Implementation of membrane technology in a Base Metal Refinery

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Proverbs 3:5 Trust in the LORD with all thine heart; and lean not unto thine own understanding.

DECLARATION

I, Franco Mocke, the under signed, hereby declare that this dissertation, ‘Implementation of Membrane Technology in a Base Metal Refinery’, is my own work.

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ABSTRACT

In this study, the implementation of membrane technology at Anglo Platinum's base metals refinery to separate acid from metal containing solutions was investigated. The refinery includes a circuit known as the "sulphur removal section", where the acid in the spent nickel electrolyte is neutralized with caustic soda to remove the excess sulphur from the overall process. Reagent costs associated with acid neutralisation, result in high operating expenditures. An alternative process route is required to improve efficiencies and stay competitive. Nanofiltration was investigated to separate acid from nickel, with the aim of recovering the acid and thereby reducing the need for expensive neutralisation.

The objectives of this study were twofold: (1) investigate and simulate the current base metals refinery, and (2) use the understanding and process know-how to investigate the use of nanofiltration by modifying the simulation to include for this technology. The modified process simulation was then used to evaluate the type of membrane required for technical viability.

The process investigation of the refinery proceeded with literature studies done on base metals recovery process, chemical reactions and design criteria applicable to the process. A simulation of the base metals refinery was undertaken in Aspen Plus using the information established in the process investigation. The simulation provided insight into the operational issues across the flowsheet, and identified key areas of the process which were sensitive to parameter changes in the sulphur removal section. Areas which were impacted were the electrowinning and copper removal section. The simulation therefore provided a useful tool to predict process variabilities as a result of plant modifications.

The investigation into nanofiltration found that it can successfully be used to separate metal ions from acid, subject to the constraints of metal ion concentrations. Pre-treatment of the nickel spent electrolyte was required to remove most of the sodium sulphate in solution, since this can cause fouling and thereby degrade membrane performance. For this reason, a cold crystallization process was introduced for the removal of sodium sulphate. However the sodium removal process caused the sodium sulphate levels in the electrowinning feed to drop below 100 g/l. Therefore minor modifications had to be made to the electrowinning pre-treatment process. The nanofiltration process itself consisted of a series of six nanofiltration stages with dilution of the interstage feed to allow the system to operate below osmotic pressure and wash out all the acid from the system.

The modified simulation including the new sulphur removal circuit (nanofiltration process) was completed by integrating the current base metals refinery simulation with the new sulphur removal process, thereby providing a tool where different membrane characteristics could be varied to enable the performance of the overall process to be evaluated.

The membrane parameters varied were the nickel rejection, the sodium rejection and the acid rejection. The simulation predicted that each of the cases which varied the mentioned parameters would be technically feasible, although not necessarily economically feasible. The process was most sensitive to acid rejection. The key variables were the amount of water used for dilution, and the membrane size. An exponential distribution was present for the sensitivity of membrane size versus acid rejection; thus realistic membrane sizes can only be achieved if the acid rejection is -100% or less. Furthermore, the addition of dilution water results in the nickel being washed out with the acid, despite nickel rejection being in the region of 99.5%. This demonstrates the importance of the membrane nickel rejection to be as high as possible.

Keywords:

Base metals refinery; process simulation; nanofiltration; acid separation

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LIST OF ABBREVIATIONS

Abbreviation	Description
AC	Alternative Refinery Case
BC	Base Refinery Case
BMR	Base Metals Refinery
CAPEX	Capital Expenditure
HPP	High Pressure Pump
NCM	Nickel-Copper-Matte
NF	Nanofiltration
R&D	Research & Development
RBMR	Rustenburg Base Metals Refinery
RBMR-NF	RBMR with Nanofiltration
SG	Specific gravity

NOMENCLATURE

Symbol	Description	Units
Symbol		
A	Area	ft^2,m^2
$c_{p,i}$	Permeate concentration of ion	$g.L^{-1}$
E_w	Washing efficiency	
E_f	Filter efficiency	
J_M	Mass flux through membrane	$kg.m^{-2}.hr^{-1}$
M	Total Mass flow rate	$ton.hr^{-1}$
M_i	Mass flow rate of specie i	$ton.hr^{-1}$
M_P	Mass flow rate of permeate	$ton.hr^{-1}$
MF_i	Mass fraction of specie i	
SF_{liq}	Liquid split fraction	
P	Pressure	bar
R_i	Ion rejection of specie i in membrane	
S	Amount of washing stages	
V	Volume flow rate	$m^3.hr^{-1}$
X	Split fraction of liquids	
Y	Split fraction of water	
Greek		
π	Osmotic Pressure	Pa
ρ	Total density	

1. INTRODUCTION

Overview

In this chapter, a broad overview of the contents of this investigation will be presented. The chapter is subdivided into four sections, starting with the background and motivation for this investigation in Section 1.1. The objectives of the investigation are formulated in Section 1.2, and Section 1.3 consists of the scope of the investigation

1.1. BACKGROUND AND MOTIVATION

The Anglo Platinum Bushveld Complex near Rustenburg, South Africa, is well known to comprise of the world's largest reserves of platinum group metals. There are enough deposits to supply the world for many decades to come(Crawthorn, 1999; Crawthorn, 2010). Base metals are mined together with platinum group metals at the Bushveld Complex, and although the primary operations are the platinum group metals, it is feasible to refine the base metals as well. The platinum and base metals refineries are located at two separate sites, due to the different processes used to separate the metals. The base metal refinery mainly consists of cobalt, selenium, copper and nickel refining. The process is based on the Sherritt process, but modifications have been made over the years to make the refinery more efficient (Bryson *et al.,* 2008).

The nickel refining circuit in the base metals refinery produces a spent electrolyte stream, which is highly concentrated with nickel sulphate, sodium sulphate and sulphuric acid. The sulphates need to be selectively removed from the process and to accomplish the task at hand a precipitation process is used to precipitate nickel as nickel hydroxide and neutralize the free acid. The neutralizing chemical used is caustic soda, and the commodity price of caustic soda in 2011 was $500 per metric ton (ISISpricing, 2011). After the nickel hydroxides are separated from the sulphate solution via filtration, the sulphates, which are present as sodium sulphate, are processed in an evaporative plant to produce sodium sulphate crystals. The commodity price of sodium sulphate as of 2010 was $127 per metric ton (USGS, 2011). It is clear from the process description summary and the comparison of the commodity prices of the main reagent and product that the nickel-sulphur separation process produces a product of less worth compared to the reagent used. It is also clear that the energy requirements are high due to an evaporator that is used to crystalize the sodium sulphate from solution.

Due to the high operating costs involved in the nickel-sulphur separation process, Anglo Platinum is currently investigating alternative process routes to create a more favourable process which will decrease operating expenditures as well as promote sustainable technology with a lower environmental impact. Since the major cost driver is the sulphuric acid, a process which can selectively separate sulphuric acid from solution can potentially be an alternative process.

Many processes exist where acid can be separated from metal containing aqueous solutions and the most reported processes are (1) solvent extraction, (2) ion exchange and (3) membrane technology.

(1) Solvent extraction is a widely used technology to separate low concentrations of ions from aqueous solution by using an organic extractant. Solvent extraction is not a favourable process route for the nickel-sulphur removal process due to the nickel-sulphur removal process having to treat an aqueous stream with high nickel and acid concentrations (Reddy *et al.*, 2009; Cheng *et al.*, 2010).

(2) Ion exchange, like solvent extraction is a widely used technology. In ion exchange ions are loaded onto a resin selectively. Ion exchange is very similar to solvent extraction in terms of what can be processed: the technology is used to adsorb low concentrations of ions and thus is not a favourable process route for an alternative nickel-sulphur removal process (Menes & Martins, 2005).

(3) Membrane technology is not widely used in the hydrometallurgical environment, but recent studies indicated that nanofiltration (NF) membranes can be used for the separation of acid from metallic ions in aqueous solutions at high metal ion concentrations. (Tanninen & Nyström, 2002; Tanninen & Nyström, 2006; Stolp, 2006).

From the evaluation of the different technologies available the potential exists for membrane technology with focus on NF to replace the current nickel-sulphur separation process, since NF is proven in literature to have the capability to separate acid from metal containing aqueous solutions.

The Anglo Platinum base metals refinery is a complicated process, and thus to be able to investigate if NF is a viable alternative process route for the nickel-sulphur removal section of the process, the entire processing plant will need to be investigated and simulated. Simulation of the base metals refinery will enable a global perspective on the overall process with the capability to introduce NF into the process and observe process-wide implications.

1.2. OBJECTIVES

The main objective for this study is twofold:

(1) Develop a process simulation of current RBMR
(2) Design, develop and simulate a process of the current RBMR with NF technology

The two objectives can be broadly defined as follows:

(1) Base metals refinery investigation (BMR)

- Investigate and describe the current RBMR process
- Develop a simulation with mass and energy balances to describe the current RBMR

(2) Base metals refinery with NF technology (RBMR-NF)

- Investigate the potential of using NF technology within a base metals refinery process
- Develop a conceptual flow-sheet and simulation that apply NF technology for the separation of nickel and sulphur in the RBMR.
- Investigate case studies to ascertain the effect of applying NF to the RBMR.
- Investigate case studies to ascertain the needed performance parameter to apply NF to the RBMR.

1.3. SCOPE OF INVESTIGATION

The basic scope of this investigation is summarised in Figure 1.1. The dissertation is subdivided into five chapters that consist of the following contents:

In **Chapter 2** the design methodology of the design procedure is discussed, together with process conditions, process boundaries and the software tools that are used to carry out process simulations.

In **Chapter 3** the RBMR is described with a detailed literature study, and the RBMR is simulated. The focus in Section 3.2 is to obtain an in-depth knowledge of the base metals refinery by means of a total literature study on the available literature that is available to the public as well as the literature that is confidential property of Anglo American. Section 3.3 is focussed on the discussion of the technical aspects of the base metals refinery plant and how the simulation was built, together with the results obtained. Section 3.4 validates the simulation by comparing key streams with information supplied by Anglo American (2012).

Chapter 4 entails the study, development and simulation of the RBMR-NF. Section 4.1 is a literature study around relevant topics required for the development of the RBMR-NF process and the simulation of the RBMR-NF process. Section 4.2 contains a process description for the relevant process sections of the RBMR-NF process. Section 4.3 discusses the simulation of the RBMR-NF, and finally Section 4.4 discusses the results of the effect of different NF membrane characteristics (case studies) on key process variables.

Finally, **Chapter 5** summarizes the main conclusions of the work described in this dissertation and gives an outlook and suggestions for future work.

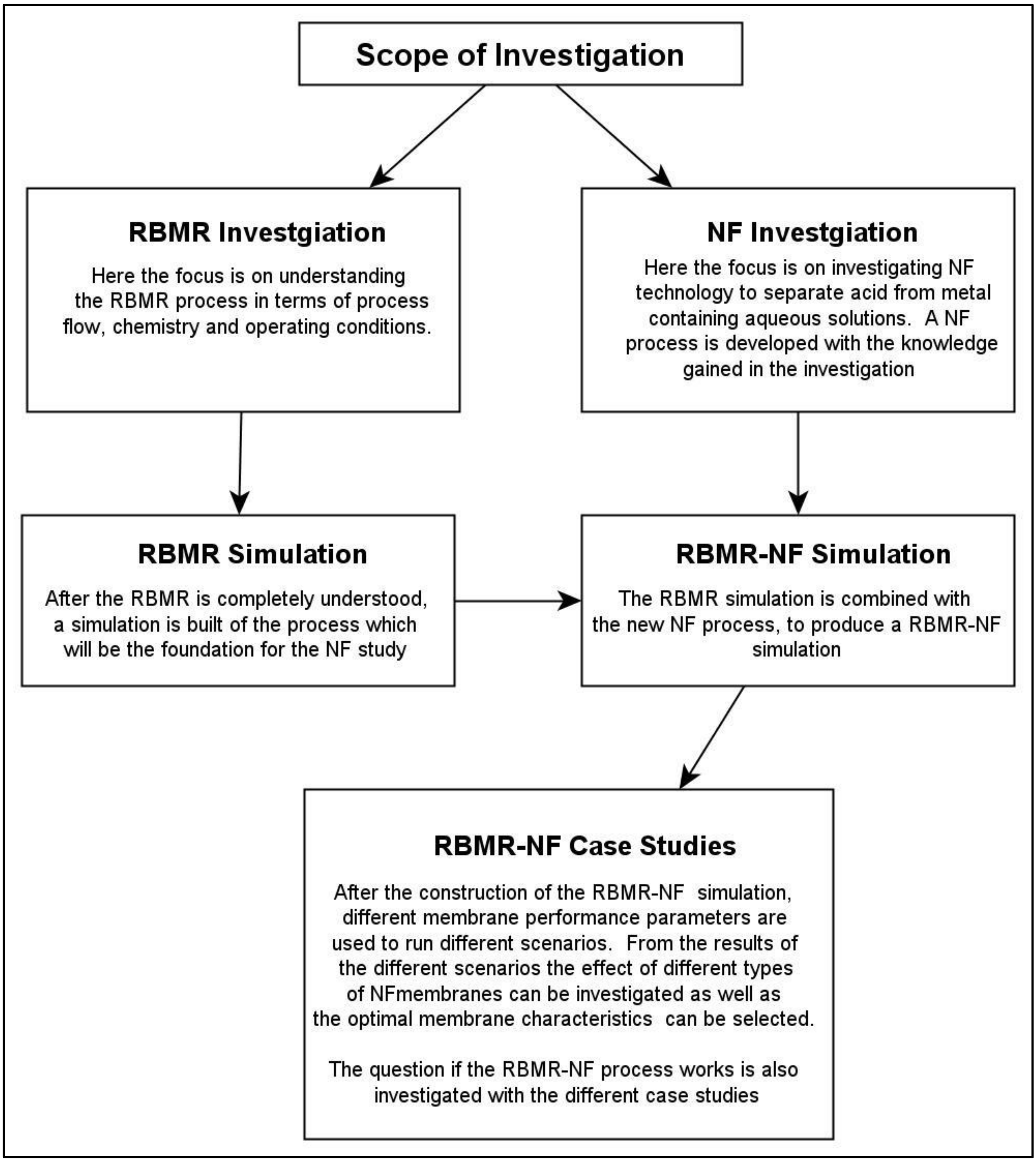

Figure 1.1: Schematically representation of the scope of this investigation

2. DESIGN METHODOLOGY

Overview

Chapter 2 gives the methodology used in which the dissertation is structured, as well as additional information required to proceed to Chapter 3. Section 2.1 discusses the research and design philosophy used in this investigation, and ties up the research and design philosophy to a conceptual framework which graphically illustrates the goals and workflow of this investigation. Section 2.2 discusses the characteristics of the BMR process, different simulation packages as well as thermodynamics. Thus Section 2.2 contains the necessary information required to select the appropriate simulation package as well as thermodynamic model. Finally Section 2.3 gives the battery limits of the RBMR and RBMR-NF simulation.

