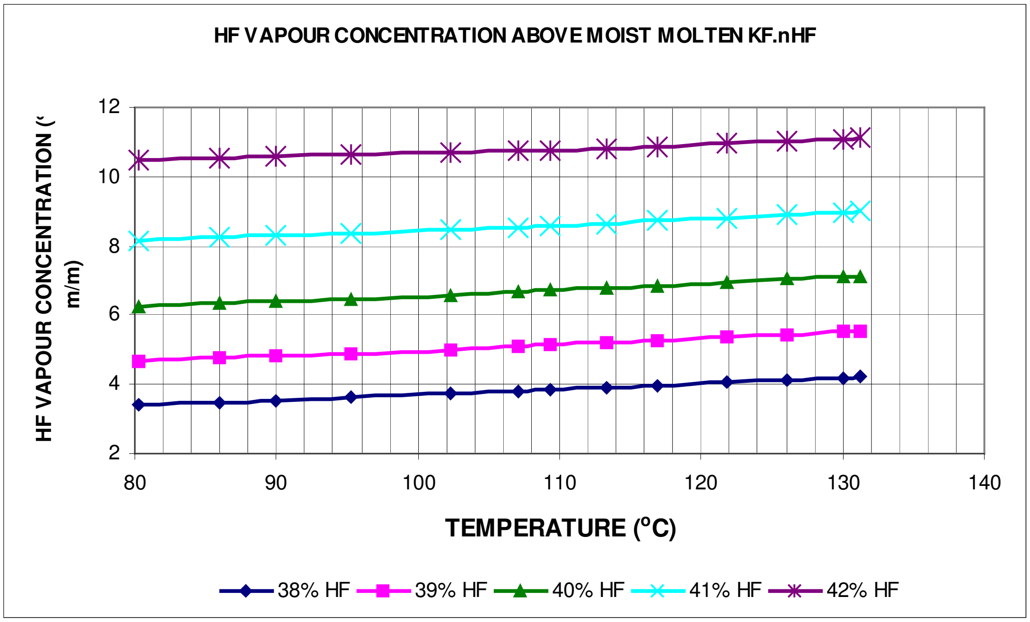

Fig 1E: HF vapour concentration above moist molten KF.nHF