NICKEL RECOVERY FROM SPENT ELECTROLYTE BY NANOFILTRATION

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This dissertation is presented in partial fulfilment of the requirements for the degree Masters of Engineering in the School of Chemical and Minerals Engineering at North-West University, Potchefstroom Campus.

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Declaration

I, Wynand Stolp, hereby declare that the dissertation with the title: **Nickel recovery from spent electrolyte by nanofiltration,** in partial fulfilment of the requirements for the M. Eng. degree, is my work and has not been submitted at any other university either in whole or in part.

Signed at Potchefstroom.

Wynand Stolp	Date

Abstract

South Africa is the world's leading producer of Platinum Group Metals (PGMs) and holds more than 80% of the world's reserves. Although PGMs are the most important products in the ores, base metals are valuable by-products, particularly nickel. Metallic nickel is produced by electrowinning from the acidic nickel sulphate solution, and the spent electrolyte still contains high levels of nickel. In the current process, the spent electrolyte is neutralised by the addition of caustic that results in precipitation of nickel hydroxide in a sodium sulphate solution. The main disadvantages of this process are that low-value sodium sulphate is produced by adding high-value caustic and that three major process units are required.

In this paper the possibility of using a DOW NF membrane to separate the nickel from an acidic solution is studied under simulated industrial conditions. The experiments were carried out in a lab-scale, cross flow, flat-sheet membrane contactor. The experimental conditions include a nickel concentration at 30 to 50 g/L, a pH range of 1 to 2 and a temperature of 25 to 40°C. Pressure differences of 20 to 55 bar were chosen to examine the effect of pressure on the selectivity of the system and to achieve meaningful flux values.

The nickel rejection was > 97.5% for all the chosen combinations of operating conditions and as high as 99.2% at pH 2 and nickel concentration of 40 g/L. Overall the rejection of nickel was higher at pH 2 compared to pH 1. With respect to the hydronium ions, negative rejection was observed. The flux depended on the nickel concentration of the feed, pressure difference over the membrane and temperature of the solution, with no significant influence by pH. Although temperature had a large affect on the flux, no influence on nickel rejection was observed. With the introduction of sodium the flux reduced immensely but only a 10% reduction in rejection of nickel was found. Fouling caused by scaling occurred and a notable reduction of flux was found during the long run. From this experimental work, it can be concluded that the results are very promising towards the introduction of nanofiltration technology into the challenging world of hydrometallurgical separations in the minerals process industry. The nickel can be separated from the sulphuric acid with large rejections (> 97.5%), and reasonable fluxes (20 – 50 kg·m^{-2}·h^{-1}). Sodium, which is present as sodium sulphate, significantly decreases the flux, and further studies should be carried out on the replacement of sodium sulphate in the electrowinning process.

Opsomming

Suid-Afrika is die wêreldleier in die produksie van Platinum Groep Metale (PGMs) en beskik oor meer as 80% van die wêreld se reserwes. Alhoewel PGMs die belangrikste produk in die erts is, word ander byprodukte ook geproduseer. Dit staan bekend as basismetale waarvan nikkel een van die belangrikstes is. Nikkel metaal word geproduseer deur middel van `n elektroplaterings proses van uit `n aangesuurde nikkelsulfaat elektroliet. Die oorblywende elektroliet bevat nog steeds hoë konsentrasies nikkel in oplossing. Die elektroliet word geneutraliseer met natriumhidroksied wat lei tot die presipitasie van nikkel-hidroksied. Die grootste tekortkominge van die proses is die vorming van natrium sulfaat wat `n baie lae markwaarde het in vergelyking met die natriumhidroksied en dat daar drie groot prosesse in die herwinning van nikkel is.

Die skripsie handel oor die ondersoek na die moontlike gebruik van `n DOW NF membraan om die nikkel van die suur oplossing te skei in gesimuleerde industriële toestande. Die eksperimente is uitgevoer in `n laboratoriumskaal, kruisvloei, plat membraan module. Die toestande behels `n nikkel konsentrasie van 30 tot 50 g/L, `n pH van 1 en 2, en temperature tussen 25 en 40°C. Om die effek van druk op die selektiwiteit van die sisteem te toets, asook bruikbare vloed te kry, is toegepaste druk tussen 20 to 55 bar gevarieër.

Nikkel verwerping was > 97.5% vir al die gekose kombinasies van bedryfstoestande en was selfs so hoog as 99.2% by `n pH van 2 en nikkel konsentrasie van 40 g/L. Die verwerping van nikkel was algeheel groter vir pH 2 as pH 1. Negatiewe verwerping is waargeneem vir die hidronium ione. Die vloed was beïnvloed deur nikkel konsentrasie in die voerstroom, die drukval oor die membraan en die temperatuur van die oplossing. Die pH het geen noemenswaardige verandering in die vloed veroorsaak nie. Alhoewel die temperatuur `n groot uitwerking op die vloed gehad het, het dit nie die verwerping van nikkel beïnvloed nie. Met die toevoeging van natrium het die vloed drasties gedaal, maar slegs `n 10% afname in verwerping van nikkel is opgemerk. Membraan vervuiling het `n merkbare afname in vloed veroorsaak. Dit was veral prominent tydens die lang lopie.

Die resultate van die eksperimentele werk toon duidelik dat nanofiltrasie tegnologie potensiaal het om `n rol te speel in die uitdagende wêreld van hidrometallurgiese skeidings in die mineraalprosesserings industrie. Nikkel kan van swawelsuur geskei word met groot verwerpings (> 97.5%), teen aanvaarbare vloed (20 – 50 $kg.m^{-2}.h^{-1}$). Natrium, wat teenwoordig is as natriumsulfaat, verlaag die vloed noemenswaardig en `n studie sal uitgevoer moet word om `n plaasvervanger daarvoor te vind in die elektroplaterings proses.

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Normal

A	Area (m^2)
C	Concentration (g/L)
D	Diameter (m)
J	Flux ($kg.m^{-2}.hr^{-1}$)
P	Pressure (bar)
R	Rejection (%)
T	Temperature (°C)

Greek

π	Osmotic pressure (bar)

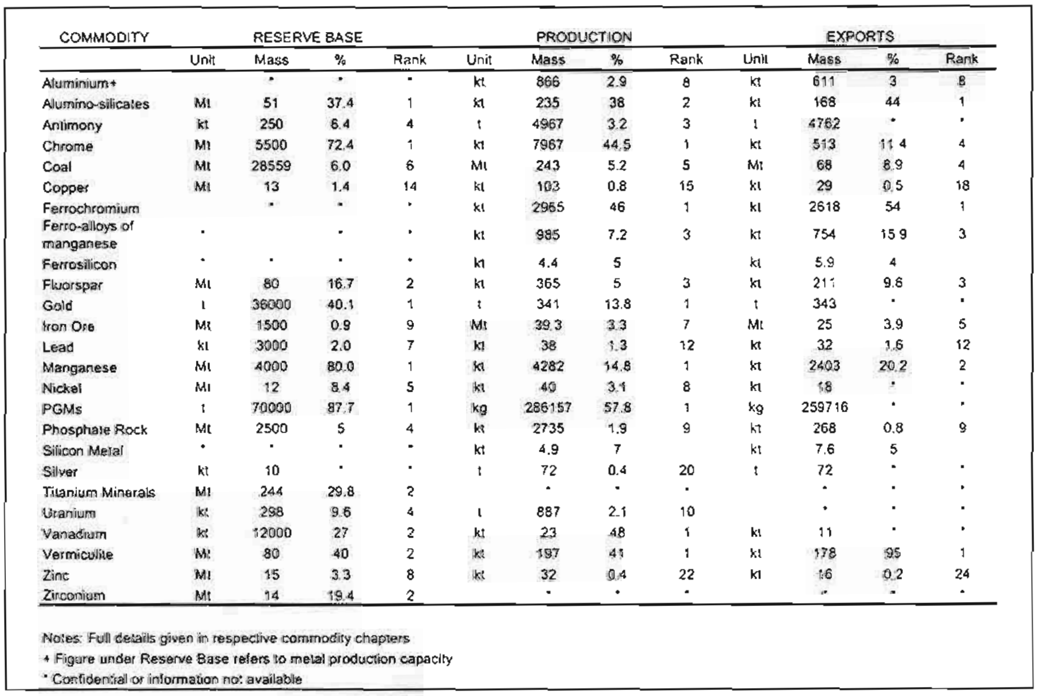
Subscripts

aq	Aquatic phase
f	Feed
p	Permeate
s	Solid phase
0	Initial

1. Introduction

1.1. Background

South Africa is the largest producer of gold, PGMs, chrome, ferrochrome, manganese and vanadium, as well as the world leader in other minerals, as can be seen in Figure 1.1. At a total commodity sale's income of R 118 000 million (Mwape *et al.*, 2005:13), it is clear that minerals play an extremely important role in South Africa's economy.



COMMODITY	RESERVE BASE				PRODUCTION				EXPORTS			
	Unit	Mass	%	Rank	Unit	Mass	%	Rank	Unit	Mass	%	Rank
Aluminium+		*	*	*	kt	866	2.9	8	kt	611	3	8
Alumino-silicates	Mt	51	37.4	1	kt	235	38	2	kt	168	44	1
Antimony	kt	250	6.4	4	t	4967	3.2	3	t	4762	*	*
Chrome	Mt	5500	72.4	1	kt	7967	44.5	1	kt	513	11 4	4
Coal	Mt	28559	6.0	6	Mt	243	5.2	5	Mt	68	6.9	4
Copper	Mt	13	1.4	14	kt	103	0.8	15	kt	29	0.5	18
Ferrochromium		*	*	*	kt	2965	46	1	kt	2618	54	1
Ferro-alloys of manganese	*		*	*	kt	985	7.2	3	kt	754	15 9	3
Ferrosilicon	*	*	*	*	kt	4.4	5		kt	5.9	4	
Fluorspar	Mt	80	16.7	2	kt	365	5	3	kt	211	9.6	3
Gold	t	36000	40.1	1	t	341	13.8	1	t	343	*	*
Iron Ore	Mt	1500	0.9	9	Mt	39.3	3.3	7	Mt	25	3.9	5
Lead	kt	3000	2.0	7	kt	38	1.3	12	kt	32	1.6	12
Manganese	Mt	4000	80.0	1	kt	4282	14.8	1	kt	2403	20.2	2
Nickel	Mt	12	8.4	5	kt	40	3.1	8	kt	18	*	*
PGMs	t	70000	87.7	1	kg	286157	57.8	1	kg	259716	*	*
Phosphate Rock	Mt	2500	5	4	kt	2735	1.9	9	kt	268	0.8	9
Silicon Metal	*	*	*	*	kt	4.9	7		kt	7.6	5	
Silver	kt	10	*	*	t	72	0.4	20	t	72	*	*
Titanium Minerals	Mt	244	29.8	2		*	*	*		*	*	*
Uranium	kt	298	9.6	4	t	887	2.1	10		*	*	*
Vanadium	kt	12000	27	2	kt	23	48	1	kt	11	*	*
Vermiculite	Mt	80	40	2	kt	197	41	1	kt	178	95	1
Zinc	Mt	15	3.3	8	kt	32	0.4	22	kt	16	0.2	24
Zirconium	Mt	14	19.4	2		*	*	*		*	*	*

Notes: Full details given in respective commodity chapters

+ Figure under Reserve Base refers to metal production capacity

* Confidential or information not available

Figure 1.1: South Africa's role in world mineral reserves, production and exports, 2004, (Mwape *et al.*, 2005:5)

One of the mining companies in South Africa, Anglo Platinum LTD, mines the Merensky and UG2 reefs in the Bushveld Complex, near Rustenburg. This region boasts an array of mineral deposits with the most important being the platinum group metals (PGMs). PGMs are the collective name for platinum, palladium, rhodium, iridium, osmium and ruthenium. In mining these precious metals, other metals such as nickel, titanium, manganese and aluminium, are also found at an economic exploitable level. These metals are often referred to as the base metals and have an array of industrial applications.

The petrography of the UG2-Merensky interval, as described by Maier and Eales (1997), consists mainly of anorthosites, leuconorites, norites, melanorites, pyroxenites, troctolites, poikilitic harzenburgite, granular harzburgite, chromites and dunite. The minerals are dispersed in different compositions within the ore and cannot be mined independently, which asks for very a creative separation process. Even the simplified schematic representation given in Figure 1.2 seems complex.

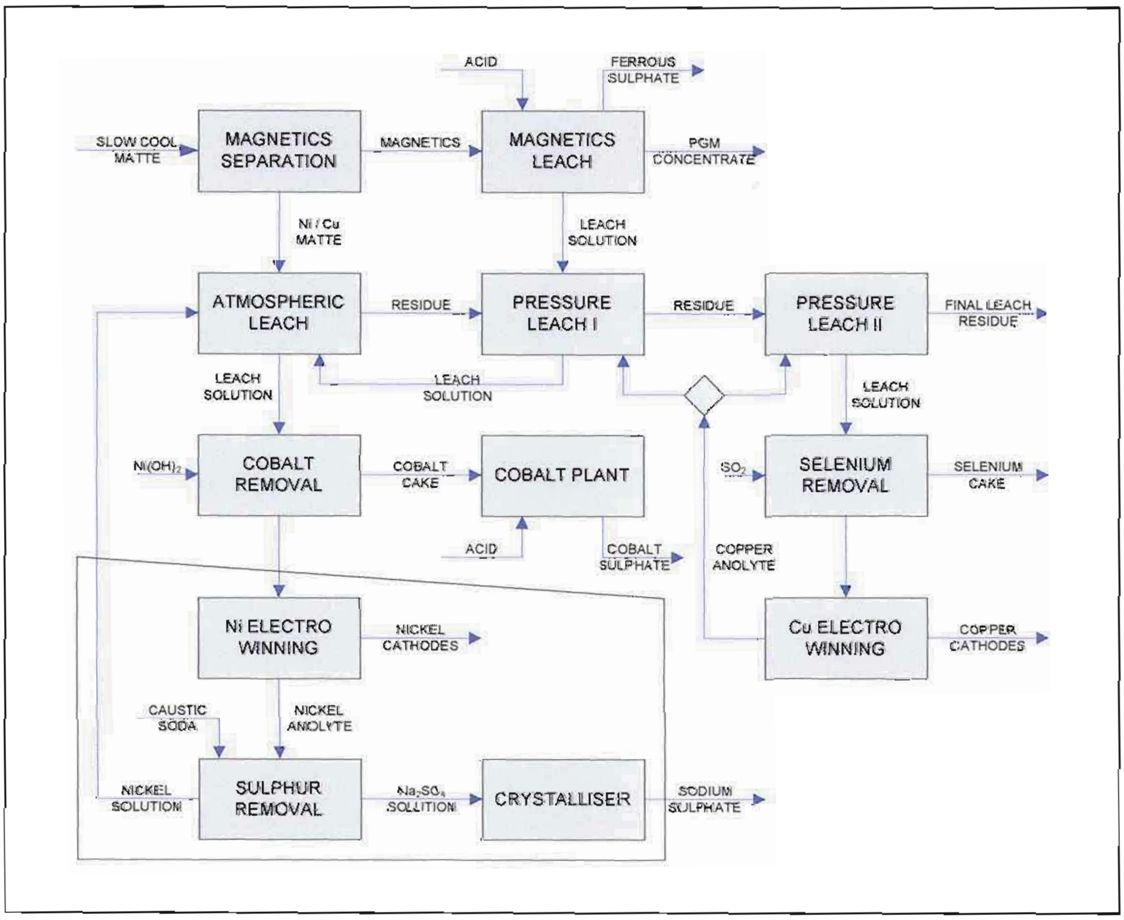


Figure 1.2: Simplified schematic of a recovery process for PGMs and base metals

The ore is mined, crushed and milled to reduce the size and expose the PGM containing minerals. This is dosed with a leaching solution and sent to a flotation unit to increase the PGM concentration up to 1000 grams per tonne. The concentrate is dried and melted in an electric furnace, separating the PGM containing matte from unwanted minerals in the slag, increasing the PGM concentration to above 1400 grams per tonne (Platinum Today, 2006).
The next step is to separate the PGMs from the base metals which in turn are send to the base metal refinery (BMR) as shown schematically in Figure 1.2.

In the complex treatment of the base metals, in order to produce mainly nickel, copper and cobalt sulphate, the recovery of nickel is of special interest in this study.

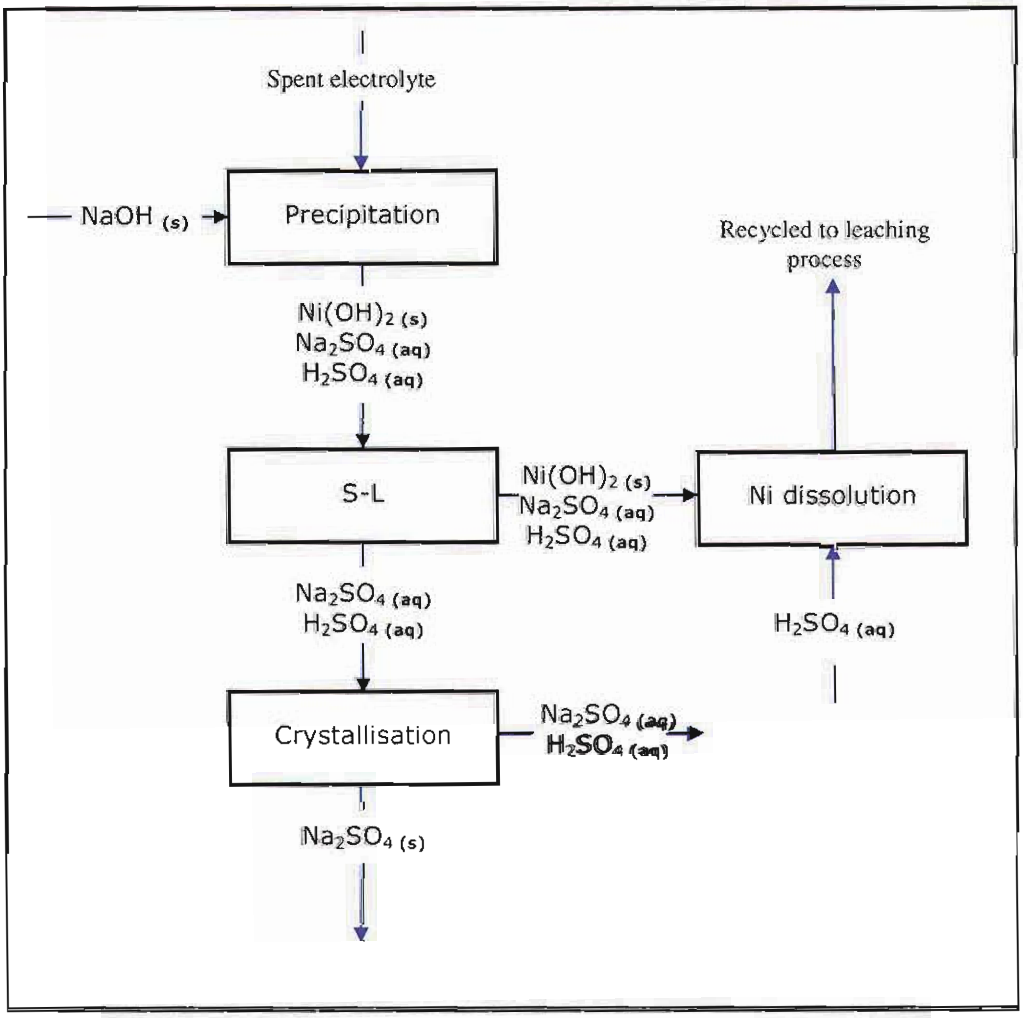


Figure 1.3: Sodium hydroxide treatment of the spent electrolyte

The nickel feed concentration is in the region of 80 g/L at a pH between 1 and 2 and is recovered from the solution by means an electrowinning process. The process recovers approximately 50% of the nickel in the solution, but a further reduction of the nickel concentration decreases the current efficiency and the process becomes uneconomical from energy consumption considerations (Venkatachalam, 1998). In order to make the nickel production profitable, it is essential to recycle the nickel.

Currently this is achieved in a complex process that requires the addition of sodium hydroxide to the spent electrolyte, schematically given in Figure 1.3. Firstly, nickel hydroxide precipitation is caused by caustic soda according to:

$$2NaOH_{(aq)} + NiSO_{4\,(aq)} \rightarrow Ni(OH)_{2\,(s)} + Na_2SO_{4\,(aq)} \qquad (1\text{-}1)$$

and the precipitate is separated from the solution via a solid-liquid separator. The solid nickel hydroxide is consecutively re-dissolved with sulphuric acid and recycled to the atmospheric leaching unit. Sodium sulphate is recovered from an evaporative crystallisation unit and forms a by-product in the production of nickel. The market value of sodium sulphate has however drastically decreased since the mid 70's and together with this the economic potential of the process (Mason, 1999). Other drawbacks of the current process are that the separation is carried out in three steps and the excessive chemicals and energy input required for the precipitation of the nickel hydroxide and the evaporative crystallisation respectively. A gain of this process however, is the successful removal of excess sulphur from the system in the form of sodium sulphate.

1.2. Motivation and objectives

Anglo Platinum is constantly looking for alternative process routes, in order to decrease capital and running costs, decrease energy and chemical consumption and to promote sustainable technology. Improving and optimizing existing processes and replacing outdated processes with new cutting edge technology can help to achieve this goal.