2.1. CONCEPTUAL FRAMEWORK

The main objective of this investigation is to ascertain the feasibility of applying NF in the RBMR for the separation of acid from an aqueous solution containing high concentrations of nickel. To achieve this goal, the following steps need to be taken:

- Replicate the original RBMR process mathematically in a simulation environment
- Design a new RBMR-NF process – complete integration with the RBMR is required
- Simulate the new RBMR-NF process by modifying the RBMR simulation to include the NF process
- Study the influence of different NF characteristics on the RBMR-NF

To achieve the goals mentioned, a conceptual framework based on engineering design is required. A conceptual framework is a visual or written product, that explains narratively or graphically the main things to be studied, the concept, key factors or variables, and most importantly the relationship between them (Maxwell, 2004).

The conceptual framework is illustrated in Figure 2.1.

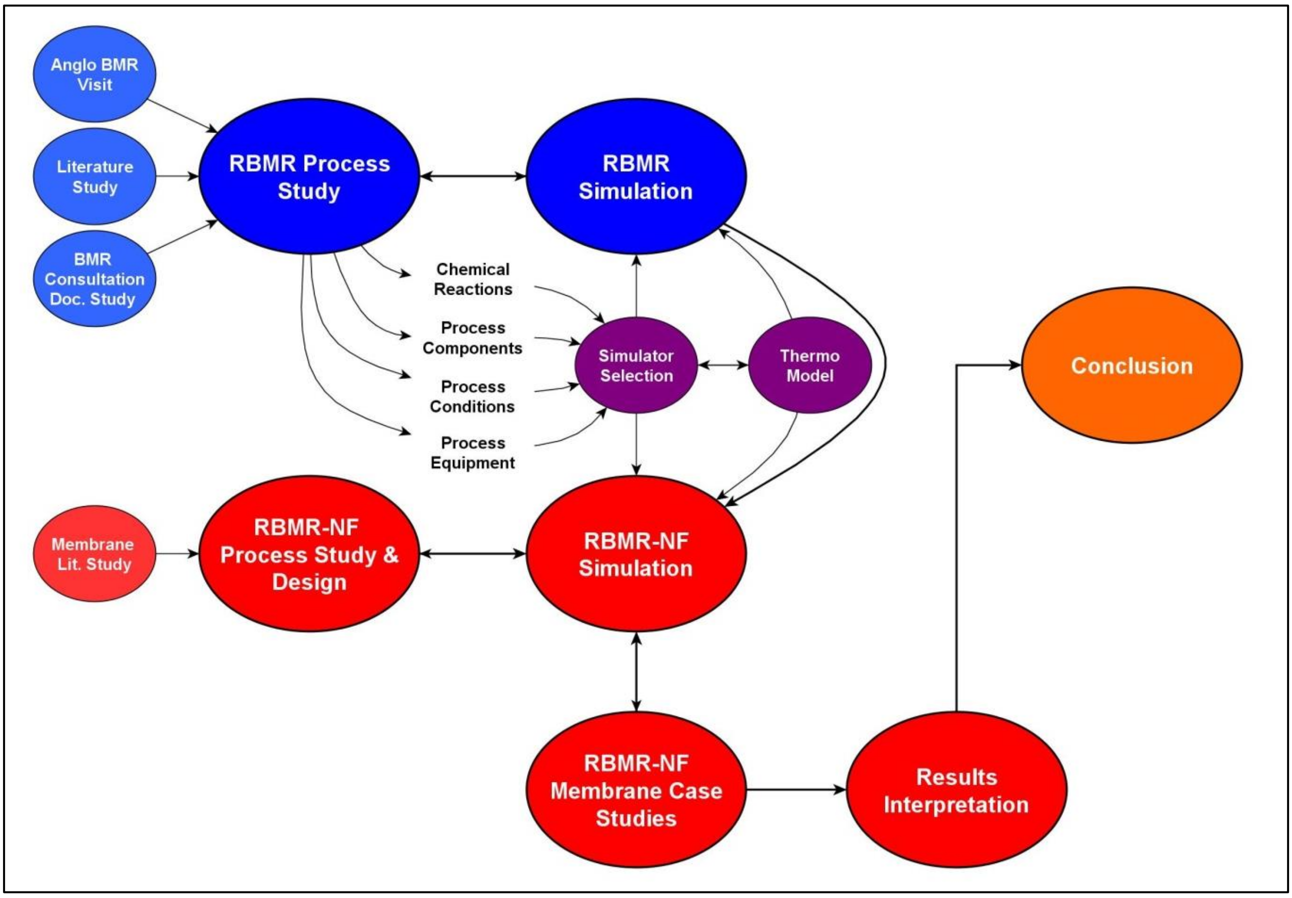

Figure 2.1: Conceptual Framework

From the conceptual framework it can be seen that there are two primary investigations, namely the RBMR investigation and the RBMR-NF investigation. The RBMR investigation consists of studying the process and simulating the process. The RBMR-NF investigation consists of studying and designing the RBMR-NF process, simulating the process and doing case studies on the RBMR-NF process. The results of the case studies are then interpreted to come to the conclusion of the dissertation.

The RBMR process study requires visits to the processing plant, literature study from reliable sources about the refinery, and also studies on documents provided by consultation for the refinery such as mass and energy balances. The data obtained will then be used to construct process design specifications on which the simulation will be based. After the study is finished the respective computer simulation software can be chosen as well as the property model (thermodynamics) that the simulation will be based on; this is then used to simulate the RBMR. The completion of the RBMR simulation will then be scrutinized and validated by comparing the RBMR simulation with data given by Anglo American (2012).

At the completion of the RBMR study, the RBMR-NF investigation will start. Literature studies are done on NF in the context of acid separation from metal containing aqueous solutions. After the literature study is completed, the RBMR-NF process is designed and described with the new nickel-sulphur removal process as well as modifications made to the RBMR. The new RBMR-NF process is then simulated by modifying the RBMR simulation.

After the completion of the RBMR-NF simulation, different case studies with different membrane parameters are run to study the effect of different membrane characteristics on the overall RBMR-NF process, and to conclude if the technology is applicable to separating acid from aqueous solution containing high concentrations of nickel.

It should be noted that the end goal of the study is to conclude if NF will work in the RBMR from a technical point of view. If it will be economically viable is a different question and outside the scope of the project.

2.2. DESIGN BASIS

The basis of design is the information required to establish the foundation of the process description and design parameters.

The characteristics of the RBMR process are discussed so that enough information is available to be able to choose a property (thermodynamic) model. The process battery limits are also discussed to define the boundaries of the simulation.

2.2.1. RBMR PROCESS CHARACTERISTICS

This section is a brief overview of the RBMR process characteristics, to define the necessary information needed for the selection of the simulation software and thermodynamic model.

Anglo Platinum Base Metal Refinery is a hydrometallurgical base metals plant consisting of mainly leaching, salt precipitation and electrowinning. The chemistry in the leaching sections of the process is fairly complex consisting of dissolution, hydrolysis and metathesis reactions. The other sections use methods such as electrolysis to recover metals and precipitation to selectively remove unwanted dissolved species (Hofirek & Kerfoot, 1992; Hofirek & Nofal, 1995)

According to Habashi (2009) hydrometallurgy is a technique within the field of extractive metallurgy involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials. Kotz *et al.* (2006:176) defines aqueous chemistry as solutions where water is the solvent. The clear understanding of the type of process is required for the thermodynamic model selection. To further understand the process, the components used in the process need to be defined. Table 2.1 contains the most important components used in the process as given by Hofirek & Halton (1990), Hofirek & Kerfoot (1992), Hofirek & Nofal (1995), Bryson *et al.* (2008) and Anglo American (2012).

Table 2.1: BMR Components & maximum operating conditions

Component	Max Temperature (°C)	Max Pressure (kPa)
Mineral Components		
$M_xS_yOH_z$*	155	688
Solid Components		
$NaOH$	155	688
Na_2SO_3	155	688
$Ba(OH)_2$	155	688
$M_x(SO4)_y$*	155	688
Liquid Components		
H_2SO_4	155	688

Component	Max Temperature (°C)	Max Pressure (kPa)
H_2O	155	688
Gaseous Components		
H_2	60	88
O_2	155	688
N_2	155	688

* M = metals such as Ni, Fe and Cu

All of the mineral, solid, liquid and gaseous components in Table 2.1 are dissolved (where possible) in the solution consisting of mainly water. Thus aqueous electrolyte solutions play a big part in the chemistry of the RBMR process. The maximum temperature and pressure in the system is 155°C and 688kPa, which will influence the decision on which thermodynamic model to use.

Due to the aqueous/electrolyte nature of the solutions, the simulation of the RBMR and RBMR-NF will require software and mathematics that can adequately describe electrolyte solutions as well as solids.

2.2.2. PROCESS BATTERY LIMITS

To understand the level of design required, battery limits need to be applied to the RBMR and RBMR-NF. This section will define the battery limits of the RBMR and RBMR-NF simulation.

2.2.2.1. RBMR

The following streams/sections of the RBMR plant will not be included in the simulation:

- Matte furnace – The nickel-copper matte will be a feed stream to the process
- No reagent make-ups will be simulated. Only the final reagent stream will be introduced into the process
- No process water simulations will be done. Process water used in the process is assumed to be pure water
- The magnetic concentrate solution from the platinum refinery is fed to the RBMR as a feed stream. Thus the production of the magnetic concentrate solution is not simulated.
- The cobalt treatment plant is not simulated
- The sodium sulphate plant is not simulated
- Any product/reagent handling is not simulated

2.2.2.2. RBMR-NF

The RBMR-NF simulation includes all the battery limits of the RBMR simulation, with the following addition:

- The permeate product from the NF plant requires further treatment to recover permeated nickel, to concentrate the acid and to recover process water. The treatment of the permeate product is outside the scope of this project and will not be simulated/investigated.

2.3. SIMULATION SOFTWARE

2.3.1. SELECTION OF SOFTWARE

Chemical process simulators are software programs designed to model process plants. Chemical process simulators are increasingly important in modelling non existing systems or systems that are too expensive to experiment many process variations in pilot plants. Being able to simulate an entire process from scratch is an enormous advantage that no process design company can do without today (Casavant & Côtè, 2004).

The process simulation software industry has rapidly evolved over the past 25 years since the role of simulation has changed from the simplest task of automating design calculations to being the centre of the conceptual design process, process design and plant troubleshooting. Process design companies are also making use of software engineering technologies such as process synthesis, economic evaluation, dynamic modelling and detailed equipment modelling in

A good simulation package is defined as one which consists of good numerical routines, property packages, property database, unit operations, optimization and sensitivity analysis capabilities Raman (1985:502).

A total of 53 chemical process simulators are recorded by Wikipedia (2012). To narrow this down to a handful of the most trusted simulators industry wise, a document, WinSim (2012) compared the leading process simulators in the industry.

The simulation software are WinSim DESIGN II, Hysys , Pro/II , ProMax, Aspen Plus and Chem CAD. WinSim (2012) reported that there are little differences between the simulation package software when it comes to obvious features such as component libraries, thermodynamic options and recycle convergence. Due to costs involved and availability of software the only option for this study is Aspen Plus. Since no direct advantages is present from other software Aspen Plus only needs to prove that it can accomplish the task at hand.

Aspen Plus is widely used by international companies in the chemical process industry for the past thirty years. Wide usage by many industries evolved Aspen Plus into being able to provide many inbuilt user operation models to cater for a wide range of their client basis. Since no simulation package can provide everything needed to the client basis, custom user models are available which can be used to build a specific unit operation model for the user's needs (Aspen Technology, 2009).

Due to the long period of development as well as the large client basis, Aspen Technology evolved into an experienced company which is able to deliver robust software. The Aspen Plus software can be applied to the simulation of diverse processes (Sinnott, 2005).

Aspen Plus features include but are not limited to the following (Aspen Technology, 2009; Aspen Technology, 2012):

- 30+ year proven track record of providing substantial economic benefits from conceptual design to engineering production
- Enables companies to rapidly design new processes, deliver new products to market s faster and optimize production
- World's largest database of pure component and phase equilibrium data for conventional chemicals, electrolytes, solids and polymers
- Regularly updated from U.S. National Institute of Standards and Technology
- Large database of experimental property and data parameters
- Custom property additions
- Up to 90 property methods and thermodynamic models available to choose from
- Many processes can be simulated out of the box
- Comprehensive library of unit operation models which addresses a wide range of solid, liquid and gas processing equipment
- Build custom libraries using Aspen Custom Modeller® or programming languages such as FORTRAN
- Can model a wide range of industrial processes such as power, chemicals, speciality chemical, polymers, metals and minerals
- Can simulate a wide range of special equipment for continuous batch and semi-batch processes
- Many workflow automation features such as linking to Microsoft Excel®
- Open environment to third party integration such as linkage to other widely used tools
- Offers the sequential modular approach as well as the equation oriented approach simulation approaches

- Analytical capabilities such as sensitivity analyses, optimization, constraint analysis and regression tools

It is clear that Aspen Plus is more than capable to handle most of the processes currently used in the world today. The variability of Aspen Plus makes it possible to add any operation models that are not included as standard models, as well as any required components. From Section 2.2 it is also clear that the software will need to simulate a hydrometallurgical process which makes use of electrolyte components. Aspen Plus is more than capable to simulate hydrometallurgical plants, with a total of 7 electrolyte property methods (Aspen Technology, 2009).

Thus in conclusion Aspen Plus will be used for the conceptual design and simulation of the BMR and BMR-NF processes.

2.3.2. ASPEN PLUS APPLICATIONS IN HYDROMETALLURGY

To verify if Aspen Plus is a good simulation package for hydrometallurgy (with focus on base metals), a literature survey is required on previous applications of Aspen Plus in a hydrometallurgical environment in context of base metals. Although literature in the simulation field of hydrometallurgical circuits is scarce, the sources as indicated in Table 2.2 were obtained where Aspen Plus was used to do either hydrometallurgical circuit simulations or to do solution chemistry calculations.

Table 2.2: Literature sources on hydrometallurgical Aspen Plus simulations/calculations

Source	Research
Casas *et al.* (2000)	Aqueous speciation of sulphuric acid and cupric sulphate solutions
Cifuentes *et al.* (2006)	Temperature dependence of the speciation of copper and iron in acidic electrolytes
Daoguang & Zhibao (2006)	Chemical modelling of nesquehonite solubility in Li, Na, K, NH_4, Mg, Cl and H_2O system
Yuan *et al. (*2010)	Measurement and modelling of solubility for calcium sulphate dehydrate and calcium hydroxide in NaOH/KOH solutions
Dry & Harris (2010)	Process simulation studies on the extraction of nickel from nickelliferous pyrrhotite
Dry (2008)	Aspects of modelling a complex chloride leach circuit for nickel and copper

Source	Research
Dry (2009)	Process simulation of water and carbonate balances in an alkaline uranium extraction circuit
Dry (2013)	Early evaluation of metal extraction projects

Authors such as Casas *et al.* (2000), Cifuentes *et al.* (2006), Daoguang & Zhibao (2006) and Yuan *et al.* (2010) used Aspen Plus to either provide solution chemistry data, or to do the calculations. The calculations were done in Aspen Plus using the Pitzer's model which is a thermo-chemical routine. All of the authors were able to successfully model solution chemistry, and where Aspen Plus gave deviated results from experimental data such as in the study done by Daoguang & Zhibao (2006), the parameters were easily adjusted to give the correct results.

Literature where process simulation was done was not available in published articles, and thus sources from papers in the public domain were obtained. Dry & Harris (2005), Dry (2008), Dry (2006) and Dry (2013) successfully modelled complicated hydrometallurgical circuits using Aspen plus™. The study done by Dry & Harris (2005) and Dry (2008) are in particular interest since the modelling are done on a base metals system containing nickel and copper, which is similar to the RBMR case.

Dry & Harris (2005) modelled four circuits, two using fairly conventional sulphate chemistry and two using novel chloride chemistry to extract nickel from nickelliferous pyrrhotite. The reagent and utility consumptions were extracted from the simulation and used with estimated unit prices to calculate the operating expenditures of each circuit. Thus the circuits were successfully compared from an economic point of view.

Dry (2008) modelled a hydrometallurgical process where high concentrations of chloride solution is used to hydrolyse ferrous to hematite. Sulphuric acid is used for the oxidative and non-oxidative leaching of the minerals. The process was successfully modelled, showing that the circuit is self-efficient in terms of energy, and that the circuit will work without combustion of fossil fuels.

Dry (2013) showed how computational methods can be used to evaluate new metal extraction projects before a substantial amount of time and money is spent on detailed engineering studies. Two detailed nickel leaching process models were constructed: (1) atmospheric acid leaching process and (2) a high pressure acid leach process. The circuits were successfully modelled with detailed operating expenditure analysis.

From the literature investigate it can be seen that Aspen Plus was used successfully in the modelling of hydrometallurgical circuits, as well as solution chemistry prediction. Thus Aspen Plus is a valuable tool for the simulation of the RBMR.

2.3.3. SELECTION OF PROPERTY METHOD

To select a property method, the system in question needs to be defined by specifying its components and operating conditions. The process type and definition has already been done in Section 2.2, and it was concluded that the process makes use of solid minerals such as nickel and copper sulphides, dissolved metals, liquids such as sulphuric acid and water. Gasses present are oxygen, nitrogen and hydrogen. The maximum temperature and pressures experienced are 155°C and 688kPa.

From the information in Section 2.2, it was determined that the system is a hydrometallurgical system where electrolytes play a big role in the chemistry. It was also found that the system is mostly in liquid form. It is already obvious that strong non-ideality in the liquids might be present due to high temperatures and large amounts of different electrolytes. According to Christian (2003) solution chemistry is mainly a function of equilibrium thermodynamics.

To make the selection of the property method more systematic, methods of selecting property methods were used as found in Seider *et al.* (2004). The property selection algorithms are the Bob Seader method and the Eric Carlson method.

The property selection algorithms, with the decisions taken (the decided paths are in bold), is given in Figure 2.2 for Eric Carlson and Figure 2.3 for Bob Seader.

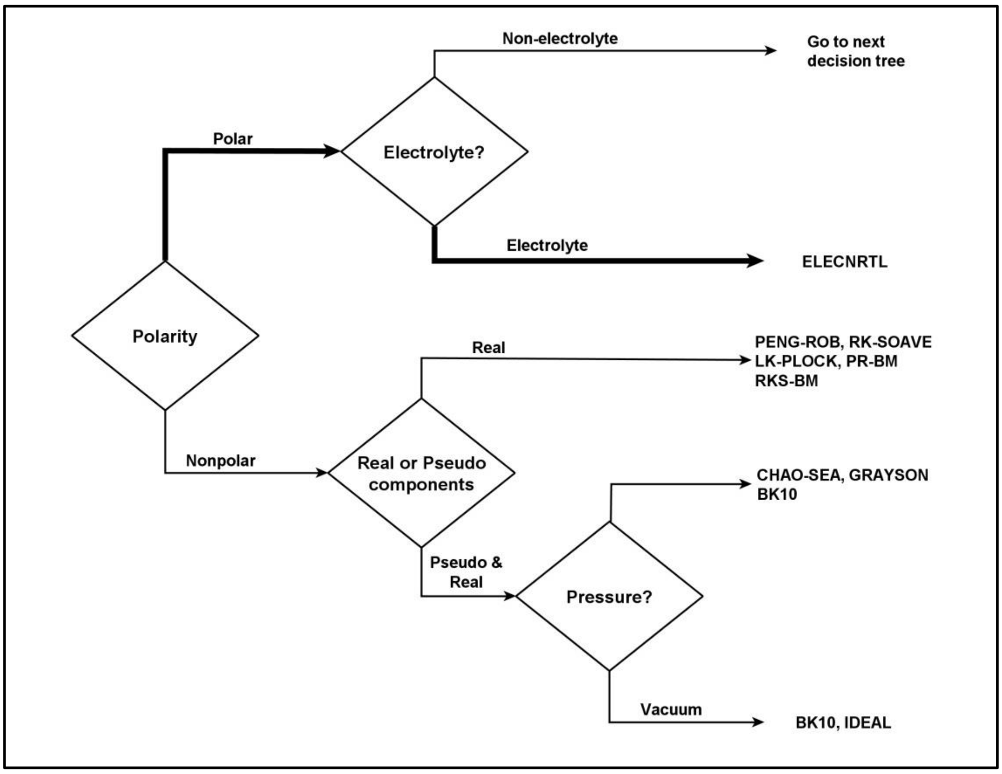

Figure 2.2: Eric Carlson property selection algorithm

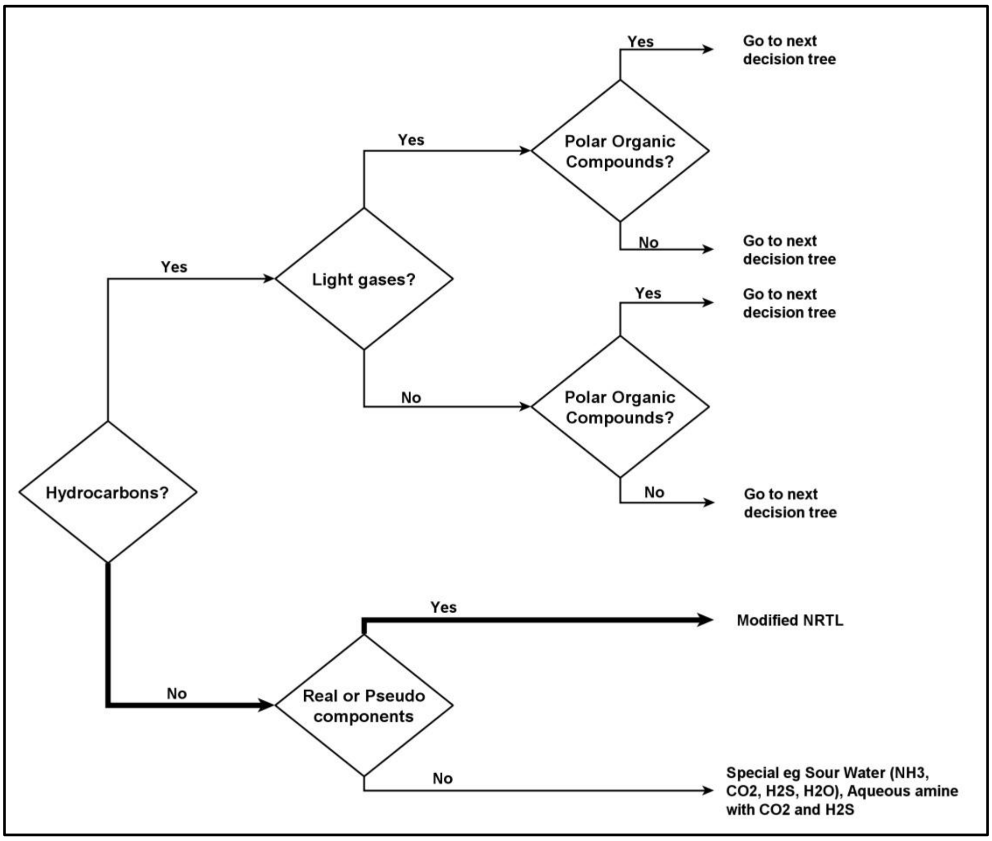

Figure 2.3: Bob Seader property method selection algorithm

The Eric Carlson algorithm recommended the ELECNRTL method whereas the Bob Seader algorithm recommended the Modified NRTL method.

According to Aspen Technology (2010) the ELECNRTL property method is an activity coefficient model based property method, which is exactly what is required due to the equilibrium nature of hydrometallurgical solutions. The available activity coefficient calculation methods in Aspen Plus include the Non-Random-Two-Liquid (NRTL), UNIQUAC and WILSON among others. The activity coefficient calculation method used for ELECNRTL property method is the Electrolyte NRTL method, which best describes inorganic components in a solution.

The ELECNRTL model is a combination property method, as it calculates the vapour phase with the Redlich-Kwong equation of state. Thus the model provides the best of both worlds, where the liquid properties are calculated with electrolyte NRTL and the gas/vapour properties are calculated with an equation of state. It should also be considered that solids will be present in the system. According to Aspen Technology (2009) the ELECNRTL model provides for the solid thermodynamics via the Barin equations.

According to Chen & Mathias (2002) the primary thermodynamic model used for electrolytes today is the electrolyte NRTL model. Thus Chen & Mathias (2002) justifies the use of ELECNRTL.

In conclusion the ELECNRTL model was chosen, due to the information gathered from the literature study. It was found that the ELECNRTL model can provide for strong non-ideal liquids, vapour phase, as well as solid thermodynamic calculations. Chen & Mathias (2002), which was written by leaders in the industry, also falls in line with the advice given by the previous sources. All these considerations make the use of ELECNRTL the most appropriate property method for the simulation of the RBMR.

2.4. CONCLUDING REMARKS

In this chapter the design methodology with a conceptual framework, as well as the characteristics and process battery limits of the simulation of the RBMR and RBMR-NF processes was discussed. Afterwards a simulation package was chosen (Aspen Plus) and verified by a literature study done on hydrometallurgical application where Aspen Plus was used. Finally a property method was selected to simulate the RBMR and RBMR-NF with.

3. SIMULATION OF RBMR

Overview

In this chapter the RBMR process will be described in detail as well as simulated in Aspen Plus. Section 3.1 gives an introduction to the RBMR process. The following two sections are the main sections, namely the RBMR process description (Section 3.2) and the simulation of the RBMR (Section 3.3). The process description of the RBMR focusses on the three sections of the process, namely the leaching circuit (Section 3.2.1), copper circuit (Section 3.2.2) and nickel circuit (Section 3.2.3). The simulation of the RBMR describes the individual sections of the copper, nickel and leaching circuit with the unit operations, methods and parameters used to build the simulation. The next section, Section 3.4, is where the RBMR simulation is validated by comparing the simulation results with Anglo American (2012) data. Finally, a conclusion for this Chapter is given in Section 3.5

3.1. INTRODUCTION

The RBMR process is well reported in public literature (Halton, 1990; Hofirek and Kerfoot, 1992; Hofirek and Nofal, 1995; Bryson *et al.*, 2008).

The RBMR production rate changed dramatically over the past 18 years according to literature. In 1994 the BMR was upgraded to produce 21 000 tons per annum of nickel, from the production rate of 19 000 tons per annum. The upgrades that took place are reported in Hofirek & Nofal (1995). The main changes were in the leaching circuit (leaching circuit described in Section 3.2). Another expansion took place in 2011, whereas the planning of that expansion was executed since 2006. The expansion increased the nickel output to 33000 tons per annum of nickel, and the major changes are in the leaching circuit with the changes reported in Bryson *et al.* (2008). Although the RBMR was expanded twice since 1990, the information such as the chemistry of the leaching circuit and the process of the nickel and copper circuits are still valid due to the same concepts being used.

To obtain more recent plant data and information, several visits, meetings and discussions were conducted at Anglo American RBMR (Anglo American, 2012). From these discussions the public literature was verified and extra information such as mass and energy balances and process design criteria were provided. A presentation was also presented by RBMR staff where more information about the plant was made available (Taute & George, 2010).

3.2. PROCESS DESCRIPTION

To describe the RBMR process, a holistic method of process description is used. A block diagram (Figure 3.1) depicting the main circuits and sections are coupled with Table 3.1 to act as a reference to the descriptions of the different sections in the process as well as the chemistry and operating conditions of the equipment within the section.

The relevant appendixes to this section are Appendix A, where the compositions of the main feeds (raw materials and reagents) to the RBMR are given, and Appendix B, where the chemistry and equipment of the RBMR process is described.