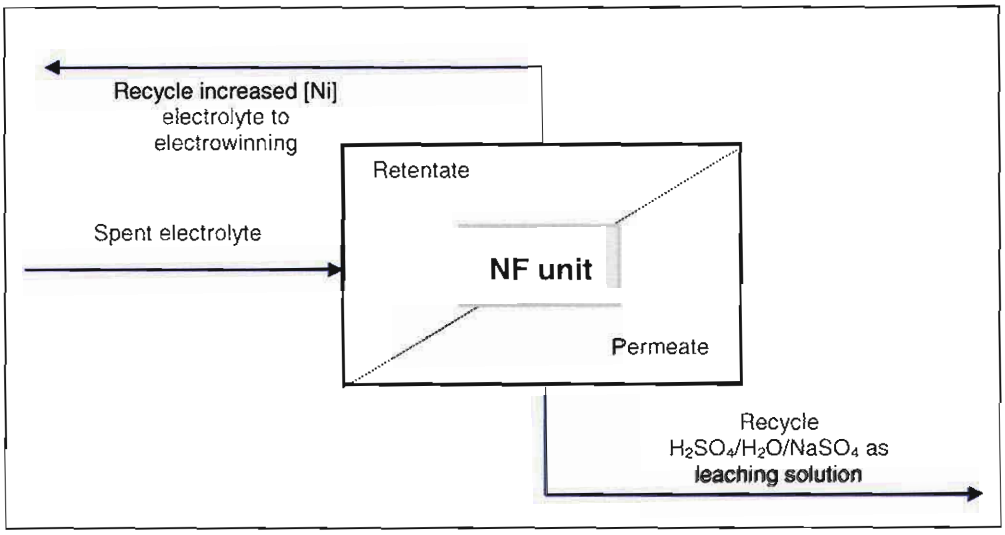


Figure 1.4: Proposed alternative nickel recovery process (Simplified)

Recent studies have shown that nanofiltration (NF) membranes can be used successfully in the separation of acids from their metal salts in ionic solutions (*e.g.* Tanninen & Nyström, 2002), and this formed the motivation for this study. If a NF-based process can be effectively applied in the nickel recovery process it will be beneficial in terms of decreasing both capital and operating costs. In the alternative NF-process, which is schematically depicted in Figure 1.4, the spent electrolyte will be send to a NF-unit, where the nickel species will be predominantly rejected, and the sulphuric acid / sodium sulphate solution will permeate the membrane. The capital costs will be decrease significantly since only one major process unit is required for the separation. Moreover, the operating costs will decrease since no additional chemicals are needed for the separation and the energy required for the crystallisation process will also be eliminated.

Research on metal acid separations, to date, have focused mainly on low metal concentrations and open source publications on nickel recovery in specific, are very limited. Therefore, the overall objective for this project is formulated as follows:

To study the separation of nickel from sulphuric acid at low pH and high nickel concentrations as an attractive alternative in the treatment of spent nickel electrolyte

In order to meet this objective, an extensive experimental program has been carried out, in which different process parameters were varied and the effect on the membrane performance was studied. To simulate the industrial conditions, the nickel concentration was varied between 20 and 50 g/L at a pH of 1 and 2. The effect of sodium addition and temperature was also studied. Since the majority of polymeric nanofiltration membranes have poor acid resistance, particularly during prolonged contact with acidic solutions (Platt *et al.*, 2004), a membrane duration test was also carried out.

1.3. Scope

This dissertation on the use of nanofiltration for the recovery of spent nickel is divided into 5 chapters. Chapter 1 presents a general introduction to, the motivation for, and the objectives of this study. Chapter 2 gives a literature background on membrane technology and specifically nanofiltration. This is followed by a discussion of the relevant literature on metal acid membrane separations. In Chapter 3, the experimental set-up, and the experimental and analytical procedures are given. In Chapter 4, the experimental results are presented, analysed and discussed, and where possible compared to literature. Finally, the conclusions and recommendations of this study are listed in Chapter 5.

2. Literature Review

2.1 Introduction

A large part of any chemical or minerals plant involves separation processes. Various technologies evolved out of the need to separate and purify products, driven by the demand of the clients, environmental considerations and process requirements. Membrane processes are relative new, and have some distinct advantages above other separation processes, in which the operation under mild conditions, the relative low energy input and the absence of chemicals are the most distinct ones. This has, amongst others, led to the building of a membrane based desalination plant in Ashkelon, Israel, designed to produce 330 000 m^3 potable water per day from sea water and hereby providing about 15% of the region's households with fresh water. The membrane installation includes 40 000 RO elements in 32 RO treatment trains (Anon, 2006). The applications are however mostly limited to the treatment of water under mild conditions, mainly due to limitations in membrane stability and/or the absence of a sufficient rejection or flux of the membrane.

In this literature study, a brief introduction to membrane technology (Section 2.2) will be given and the principles and applications nanofiltration will be presented in more detail (Section 2.3). The specific application of metal acid separations will be discussed in Section 2.4, followed by a conclusion on this in Section 2.5.

2.2 Membrane Technology

The broad definition of filtration is the passing of a fluid through a filter medium to remove suspended particles. The filtering medium can be a solid, a fluid or a combination of both. This medium acts as a selective barrier between the two phases. Sieving, on the other hand, refers to the separation of particles based on their size. In this case a heterogeneous mixture (phase, shape or size) is passed over a screen with a specified mesh size, only allowing particles smaller than the cut-off size to pass.

A membrane can be described as a selective barrier between two phases and as a screen that allows the passing of suspended solutes\molecules with a certain size and/or charge, and can therefore be classified as a separation medium with both filtration and sieving characteristics. Membranes are used in the rejection of contaminants ranging from ions (order of Angstroms) to bacteria and yeasts (micrometer scale), and a general classification of the different processes and possible applications is given in Figure 2.1.

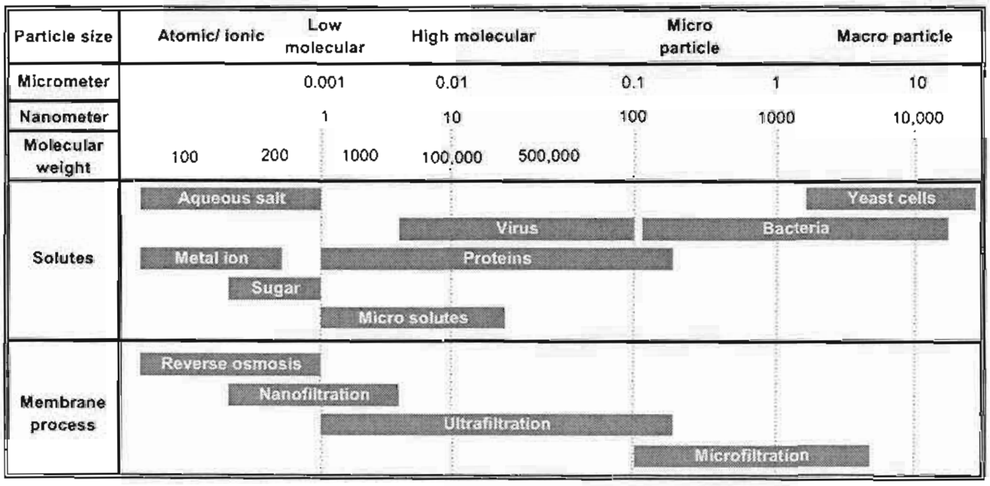


Figure 2.1: Membrane process application range (Adapted from Mulder)

Popular materials for the construction of membranes include metals, ceramics and polymers, in which the last group of is often preferred due to the low production costs. Ceramic membranes are known to be superior in terms of stability and robustness, but the installation costs are approximately a tenfold higher compared to their polymeric counterparts (Guibault, 2004). Also, polymeric membrane technology is much more matured, and an array of different commercial membranes is available, which made polymeric membranes the preferred choice in this study.

Nanofiltration is a specific class of membrane application and has received increased attention recently. The number of publications on nanofiltration has increased approximately a tenfold over the period of 1994 – 2002 and the industrial capacity have grown with a factor six in the period of 1992 – 2000 (Schäfer *et al.*, 2005). The main characteristic that is unique for nanofiltration is that monovalent ions can be separated from divalent ions, mainly due to the charge of the membrane. This feature makes fractionation of salts possible, and this can broaden the application field of nanofiltration to the chemical and minerals process industry. The separation of nickel from acidic solutions, relevant to the BMR of Anglo Platinum is an example of this. Nanofiltration will be discussed in more detail in the following section.

2.3 Nanofiltration

According to Schäfer *et al.* (2005:6) nanofiltration membranes exists from the 1960s, but was referred to as either loose RO membranes or tight UF membranes up to the late 1980s. The term Nanofiltration was first introduced by FilmTec, referring to the cut-off of non-charged solutes with the approximate size of 1 nm.

Nanofiltration membranes can provide higher flux values than Reverse Osmosis (RO) membranes at lower operating pressures and provide higher retention of multivalent ions and organic material than Ultrafiltration (UF) membranes. Therefore, NF is classified between RO and UF membranes, illustrated in Figure 2.2.

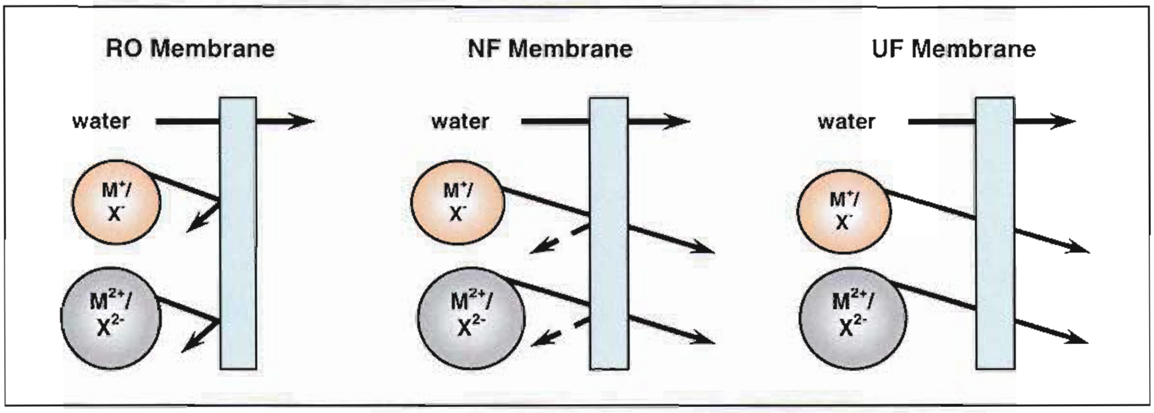


Figure 2.2: Rejection comparison between RO, NF and UF membranes

NF processes are currently used in water treatment, mainly for the production of potable water, water reclamation and ground water remediation. Also, a significant amount of NF processes can be found in the textile dye industry, mainly relevant to effluent treatment. Fewer applications are in the chemical processing industry, in which the dewaxing of solvents is an example. The separation of metals from acidic solutions has received some attention recently and can be a novel attractive application field of NF, based on the unique characteristics of this membrane process. The basic principles of NF, in relation to this application will be summarised in the following sections.

2.3.1. NF principles

As stated, NF can be classified between RO and UF. RO membranes are normally assumed to be dense and, for water applications, only water will permeate significantly, and all the salts are rejected for more than 90%. Large rejections of salts can be contributed to the weak interaction between membrane and ions. UF, on the other hand, shows very little or no retention to salts, mainly due to the relative large size of the pores compared to the ions in solution. It is often discussed whether RO membranes are non-porous or dense, but an absolute answer cannot be distilled from literature. Despite this ambiguity, the behaviour of RO membranes can be explained by a combination of interaction of the ions with the membrane and size of the ions, in which the interaction effect is often dominant. The interaction effect is mainly caused by the membrane charge in combination with the charge of the contaminants in solution, and is discussed in the following section.

Membrane surface charge

In Schafer *et al.* (2005:107), it is stated: *"The appearance of charge determines to a large extent the properties of NF membranes towards charged solutes. In contact with water membranes will acquire an electric charge, through several possible mechanisms. These mechanisms may include dissociation of functional groups,* *adsorption of ions from solution and adsorption of polyelectrolytes, ionic surfactants and charged macro molecules."*

Although a lot of work has been done on this subject and various models exists describing different charged layers, this topic is only discussed on a qualitative level. When a membrane is put in contact with a solution, functional groups on the membrane-solution interface will interact with species from the solution, which can induce a charged layer on the interface of the membrane. This effect can be quantified by the zeta potential, via streaming potential measurements, but this falls outside the scope of this study. However, whether this charged layer is positive or negative can easily be determined from the isoelectric point (IOP) of the membrane, which is determined by the material of construction. Ceramic membranes have often IOP's in the range of 6-9, but different studies (*e.g.* Schaep *et al.*, 2001, Mänttäri *et al.*, 2004 and Veríssimo *et al.*, 2006) report on an IOP of 4-5 for various polymeric NF membranes.

The combined effect of charge and size is nicely illustrated by the work of Schaep et al. (2001), where 4 different membranes were studied, and amongst others, the rejection of different salts (NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$) were tested. One membrane, the CA30 membrane showed poor rejections to all salts, mainly due to the relative large molecular weight cut off (MWCO) of the membrane and the material of construction, cellulose acetate, only having a weakly charged membrane interface. The NF40 and UTC20 membrane were made of polypiperazine-amide and had a relative low MWCO, and high rejections for the salts dissociating in one or more large ions ($MgSO_4$, Na_2SO_4 and $MgCl_2$), and poor rejections for the salts dissociating in small ions (NaCl), were obtained. The fourth membrane, NTR7450, a sulphonated polyethersulphone membrane, characterised with a high negative membrane charge and an intermediate MWCO, showed the most interesting results. Due to the negative charged membrane, the multivalent negative sulphate ion was rejected most. Between $MgSO_4$ and Na_2SO_4, Na_2SO_4 was rejected most, because of the single valent positive sodium ion, despite the larger Stokes radius of the magnesium ion. The same was valid for the chloride salts, leading to the following rejection order: $Na_2SO_4 > MgSO_4 > NaCl > MgCl_2$.

Application to nickel sulphate/sulphuric acid separation

Since the intended application of the separation of nickel from sulphuric acid solutions is operated at a pH < 2, the charge of the membrane will be positive. It is therefore expected that the divalent cation Ni^{2+} will largely be rejected. The monovalent cation H^+ will diffuse through the membrane and to obtain electro neutrality the sulphate will permeate as well. The interaction of the divalent ion with the membrane can be so strong that the concentration of the monovalent ion at the permeate side is larger than the feed side. This effect, which is called the push-out effect, is not uncommon in NF application, as also reported by Krieg (2005). A schematic representation of the proposed separation mechanism is given in Figure 2.3.

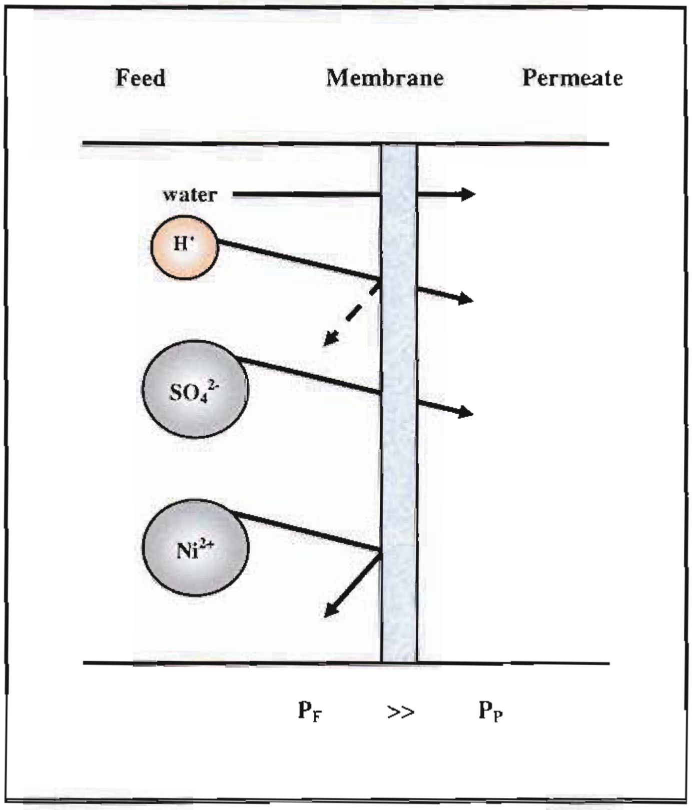


Figure 2.3: Solute-membrane charge interaction

The rejection, also often termed retention, is quantified as the fraction of ions retained by the membrane and is defined by:

$$R = \frac{C_f - C_p}{C_f} = 1 - \frac{C_p}{C_f} \qquad (2.1)$$

Where C_f and C_p are the ion feed and permeate concentration respectively (Mulder, 1999:9). Thus if the permeate concentration is higher than the feed concentration, as with the case of H^+, a negative retention value is obtainable. It is also common practice to express retention in a percentage value.

Acid stability

Since the intended operation is carried out a relative low pH, the stability of the membrane is an important issue. Aggressive chemicals can attack and irreversibly degrade polymeric membranes through means of oxidation, nitration, hydrolysis and acid–catalysed hydrolysis according to Platt *et al* (2004). The degradation is caused by chain scission, cross-linking and chemical modification. The following features are given as indicators of chemical degradation:

- embrittlement;
- surface cracking;
- blistering;
- pock-marks on the surface (due to etching);
- swelling or distortion;
- discoloration (due to oxidation);
- voids or holes (caused by selective dissolution).

Membrane fouling

Next to the relative low pH, another difference with conventional NF processes is the relative high concentrations of the contaminants. This feature may give rise to an increased fouling of the membrane and is discussed shortly.

Membrane fouling can be express as any reversible or irreversible process that reduces the efficiency of the membrane in such a way that the flux decreases, and/or influences the desired retention value. Settling of suspended solids on the membrane surface or inside the membrane pores and concentration polarization both qualify as fouling agents.

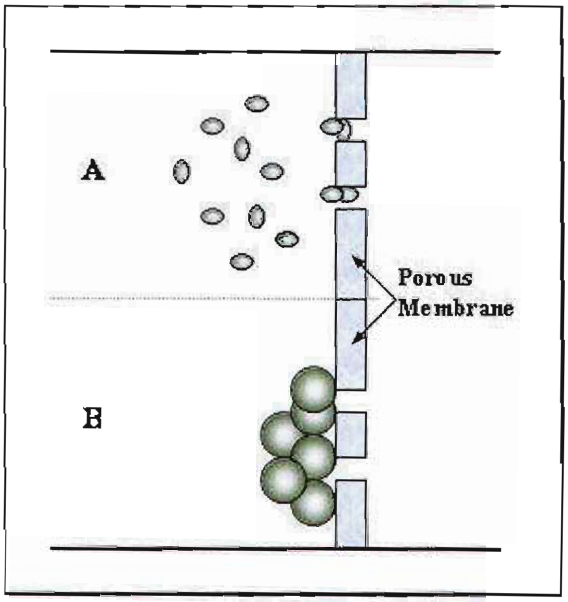


Figure 2.4: Fouling mechanisms: (A) Membrane pore fouling; (B) Membrane surface fouling

Figure 2.4 gives a graphic illustration of the difference between fouling due to settling or adsorption of particles or ions in membrane pores (A) and on the membrane surface (B). Both these cases will lower the flux as the fouling grade increase.

Concentration polarisation

Another feature, which is often associated with NF operation, especially in the case of high salt concentrations, is concentration polarization. Concentration polarization is a regular occurrence with dead-end operation of membranes, but it can also occur if the turbulence along the membrane is low during cross-flow operation. In membrane operation, the convective flux towards the membrane causes the concentration of the rejected constituent to increase near the membrane interface. The concentration difference that now occurs induces molecular transport of this constituent back to the bulk, and is often termed back-diffusion in membrane operations. Normally, the convective flow is rate determining, but in the case of a large flux through the membrane and a high salt concentration, the back-diffusion may become rate limiting, which is called concentration polarisation.

Specifically on the intended application of metal separation from acidic solutions the following was reported: In an article published by Nyström *et al* (1994), NF membranes are referred to as having free volume rather than pores. If a membrane has relatively little free volume (tight structure) it has more RO characteristics, and if it has relatively large free volume (open structure) it is more like a UF membrane. This indicates that the retention characteristics of a NF membrane are dependent on the amount of free volume in the active membrane layer. The free volume can be influenced by solvent and solute interaction with the skin layer due to internal electrostatic repulsion. This is caused by dissociation of functional groups on polymeric strands of the membrane or sorption of charged particles in the free volume. Depending on the effect it has it can decrease or increase the rejection and/or decrease or increase the flux.

This corresponds well with the shrinking skin theory of Freger *et al.* In this study, different model substances were chosen to see what influence they have on the membrane and to report fouling if any occurred. The model substances include; salts: NaCl, $MgCl_2$, NH_4Cl, organic molecules: sucrose, vanillin, humic acid, lignoslfonates: LS-PN and LS-PC, potato and maize starch and wastewater from three chemical pulp bleaching stages. An important finding concerning this study is that the salts only foul at certain pH values where they precipitate and forms scaling or forms some type of gel. Overall it was reported that the more open membranes fouled easier especially if they were permeable for the model substance. Thus the better a substance was retained the less fouling it caused.