Table 3.1: RBMR process description, chemistry and equipment

Process Section	Function	Description	Chemistry	Equipment
Leaching Circuit	Selective leaching of nickel and copper in the matte takes place	3.2.1		
Copper Removal	Removal of copper from leach solution as well as leaching of fast reacting nickel minerals	3.2.1.1	B2.1	B2.2
Nickel atmospheric leach	Selective leaching of fast reacting nickel minerals	3.2.1.2	B3.1	B3.2
Pressure Iron Removal	Removal of iron from solution	3.2.1.3	B4.1	B4.2
Nickel non-oxidizing leach	Selective leaching of nickel from slow reacting nickel minerals	3.2.1.4	B5.1	B5.2
Copper pressure leach	Leaching of slow reacting copper minerals as well as remaining nickel minerals	3.2.1.5	B6.1	B6.2
Copper Circuit	Copper cathode and acid production	3.2.2		
Se/Te removal	Removal of selenium and tellurium from copper rich solution	3.2.2.1	B7.1	B7.2
Copper electrowinning	Production of copper electrodes and recycling of produced acid to leaching circuit	3.2.2.2	B8.1	B8.2
Nickel Circuit	Nickel cathode production and water, sodium and sulphur removal	3.2.3		
Lead removal	Removal of lead from nickel rich solution	3.2.3.1	B9.1	B9.2
Cobalt removal	Removal of cobalt from nickel rich solution	3.2.3.2	B10.1	B10.2
Nickel electrowinning	Production of nickel cathodes and recycling of acid to leaching circuit	3.2.3.3	B11.1	B11.2
Sulphur removal	Neutralization of acid and removal of excess sulphur, sodium and water from the process	3.2.3.4	B12.1	B12.2

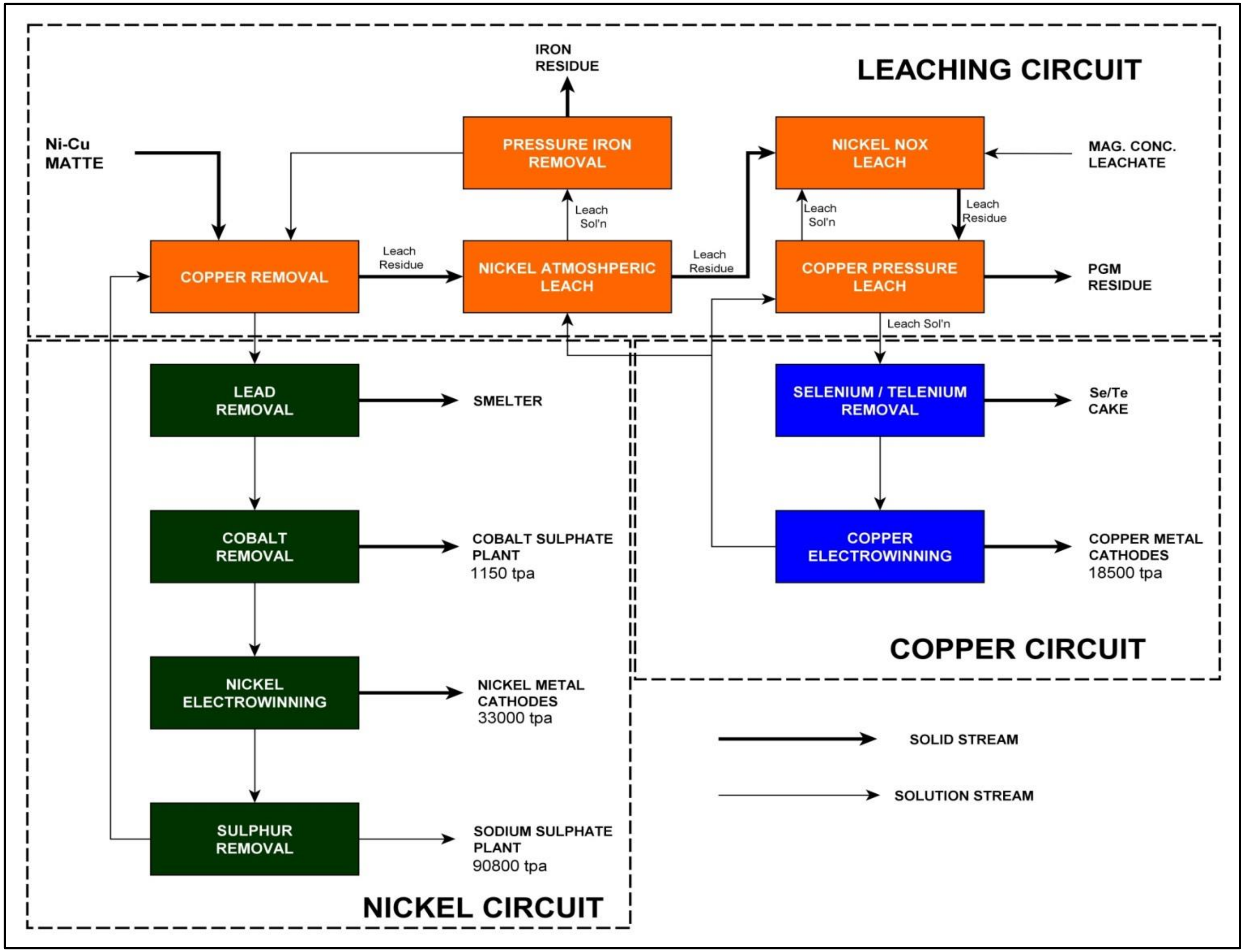

Figure 3.1: RBMR Block Diagram

3.2.1. LEACHING CIRCUIT

The main purpose of the leaching circuit is to selectively dissolve nickel, copper and cobalt from nickel-copper-matte (NCM). The leaching circuit consist out of five leaching stages, namely (1) copper removal, (2) nickel atmospheric leach, (3) pressure iron removal, (4) nickel non-oxidizing leach and (5) copper pressure leach.

1. The copper removal stage removes copper and iron from the primary leach solution which is in contact with the NCM.

2. The nickel atmospheric leach selectively dissolves nickel and iron in the presence of oxygen. The dissolved nickel and iron is introduced into the pressure iron removal section whereas the residue stream is sent to the nickel non oxidizing pressure leach stage.

3. The pressure iron removal is a pressure process where iron is precipitated from the solution in the presence of oxygen. The product solution is recycled back to the copper removal section.

4. The nickel non oxidizing leach stage dissolves the remaining nickel by means of copper metathesis inside an autoclave. Oxygen is absent from this stage. The product solution is recycled back to the nickel atmospheric leach stage whereas the product residue is sent to the copper pressure leach stage.

5. The copper pressure leach stage, which is the last stage of the leaching circuit, dissolves the copper together with any remaining nickel as well as other base metals inside an autoclave in the presence of oxygen.

To better understand the leaching characteristics and chemistry of the leaching circuit, a brief literature study on the reactivity of the minerals leached in the leaching circuit can be found in Appendix B.1.2.

3.2.1.1. Copper removal leach

The copper removal leach ensures that all iron and copper are removed - Iron and copper concentrations of less than 10 - 20 mg/l is adequate. Although the objective of the atmospheric leach is to dissolve copper and iron, approximately 10 – 15% of nickel is also dissolved, which is sent directly to the Nickel Circuit after liquid/solid separation (Bryson *et al.*, 2008; Hofirek & Nofal, 1995). The process flow of the copper removal leach is given in Figure 3.2.

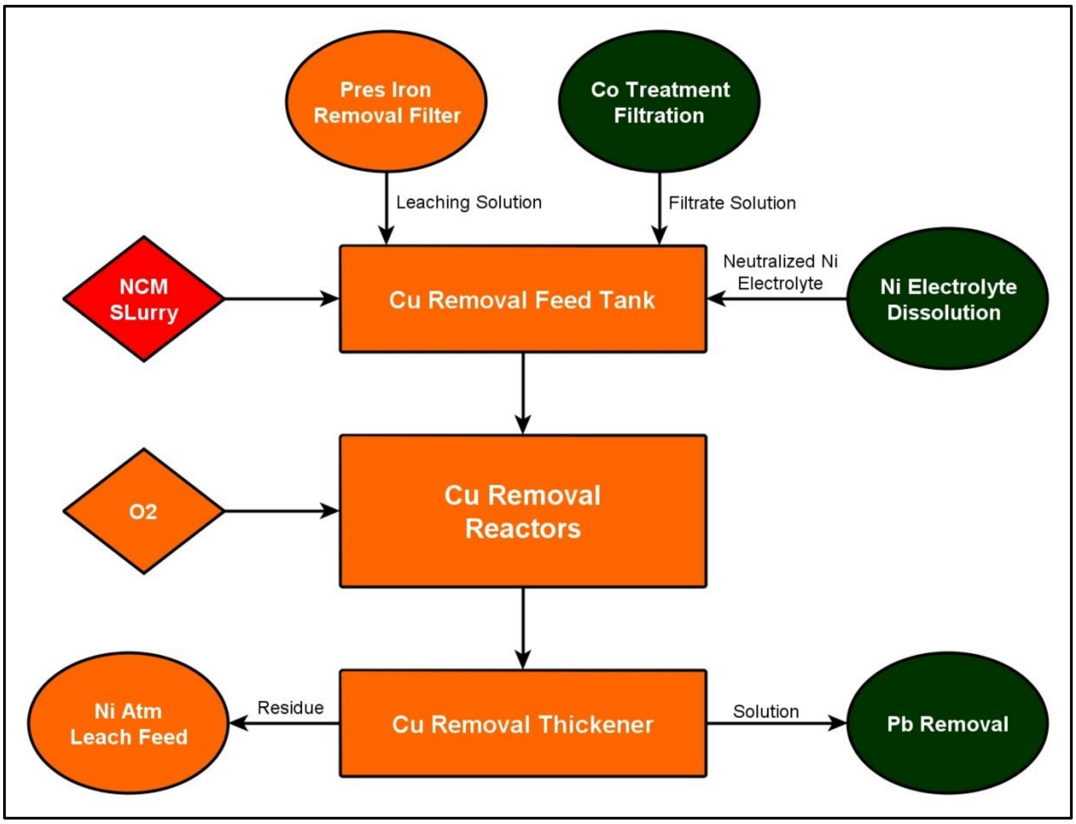

Figure 3.2: Copper Removal Leach Process

Fresh NCM is mixed with the product solution from the pressure iron removal section, the filtrate from the cobalt treatment plant as well as neutralized spent nickel electrolyte from the sulphur removal section. The resulting blend has a pH of approximately 2.5 (Hofirek & Kerfoot, 1992).

The copper removal leach is composed of four reactors in series, with an approximate total residence time of 12 hours. Each reactor is mechanically agitated with a system of three impellers on one shaft, as well as aerated with pure oxygen. The temperature within these reactors is operated at 75 - 80°C. The pH of the final product is approximately 6.4 to 6.6 depending on the control of the feed mixtures (Hofirek & Nofal, 1995; Anglo American, 2012).

The discharge from the reactors is introduced into a thickener, where the solids are separated from the liquids. The solution (overflow) is sent to the lead removal section (nickel circuit), whereas the residue (underflow) is sent to the nickel atmospheric leach feed unit.

3.2.1.2. Nickel Atmospheric Leach

The objective of the nickel atmospheric leach stage is to extract nickel and iron, precipitate incoming copper as copper sulphides, retain the iron in the solution as ferrous, and produce a product liquor containing 10 g/l Cu and 15 g/l H_2SO_4. The leaching is conducted at atmospheric conditions (Anglo American, 2012). The nickel atmospheric leach process is given in Figure 3.3.

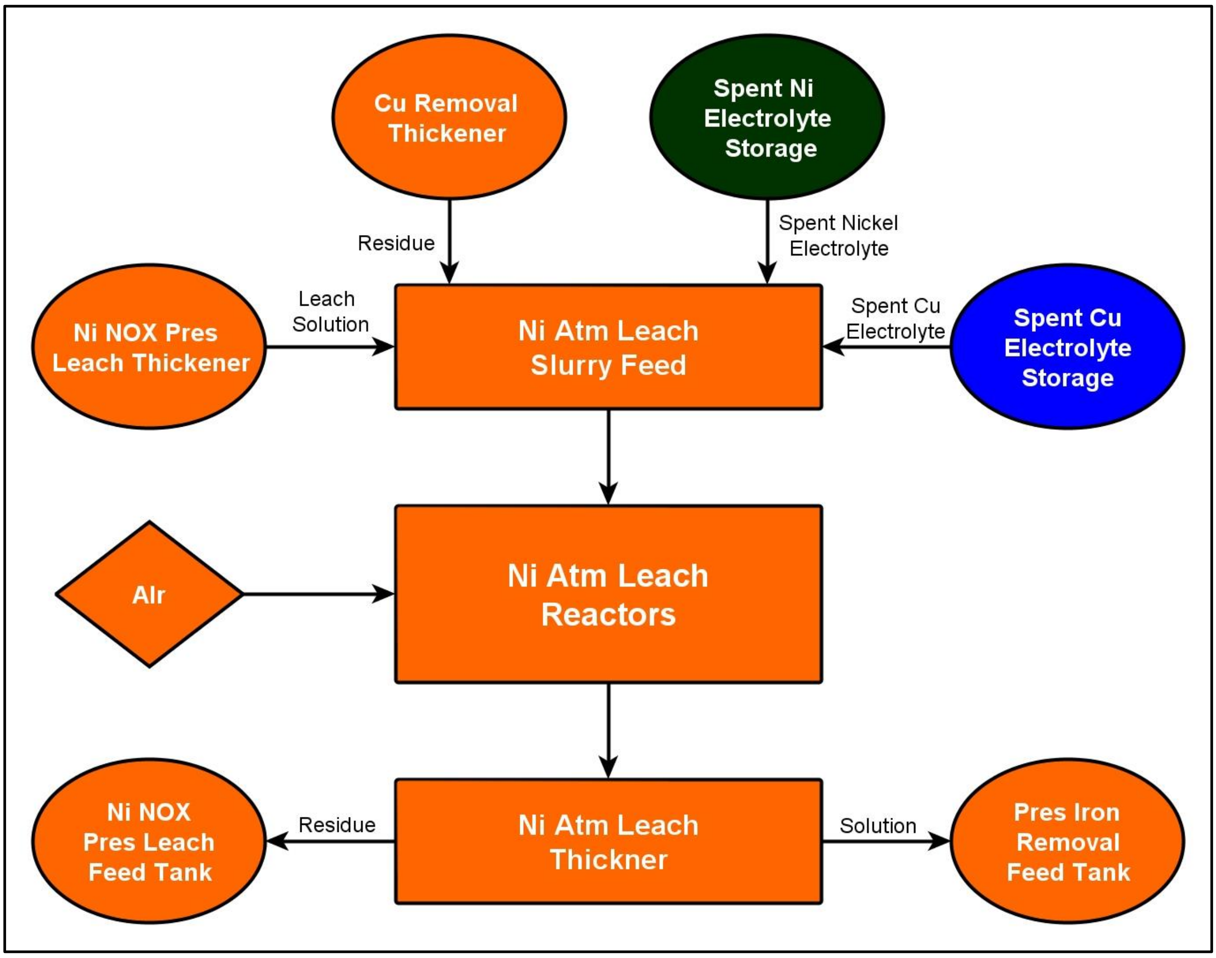

Figure 3.3: Nickel Atmospheric Leach Section

Residue from the copper removal stage is mixed with nickel spent electrolyte, copper spent electrolyte and leach solution from the nickel non-oxidizing leach stage. The oxidant used is air, although the entire leaching period is not operated under oxidative conditions. A part of the leaching is done in an oxygen free environment to ensure that metathesis reactions take place.

A series of stirring reactors is used, which operates at a temperature between 80 - 95°C (Anglo American, 2012).

The discharge from the reactors is sent to a thickener to separate the solution from the solids. The solution (overflow) is sent to the pressure iron removal stage whereas the residue (underflow) is sent to the nickel non oxidizing pressure leach stage.

3.2.1.3. Pressure Iron Removal

The main objective of the pressure iron removal section is to remove all of the iron introduced by the matte and the magnetic PGM concentrate leach solution. The iron from the matte is mainly dissolved in the nickel atmospheric leach, nickel non-oxidizing leach and the copper pressure leach sections of the leaching circuit. The pressure iron removal process is given in Figure 3.4.

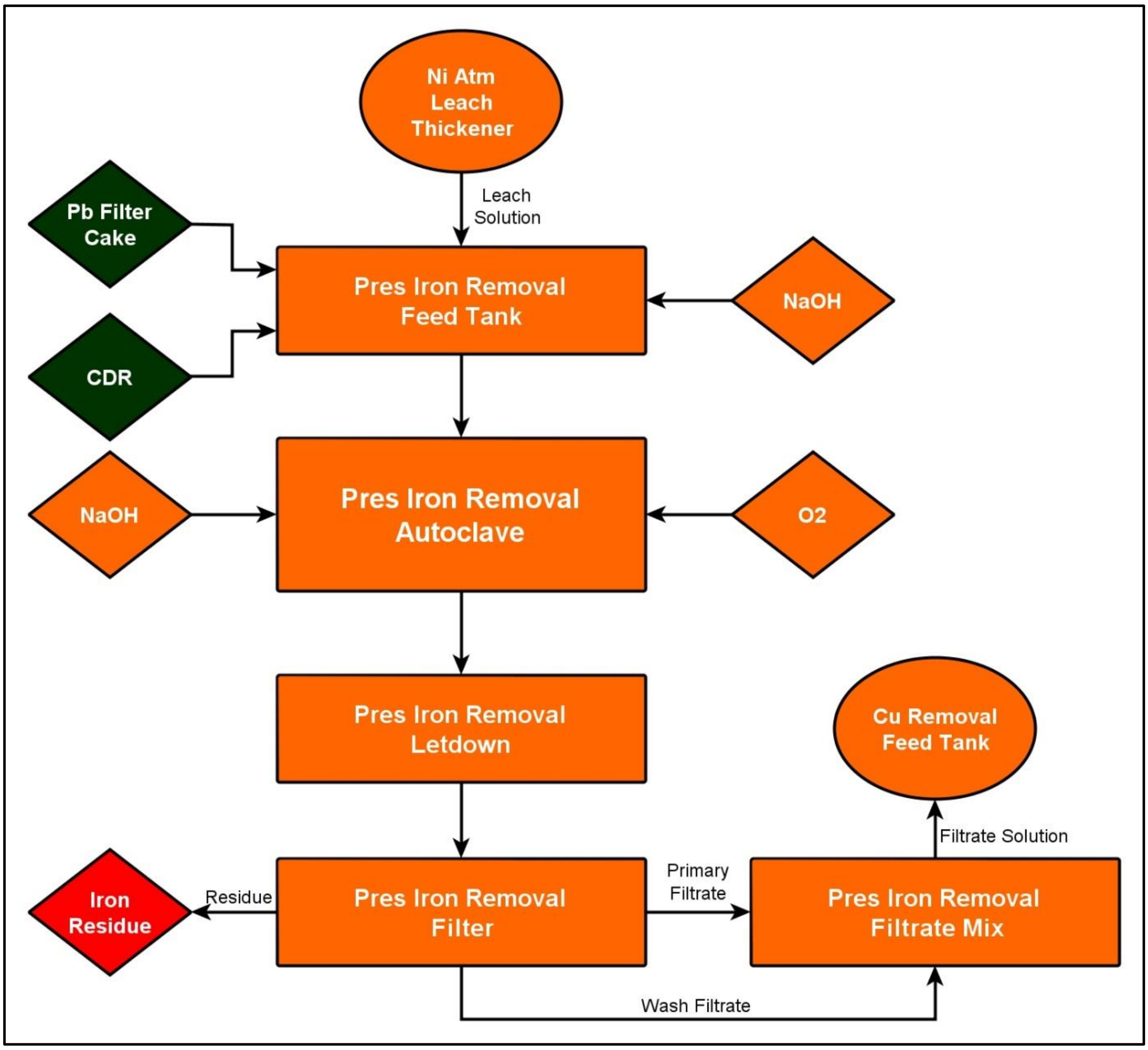

Figure 3.4: Pressure Iron Removal Section

Leach solution from the nickel atmospheric leach thickener, cobalt dissolution residue (from the cobalt plant), sodium hydroxide and filter cake from the lead removal section is introduced into a feed tank. The mixed solution is then introduced into the pressure iron removal autoclave, which is operated at a pressure of 6 bar gauge, and a temperature between 140 - 150°C (Anglo American, 2012).

The discharge from the autoclave is de-pressurized, and then directed to a filter. The filtrate and the wash filtrate from the filter is mixed, and sent to the copper removal section.

3.2.1.4. Nickel Non-Oxidizing Leach

The primary objective of the nickel non-oxidizing leach is to dissolve additional nickel and iron by means of metathesis with copper ions. The process conditions are at elevated temperatures and pressures under a non-oxidizing environment. The nickel non-oxidizing leach process is illustrated in Figure 3.5.

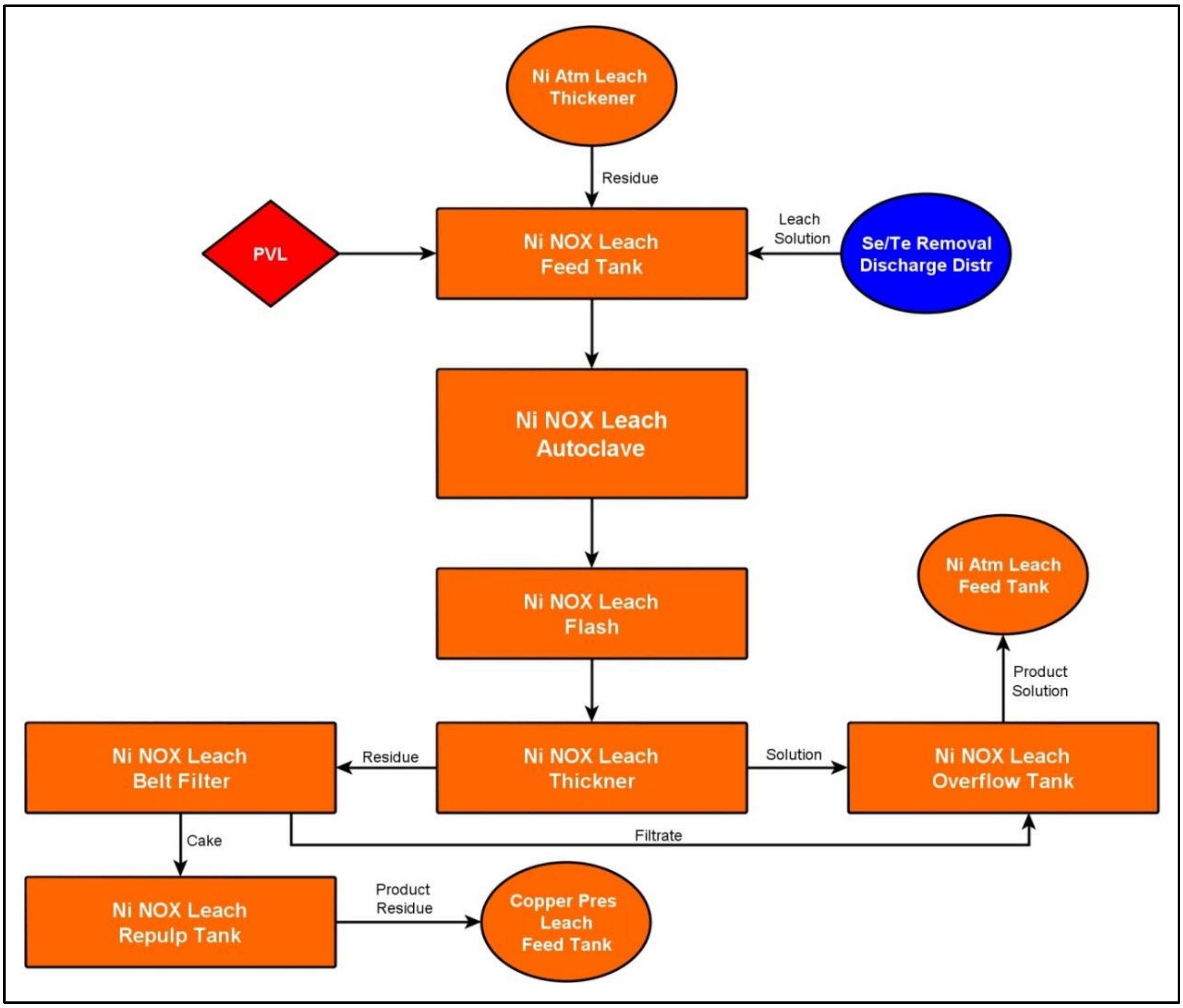

Figure 3.5: Nickel Non-Oxidizing Leach Section

The residue (thickener underflow) from the nickel atmospheric leach, liquor from the PGM plant as well as leach solution from the selenium/tellurium removal stage is introduced in a feed tank. The mixed slurry is then sent to an autoclave, which operates at a pressure of 6 bar gauge and a temperature of 155°C (Anglo American, 2012).

The discharge from the autoclave is flashed to reduce the pressure to atmospheric, and sent to a thickener where the solids are separated from the solution. The separated solids are at a solids concentration of approximately 45%, and thus the solids need to be filtered in a belt filter. The solution from the thickener and filter is sent to an overflow tank, and recycled back to the nickel atmospheric leach feed tank. The cake from the filter is re-pulped and directed to the copper pressure leach section.

It is important for the residue/cake to contain Cu:Ni ratio in the range of 6:1 to 8:1 to prevent excessive acid in the nickel atmospheric leach stage (Bryson *et al.*, 2006).

3.2.1.5. Copper Pressure Leach

In the copper pressure leach the nickel non-oxidizing leach residue is leached under oxidizing conditions at elevated temperatures. The main objectives of the copper pressure leach is to leach the copper and the remaining nickel in the nickel non-oxidizing pressure residue and to produce a platinum group metals containing residue that is suitable for further upgrading or treatment elsewhere. The copper pressure leach process is given by Figure 3.6.

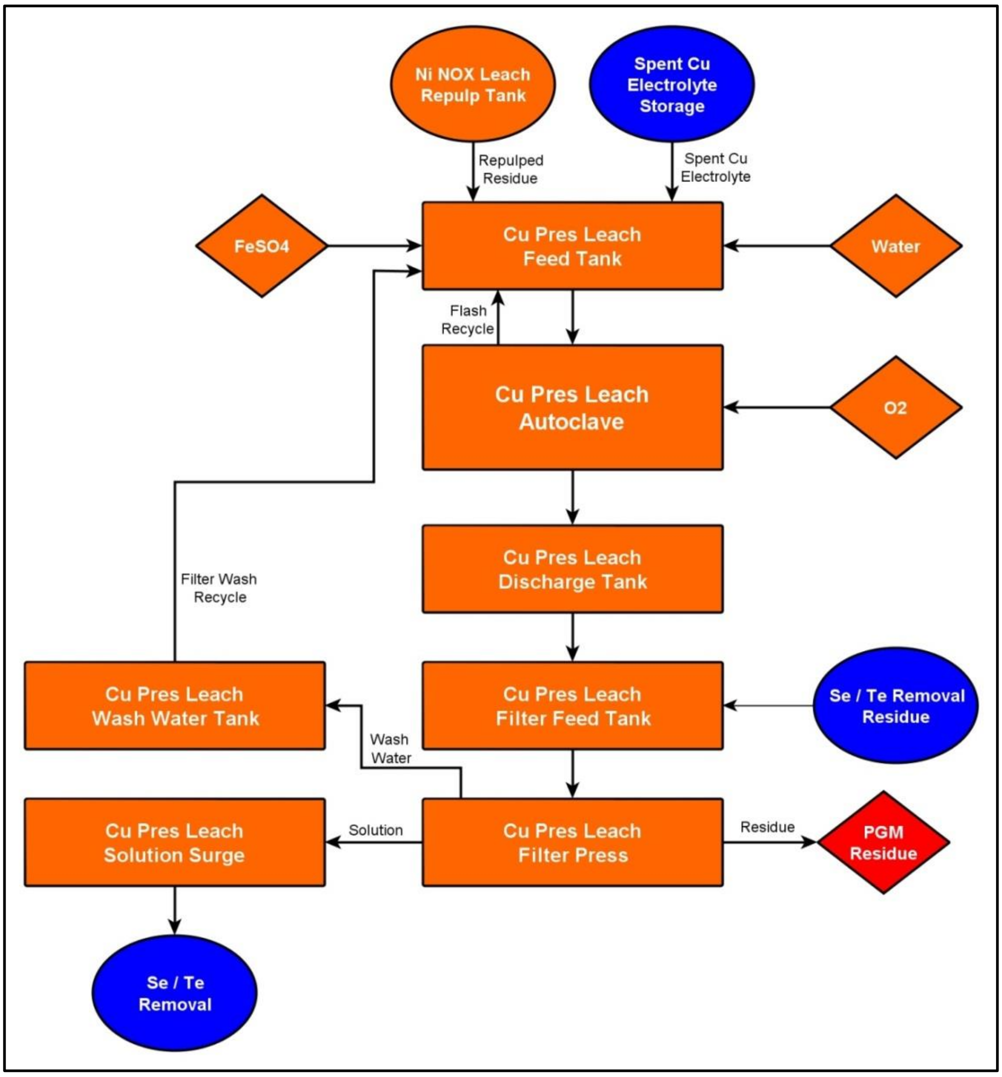

Figure 3.6: Copper Pressure Leach Section

Iron sulphate, residue from the nickel non-oxidizing stage, spent copper electrolyte and water is mixed in a feed tank and directed to the autoclave which operates at a temperature of 140°C and a pressure of 6 bar gauge. The autoclave has a cooling coil in compartment 2 and 3 to control the temperature of the reactor. A flash recycle is also present after compartment 1 to control the temperature in compartment 1. (Anglo American, 2012).