2.3.2. Operating methods

For research purposes the most commonly used membrane set-up are flat-sheet membrane modules. This type of set-up is relatively easy to construct and makes the control of the different operational constraints easy. Two different arrangements are possible:

- Dead-end module (Batch);
- Cross-flow module (Continuous).

The pressure in a dead-end module set-up is normally applied by an inert gas such as nitrogen. In the case of cross-flow pressure is applied mechanically with a pump and backpressure regulator. The advantages and disadvantages of both setups are compared in Table 2.1. Since concentration polarisation is to be expected, and to simulate industrial modules better, a cross flow model was used in this study.

Table 2.1: Dead-end versus Cross-flow

	Dead-end	**Cross-flow**
Advantages	Easy to operate	Decrease concentration polarisation
	Applied pressure is tangent on the membrane surface	Continuous operation
	Good for membrane characterisation experiments	Pseudo constant feed concentration
Disadvantages	Tends to form concentration polarisation	More complicated to operate
	Batch	Still differences in results compared with spiral wound modules

2.3.3. Speciation

Nickel sulphate

Ionic salts dissociate in aqueous solution due to the dipolar characteristic of water. The degree and rate of dissociation is related to the solubility of the chemicals, which in turn are related to the temperature, pH, pressure and the concentration of the salt in the solution. The ions can form different species within the solution and these species are extremely dependent on the free protons in the solution. The efficiency of nanofiltration, as already explained, can be very dependent on both size and charge of the ions in the solution. Thus knowing what species will be present for the given conditions in the solution, one can predict the retention of the membrane and explain some phenomena occurring during separation.

Considering the aqueous solution of water, sulphuric acid and nickel sulphate, Zijp (2006) proposed that the following species to be present:

- Ni^{2+}
- $Ni\ (OH)_{2\ (aq)}$
- $Ni\ (OH)_3^-$
- Ni_2OH^{3+}
- HSO_4^-
- H^+
- $NiOH^+$
- $NiSO_{4\ (aq)}$
- $Ni\ (OH)_4^{2-}$
- $Ni_4(OH)_4^{4+}$
- SO_4^{2-}
- OH^-

A speciation-modelling program, HCS, was used to predict the distribution of the species for the proposed operation conditions (see Figure 2.5).
From this list the following species was chosen to be the most probable species present at the operating conditions between pH 1 and 2.

- Ni^{2+}
- HSO_4^-
- H^+
- $NiSO_{4(aq)}$
- SO_4^{2-}

Figure 2.5 is a speciation diagram of 50 g/L Ni in a water-sulphuric acid solution generated by the HCS program. It is important to note that the nickel sulphate is only fractionally dissociated and also that the monovalent bisulphate is present in significant quantities.

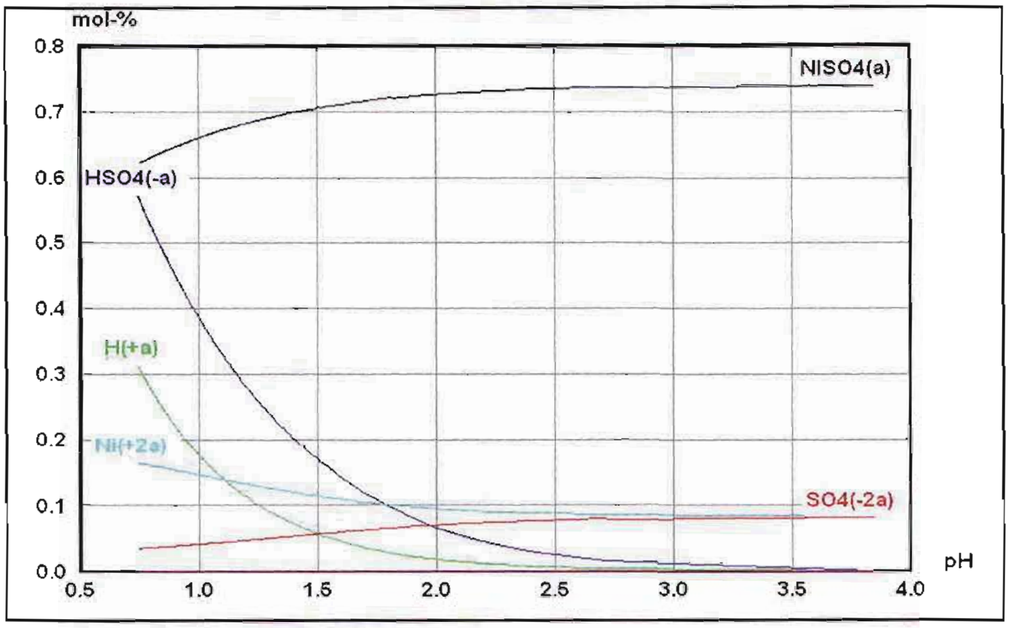


Figure 2.5: Species diagram

Sulphuric acid

Sulphuric acid is classified as a polyprotic acid in Kotz and Treichel (1999:789), meaning that each H_2SO_4 molecule can donate two protons to an aqueous solution. Sulphuric acid's dissociation into water can be represented by the following two equilibrium reactions as described by Visser (2000:9).

$$H_2SO_{4\,(aq)} \leftrightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)} \tag{2.1}$$

$$HSO_4^-{}_{(aq)} \leftrightarrow H^+_{(aq)} + SO_4^{2-}{}_{(aq)} \tag{2.2}$$

Below a pH of 2 the bisulphate ion (HSO_4^-) is more abundant than the sulphate ion (SO_4^{2-}). This is caused by the extreme concentration of protons at this pH, forcing reaction 2.2 to the left.

2.3.4. Osmotic pressure

The principle of osmotic pressure lies in the chemical potential difference between two phases, separated by a semipermeable membrane, with different solute concentrations.

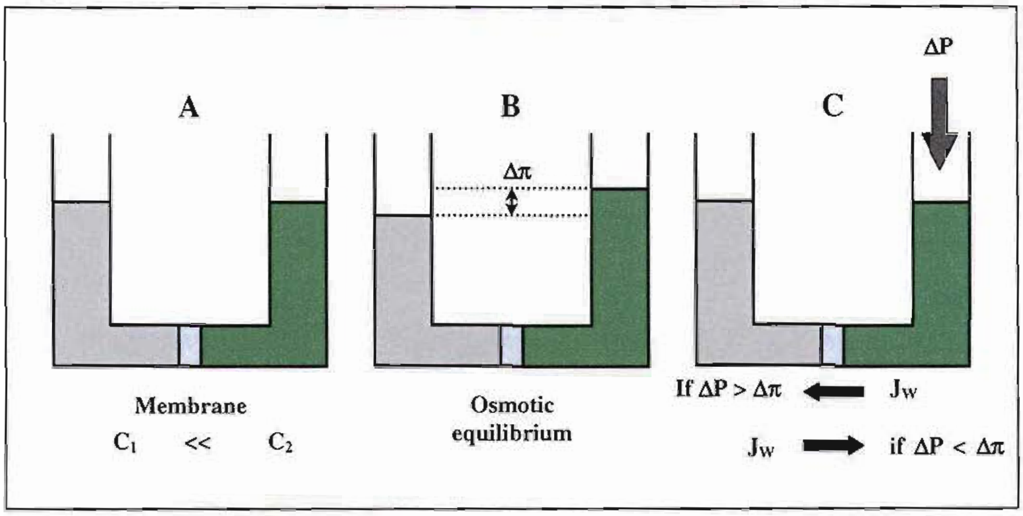


Figure 2.6: The osmotic effect

A solvent with the low concentration solute has a more negative chemical potential than the same solvent with a high concentration solute. Subsequently solvent flow from the dilute phase to the concentrated phase will arise.

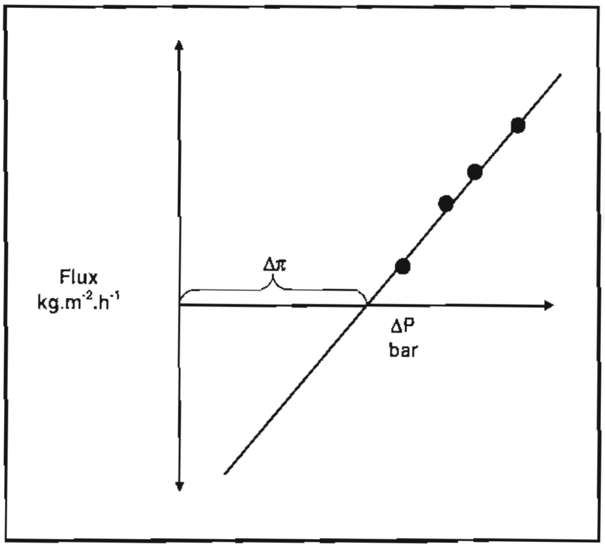


Figure 2.7: Determining osmotic pressure from flux data

For a set-up, as illustrated in Figure 2.6 (B), the osmotic pressure can be calculated with (Mulder):

$$\pi = c_j\,RT/\,M \tag{2.3}$$

Another way of presenting and calculating osmotic pressure is by extrapolating a trend line fitted through flux measurements back to the intersection of the x-axis, as illustrated in Figure 2.7.

2.4 Studies on the use of NF for ion separation

The study on applications of NF membranes for ion recovery is relatively new. A lot of work went into RO membranes for desalination processes in the mid sixties, but it was only in the late eighties that an investigation into the potential of NF membranes for ion separation started to catch on.

A study done by Mehiguene *et al* (1998) on the retention of copper and cadmium showed a relation between the hydration energy and charge valency of the permeating co-ions. It was shown that for both Cu^{2+} and Cd^{2+} the retention increased with anion hydration energy. The retention of Cd^{2+} was found as 35.2% when the permeating anion was NO_3^- (hydration energy of 310 $kJ.mol.l^{-1}$), compared with retention of 99.1% with SO_4^{2-} (hydration energy of 1047 $kJ.mol.l^{-1}$).

In a study on the recovery of sulphuric acid by Visser *et al* (2000), it was reported that SO_4^{2-} rejection between 95 – 99% could be achieved with several different NF membranes at neutral conditions, but these values decreased dramatically at lower pH values. A change in membrane charge and an increase of the formation of HSO_4^- at lower pH is given as an explanation for this occurrence.

Taleb-Ahmed *et al* (2002) studied the recovery of Cr^{3+} and Cr^{5+} from tannery wastewater, and their results showed that the retention of chrome is strongly governed by speciation, which in turn is dependent on concentration and pH. Rejection between 99.5% and 99.9% is reported for Cr^{3+} in a chloride solution with no significant influence of concentration or applied pressure. There was little change in rejection with the addition of NaCl to the solution, but $NaSO_4$ decreased it dramatically to well below 95%.

Between a pH of 1 and 6 there are two possible species of Cr^{5+} dependant on the concentration of chrome. Up to 10 $mMol.L^{-1}$ the monovalent species $HCrO_4^-$ exists and above this $Cr_2O_7^{2-}$. At very low concentrations, below 2.5 $mMol.L^{-1}$, extremely good separations were achieved. From 2.5 $mMol.L^{-1}$ to 10 $mMol.L^{-1}$ a steady decrease to a rejection of 45% is reported. Upwards from 10 $mMol.L^{-1}$ it increase again but stabilised at 60% rejection.

Nyström & Tanninen (2002) showed that nanofiltration could be used to separate acids from their metal salts in ionic solutions. They studied the retention characteristics of NF 45 and Desal-5 DK for Na^+ and Mg^{2+} in their nitrate solutions. The Mg^{2+} concentrations where varied over a pH range of 0.7 to 5. The NF 45 showed very good rejection for Mg^{2+}, 97.5 to 99.5%, from neutral to extreme acidic conditions. The retention values for Desal-5 DK were lower at 92.5 to 94.5%. A maximum rejection of Na^+ was achieved at approximately pH 2.5, decreasing with increasing Mg^{2+} concentration. The retention of Na^+ in a pure solution dropped from 60% to as low as 14% with the addition of Mg^{2+}. At extreme acidic conditions the monovalent ion permeation is poor due to the permeation of the abundant and more mobile H^+ ion. This indicates that by choosing the correct operating conditions, NF membranes can be used to separate divalent from monovalent ions.

Tanninen *et al.* (2005) did a similar study on the rejection of copper in an acidic copper sulphate solution. The NF45 membrane, similar to the NF membrane used in this study, provided rejection of copper between 96 and 98% at 0.47 M $CuSO_4$ ($\approx$30g/L Cu^{2+}). Although the pH influenced the rejection of sulphuric acid, it had little effect on the retention of copper.

A variation of operating conditions on recovery of indium was studied and presented by Wu *et al* (2004). They showed that the best recovery was at neutral conditions where the indium formed polymerised hydrolysis products or complexes that aided separation. In acidic conditions the rejection varied. This can be ascribed to the use of membranes that were negatively charged in acid conditions.

Another study on the effect of varying pH was done on the recovery of sodium. The study by Qin *et al* (2003) looked at the rejection of Na^+ over a pH range of 1 to 7. The feed was prepared using NaCl and $NaNO_3$ to examine the effect of different counter-ions. They showed that rejection of Na^+ and the permeate pH is dependant on the feed pH. This is caused by the change of membrane surface charge at the isoelectric point, which was in this case at pH 4.

Freger *et al* (2005) used sodium chloride and lactic acid mixtures as a model solution to study the separation organic/inorganic mixtures with a FILMTEC™ NF-200B membrane. Their study concentrated on the effects that pH, salt concentration and temperature had on the flux and lactate rejection.

It was found that there was a decrease in flux with an increase in concentration but an increase in flux with increasing pH. The rejection decreased with increasing concentration and a maximum rejection was found at a neutral pH.

The decreasing flux at higher concentrations are attributed to an increasing osmotic difference between the feed and the permeate. Shrinking of the skin layer caused by the differences in the hydration of the ionised groups and counter ions due to varying pH is given as the reason for the rise in flux with increasing pH.

The decreasing rejection above and below neutral pH could not be explained with the combination of charge repulsion and sieving alone. It was thought that the effect of sorption leading to diffusion leakage played an important role.

The fluxes increased with temperature and the rejection, for all the concentrations, decreased. Higher activation energy of at the lower fluxes is given as the reason. This confirms their theory that the shrinking skin layer causes the decrease in flux.

A study on the separation of nickel sulphate and nickel nitrate from their acids was done by Nyström *et al* (2000). Three different membranes (NF45, Desal-5 DK, and PVDS-1) were tested for permeability and Ni^{2+} ion rejection under various conditions. For this study they varied the Ni^{2+} concentration between 0.5 and 10 g/L. The NF45 showed very good results at 99% rejection of Ni^{2+} in the sulphuric acid solution. A decrease in flux with increasing $NiSO_4$ concentration is reported, but no real change in flux with increasing H_2SO_4 concentration. A 10% decrease in retention of Ni^{2+} was found with the addition of nitric acid indicating the important role of the counter-ion(s) in a charged NF membrane process.

2.5 Conclusion

The use of NF for the separation of different metal ions from their acidic solution holds a lot of promise for the metal recovery industry. It should be clear from the information given above that excellent rejection values have been observed under different operating conditions for various metals. But thus far most studies only considered low ion concentrations. The highest Ni concentration reported was 10 g/L by Nyström *et al* (2000). In this study the focus will be shifted to how effective the NF processes will be under high metal ion concentrations and low pH, reflecting the industrial conditions experienced at Anglo Platinum.

3. Experimental

3.1 Introduction

In this chapter, details about the experiments, as presented in Chapter 4, are described. The different materials used are listed in Section 3.2, the experimental set-up is discussed in Section 3.3, and the experimental procedures are given in Section 3.4. Since the experimental set-up is designed and constructed in house, the reproducibility has been tested, which is the subject of Section 3.5.

3.2 Materials

3.2.1. Membrane

From initial experiments, it was shown that the membrane from a FILMTEC NF-2540 (further referred to only as NF) spiral wound module, a polypiperazine amide thin-film composite membrane from DOW, harnessed the most potential in the separation of nickel from sulphuric acid solutions (Rautenbach, 2005 and Groenewald, 2005). The membrane was unwounded from the module, and all experiments were carried out with circular cuts from this sheet. A technical data sheet, as provided by DOW is given in Appendix B.

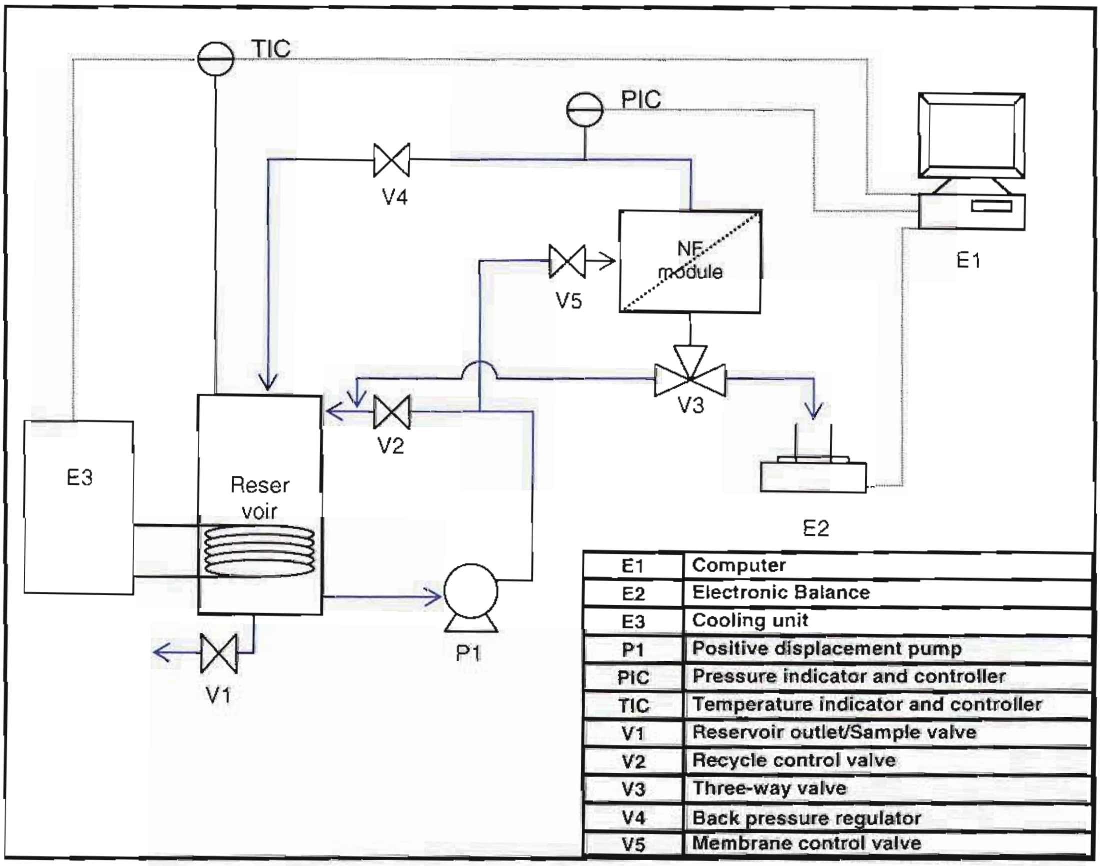
3.2.2. Chemicals

Two forms of hydrated nickel sulphate were used. Analytical grade nickel sulphate hexahydrate ($NiSO_4{\cdot}6H_2O$) was purchased from Merck (purity > 98 mass%) and used as received. Anglo Platinum LTD provided nickel sulphate ($NiSO_4.xH_2O_{(s)}$) in solid form, and this is termed industrial nickel sulphate in this thesis. The hydration number, x, was found to be 5.2 by comparing the industrial sample with the analytical one (Appendix A). The industrial nickel sulphate was purified before use (see Section 3.4.1). Anhydrous sodium sulphate was purchased from Merck (purity >

99%) and used as received. Sulphuric acid was used to adjust the pH, and was obtained from Fluka with an assay of > 98%. Pure water (conductivity < 0.05 μSiemens) was used for all experiments and was purchased from Immuno-Vet Services.

3.3 Experimental set-up

The experimental set-up is schematically depicted in Figure 3.1. The important features of the set-up, the reservoir, the pump and the membrane module, are interconnected with stainless steel (SS-316) ¼" pipes and connected with Swagelok® coupling pieces. Only the connection between the reservoir and pump was made of a flexible silicon rubber hose.



E1	Computer
E2	Electronic Balance
E3	Cooling unit
P1	Positive displacement pump
PIC	Pressure indicator and controller
TIC	Temperature indicator and controller
V1	Reservoir outlet/Sample valve
V2	Recycle control valve
V3	Three-way valve
V4	Back pressure regulator
V5	Membrane control valve

Figure 3.1: Schematic representation of experimental set-up

The reservoir was constructed from a 316 stainless steel plate and has a capacity of 6 litres. The inner side of the reservoir contained a spiral, which was connected to a refrigerant unit (E3) for temperature control, purchased from Grant (Optima Series GP200). This unit uses ethylene glycol as refrigerant.