The discharge from the autoclave is filtered and washed and the residue is sent to the PGM plant whereas the solution is sent to the Se / Te removal section.

3.2.2. COPPER CIRCUIT

The main purpose of the copper circuit is to produce copper cathodes as well as acid that are recycled to the leaching circuit. The copper circuit consist out of a (1) selenium/tellurium removal section as well as a (2) copper electrowinning section.

1. The selenium/tellurium removal stage selectively removes selenium and tellurium from the copper rich leach solution. A precipitation process involving sodium sulphite in a pipeline reactor is used to precipitate the unwanted minerals from the solution

2. After the selenium/tellurium is removed the solution is sent to the copper electrowinning section where dissolved copper is plated on metal cathodes to produce copper cathodes. The acid rich copper spent electrolyte is then recycled to the nickel atmospheric leach and copper pressure leach to supply the required acid for the dissolution of the base metal species.

3.2.2.1. Selenium/Tellurium Removal

The filtered solution from the secondary pressure leach requires Se/Te removal due to high quantities of the impurities in the solution, which were dissolved in the harsh conditions of the copper pressure leach autoclave. During this purification step, a significant portion of the dissolved PGMs may also be precipitated. The Se/Te removal process is given in Figure 3.7:

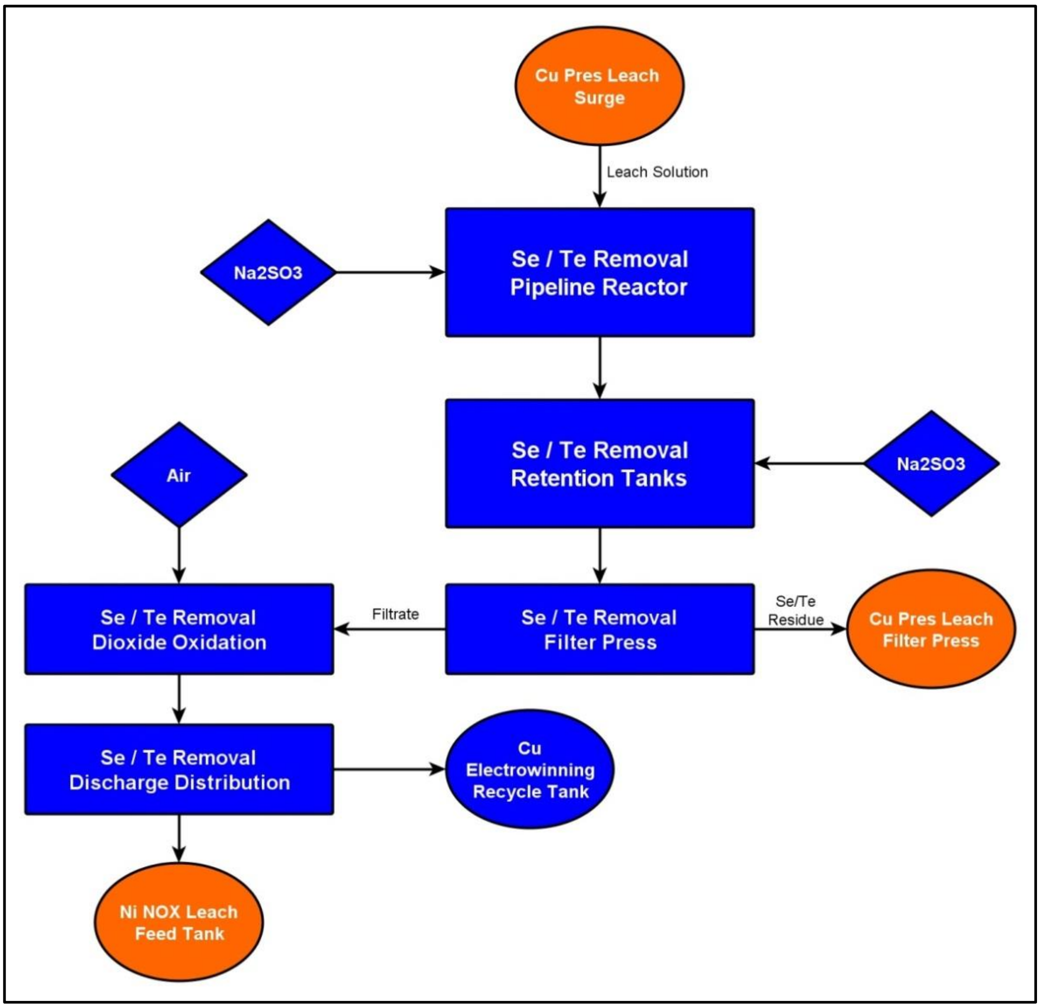

Figure 3.7: Selenium/Tellurium Removal Section

Selenium is removed from the solution by adding $NaSO_3$, which in turn is produced with NaOH and SO_2 on-site. Pure SO_2 can also be used to achieve the same results. The selenium removal process operates at a temperature of 90°C (Anglo American, 2012).

Copper pressure leach solution and Na_2SO_3 are added to a pipe reactor, where most of the selenium/tellurium is removed. The discharge is sent to retention tanks, where further selenium/tellurium is removed. The final product solution contains 10mg/l selenium whereas tellurium is completely removed at below 0.2mg/l. The solution is then sent to a filter press, where the solids and liquids are separated. The liquids are oxidized and split to feed the electrowinning as well as the nickel non-oxidizing leach sections (Bryson *et al.*, 2008).

The residue from the filter is sent to the copper pressure leach filter press where it is removed with the remaining impurities.

3.2.2.2. Copper electrowinning

The main goal of the copper electrowinning is to produce pure copper cathodes with maximum energy efficiency. The copper electrowinning process is detailed in Figure 3.8.

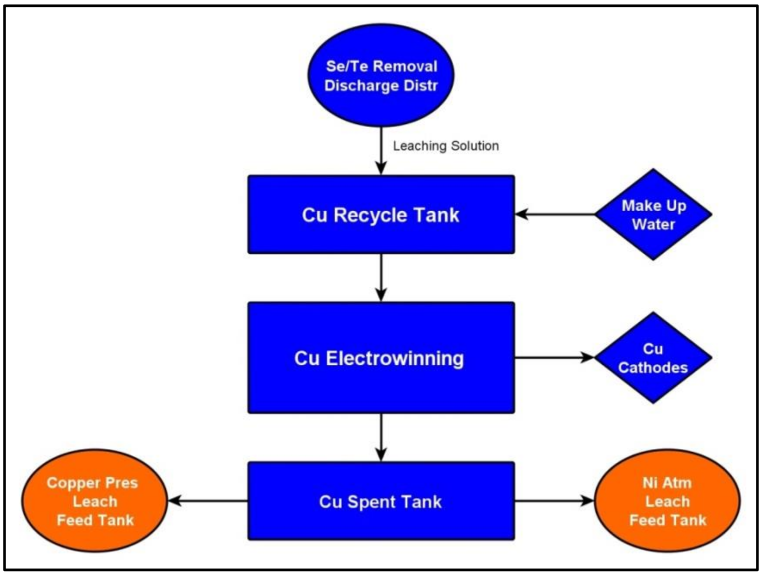

Figure 3.8: Copper Electrowinning Section

The discharge solution from the selenium/tellurium removal is cooled in a plate heat exchanger to a temperature of 60°C (to prevent acid mist) before entering the copper electrowinning section. The anodes used are made from lead whereas the cathodes are copper (Anglo American, 2012).

Due to the unique electrochemical voltage of copper, no other metals are plated on the copper cathodes, although high iron concentrations can result in a loss of current efficiency which causes a reduction in current efficiency and other harmful scenarios such as dissolution of copper straps which holds the cathodes in suspension.

The spent copper electrolyte is recycled to the copper pressure leach stage as well as the nickel atmospheric leach stage.

3.2.3. NICKEL CIRCUIT

The main purpose of the nickel circuit is to produce nickel cathodes as well as remove excess sulphur, sodium and water from the process. The nickel circuit consist out of (1) a lead removal section, (2) a cobalt removal section, (3) a nickel electrowinning section as well as (4) a sulphur removal section.

1. The copper removal product leach solution is rich in nickel, but is contaminated with lead and is processed in the lead removal section to remove the lead. The lead is selectively removed from the solution by the addition of barium hydroxide to precipitate the lead out of the solution.

2. The lead free solution is then processed in a cobalt removal section, where nickelic, a chemical produced in-house is used to precipitate cobalt out of the solution.

3. The cobalt and lead free nickel solution is then fed to the nickel electrowinning section where nickel cathodes are produced by means of electrowinning. The spent nickel electrolyte which is rich in acid is then recycled to the leaching circuit and the remaining solution is recycled to the sulphur removal section.

4. The sulphur removal section neutralizes the excess acid, by addition of caustic soda. The excessive sodium, water and sulphur are then removed from the process, where the resulting acid-free nickel solution is recycled to the nickel and leaching section of the process.

3.2.3.1. Lead removal

In the electrochemical series, nickel has an electro potential of -0.26V, thus it is required to remove other elements with negative electro potentials such as lead (-0.13V) and cobalt (-0.28V). If not removed the elements will cause problems in the electrorefining process of nickel (Murdoch University, 2006).

Other impurities such as manganese and zinc are also problematic but most of them are removed with the lead/cobalt removal steps.

Lead is present in the oxidized form of PbS, which was introduced into the process by the Ni-Cu matte. The lead anodes in the nickel and copper electrowinning are also a source of lead due to the slow dissolution of the lead anodes. Thus the main objective is to reduce the lead concentration from 5 – 15mg/l to < 1mg/l (Taute & George, 2010).

The lead removal process is illustrated in Figure 3.9.

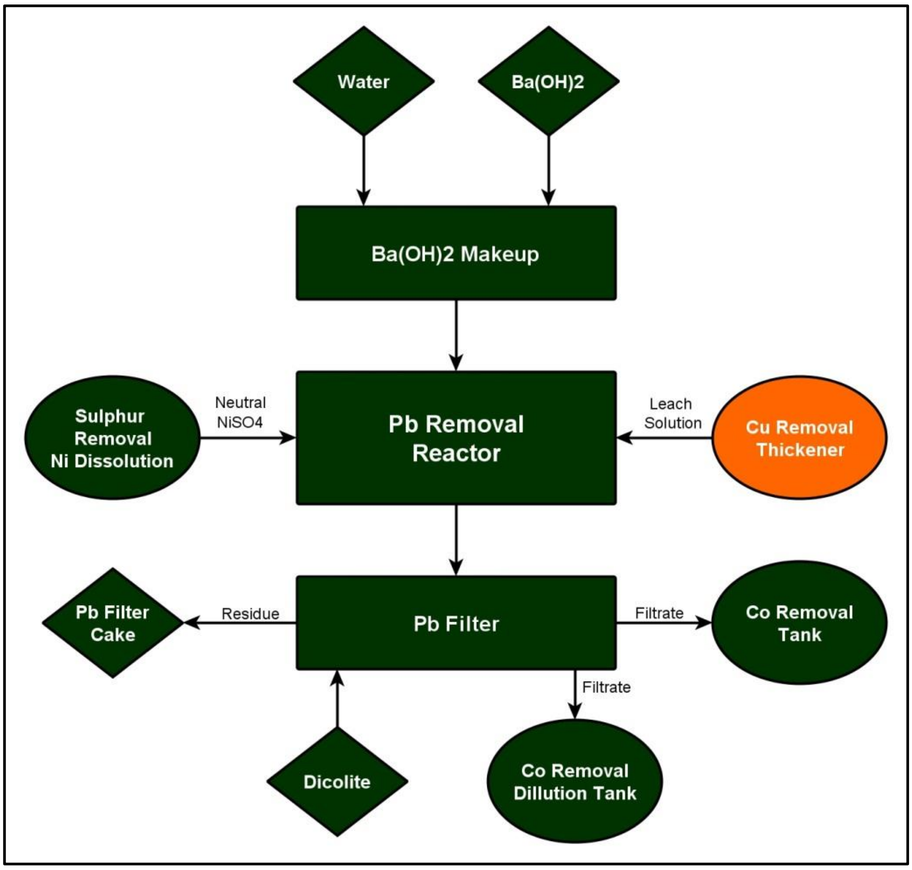

Figure 3.9: Lead Removal Section

To remove the lead, $Ba(OH)_2$ is injected into the solution (solution is made up of sulphur removal neutralized nickel solution and copper removal leach solution) in pipe reactors where the lead is then immediately precipitated in the form of $BaSO_4.PbSO_4$.

The cake from the filtration section containing lead and other trace metals are sent to the Waterval smelter, where it is disposed of as a waste product in the smelter slag.

3.2.3.2. Cobalt removal

Cobalt sulphate is a valuable commodity and thus it is important to recover as much cobalt as possible. Thus the main objective is to selectively remove cobalt as efficiently as possible. The cobalt removal process is given by Figure 3.10.

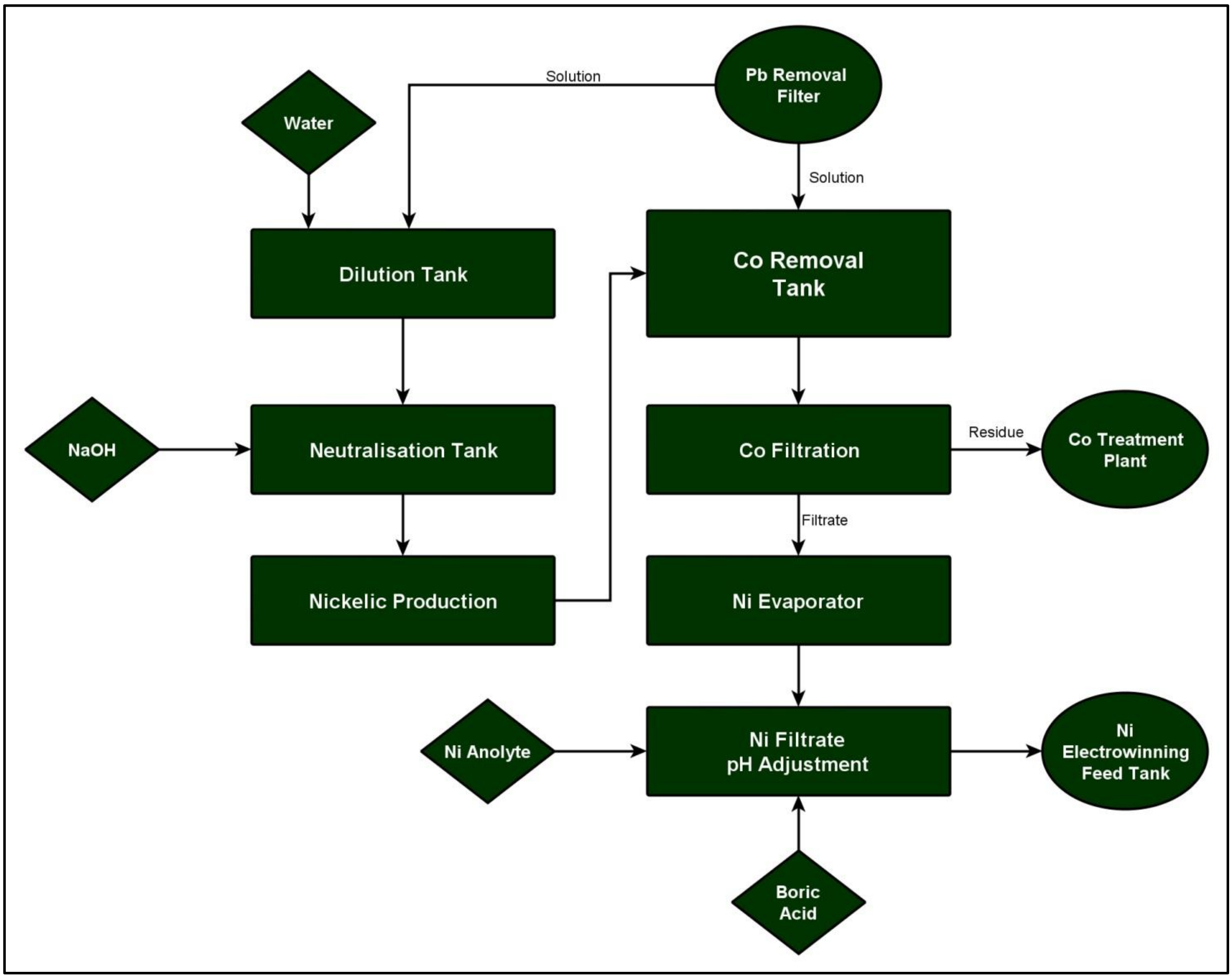

Figure 3.10: Cobalt Removal Section

To accomplish the removal of cobalt, a process is used which takes advantage of the differences in stability of the oxidised hydroxides of cobalt and nickel in the pH range of 5.6 – 5.7. Four cobalt precipitation reactors are online which operates at a temperature of 80°C (Taute & George, 2010).

$Ni(OH)_3$, which is not commercially available, is produced in-house in the nickel electrowinning tank house. This unique chemical has great oxidation abilities and is used to oxidize the cobalt as well as other available impurities such as Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}. $Ni(OH)_3$ is produced electrolytically by making use of a fraction of the incoming lead free solution stream rich in nickel as well as a small quantities of caustic soda.

$Ni(OH)_3$ is reacted with the nickel solution, and filtered to separate the cake from the solution. The cake is sent to the cobalt treatment plant where the process of cobalt refining continues. Any remaining $Ni(OH)_2$ is dissolved in a cobalt treatment reactor using spent nickel electrolyte. The reactor operates at pH of 3.2 and temperature of 75°C (Taute & George, 2010).

The solution is treated in an evaporator to remove excess water, and spent nickel electrolyte is further used to correct the pH of the solution. This is done to ensure the correct pH and nickel concentration for the nickel electrowinning process.

3.2.3.3. Nickel Electrowinning

The nickel electrowinning stage reduces Ni^{2+}(aq) to Ni(s) with the use of electricity. Lead anodes and nickel cathodes are used. The nickel electrowinning process is illustrated in Figure 3.11.

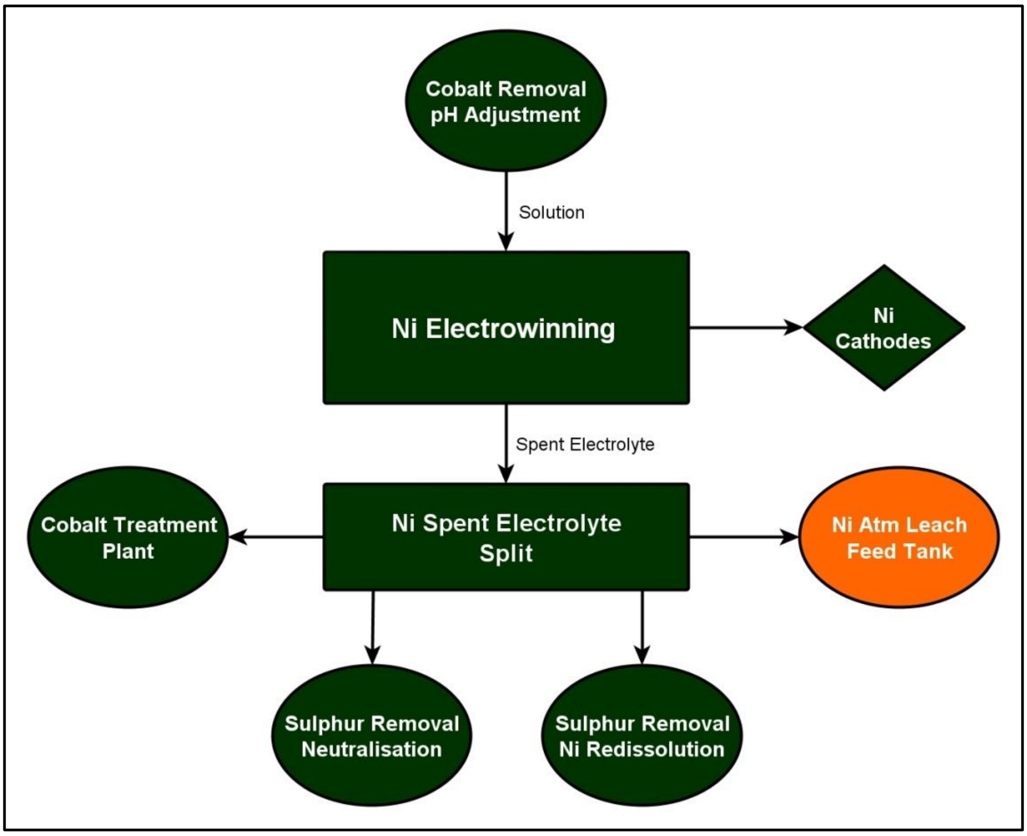

Figure 3.11: Nickel Electrowinning Section

Solution from the pH adjustment section is electrowon, and the product is nickel cathodes and spent nickel electrolyte. The spent nickel electrolyte is directed to the Leaching Circuit (nickel atmospheric leach), the sulphur removal section as well as to the cobalt treatment plant.

Due to the highly negative electro voltage, other metals will also plate with the nickel. Thus it is of vital importance for the nickel stream to be clean of all impurities. (Murdoch University, 2006).

The feed temperature is at a temperature of 60 - 65°C and a pH of 3.2 – 3.5 (Taute & George, 2010).

The impurities in the section, if according to specifications, will be: Cu < 5ppm and Fe < 5ppm. The spent composition nickel concentration is 50 – 55g/l and the acid is 40 – 45g/l (Taute & George, 2010).

Although the spent electrolyte composition is given as having a nickel concentration of between 50 – 55g/l, Anglo American (2006) specified the concentration as 62.7g/l showing that the concentration is dependent on the incoming concentration of nickel to the electrowinning section.

3.2.3.4. Sulphur Removal

The last stage of the Nickel Circuit is the sulphur removal stage, where nickel is separated from sulphur. Na_2SO_4 is produced with the removal of water, acid and sulphur from the process. The sulphur removal section is illustrated in Figure 3.12.

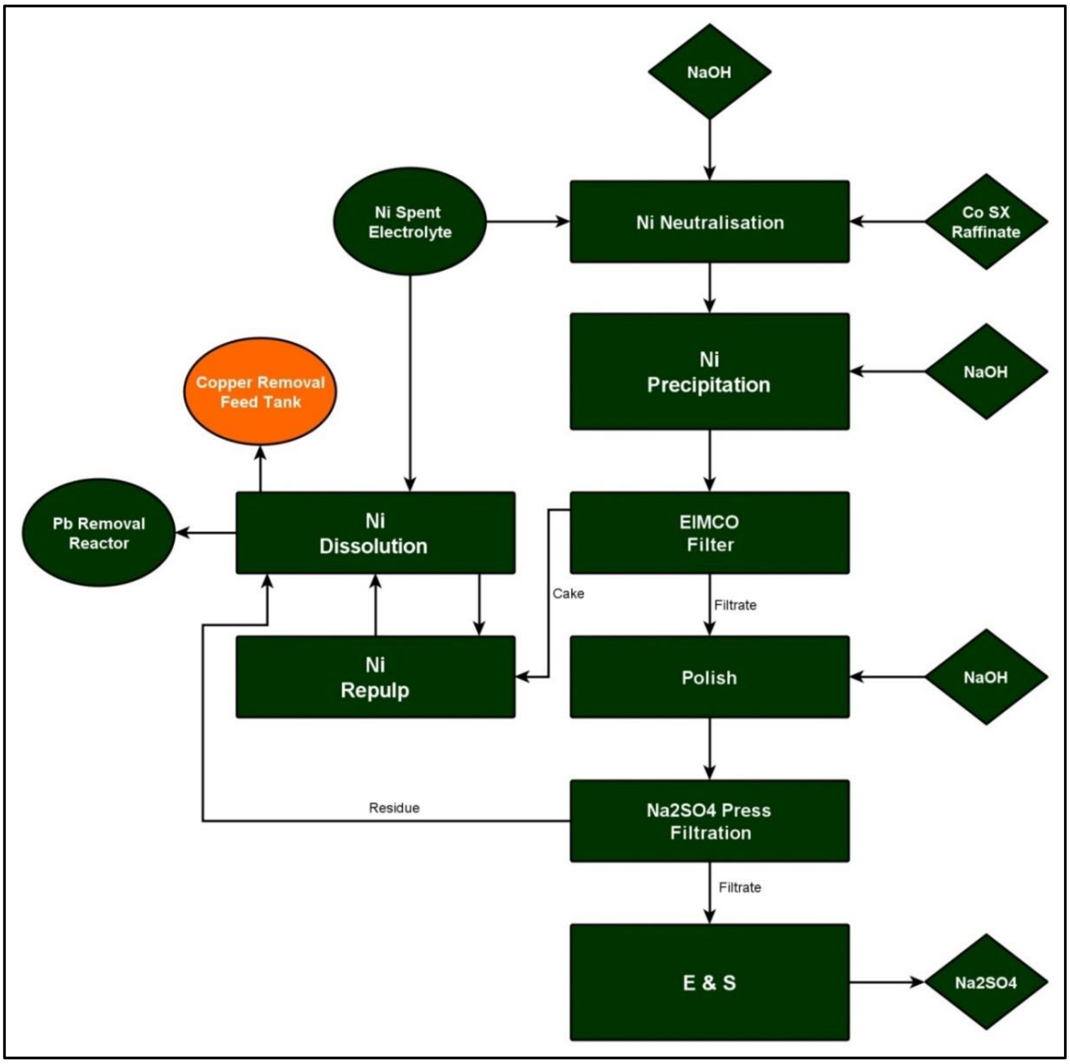

Figure 3.12: Sulphur Removal Section

Nickel spent electrolyte and a small stream from the cobalt plant is neutralized with caustic soda to a pH of about 5.8. The neutralized solution is then sent to the precipitation reactors where the pH is raised to 8.8 to achieve $Ni(OH)_2$ precipitation (Taute & George, 2010).

The liquid/solid stream is then filtered in an EIMCO filter, where the nickel rich cake is produced which is repulped and dissolved with Ni spent electrolyte. The sodium sulphate from the filter is polished to a pH of 9.1, filtered again to remove the last bits of nickel and sent to the sodium sulphate crystallizer plant (Taute & George, 2010).

3.3. DEVELOPMENT AND SIMULATION OF RBMR

3.3.1. INTRODUCTION

The Aspen Plus flowsheet were developed by modelling the base metal refinery as discussed in Section 3.2. The flow sheet is based on a hierarchal design where each section is built into a hierarchy with relevant inputs and outputs. The global view of the Aspen Plus flowsheet with the respective hierarchies can be seen in Figure 3.13. All of the hierarchy inputs are viewed whereas only the most important outputs are specified in the global flow sheet.