A positive displacement pump (P1), with a stainless steel pump head, purchased from Fluid Controls (Cucchi, CPP 3/25 XV 110S), induced the pressure and flow in the system. From the reservoir, the fluid is pumped to the flat-sheet module (Figure 3.2) that was designed and constructed in-house and has an outer and effective diameter of 120 and 59.3 mm respectively. Viton sealing is used and a porous stainless steel plate was used as support for the membrane. The cross flow volumetric flow rate was regulated by the pump to 60 L/h. This volumetric flow-rate corresponds with an average linear velocity of 10 cm.s^{-1}, and a Reynolds number of about 600. The liquid is injected in the module with a velocity larger than 2 m/s, via the 1/8" inlet pipe, and sufficient mixing was observed, via dye experiments, by Rautenbach (2005).

- Outer diameter: $D_{out} = 120 \times 10^{-3}$ m
- Inner diameter: $D_{in} = 59.3 \times 10^{-3}$ m

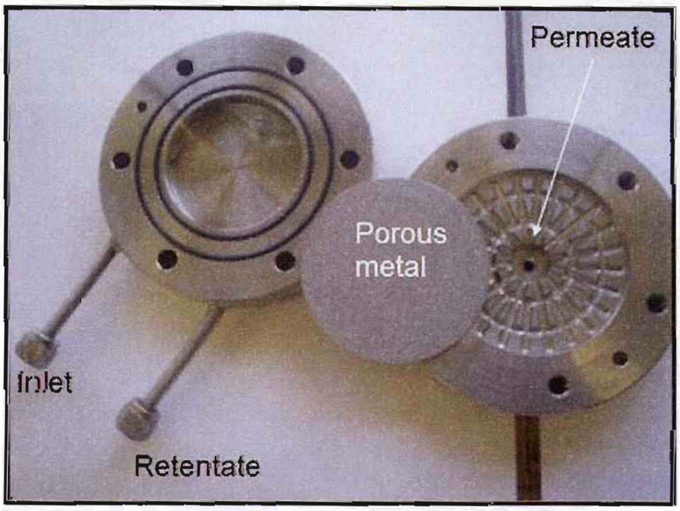


Figure 3.2: Flat-sheet membrane module

A pseudo constant feed concentration can be achieved by recycling both permeate and retentate to the reservoir, by closing valve V2, and opening valve V5. The pressure is than regulated by a backpressure regulator V4, purchased from Tescom (26-1700 series), and the three-way valve V3 is used to direct the permeate to the reservoir.

When a sample is taken all the valves stay in the same configuration except for the three-way valve V3, which is opened in the direction of the sample discharge tube for the duration of sampling.

An electronic balance (E2) is used to determine the permeate mass for flux calculations, and was purchased from Denver Instruments (PI – 403). The balance is connected to a Compaq Descpro PC (E1) for automatic logging using the RS-232 port. The software package used for the mass logging was developed by TAL Technologies specifically for Denver Instruments balances. The data could be transferred to Excel® for further processing.

The pressure in the system was measured with an electronic WIKA Universal Pressure Transmitter UniTrans 10 (UT – 10) gauge. This was used in conjunction with the mechanical pressure gauge already connected to the system. The advantage of the electronic gauge is threefold. Firstly the pressure pulse generated by the positive displacement pump could be electronically damped by the gauge, giving an average continuous readout over 40 second intervals. Secondly the gauge was coupled to a controller, allowing emergency shutdown of the pump for either too high or too low pressure situations and lastly it allowed continuous logging of the pressure for the duration of the experiment.

The temperature was measured with a WIKA Standard RTD, simplex with potseal. Both the pressure gauge and the temperature probe where connected to Shinko programmable DIN rail mount controllers, which were connected to a Shinko RS 485/RS - 232 Converter/ repeater interface. The output from the converter is also connected to a Compaq Descpro PC (E1) using RS -232 connections. The software package JC-300 (DCL-300) SWM-JC001M, version 1.0.9, was used for control and logging and was develop by Shinko Technos CO., LTD. This data could also be transferred to Excel® for further processing.

3.4 Experimental Procedure

3.4.1. Industrial nickel sulphate purification process:

The purification process of the industrial nickel sulphate consisted of the following steps:

Step 1:	Preparation of saturated solution of $NiSO_4$ at 50 °C.
Step 2:	Filtration of the solution to remove suspended solids.
Step 3:	The solution was allowed to cool down to ambient temperature and left for 24h to crystallise
Step 4:	The crystals were separated from the solution with vacuum filtration.
Step 5:	The crystals were gently rinsed on the filter with cold water.

Although this process is fairly successful in removing suspended solids, some amount of soluble impurities still remains in the nickel sulphate crystals. The results of Inductively Coupled Plasma (ICP) spectroscopy on the industrial $NiSO_4$ are displayed in Appendix D. Note that large amounts of iron and cobalt are present in these impurities.

3.4.2. Solution preparation:

The 30, 40 and 50 g/L Ni stock solutions were prepared respectively with 634.76, 846.71 and 1058.84 g industrial nickel sulphate. Purified water was added to the Erlenmeyer flask until a mass of approximately 4.8kg was reached. Next the desired pH was obtained with the addition of H_2SO_4. The amount of acid added was noted and the solution was topped up to 5 L with the purified water. It was found that the industrial nickel sulphate was heterogeneous and with the preparation method slightly lower concentrations were prepared. Note that the exact Ni concentration and pH values were not calculated from the preparation data but analysed and found to be 27 ± 3, 35 ± 3 and 45 ± 3 g/L respectively for the 30, 40 and 50 g/L solutions. The stock solution was left overnight to allow settling to proceed, and was decanted and filtrated to remove the solids. Notably more solids formed for pH 2 than for pH 1. When no visible solids remained on the filter paper the solution was transferred to the reservoir.

3.4.3. Membrane preparation:

Circular pieces where cut out of the single sheet of membrane material and conditioned by permeating at least 100 g water through the membrane at a pressure difference of 24 bar. One piece of membrane was used for each solution that was studied.

3.4.4. Analysis:

A Pharmacia Biotech Ultrospec 3000 was used for UV/Visible spectrometry to determine the nickel concentration for all samples taken. UV/Visible spectrometry works on the principle that elements have a unique absorbance of light at a certain wavelength, which is at 393 nm for nickel (Reusch, 1999).

The absorbance is a function of the nickel concentration and a calibration curve is given in Figure 3.3. From the figure, it can be seen that the relationship between absorbance and concentration is linear, and Equation 3.1 is used for the determination of the nickel concentration in feed, retentate and permeate. The apparatus was re-calibrated throughout the course of the project, and deviations of < 1% were found.

$$[\mathrm{Ni}] = 12.102 \times \mathrm{Absorbance} \tag{3.1}$$

The absorbance of nickel above 35 g/L is larger then the detection range of the apparatus, and for these concentrations it was necessary to dilute the samples before analysis.

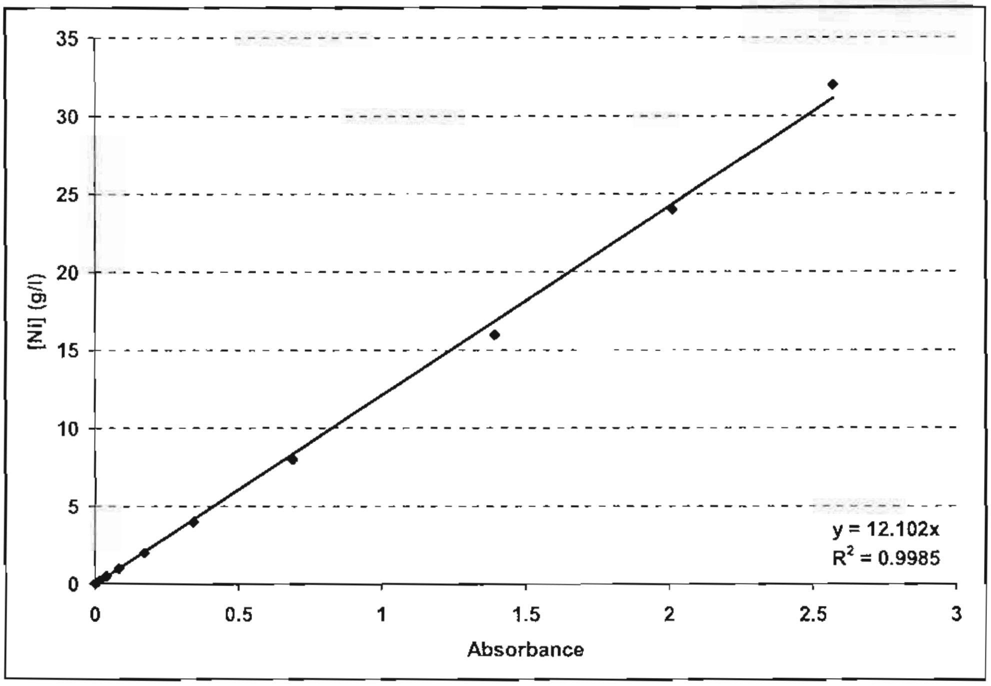


Figure 3.3: UV/Visible spectrometry calibration curve

The pH for all samples was measured with a Metrohm 827 pH meter. The pH was converted to the hydronium concentration, $[H^+]$, with the logarithmic relation between pH and $[H^+]$:

$$pH = -\log[H^+] \qquad (3.2)$$

With the hydronium concentrations calculated in both feed and permeate it is possible to calculate the rejection of the H^+ with Equation 2.1, which is also used for nickel.

As explained in Section 3.4 a balance was used to measure the sample mass. The balance transmitted the sample mass at five-second intervals to a computer with a software package that logged the data in an Excel spreadsheet format. The flux can be calculated by dividing the slope of the graph plotted with mass versus time (an example is given in Figure 3.4) with the effective membrane area, Equation 3.3.

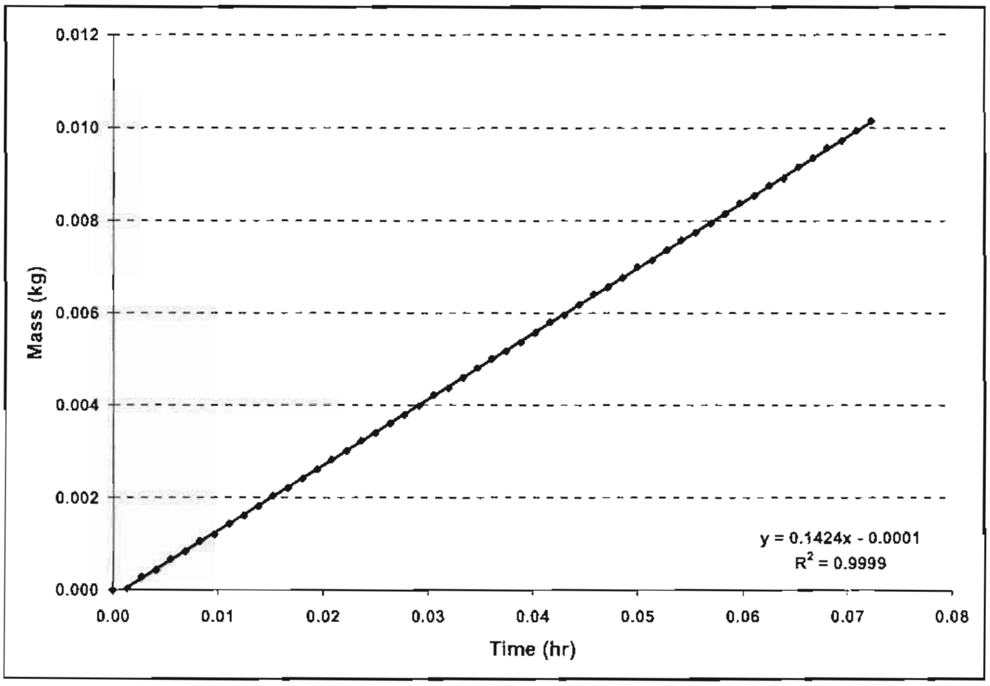


Figure 3.4: A graph of mass versus time used for flux calculations

$$J = \frac{slope}{A_{mem}} \tag{3.3}$$

For clean water experiments, the mass flux was converted to the volumetric flux, using a density of 998,4 kg/m^3 (Perry)

New and unused membranes were studied and compared with a Phillips XL 30 scanning electron microscope for any traces of severe damage due to the acidic medium. In conjunction with the SEM a CDU Leap Detector was used to determine the composition of fouling agents, if any were observed.

3.5 Experimental Planning

To recall the objectives of this study it is of interest to determine the performance of the NF membrane under simulated industrial conditions. In regards to the statement above it was necessary to determine the flux and Ni rejection under different operating conditions, examine the influence of the impurities in the industrial nickel sulphate provided by Anglo Platinum LTD, test specifically for the influence of sodium and test the stability of the membrane.

3.5.1. Influence of process parameters on membrane performance

The controllable operating conditions for the experimental set-up included pH, pressure, temperature, and Ni concentration.

Table 3.1: Parameters for data matrix

Operating Matrix		Pressure (bar)			
		20	30	40	50
Concentration (Ni g/L)	30	pH: 1,2	pH: 1,2	pH: 1,2	pH: 1,2
	40	pH: 1,2	pH: 1,2	pH: 1,2	pH: 1,2
	50		pH: 1,2	pH: 1,2	pH: 1,2

The focus was on the filtration of high concentration nickel solution at low pH to replicate the industrial operating conditions. The effluent of the Ni electrowinning has a concentration in the order of 40g/L Ni. 10 g/L below and above this value was chosen to compensate for any fluctuations that might occur in such an operation. The pH in the electrowinning unit varies between 1 and 2 and these limits have been studied for this reason.

Different pressure difference values were chosen to establish the effect on rejection and flux of the membrane. The pressures were chosen in such a way as to have a sufficient flux, which is mainly determined by the concentration (osmotic pressure) of the solution and by the maximum capacity of the pump.

The different experiments are summarised in Table 3.1

3.5.2. Impurity influence

A stock solution with a nickel concentration of 40 g/L at pH 2 was prepared with the laboratory grade nickel sulphate hexahydrate. Experiments were conducted in the cross-flow membrane set-up at 20, 25, 30, 35 and 40 bar at 20°C, the same operating conditions that were used for the industrial nickel sulphate provided by Anglo Platinum LTD. This made it possible to compare the results of the rejection and flux of both the laboratory grade and industrial nickel sulphate to examine the influence of the impurities.

3.5.3. Sodium influence

There are high concentrations of sodium in the spent electrolyte. The influence of sodium was monitored by preparing a solution of 100 g/L sodium sulphate (Na_2SO_4) and 40 g/L Ni solution. Any difference in Ni and H^+ rejections where monitored as well as changes in the flux due to the presence of Na^+ ions in solution.

3.5.4. Long run

Lastly a long run experiment was done over a period of five days to get a clearer view of the fouling effect of the impurities on the membrane efficiency. A solution of industrial nickel sulphate with a concentration of 40 g/L at pH 2 was used in this experiment. Both permeate and retentate were recycled back to the reservoir with samples taken every 24 hours. Again the Ni and H^+ rejections and the flux were checked for any changes cased by fouling over a longer time period.

3.6 Steady-state and reproducibility:

Since the experimental apparatus was designed and constructed in-house, it was found to be necessary to test the reproducibility of the set-up, and find an indication of the time needed to reach steady state conditions.

For this reason, three independent experiments were carried out with a nickel concentration of 30 g/L, a pH of 1 and a trans-membrane pressure difference of 20 bar. The results are summarised in Figure 3.5.

From Figure 3.5, it can be seen that steady-state conditions are reached after approximately 55 minutes, where both rejection and flux remain constant in time.

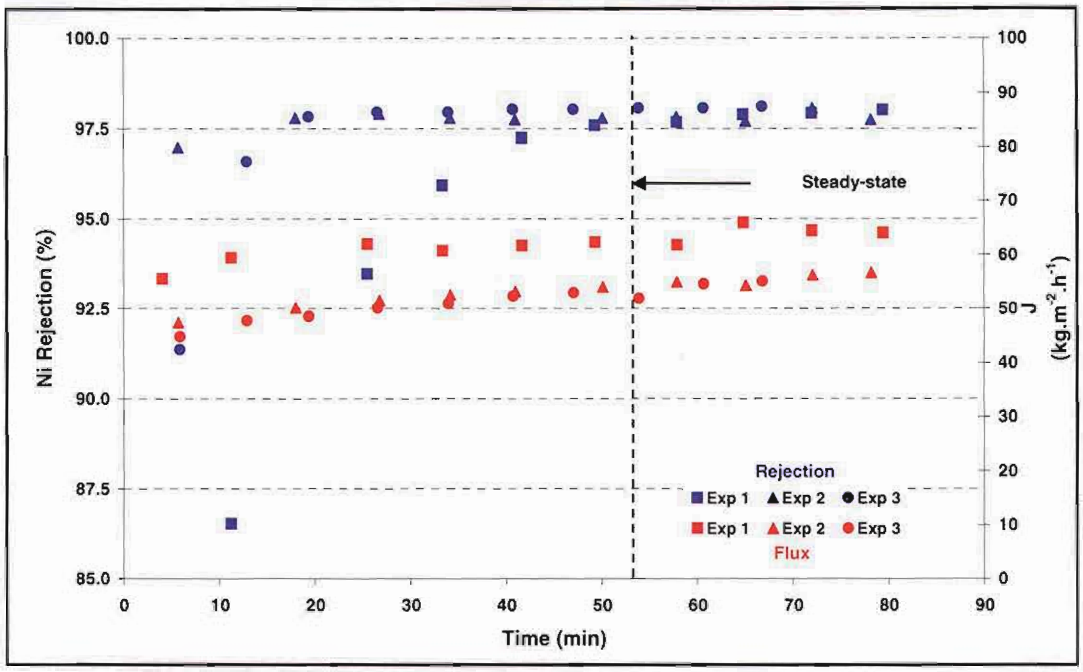


Figure 3.5: Steady-state and reproducibility data

The reproducibility was tested by calculating the standard deviation of the experiments and the 95% confidentiality interval was used as characteristic for the experimental error. Ten samples were taken in time and the results are summarised in Table 3.2.

Table 3.2: Statistical analysis of reproducibility data of experiment 1, 2 and 3

Sample	J (kg.m^{-2}.h^{-1})	R (%)	Standard deviation J	Standard deviation R	% error J	% error R
1	49.2	89.6	5.6	8.4	11.4	9.4
2	52.4	93.6	6.2	6.2	11.8	6.6
3	54.0	96.4	7.1	2.5	13.1	2.6
4	54.4	97.2	5.6	1.1	10.2	1.2
5	55.3	97.6	5.7	0.4	10.4	0.4
6	56.2	97.8	5.4	0.2	9.6	0.2
7	56.5	97.8	4.7	0.2	8.3	0.2
8	57.3	97.9	7.5	0.2	13.1	0.2
9	58.4	98.0	5.3	0.1	9.1	0.1
10	58.6	97.9	4.8	0.2	8.1	0.2

The error for the rejection in the first points is relatively large since steady-state conditions were not yet reached. At steady state conditions, however, the rejections convert to a steady value with a very small error margin. From this initial experiment it could be concluded that the time to reach steady state is approximately an hour, and all the results presented in Chapter 4 are taken after this period. The experimental error for the rejection and flux was respectively estimated at <0.2% and <10%.

Chapter 4

4. Results and Discussion

4.1 Introduction

The following results were obtained from the concluded experiments as described in Chapter 3. Firstly the membrane was characterised with SEM and clean water experiments. The Ni and H^+ rejection data concerning variations in pH and concentration are given and discussed and compared to related studies. The influence of the different operating conditions on the fluid flux is also given and discussed. The influence of temperature on the fluid flux and nickel rejection characteristics of the membrane is given. This is followed by the results of the influence of impurities and sodium on the efficiency of the membrane. The results of the long run are given and discussed, which is followed by the effect of membrane fouling that occurred during the experimentation. Lastly the acid stability of the DOW NF membrane used in the study is commended on.

4.2 Membrane characterisation

The pure water permeability coefficient (L_P) is by far the most basic method for membrane characterisation (Schafer, 2005). It is determined by measuring the pure water flux through a membrane at different pressures, and the result is given in Figure 4.1. The slope of the trend line fitted through the pressure-flux data points gives the pure water permeability coefficient, and was found to be $L_P = 9.1\ L.m^{-2}.h^{-1}.bar^{-1}$. This value, compared to values reported in Schafer *et al*, $1.0 - 6.6\ L.m^{-2}.h^{-1}.bar^{-1}$ for 20 commercial membranes, does indicate that the DOW FilmTec NF membrane is a more open structured NF membrane than the others. The lower values are merely obtained from spiral wound modules and not in a flat-sheet module, since also significant pressure losses can occur in spiral wound modules, other than the trans-membrane pressure drop (*e.g.* spacers).

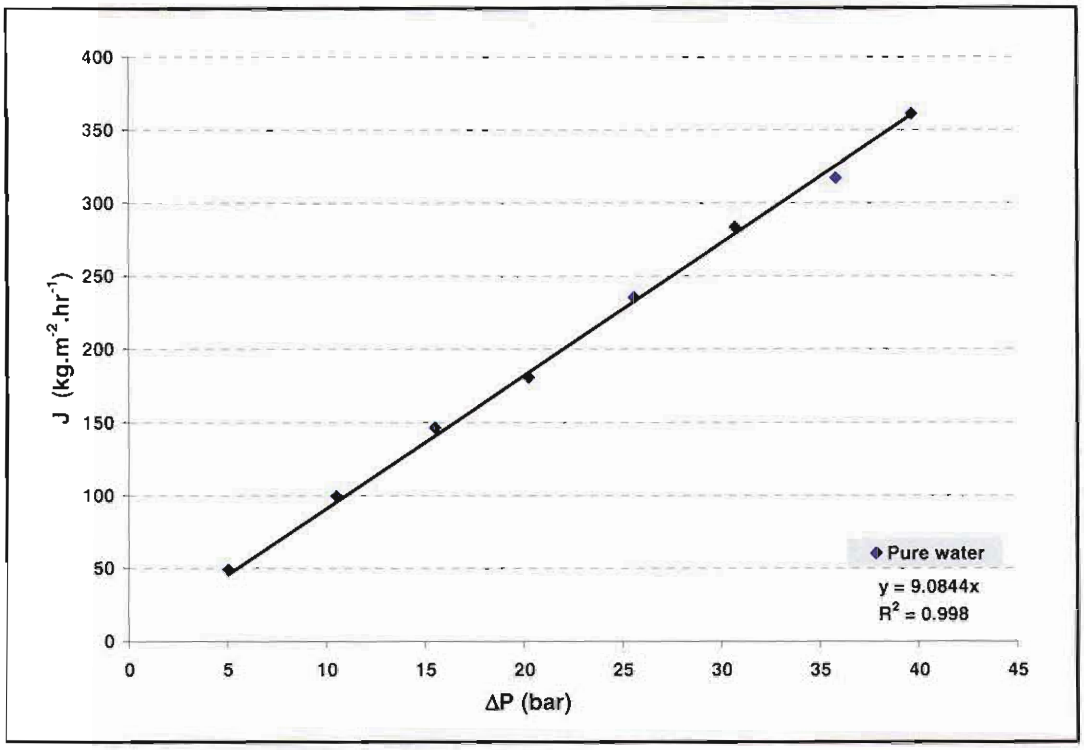


Figure 4.1: Pure water permeability

Figure 4.2 shows a cross-section SEM photograph of a DOW FilmTec NF membrane. From this figure, it can be seen that the membrane consists of three layers and that the average thickness of the active membrane is in the order of 1.0 μm.

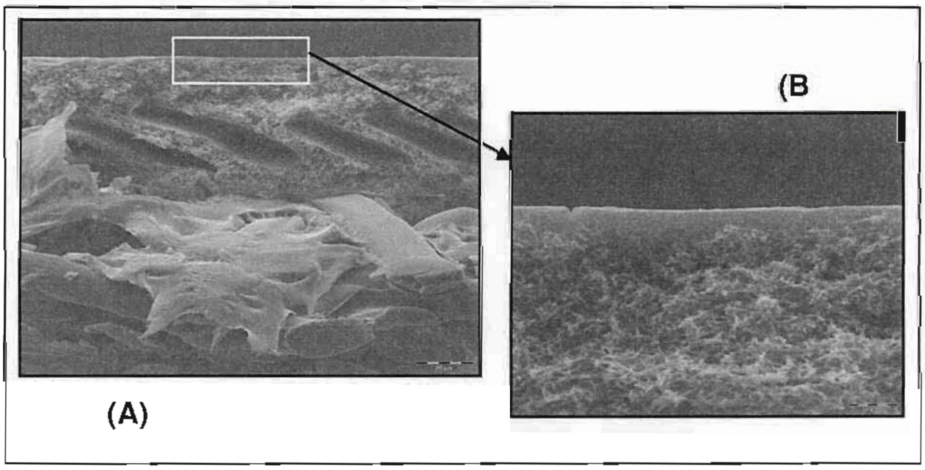


Figure 4.2: (A) A cross-section SEM photograph of DOW FilmTec NF membrane. (B) Close-up of the active membrane layer

4.3 Ni rejection

Figure 4.3 gives the different rejection values for pH 1 and 2 at 30, 40 and 50 g/L Ni concentrations over the pressure range of 20 to 55 bar. Each data point represents the average of three samples taken at each operating condition. At pH 1 there are two clear trends: the rejection decreases with increasing concentration; and the rejection increase with increasing applied pressure, this is in accordance to the results of Nyström & Tanninen (2002) discussed in Section 2.4.

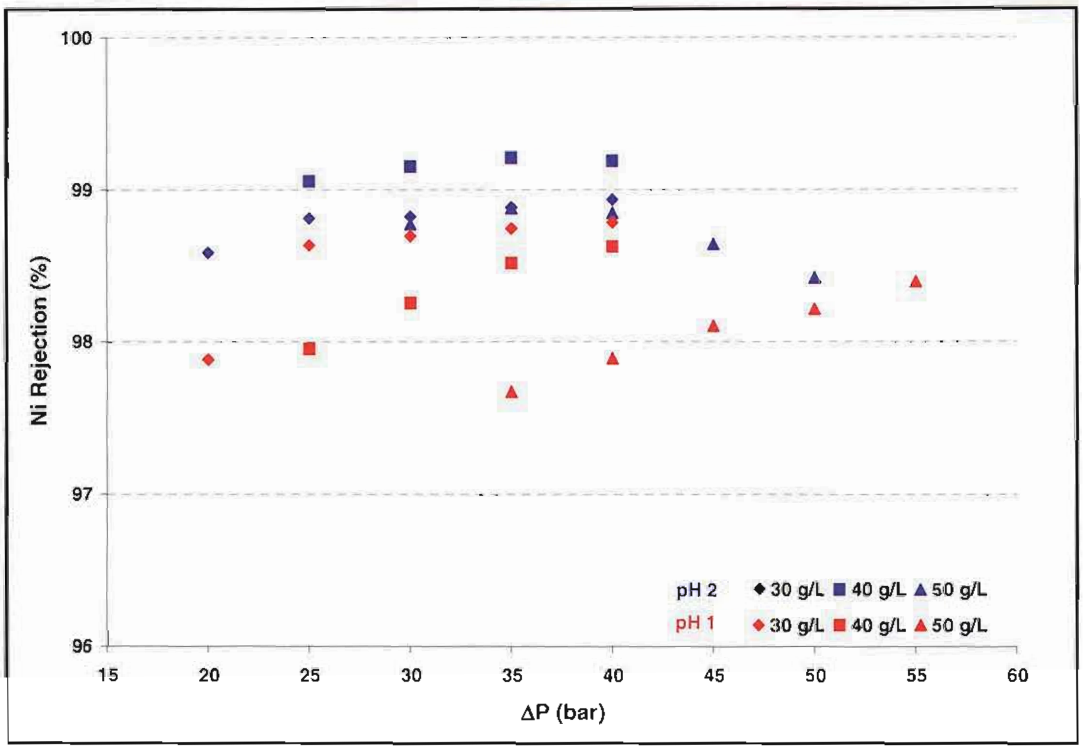


Figure 4.3: Rejections versus trans-membrane pressure for different pH and Ni concentrations

This is not exactly the case for pH 2. Overall, the rejection is higher for pH 2, but the rejection for 40 g/L concentration is higher than that of 30 g/L. Another interesting occurrence is the decrease of rejection with increasing applied pressure for 50g/L. During the experimentation serious fouling was observed for pH 2. This can be the main cause for this erratic behaviour. More is said in Section 4.10 on the subject of fouling and the influence thereof on the efficiency of the membrane.

4.4 H^+ rejection

The pH of both the feed and permeate samples was measured and used to calculate the concentrations of the hydronium ion. The rejection of H^+ was calculated in the same way as the rejection of Ni. The rejection values for the experiments conducted at pH 1 and pH 2 over a range of different concentrations of Ni and pressure differences are compared in Table 4.1.

Table 4.1: Hydronium rejection values

	pH 1		pH 2	
[Ni] (g/L)	ΔP (bar)	R_{H+} (%)	ΔP (bar)	R_{H+} (%)
30	20	-15	20	-83
30	25	-15	25	-83
30	30	-20	30	-82
30	35	-10	35	-77
30	40	-8	40	-83
40	25	-21	25	-104
40	30	-17	30	-91
40	35	-12	35	-92
40	40	-36	40	-79
50	35	-16	30	-62
50	40	-34	35	-68
50	45	-11	40	-66
50	50	-6	45	-66
50	55	-14	50	-71

The negative rejection values indicates that the hydronium concentration is higher in the permeate than in the feed. Nyström & Tanninen (2002) reported similar results. This shows that excellent acid permeation is obtained. Although there is little to say about a trend in the rejection at different operating conditions, there is a clear difference in the rejection between pH 1 and pH 2. Form Table 4.1 it can be seen that there is a higher negative rejection at pH 2 than for pH 1. This is an indication of more severe interaction between the solution and the membrane at a pH of 2. This also strengthens the theory that below pH 2 the charge characteristics become less important than the sieving characteristics.

4.5 Flux

The second measured parameter in the experiments was the mass of the permeate samples. This was converted to flux, see Appendix A for sample calculations, and the comparative values for pH 1 and 2 are presented in Figure 4.4.

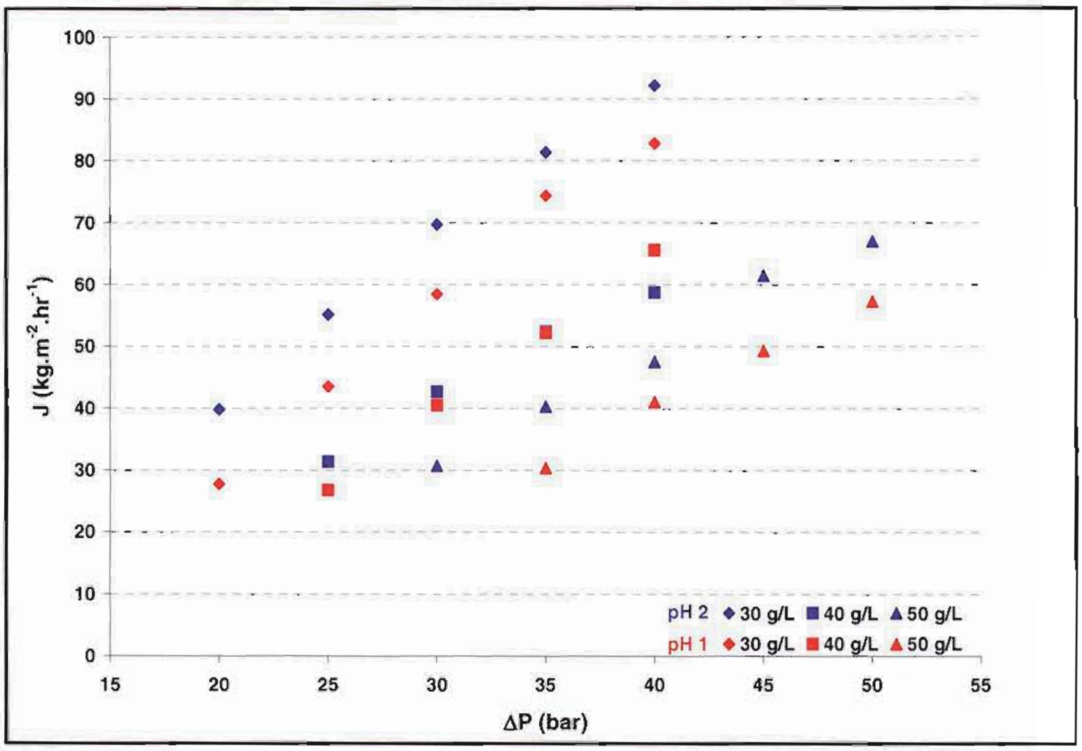


Figure 4.4: Flux versus trans-membrane pressure difference for different pH and Ni concentrations

Again higher values were obtained for pH 2, with the exception of the 40 g/L Ni solution, where very similar values are observed. There is also a clear decrease in flux with an increase in concentration. This is due to the increase in osmotic pressure along with the increase in concentration, which results in an overall decrease in the effective applied pressure.

Comparing these values with that of pure water, another phenomenon is observed. Note in Figure 4.5 how the slope of the lines fitted through the data points at each of the concentrations decreases with increasing concentration.

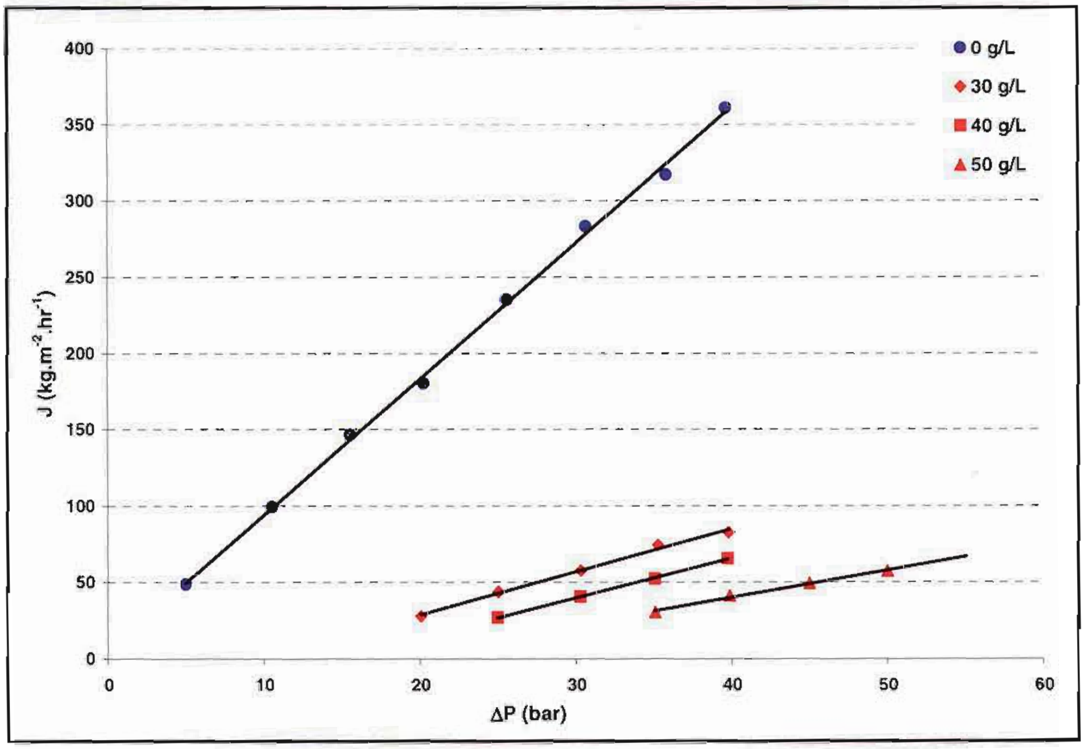


Figure 4.5: Flux versus trans-membrane pressure for pure water and Ni concentrations of 30, 40 and 50 g/L at pH 1

This is further illustrated in Figure 4.6 and indicates that the permeability of the membrane is not constant, but decreases with increasing solute concentration. The decreasing permeability can be attributed to the increased viscosity of the solution, which is that of water in the pure water experiments, and a sulphuric acid solution (with small amounts of nickel sulphate) in the case of the nickel experiments. A study on the permeation of sulphuric acid through different NF membranes (Fitchat, 2006) has shown that the permeability of sulphuric acid (pH 1) is about 50% of that of water. The additional decrease can possibly be attributed to the nickel sulphate, which is also permeating.

If the flux data is extrapolated to the x-axis to find the osmotic pressure, an interesting observation regarding osmotic pressure is made. From the graph in

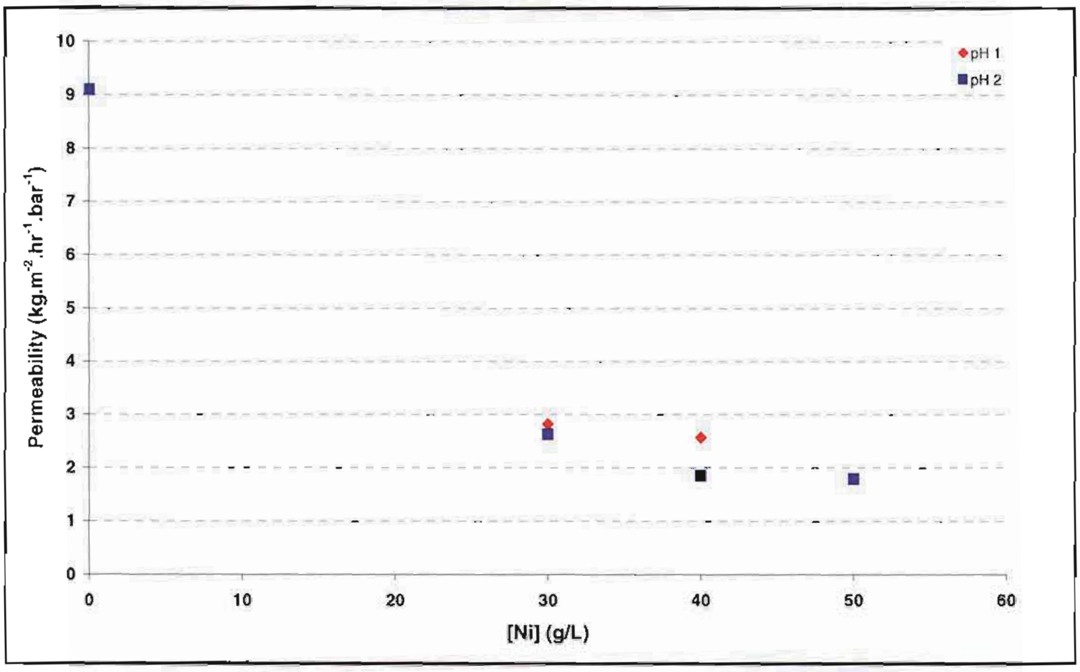


Figure 4.6: Permeability for pH 1 and 2 at 0, 30, 40 and 50 g/L Ni concentration

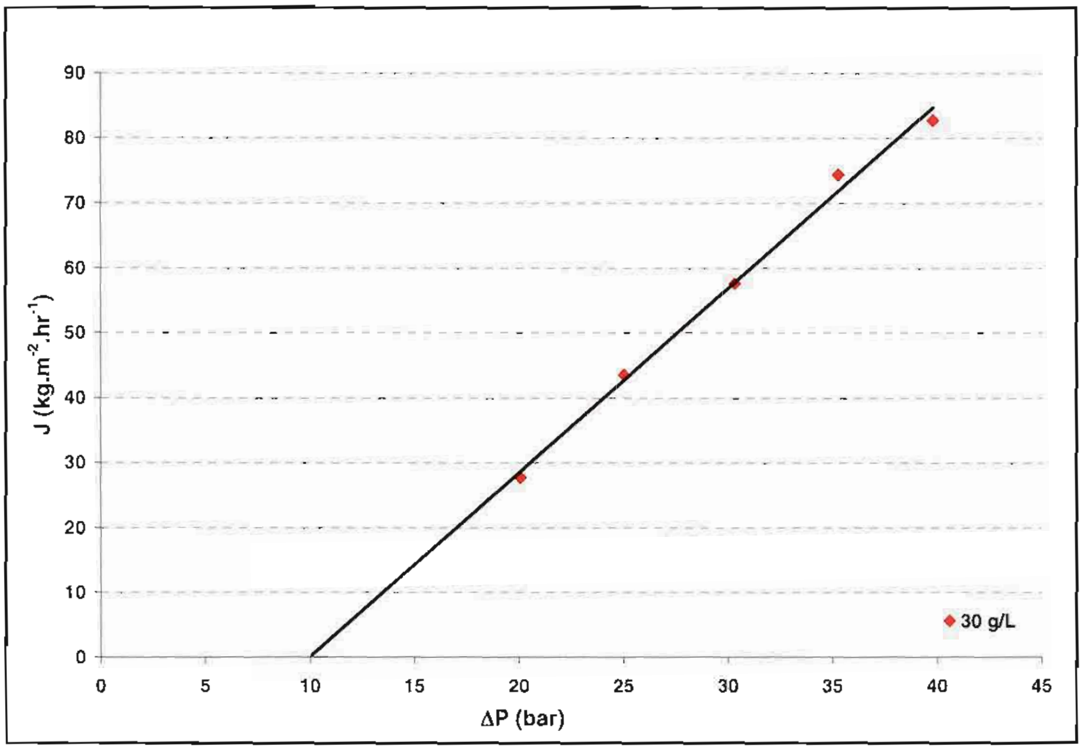


Figure 4.7: Empirical determination of osmotic pressure for a [Ni] = 30 g/L at pH 1

Figure 4.7 the extrapolation indicates that the osmotic pressure ($\Delta\pi$) is 9.7 bar, which is much smaller than the theoretical value of 25 bar, which is obtained by using Eq. 2.3 with the assumption of complete dissociation of nickel sulphate. The empirical determined osmotic pressures for the various solutions are given in Figure 4.8. This finding confirms the importance of the speciation, and correlates well with the finding of large quantities of $NiSO_{4\,(aq)}$, (see section 2.3.3).

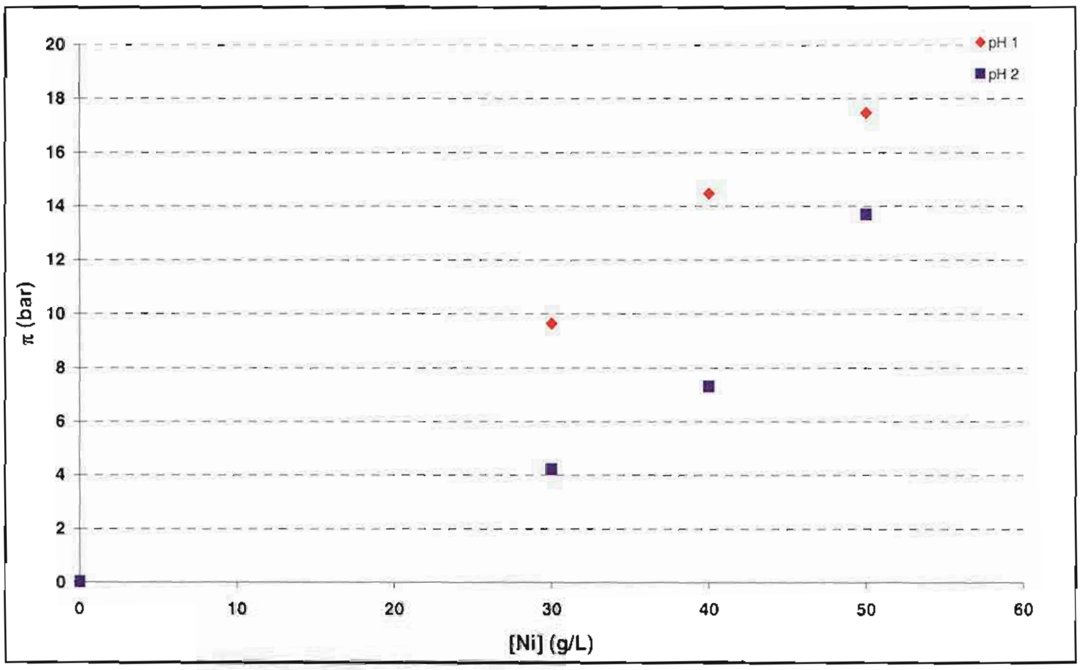


Figure 4.8 Osmotic pressures for pH 1 and 2 at 0, 30, 40 and 50 g/L Ni concentrations

4.6 Influence of temperature

Samples were taken from the same solution at different temperatures to examine what influence temperature has on Ni rejection and flux. The solution had a concentration of 30 g/L Ni and the experiment was done at 40 bar. Ni rejection and flux is shown as a function of temperature in Figure 4.9. There is a linear trend between temperature and flux, with an increase of approximately 2.5 $kg.m^{-2}.hr^{-1}$ for every increase of 1 °C in the solution temperature. This can be largely ascribed to a decrease in viscosity as the temperature rise. The flux at 40 °C is about 70% larger than that at 20 °C, while the viscosity decreases with about 55% (Perry). The increased temperature may also have an effect on the free volume of the membrane, as given by Freger *et al.* (2005), where it was explained how pH can have an influence on the free volume of a NF membrane that causes in increase in flux. Similarly higher temperatures may also cause a more open membrane and therefore a larger flux.

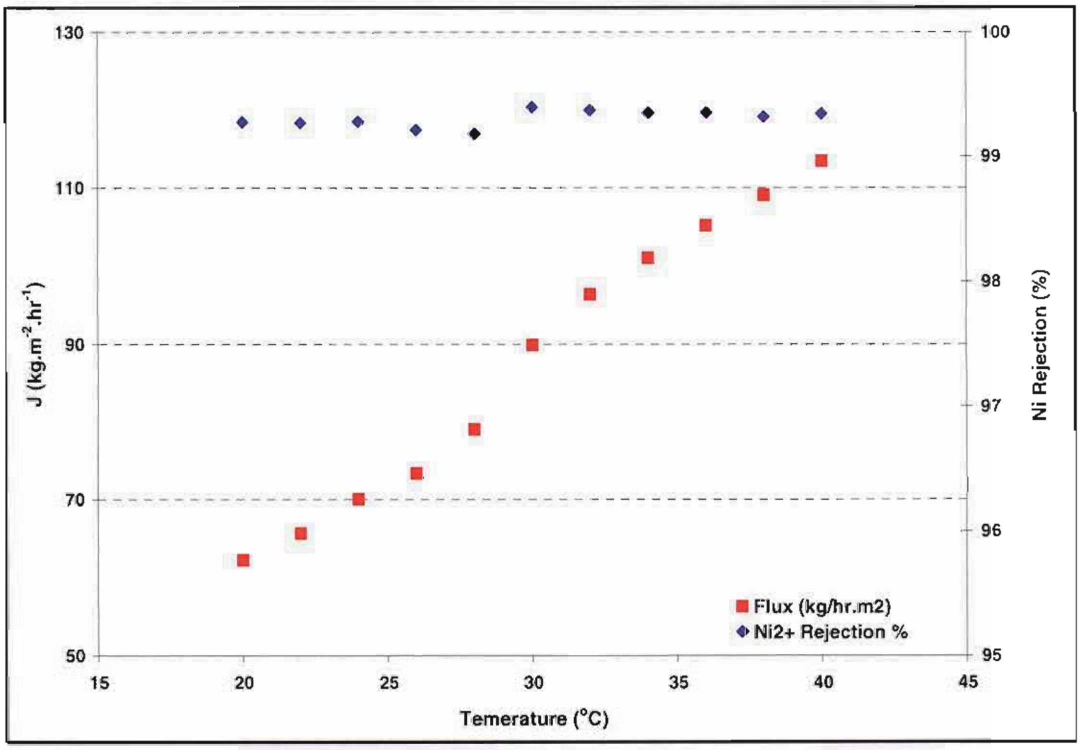


Figure 4.9: The influence of temperature on flux and rejection of [Ni] = 30 g/L, pH = 2 and ΔP = 40 bar

The rejection, on the other had is not influenced by the increasing temperature at all. An increase in the free volume of the membrane will relate to a decrease in retention, as this is not the case it can be said that a decrease in viscosity is the main contributor to the increasing flux.

4.7 Influence of sodium

In Table 4.2 a comparison is made between data collected with experiments done with the sodium-nickel solution to that with data collected from a nickel solution at similar operating conditions (pH 2, 20°C). The biggest influence of the sodium is on the flux of the membrane, which is largely reduced. This can be attributed to the increased osmotic pressure due to the additional sodium ions in the solution.

Table 4.2: Comparison of a nickel-sodium solution to a nickel only solution

	Composition		Compared Parameters			
Sample	[Ni] (g/L)	[Na] (g/L)	Flux ($kg.m^{-2}.h^{-1}$)	R_{Ni} (%)	R_{Na} (%)	R_H (%)
1	40	-	87.5	99	-	-54
2	40	37	9.3	98	> 60	28

The reduction in flux, after the addition of sodium ions, can have a large impact on the application of NF in the separation of nickel from sulphuric acid, since sodium is present in the electro-winning stream for an improved efficiency of this process. The large Na^+ retention also indicates that the next to the charge of the ion, the size of the ion also plays an important role.

4.8 Influence of impurities

A comparative study was made to establish what influence the impurities in the industrial $NiSO_4$ have on the efficiency of the membrane. The results of this study are given in Figure 4.10 and 4.11 where the Ni and H^+ rejection as well as the flux are compared. It is observed that the nickel retention and also the negative rejection of H^+ are larger for the industrial sample. Due to the complex composition of the industrial sample, a simple reason for this behaviour could not be found here, and falls outside the scope of this dissertation.

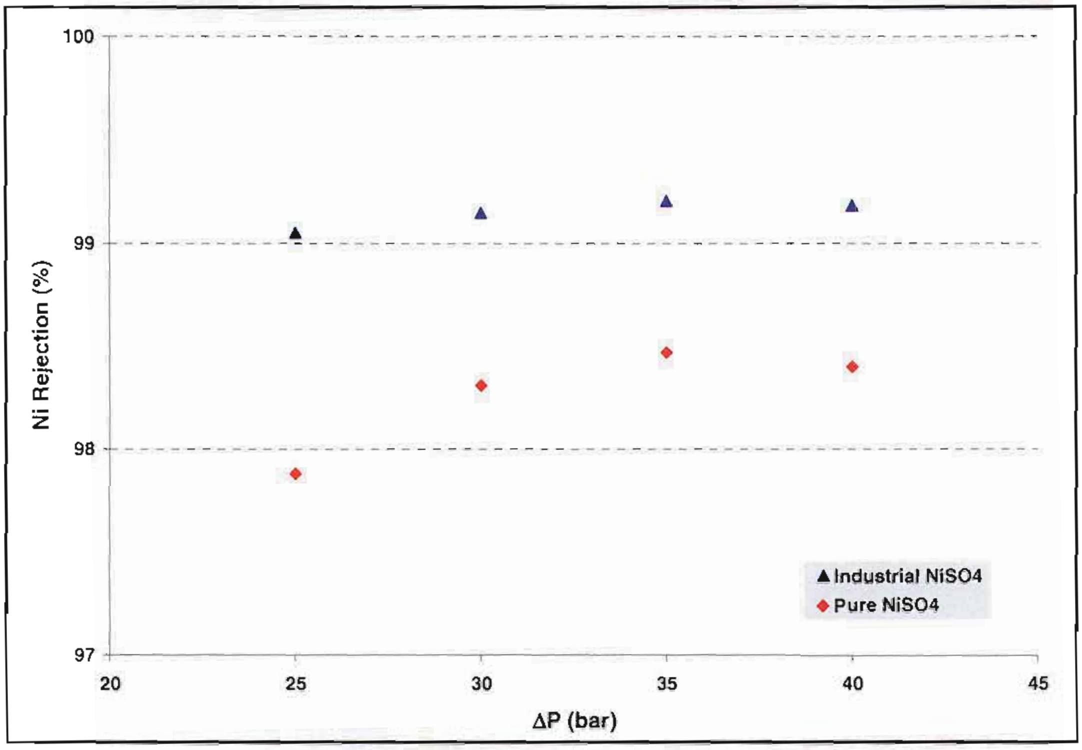


Figure 4.10: Nickel rejection versus trans-membrane pressure; laboratory grade and industrial nickel sulphate

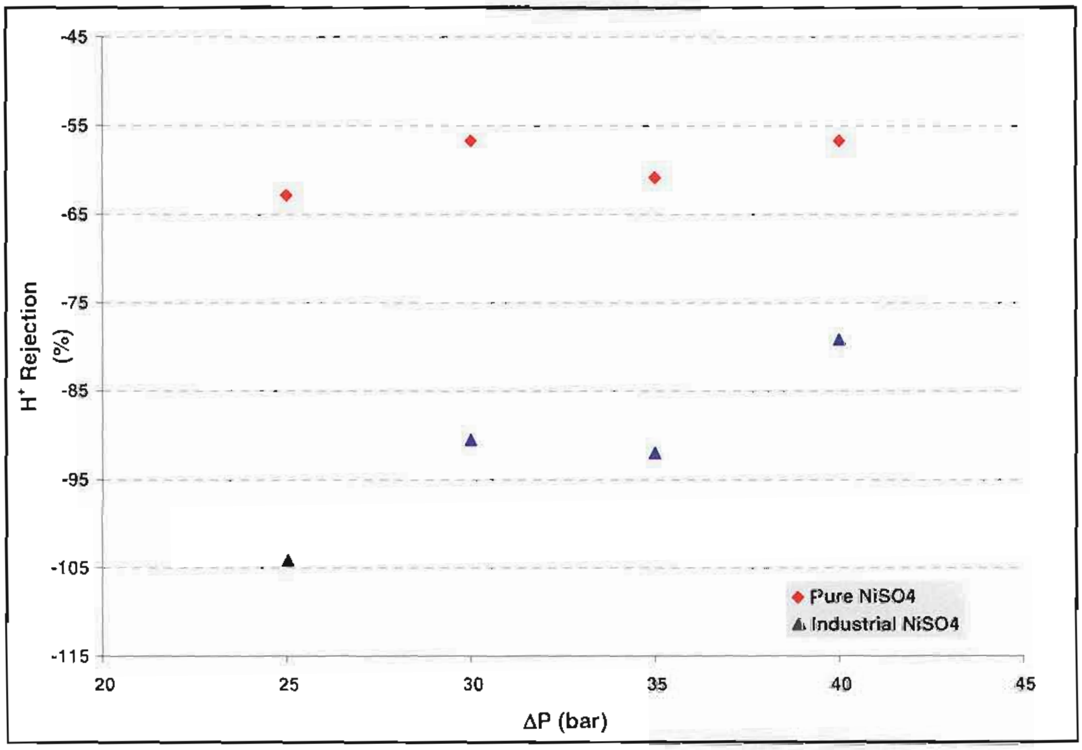


Figure 4.11: Hydronium rejection versus trans-membrane pressure; laboratory grade and industrial nickel sulphate

However, possible explanations include a more complete dissociation in the pure $NiSO_4$ solution and the possible formation of other nickel complexes for the industrial solution. These complexes are normally relative large molecules and this will facilitate the rejection of nickel. A deeper insight in the speciation is recommended here.

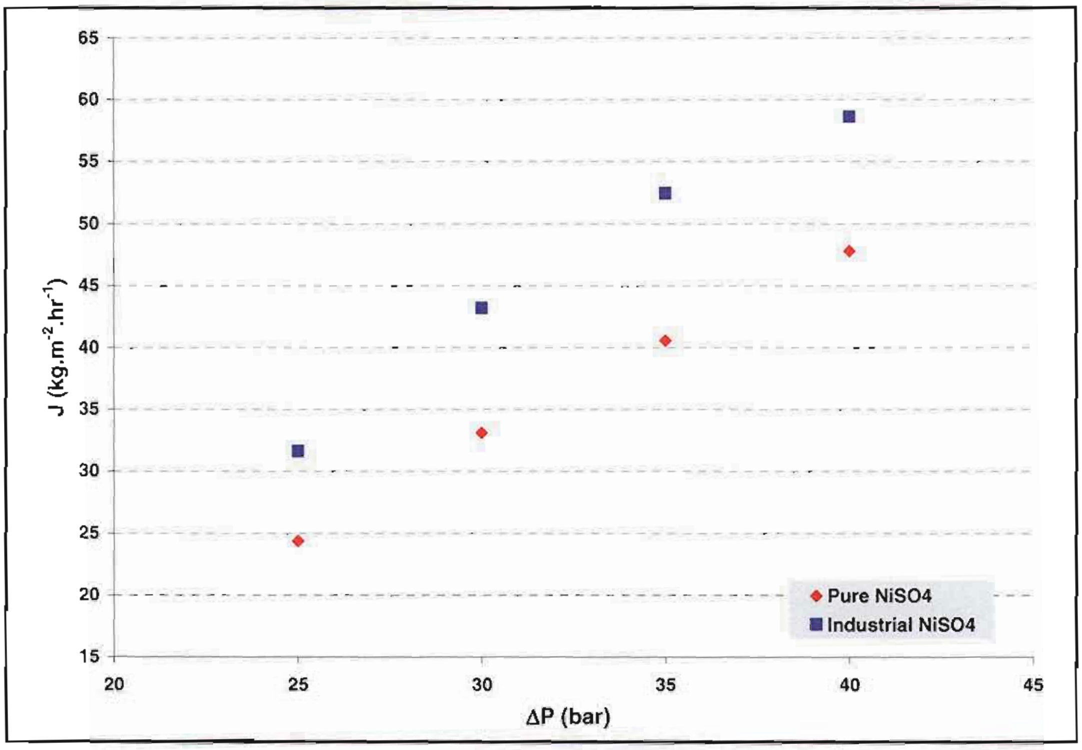


Figure 4.12: Flux versus trans-membrane pressure; laboratory grade and industrial nickel sulphate

The fact that the industrial solution has an improved flux, compared to the synthetic nickel sulphate is unexpected (Figure 4.12). The additional ions, in the industrial solution, were thought to an increased osmotic pressure and hence a decreased flux. A possible reason for the increased flux is, again, the speciation of the industrial sample.

4.9 Long run

A long run was done to observe the membrane's efficiency with prolonged exposure to the extreme industrial conditions. The set-up ran continuously for five days recycling both permeate and retentate to the reservoir. Samples of permeate and feed were taken approximately every 24 hours. There is a reduction in flux of 15% from the day one to day six (Figure 4.13). The largest reduction occurs during the first twenty-four hours, which could possibly be induced by scaling. The flux reduction reduces after one day, which is possibly connected with the fouling of the membrane. Although the reduction in flux was significant, the nickel rejection remained constant at 99 (±0.25)%.

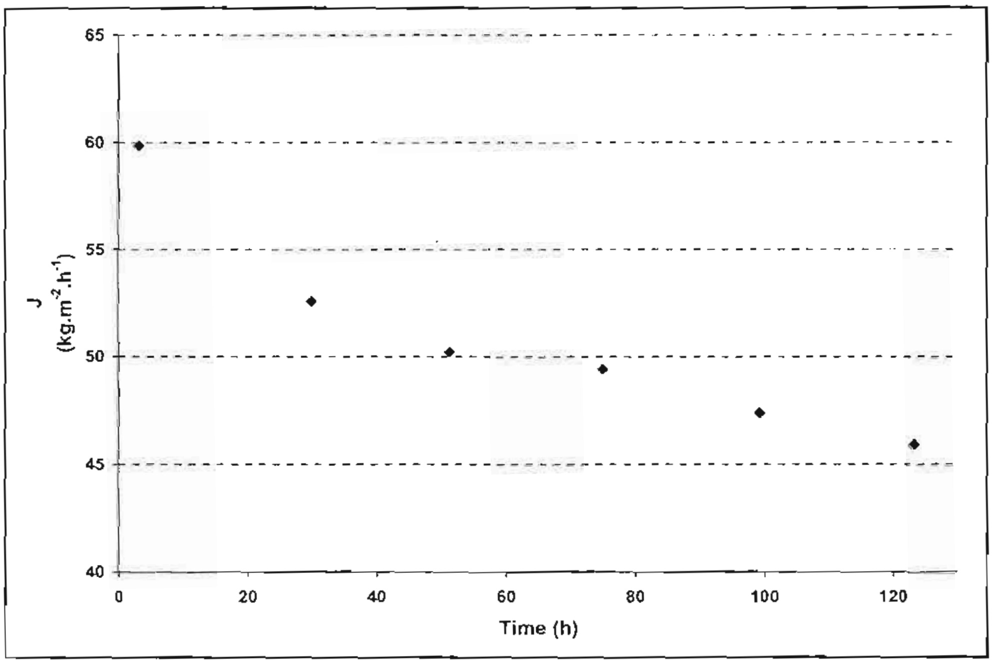
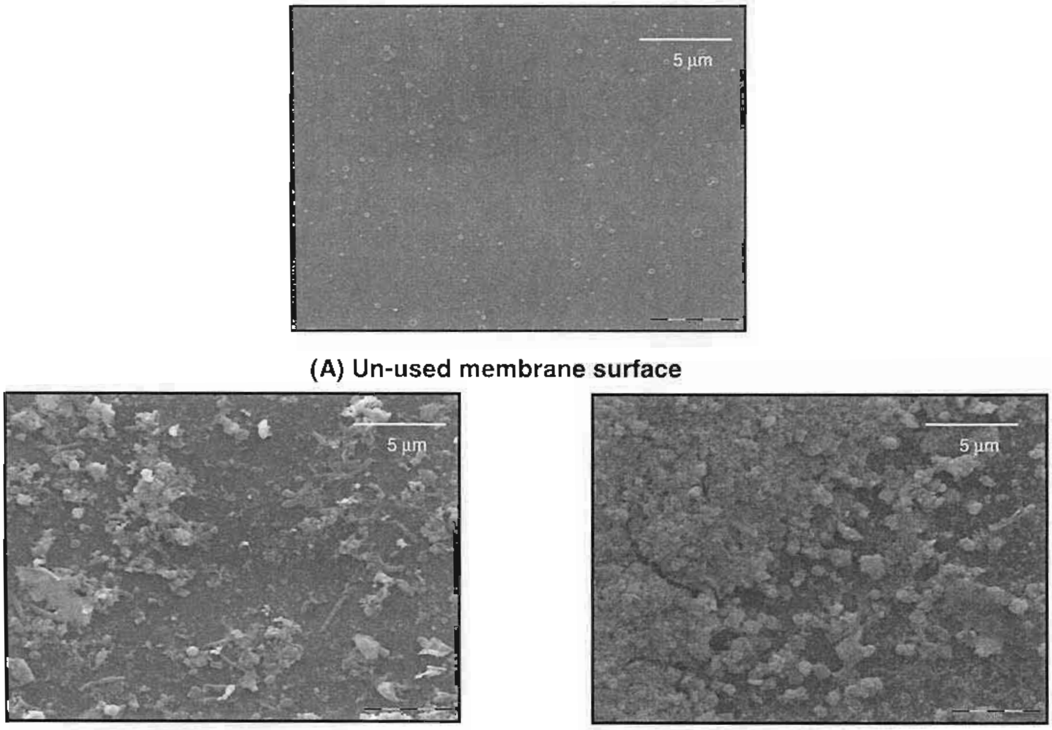


Figure 4.13: Reduction of flux over a 6 day period

4.10 Fouling

A list of impurities in the industrial nickel sulphate provided by Anglo Platinum LTD is presented in Appendix D. The suspended impurities were removed by means of filtration and re-crystallisation as described in Section 3.3. But the remaining dissolvable impurities of which the most cumbersome is the iron(III)oxide (Fe_2O_3) could not be removed with this method. At pH 2 the Fe_2O_3 precipitates from the solution and caused fouling that notably reduces the flux. The photographs (Figure 4.14) were taken at the same magnification, and it is apparent that the fouling density is larger on the membrane used for the pH 2 experiments (Figure 4.14(C)). This is clearly a case of membrane surface fouling (Figure 2.4(B))



(A) Un-used membrane surface

(B) Membrane surface, pH 1, [Ni] = 30 g/L

(C) Membrane surface, pH 2 [Ni] = 30 g/L

Figure 4.14: SEM photograph's of membrane surfaces exposed to various solutions (B, C) compared to an un-used membrane (A)

The fouling during the long run was more severe than the other shorter experiments. The cake formed by the scaling can clearly be seen in Figure 4.15. A CDU analysis on the fouling agent was done and the elements present are given in mass percentage in Figure 4.16. The nickel is probably what remained when the membrane was dried before the scan. A lot of iron(III)oxide and chrome(III)oxide are present.

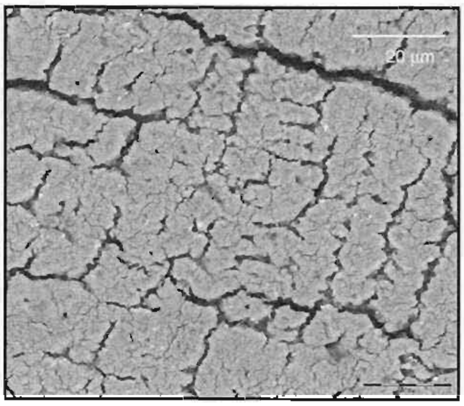


Figure 4.15: A SEM photograph of fouling cake on membrane surface

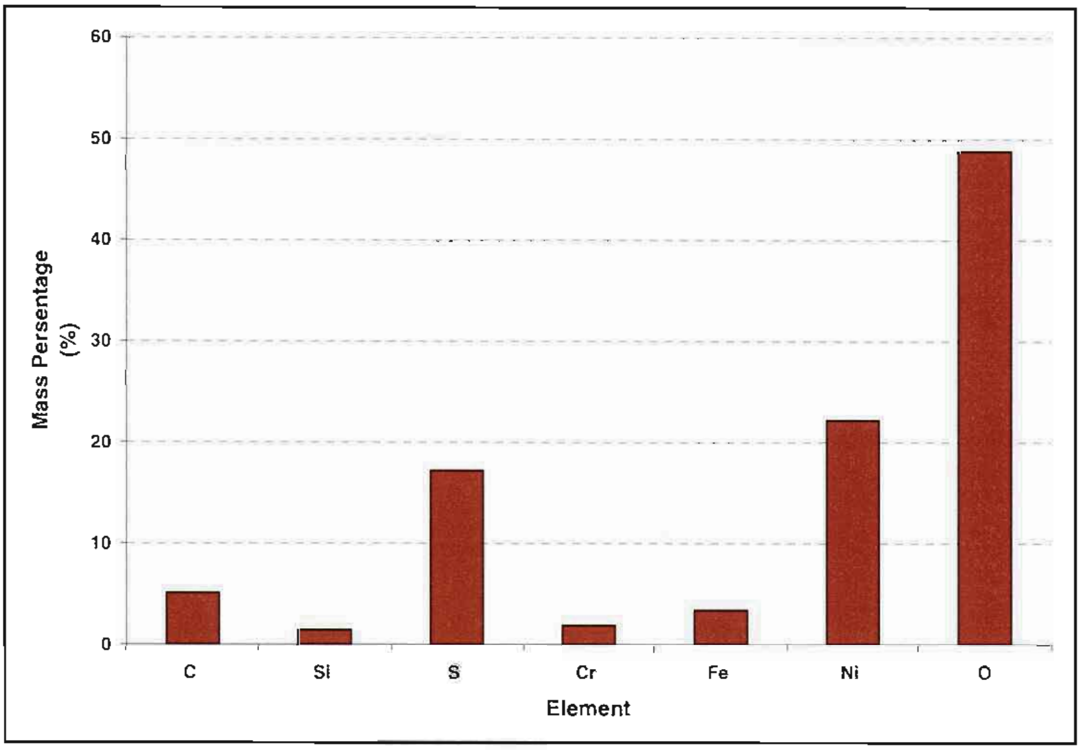


Figure 4.16: Composition of fouling cake

No real comment can be made if the fouling is reversible or not because limitations on the set-up prevented back-flush operation.

4.11 Acid resistance

For the duration of the experiments the membranes showed none of the visible signs (see Section 2.3.2) of chemical attack that an acidic solution might have on composite polymeric nanofiltration membranes. The discoloration that was observed was caused by yellowish brown Fe_2O_3 scaling. No sudden increase of fluid flux or decrease in rejection occurred that are telltale signs of membrane failing under chemical attack.

Chapter 5

5. Conclusions, prospects and recommendations

5.1. Conclusions

With the use of industrial nickel sulphate the DOW NF membrane gave excellent rejection (> 97.5%) at all the operating conditions ([Ni] = 30, 40 and 50 g/L, pH 1 – 2, ΔP = 20, 30, 40 and 50 bar), reaching > 99% for [Ni] = 40 g/L at a pH of 2. The rejection is a function of feed concentration, pH and pressure and follows the following general trend:

The rejection:

- decreases with increasing nickel concentration in the feed;
- decreases with increasing pH;
- increases with increasing trans-membrane pressure, but
- was not influenced by temperature.

An acceptable fluid flux was achieved at the all the applied trans-membrane pressure differences. The flux seemed to follow a similar trend as the rejection except that it was sensitive for change temperature. An increase in the flux was found to be approximately 2.5 $kg.m^{-2}.hr^{-1}$ for every increase of 1°C in the feed temperature.

The empirically determined osmotic pressures are less than half the theoretically determined osmotic pressures, indicating the incomplete dissociation of $NiSO_4$.

The NF membrane allows very good hydronium permeation and the interaction between the nickel and the positively charged membrane causes a push out effect and enhances the H^+ migration through the membrane. This relates to higher H^+ concentrations in the permeate than what was originally in the feed. The push out effect is more prominent for pH 2 indicating larger solution-membrane interactions.

Due to the increase of osmotic pressure caused by sodium the fluid flux decreases to such an extent that the process becomes impractical at high Na concentrations. It has a lesser influence on the rejection of the Ni and reduces the push out effect on H^+.

The impurities in the industrial nickel sulphate in some way facilitates the fluid flux and nickel rejection as both these parameters are higher for the industrial nickel sulphate compared to laboratory grade nickel sulphate solution at the same operating conditions. Lack in knowledge of the speciation of nickel in these conditions makes it impossible to fully understand this observation yet.

Fouling caused by scaling (precipitation of Fe_2O_3) was more evident at pH 2 and resulted in reduced fluid flux, especially during the long run. The fouling however did not show any effect on the retention characteristics of the membrane.

5.2. Prospects

The fact that it was possible to obtain high nickel rejection at high concentrations makes the use of NF membranes as an alternative to the current process very attractive. The principle for the separation of nickel from its acidic sulphate solution predicts that it might also hold promise for other metal recovery processes.

5.3. Recommendations

Although the focus in this study was the separation of nickel, it is evident that in the complexity of the system the impurities, especially sodium, play an important role. Some question needs to be asked and answered: To what extent does the membrane reject the impurities in the solution? What influence do the impurities have on the dissociation of nickel sulphate and the osmotic pressure of the solution? What role do the impurities play in the speciation of nickel if any occur?

It is further recommended to use actual nickel electrowinning effluent during the experimentation with an on-site pilot plant, with a scale of approximately 1000L/hr, using spiral wound membrane modules. Proposed analytical methods to determine the concentrations of the nickel and the impurities in the feed and permeate include ICP and electrophoresis. Both these methods could go a long way in answering the questions stated above.

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Appendix A – Sample Calculations

Crystal water

The assumption was made that the industrial $NiSO_4.xH_2O$ only consisted of nickel sulfate hexahydrate (x = 6). A precise solution of 35.83 g industrial $NiSO_4.xH_2O$ was prepared in a 250 mL volumetric flask. The absorbance of solution measured as 2.8 with UV/Vis spectrometry, which related to a concentration of 33.87 g/L Ni (Section 3.4.4). The total mass $NiSO_4$ was calculated as 89.31 g/L and subtracted from the total initial mass of 143.32 g/L giving the mass of H_2O as 54 g/L. The factor x was then calculated:

$$x = \frac{m_{H_2O}}{M_{H_2O}}$$

$$x = 3$$

With: m_{H2O} = Mass of water

M_{H2O} = Molar mass water

But this is only for 0.58 mol used initially. Thus for 1 mol $NiSO_4.xH_2O$:

$$x = 3 \times \frac{1}{0.58}$$

$$x = 5.2$$

Membrane area

The membrane area needs to be calculated to be able to do flux calculations. The membrane area is calculated from the inner diameter of the of the membrane module.

$$A_{mem} = \frac{\pi D_{in}^2}{4}$$

$$D_{in} = 59.3 \times 10^{-3} m$$

$$A_{mem} = 2.76 \times 10^{-3} m^2$$

Ni rejection

Before the Ni rejection can be calculated it is first necessary to calculate the Ni concentrations in the permeate sample as well as the feed sample and retentate sample. This is done with the process explained in Section 3.4.4.

For sample 5 of run 18 the absorbance was measured as 0.066, with the absorbance of the feed and retentate samples being respectively 0.827 and 0.821. By applying Equation 3.2 for sample 5 the concentration is calculated as:

$$\begin{aligned}[\mathrm{Ni}] &= 12.102 \text{ x Absorbance} \\ &= 12.102 \times 0.066 \\ &= 0.8\mathrm{g/L}\end{aligned}$$

The feed and retentate samples were diluted with a factor 5 and by taking this into account their concentrations are calculated as:

$$\begin{aligned}C_f &= 50.04\mathrm{g/L} \\ C_R &= 49.68\mathrm{g/L}\end{aligned}$$

The average of these two values, C_f = 49.86, is taken as the feed concentration for the rejection calculations. By applying Equation 2.1 the Ni rejection for sample 5 is calculated as:

$$\begin{aligned}R &= \left(1-\frac{C_p}{C_f}\right)\times 100\% \\ &= \left(1-\frac{0.8}{49.86}\right)\times 100\% \\ &= 98.4\%\end{aligned}$$

Flux

As explained in Section 3.4.4 the flux is calculated by dividing the slope of the fitted curve through a plot of mass versus time by the membrane area. For sample 5 of run 18 the slope is calculated as 0.1424 kg/hr (see Figure 3.4). Thus to calculate the flux Equation 3.5 is applied:

$$J = \frac{slope}{A_{mem}}$$

$$J = \frac{0.1424}{2.76 \times 10^{-3}}$$

$$J = 51.59 \frac{kg}{m^2.hr}$$

Appendix B – Membrane Specification Sheet

Product Information

FILMTEC Membranes

Desalting Nanofiltration Elements for Process Streams

Features

FILMTEC™ NF membrane elements are designed for process applications where a separation of solutes is desired.

- NF is a durable polypiperazine amide membrane designed to reject organics with a molecular weight above 200 while passing monovalent salts.
- FILMTEC NF membrane elements are used in a variety of applications such as desalting organic compounds, acid processing, metal recovery and antifreeze recovery.
- FILMTEC NF membrane elements replace discontinued NF45 elements.

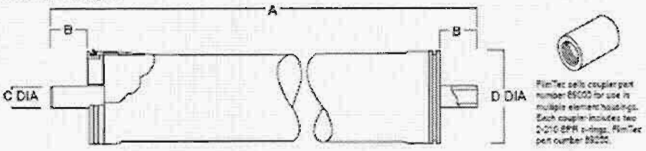
Product Specifications

Product	Part number	Active area – ft² (m²)
NF-2540	151538	28 (2.6)
NF-4040	151543	82 (7.6)
NF-400 (8040 style)	151544	400 (37.2)

1. Permeate flow and salt rejection based on the following test conditions: 2,000 ppm $MgSO_4$, 130 psig (8.9 bar), 77°F (25°C), pH 8 and 15% recovery.
2. Target water flow rates for new elements are: NF-2540 – 920 gpd (3.5 m³/d), NF-4040 – 3,050 gpd (11.5 m³/d), NF-400 – 13,700 gpd (51.9 m³/d).
3. Minimum $MgSO_4$ rejection is 98.0%. Stabilized rejection is >99%.
4. Product specifications may vary slightly as improvements are implemented.

Figure 1.

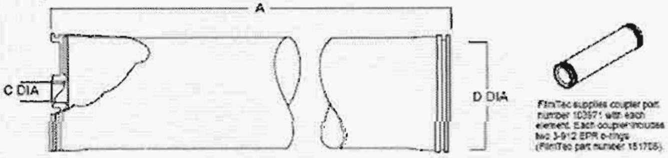
2540 and 4040 styles



FilmTec sells coupler part number 89055 for use in multiple element housings. Each coupler includes two 2-210 EPR o-rings, FilmTec part number 89255.

Figure 2.

8040 style



FilmTec supplies coupler part number 100371 with each element. Each coupler includes two 3-912 EPR o-rings (FilmTec part number 151705).

Product	Maximum feed flow rate, gpm (m³/h)	Typical recovery rate (%)	Dimensions – inches (mm) A	B	C	D
NF-2540	6 (1.4)	15	40.00 (1,016)	1.19 (30.2)	0.75 (19)	2.4 (61)
NF-4040	16 (3.6)	15	40.00 (1,016)	1.05 (25.7)	0.75 (19)	3.9 (99)
NF-400 (8040 style)	70 (16)	15	40.00 (1,016)	-	1.13 (28.6)	7.9 (200)

1. Typical recovery rate shown is for a single element. Recovery rate is calculated by dividing permeate flow rate by feed flow rate.
2. NF-2540 elements have a tape outerwrap. NF-2540 elements fit nominal 2.5 inch I.D. pressure vessel.
3. NF-4040 elements have a fiberglass outerwrap. NF-4040 elements fit nominal 4 inch I.D. pressure vessel.
4. NF-400 elements have a fiberglass outerwrap. NF-400 elements fit nominal 8 inch I.D. pressure vessel.

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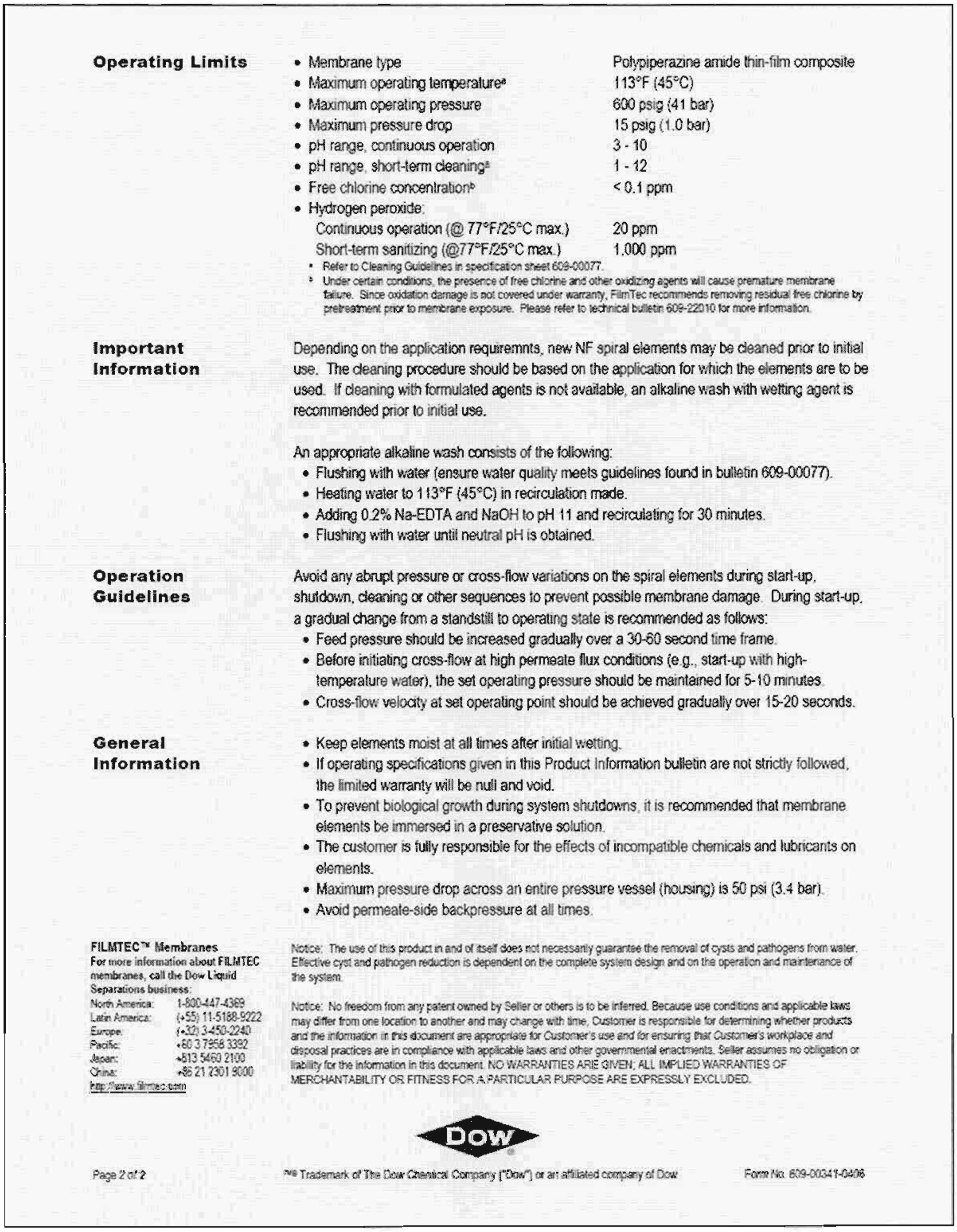


Operating Limits

• Membrane type	Polypiperazine amide thin-film composite
• Maximum operating temperature[a]	113°F (45°C)
• Maximum operating pressure	600 psig (41 bar)
• Maximum pressure drop	15 psig (1.0 bar)
• pH range, continuous operation	3 - 10
• pH range, short-term cleaning[a]	1 - 12
• Free chlorine concentration[b]	< 0.1 ppm
• Hydrogen peroxide:	
Continuous operation (@ 77°F/25°C max.)	20 ppm
Short-term sanitizing (@77°F/25°C max.)	1,000 ppm

[a] Refer to Cleaning Guidelines in specification sheet 609-00077.

[b] Under certain conditions, the presence of free chlorine and other oxidizing agents will cause premature membrane failure. Since oxidation damage is not covered under warranty, FilmTec recommends removing residual free chlorine by pretreatment prior to membrane exposure. Please refer to technical bulletin 609-22010 for more information.

Important Information

Depending on the application requiremnts, new NF spiral elements may be cleaned prior to initial use. The cleaning procedure should be based on the application for which the elements are to be used. If cleaning with formulated agents is not available, an alkaline wash with wetting agent is recommended prior to initial use.

An appropriate alkaline wash consists of the following:
- Flushing with water (ensure water quality meets guidelines found in bulletin 609-00077).
- Heating water to 113°F (45°C) in recirculation made.
- Adding 0.2% Na-EDTA and NaOH to pH 11 and recirculating for 30 minutes.
- Flushing with water until neutral pH is obtained.

Operation Guidelines

Avoid any abrupt pressure or cross-flow variations on the spiral elements during start-up, shutdown, cleaning or other sequences to prevent possible membrane damage. During start-up, a gradual change from a standstill to operating state is recommended as follows:
- Feed pressure should be increased gradually over a 30-60 second time frame.
- Before initiating cross-flow at high permeate flux conditions (e.g., start-up with high-temperature water), the set operating pressure should be maintained for 5-10 minutes.
- Cross-flow velocity at set operating point should be achieved gradually over 15-20 seconds.

General Information

- Keep elements moist at all times after initial wetting.
- If operating specifications given in this Product Information bulletin are not strictly followed, the limited warranty will be null and void.
- To prevent biological growth during system shutdowns, it is recommended that membrane elements be immersed in a preservative solution.
- The customer is fully responsible for the effects of incompatible chemicals and lubricants on elements.
- Maximum pressure drop across an entire pressure vessel (housing) is 50 psi (3.4 bar).
- Avoid permeate-side backpressure at all times.

FILMTEC™ Membranes
For more information about FILMTEC membranes, call the Dow Liquid Separations business:

North America:	1-800-447-4369
Latin America:	(+55) 11-5188-9222
Europe:	(+32) 3-450-2240
Pacific:	+60 3 7958 3392
Japan:	+813 5460 2100
China:	+86 21 2301 9000

http://www.filmtec.com

Notice: The use of this product in and of itself does not necessarily guarantee the removal of cysts and pathogens from water. Effective cyst and pathogen reduction is dependent on the complete system design and on the operation and maintenance of the system.

Appendix C – Experimental Data

[Ni] = 30 g/L, pH = 1

	ΔP = 30 Bar		$[Ni]_0$ = 26.97 g/L		pH = 0.92		
Run6	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average	
J	72.6	73.57	74.44	75.17	75.89	74.33	$kg.m^{-2}.hr^{-1}$
C	0.26	0.36	0.36	0.36	0.36	0.34	g/L
Ni Rejec	99.04	98.63	98.67	98.67	98.67	98.74	%
pH	1.17	0.87	0.87	0.89	0.89	0.94	-
H^+ Rejec	*	-12.20	-12.20	-7.15	-7.15	-9.68	%
Run7	ΔP = 40 Bar		$[Ni]_0$ = 27.83 g/L		pH = 0.93		
J	78.43	81.32	83.28	85.05	85.41	82.70	$kg.m^{-2}.hr^{-1}$
C	0.37	0.31	0.30	0.30	0.31	0.32	g/L
Ni Rejec	98.67	98.89	98.94	98.94	98.89	98.87	%
pH	0.90	0.90	0.90	0.88	0.90	0.90	-
H^+ Rejec	-7.15	-7.15	-7.15	-12.20	-7.15	-8.16	%
Run8	ΔP = 25 Bar		$[Ni]_0$ = 28.13 g/L		pH = 0.92		
J	42.44	43.56	43.38	43.85	44.35	43.51	$kg.m^{-2}.hr^{-1}$
C	0.36	0.38	0.38	0.39	0.41	0.38	g/L
Ni Rejec	98.73	98.64	98.64	98.60	98.55	98.63	%
pH	0.87	0.86	0.86	0.86	0.85	0.86	-
H^+ Rejec	-12.20	-14.82	-14.82	-14.82	-17.49	-14.83	%
Run9	ΔP = 20 Bar		$[Ni]_0$ = 28.91 g/L		pH = 0.90		
J	27.01	27.34	27.74	28.10	28.28	27.69	$kg.m^{-2}.hr^{-1}$
C	0.62	0.58	0.59	0.68	0.59	0.61	g/L
Ni Rejec	97.87	97.99	97.95	97.65	97.95	97.88	%
pH	0.84	0.84	0.84	0.84	0.84	0.84	-
H^+ Rejec	-14.82	-14.82	-14.82	-14.82	-14.82	-14.82	%

* Sample loss due to spill

[Ni] = 40g/L, pH = 1

	ΔP = 40 Bar		$[Ni]_0$ = 33.07 g/L		pH = 1.04		
Run10	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average	
J	61.65	62.46	64.09	74.05	65.34	65.52	$kg.m^{-2}.hr^{-1}$
C	0.92	0.70	0.64	0.62	0.62	0.70	g/L
Ni Rejec	97.23	97.88	98.06	98.13	98.13	97.89	%
pH	0.92	0.92	0.90	0.90	0.90	0.91	-
H^+ Rejec	-31.83	-31.83	-38.04	-38.04	-38.04	-35.55	%

Run11	ΔP = 35 Bar		$[Ni]_0$ = 36.83 g/L		pH = 0.97		
J	51.72	51.20	52.01	52.67	53.25	52.17	$kg.m^{-2}.hr^{-1}$
C	0.56	0.54	0.55	0.55	0.55	0.55	g/L
Ni Rejec	98.48	98.55	98.51	98.51	98.51	98.51	%
pH	0.93	0.93	0.91	0.91	0.92	0.92	-
H^+ Rejec	-9.65	-9.65	-14.82	-14.82	-12.20	-12.23	%
Run12	ΔP = 30 Bar		$[Ni]_0$ = 37.73 g/L		pH = 0.97		
J	39.10	39.74	40.74	41.17	41.55	40.46	$kg.m^{-2}.hr^{-1}$
C	0.58	0.58	0.58	0.60	0.60	0.59	g/L
Ni Rejec	98.45	98.45	98.42	98.42	98.42	98.43	%
pH	0.90	0.90	0.91	0.91	0.89	0.90	-
H^+ Rejec	-17.49	-17.49	-14.82	-14.82	-20.23	-16.97	%
Run13	ΔP = 25 Bar		$[Ni]_0$ = 38.35 g/L		pH = 0.98		
J	25.72	26.20	26.64	26.91	28.14	26.72	$kg.m^{-2}.hr^{-1}$
C	0.73	0.79	0.81	0.83	0.85	0.80	g/L
Ni Rejec	98.11	97.95	97.89	97.83	97.80	97.92	%
pH	0.89	0.90	0.90	0.90	0.89	0.90	-
H^+ Rejec	-23.03	-20.23	-20.23	-20.23	-23.03	-21.35	%

[Ni] = 50g/L, pH = 1

	ΔP = 40 Bar		$[Ni]_0$ = 44.65 g/L		pH = 1.04		
Run14	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average	
J	40.16	40.77	41.06	41.39	41.69	41.02	$kg.m^{-2}.hr^{-1}$
C	0.91	1.05	1.11	1.11	1.10	1.06	g/L
Ni Rejec	97.95	97.65	97.51	97.51	97.54	97.63	%
pH	0.92	0.92	0.91	0.91	0.91	0.91	-
H^+ Rejec	-31.83	-31.83	-34.90	-34.90	-34.90	-33.67	%
Run15	ΔP = 35 Bar		$[Ni]_0$ = 48.78 g/L		pH = 0.97		
J	29.09	29.62	30.45	31.03	31.56	30.35	$kg.m^{-2}.hr^{-1}$
C	1.15	1.12	1.12	1.11	1.17	1.13	g/L
Ni Rejec	97.65	97.70	97.70	97.72	97.60	97.67	%
pH	0.90	0.90	0.91	0.91	0.91	0.91	-
H^+ Rejec	-17.49	-17.49	-14.82	-14.82	-14.82	-15.89	%
Run16	ΔP = 45 Bar		$[Ni]_0$ = 49.24 g/L		pH = 0.97		
J	47.69	48.47	49.13	50.20	50.72	49.24	$kg.m^{-2}.hr^{-1}$
C	1.06	0.90	0.91	0.91	0.90	0.94	g/L
Ni Rejec	97.84	98.17	98.15	98.15	98.17	98.10	%
pH	0.95	0.91	0.91	0.91	0.94	0.92	-
H^+ Rejec	-4.71	-14.82	-14.82	-14.82	-7.15	-11.26	%

Run17	ΔP = 50 Bar		[Ni]$_0$ = 49.95 g/L		pH = 0.96		
J	50.72	58.81	58.88	58.67	58.92	57.20	kg/hr.m^2
C	0.93	0.89	0.88	0.90	0.89	0.90	g/L
Ni Rejec	98.15	98.22	98.25	98.20	98.22	98.21	%
pH	0.94	0.94	0.94	0.91	0.94	0.93	-
H$^+$ Rejec	-4.71	-4.71	-4.71	-12.20	-4.71	-6.21	%
Run18	ΔP = 55 Bar		[Ni]$_0$ = 50.85 g/L		pH = 0.97		
J	46.11	47.05	49.03	50.21	51.46	48.77	kg.m^{-2}.hr^{-1}
C	1.10	0.91	0.83	0.81	0.81	0.89	g/L
Ni Rejec	97.84	98.20	98.37	98.40	98.40	98.24	%
pH	0.96	0.93	0.96	0.96	0.96	0.95	-
H$^+$ Rejec	-14.82	-14.82	-12.20	-12.20	-14.82	-13.77	%

[Ni] = 30 g/L, pH = 2

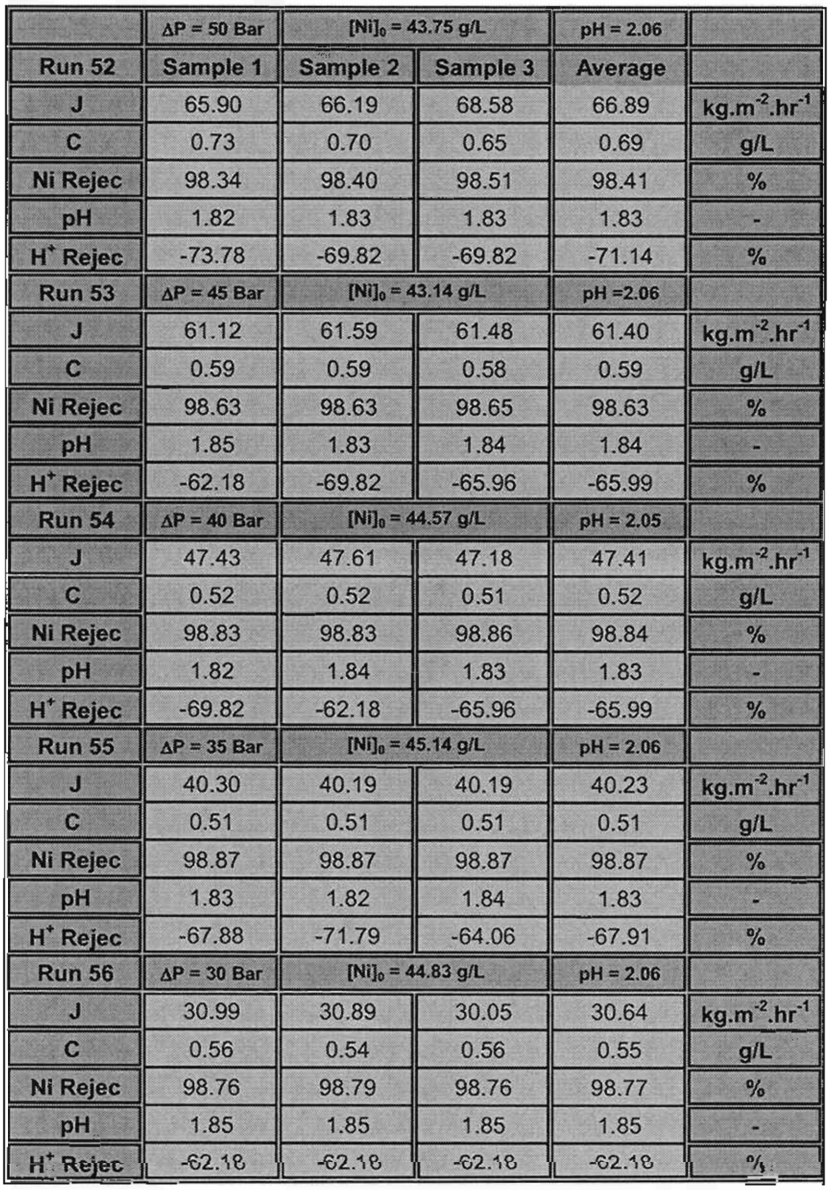
	ΔP = 40 Bar	[Ni]$_0$ = 23.72 kg/L		pH = 2.00	
Run 36	Sample 1	Sample 2	Sample 3	Average	
J	90.63	94.61	90.95	92.06	kg.m^{-2}.hr^{-1}
C	0.25	0.25	0.25	0.25	g/L
Ni Rejec	98.93	98.93	98.93	98.93	%
pH	1.73	1.73	1.74	1.73	-
H$^+$ Rejec	-84.08	-84.08	-79.89	-82.68	%
Run 37	ΔP =35 Bar	[Ni]$_0$ = 23.36 kg/L		pH = 2.00	
J	81.43	79.01	83.31	81.25	kg.m^{-2}.hr^{-1}
C	0.27	0.27	0.25	0.26	g/L
Ni Rejec	98.86	98.86	98.91	98.88	%
pH	1.76	1.73	1.75	1.75	-
H$^+$ Rejec	-71.79	-84.08	-75.79	-77.22	%
Run 38	ΔP = 30 Bar	[Ni]$_0$ = 23.54 kg/L		pH = 2.00	
J	70.46	69.55	68.79	69.60	kg.m^{-2}.hr^{-1}
C	0.27	0.29	0.28	0.28	g/L
Ni Rejec	98.87	98.77	98.82	98.82	%
pH	1.73	1.73	1.73	1.73	-
H$^+$ Rejec	-81.97	-81.97	-81.97	-81.97	%

Run 39	ΔP = 25Bar	$[Ni]_0$ = 23.35 kg/L		pH = 2.00	
J	55.47	54.60	55.04	55.04	kg.m^{-2}.hr^{-1}
C	0.31	0.30	0.29	0.30	g/L
Ni Rejec	98.76	98.81	98.85	98.81	%
pH	1.73	1.73	1.72	1.73	-
H$^+$ Rejec	-81.97	-81.97	-86.21	-83.38	%
Run 40	ΔP = 20 Bar	$[Ni]_0$ = 25.57 kg/L		pH = 1.99	
J	40.19	39.36	39.61	39.72	kg.m^{-2}.hr^{-1}
C	0.35	0.36	0.38	0.36	g/L
Ni Rejec	98.63	98.58	98.53	98.58	%
pH	1.73	1.73	1.72	1.73	-
H$^+$ Rejec	-81.97	-81.97	-86.21	-83.38	%

[Ni] = 40g/L, pH = 2

	ΔP = 40 Bar	$[Ni]_0$ = 37.03 g/L		pH = 1.98	
Run27	Sample 1	Sample 2	Sample 3	Average	
J	58.58	59.16	58.19	58.64	kg.m^{-2}.hr^{-1}
C	0.33	0.33	0.25	0.30	g/L
Ni Rejec	99.12	99.12	99.31	99.18	%
pH	1.72	1.73	1.73	1.73	-
H$^+$ Rejec	-81.97	-77.83	-77.83	-79.21	%
Run 28	ΔP = 35 Bar	$[Ni]_0$ = 36.55 g/L		pH = 1.98	
J	52.43	52.61	51.96	52.33	kg.m^{-2}.hr^{-1}
C	0.31	0.28	0.28	0.29	g/L
Ni Rejec	99.14	99.24	99.24	99.21	%
pH	1.69	1.70	1.70	1.70	-
H$^+$ Rejec	-94.98	-90.55	-90.55	-92.03	%
Run 29	ΔP = 30 Bar	$[Ni]_0$ = 36.94 g/L		pH = 1.98	
J	43.16	42.25	42.36	42.59	kg.m^{-2}.hr^{-1}
C	0.33	0.30	0.31	0.31	g/L
Ni Rejec	99.12	99.18	99.15	99.15	%
pH	1.70	1.70	1.70	1.70	-
H$^+$ Rejec	-90.55	-90.55	-90.55	-90.55	%
Run 30	ΔP =25 Bar	$[Ni]_0$ = 37.76 g/L		pH = 1.98	
J	31.61	31.36	30.99	31.32	kg.m^{-2}.hr^{-1}
C	0.36	0.35	0.36	0.36	g/L
Ni Rejec	99.04	99.07	99.04	99.05	%
pH	1.68	1.69	1.70	1.69	-
H$^+$ Rejec	-108.93	-104.17	-99.53	-104.21	%

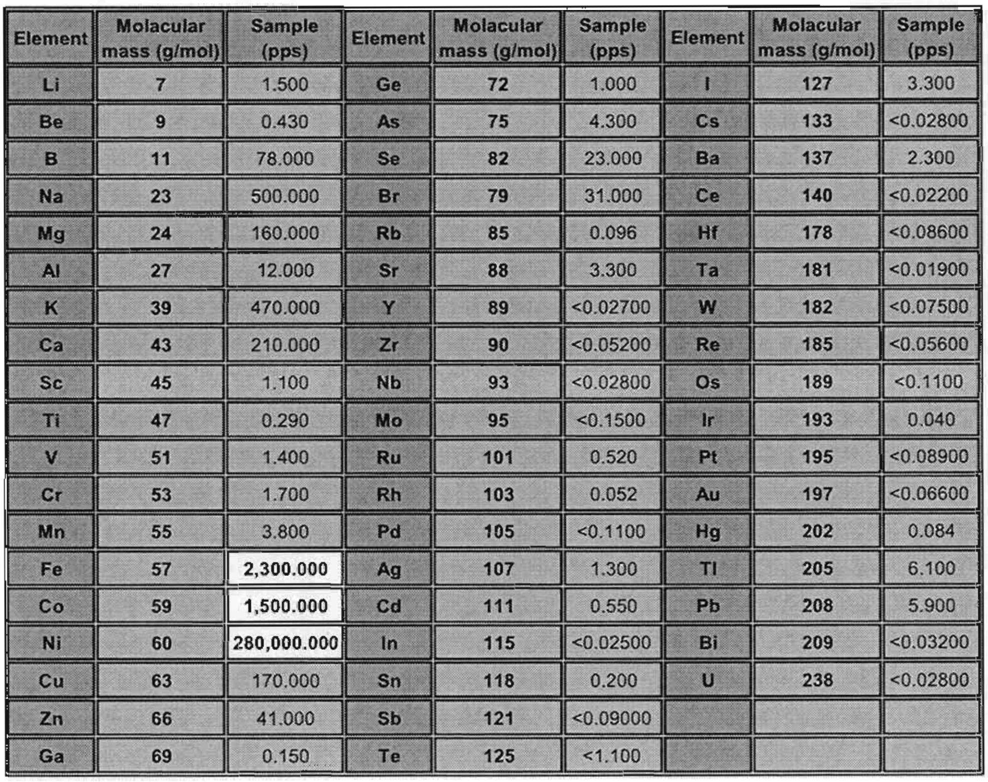
[Ni] = 50g/L, pH = 2



	ΔP = 50 Bar	$[Ni]_0$ = 43.75 g/L		pH = 2.06	
Run 52	**Sample 1**	**Sample 2**	**Sample 3**	**Average**	
J	65.90	66.19	68.58	66.89	**$kg.m^{-2}.hr^{-1}$**
C	0.73	0.70	0.65	0.69	**g/L**
Ni Rejec	98.34	98.40	98.51	98.41	**%**
pH	1.82	1.83	1.83	1.83	**-**
H^+ Rejec	-73.78	-69.82	-69.82	-71.14	**%**
Run 53	ΔP = 45 Bar	$[Ni]_0$ = 43.14 g/L		pH =2.06	
J	61.12	61.59	61.48	61.40	**$kg.m^{-2}.hr^{-1}$**
C	0.59	0.59	0.58	0.59	**g/L**
Ni Rejec	98.63	98.63	98.65	98.63	**%**
pH	1.85	1.83	1.84	1.84	**-**
H^+ Rejec	-62.18	-69.82	-65.96	-65.99	**%**
Run 54	ΔP = 40 Bar	$[Ni]_0$ = 44.57 g/L		pH = 2.05	
J	47.43	47.61	47.18	47.41	**$kg.m^{-2}.hr^{-1}$**
C	0.52	0.52	0.51	0.52	**g/L**
Ni Rejec	98.83	98.83	98.86	98.84	**%**
pH	1.82	1.84	1.83	1.83	**-**
H^+ Rejec	-69.82	-62.18	-65.96	-65.99	**%**
Run 55	ΔP = 35 Bar	$[Ni]_0$ = 45.14 g/L		pH = 2.06	
J	40.30	40.19	40.19	40.23	**$kg.m^{-2}.hr^{-1}$**
C	0.51	0.51	0.51	0.51	**g/L**
Ni Rejec	98.87	98.87	98.87	98.87	**%**
pH	1.83	1.82	1.84	1.83	**-**
H^+ Rejec	-67.88	-71.79	-64.06	-67.91	**%**
Run 56	ΔP = 30 Bar	$[Ni]_0$ = 44.83 g/L		pH = 2.06	
J	30.99	30.89	30.05	30.64	**$kg.m^{-2}.hr^{-1}$**
C	0.56	0.54	0.56	0.55	**g/L**
Ni Rejec	98.76	98.79	98.76	98.77	**%**
pH	1.85	1.85	1.85	1.85	**-**
H^+ Rejec	-62.18	-62.18	-62.18	-62.18	**%**

Appendix D – Analysis

Table D.1: Industrial nickel sulphate composition



Element	Molacular mass (g/mol)	Sample (pps)	Element	Molacular mass (g/mol)	Sample (pps)	Element	Molacular mass (g/mol)	Sample (pps)
Li	**7**	1.500	**Ge**	**72**	1.000	**I**	**127**	3.300
Be	**9**	0.430	**As**	**75**	4.300	**Cs**	**133**	<0.02800
B	**11**	78.000	**Se**	**82**	23.000	**Ba**	**137**	2.300
Na	**23**	500.000	**Br**	**79**	31.000	**Ce**	**140**	<0.02200
Mg	**24**	160.000	**Rb**	**85**	0.096	**Hf**	**178**	<0.08600
Al	**27**	12.000	**Sr**	**88**	3.300	**Ta**	**181**	<0.01900
K	**39**	470.000	**Y**	**89**	<0.02700	**W**	**182**	<0.07500
Ca	**43**	210.000	**Zr**	**90**	<0.05200	**Re**	**185**	<0.05600
Sc	**45**	1.100	**Nb**	**93**	<0.02800	**Os**	**189**	<0.1100
Ti	**47**	0.290	**Mo**	**95**	<0.1500	**Ir**	**193**	0.040
V	**51**	1.400	**Ru**	**101**	0.520	**Pt**	**195**	<0.08900
Cr	**53**	1.700	**Rh**	**103**	0.052	**Au**	**197**	<0.06600
Mn	**55**	3.800	**Pd**	**105**	<0.1100	**Hg**	**202**	0.084
Fe	**57**	**2,300.000**	**Ag**	**107**	1.300	**Tl**	**205**	6.100
Co	**59**	**1,500.000**	**Cd**	**111**	0.550	**Pb**	**208**	5.900
Ni	**60**	**280,000.000**	**In**	**115**	<0.02500	**Bi**	**209**	<0.03200
Cu	**63**	170.000	**Sn**	**118**	0.200	**U**	**238**	<0.02800
Zn	**66**	41.000	**Sb**	**121**	<0.09000			
Ga	**69**	0.150	**Te**	**125**	<1.100			