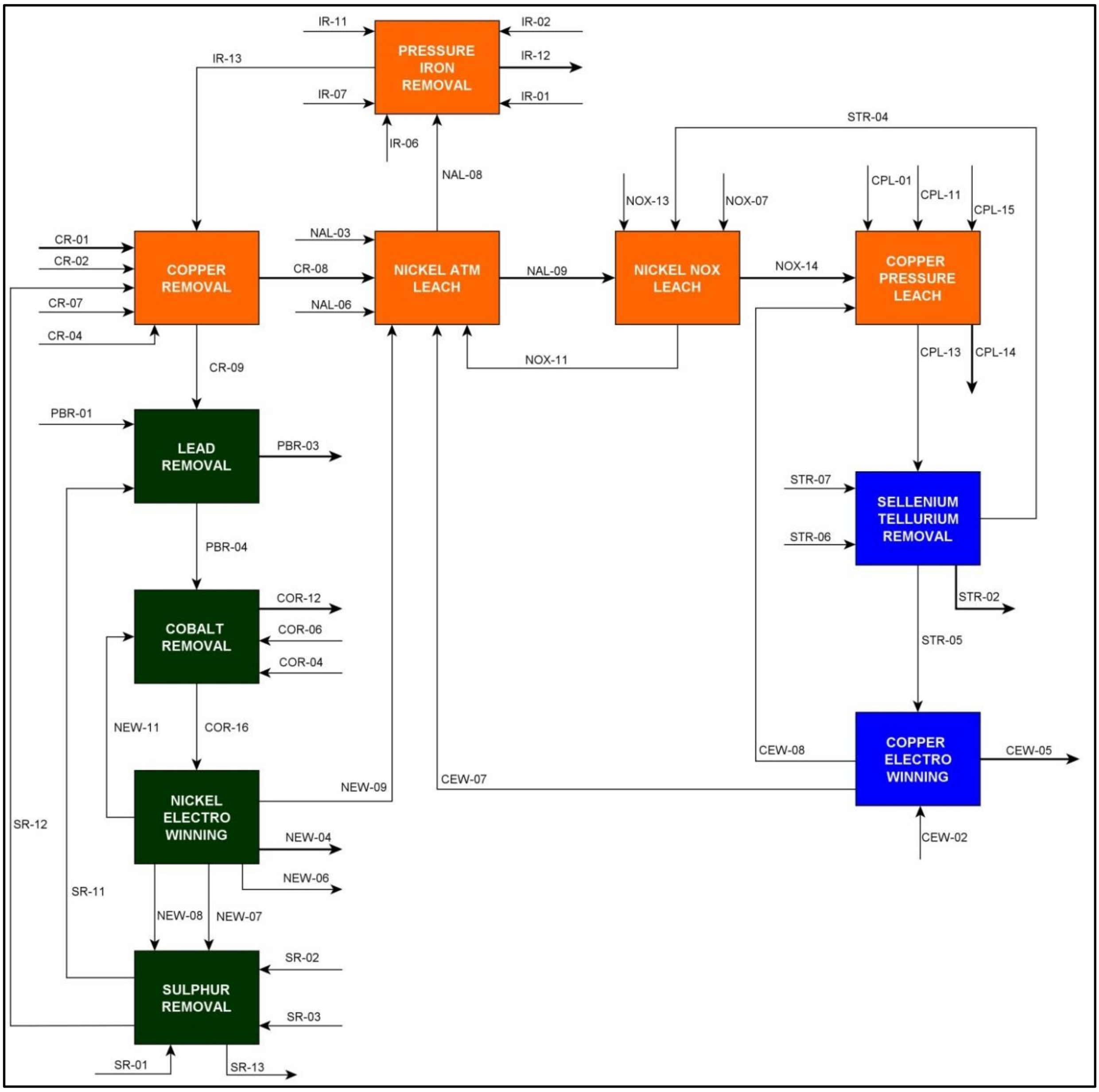

Figure 3.13: Hierarchal view of Base Case Aspen Plus Flowsheet

The raw feeds and chemicals/reagents fed to the process are specified in Appendix A

Each section will be discussed in terms of unit operation functionality; detailed design specification and process design criteria's are given in Appendix B. All of the design criteria's were taken from meetings and discussions with Anglo American personnel as well as confidential documents supplied by Anglo American (Anglo American, 2012).

Stream tables and stream definitions consisting of the results of the simulation are given in Appendix C. Algorithms used in Aspen Plus can be found in Appendix F.

3.3.2. COPPER REMOVAL SECTION

The copper removal section removes copper from the leaching solutions by precipitating it as antlerite. Nickel is also leached by the free acid present in the solutions. The Aspen Plus copper removal section flowsheet is given in Figure 3.14.

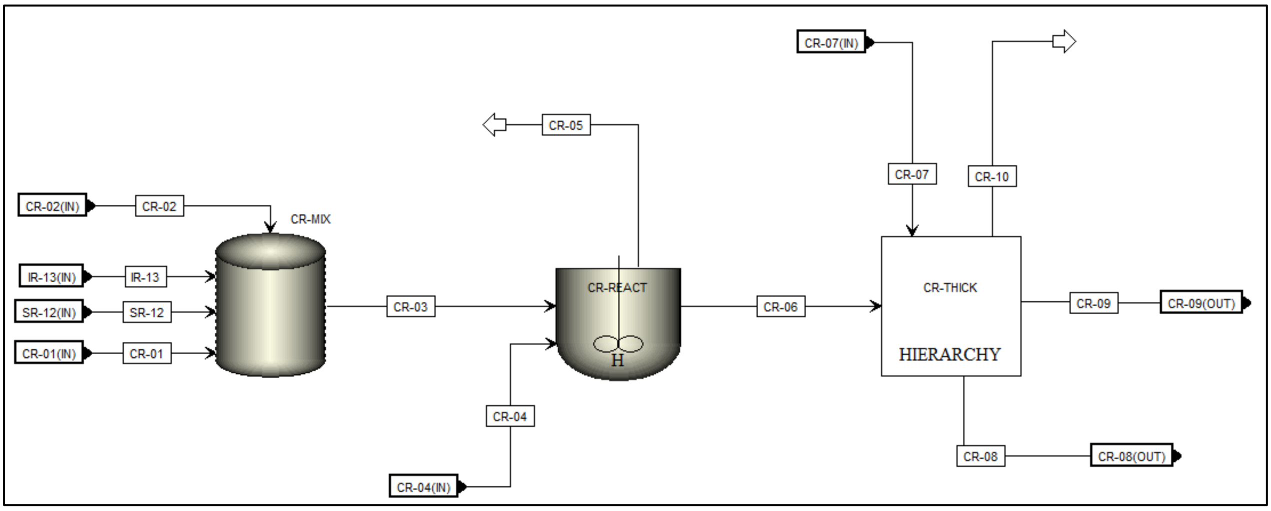

Figure 3.14: Aspen Plus RBMR copper removal section flowsheet

The copper removal section is modelled using three Aspen Plus user models, and is summarized in Table 3.2.

Table 3.2: RBMR copper removal unit operations

Equipment Name	Modelling Purpose and details
CR-MIX	Models a mixing tank that mixes the main feed streams (CR-02, IR-13, SR-12 and CR-01) to the copper removal section
CR-REACT	Represents the series of atmospheric leaching reactors that leaches fresh matte in the presence of oxygen (CR-04).
CR-THICK	Models a thickener which separates solids to the underflow (CR-08) and liquid to the overflow (CR-09), with a vent (CR-10) modelling evaporative losses.

Detailed operating conditions, controls and chemistry for the three unit operations are given in Appendix B.2.2.

3.3.3. NICKEL ATMOSPHERIC LEACH SECTION

The nickel atmospheric leach section is where the leaching of nickel containing minerals takes place. The leaching can progress according to two mechanisms, which are metathesis reactions (oxygen free environment) and acid leaching reactions (oxygen environment).

The Aspen Plus nickel atmospheric leach section flowsheet is given in Figure 3.15.

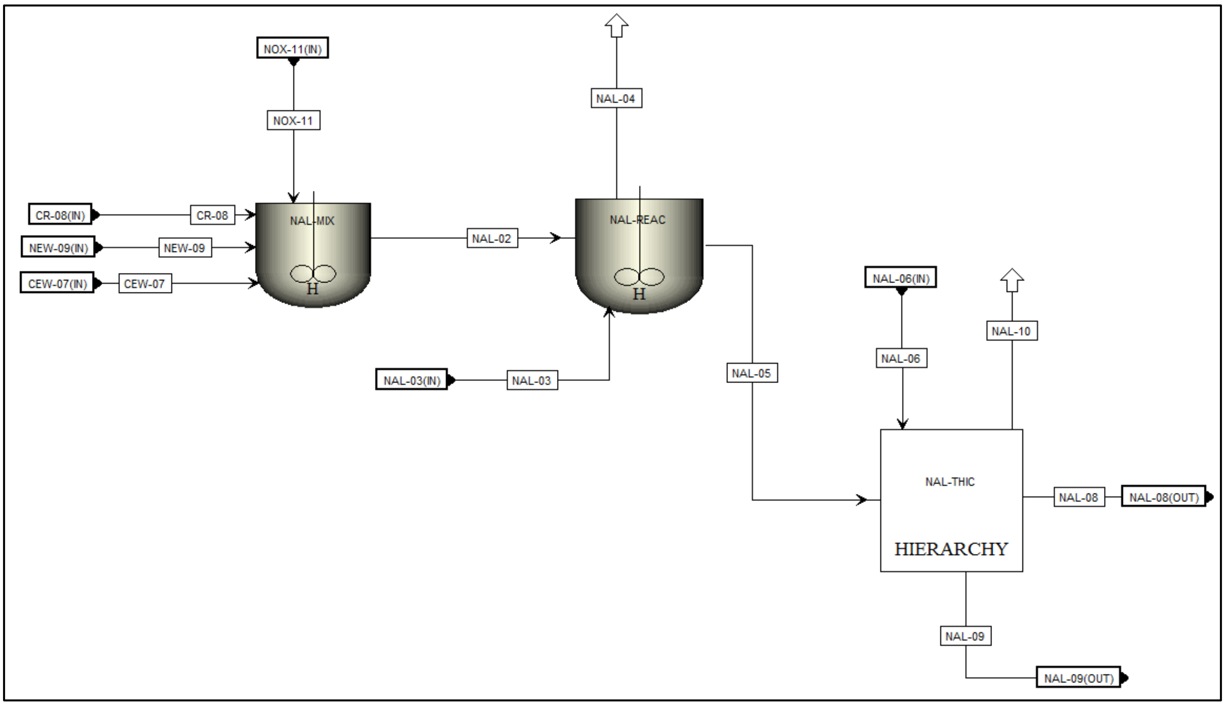

Figure 3.15: Aspen Plus RBMR nickel atmospheric leach section flowsheet

The nickel atmospheric leach section is modelled using three Aspen Plus user models, and are given in Table 3.3.

Table 3.3: RBMR nickel atmospheric leach unit operations

Equipment Name	Modelling Purpose and details
NAL-MIX	Models the mixing tank that mix the incoming feed streams (NOX-11, CR-08, NEW-09, CEW-07) to the nickel atmospheric leach section
NAL-REAC	Represents the non-oxidizing and oxidizing atmospheric leach reactors with a vent (NAL-04) that includes evaporative losses. The NAL-REAC model contains two stoichiometric reactor models, one for the oxidative leach (where the oxygen stream, NAL-03 is fed to) and one for the non-oxidative leach.

Equipment Name	Modelling Purpose and details
NAL-THIC	Represents a thickener which separates solids to the underflow (NAL-09) and liquid to the overflow (NAL-08), with a vent (NAL-10) that models evaporative losses.

Detailed unit operation operating conditions and chemistry are given in Appendix B.3.2.

3.3.4. PRESSURE IRON REMOVAL SECTION

The pressure iron removal section removes iron from the refinery by oxidizing iron ions to precipitate hematite and jarosite.

The Aspen Plus pressure iron removal flowsheet is given in Figure 3.16.

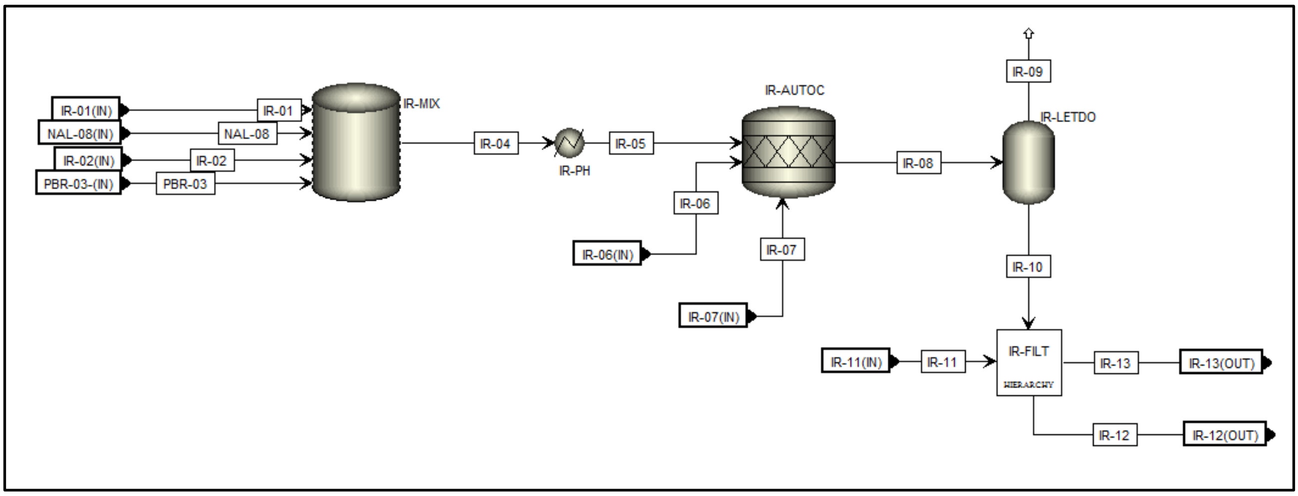

Figure 3.16: Aspen Plus RBMR pressure iron removal section flowsheet

The pressure iron removal section is modelled using numerous Aspen Plus user models, and are represented in Table 3.4.

Table 3.4: RBMR pressure iron removal unit operations

Equipment Name	Modelling Purpose and details
IR-MIX	Models the mixing tank that mixes the main feed streams (IR-01, NAL-08, IR-02, PBR-03)
IR-PH	Models the heat exchanger that heats the feed (IR-04) to the autoclave (IR-AUTOC). The heat exchanger heats the feed to 150˚C and operates at 600 kPa gauge pressure
IR-AUTOC	Models the pressure iron removal autoclave
IR-LETDO	A flash model which models the let-down effect of the autoclave discharge (IR-08). The flash column flashes the solution and

Equipment Name	Modelling Purpose and details
	vaporizes some of the water to steam due to the high temperatures and pressures of the discharge of the autoclave
IR-FILT	Represents the filter and wash system. IR-FILT simulates the separation of liquids and solids to a residue (IR-12) and filtrate (IR-13) stream due to filtration and residue washing. The algorithm responsible for the calculation of the wash water requirements are given in Appendix F.2.

Detailed unit operation operating conditions and chemistry are given in Appendix B.4.2.

3.3.5. NICKEL NON-OXIDIZING LEACH SECTION

The nickel non-oxidizing leach section selectively leaches nickel from the remaining nickel containing minerals via copper metathesis reactions. The reactions take place in a non-oxidative environment at elevated temperature and pressure conditions.

The Aspen Plus nickel non-oxidizing leach flowsheet is given in Figure 3.17.

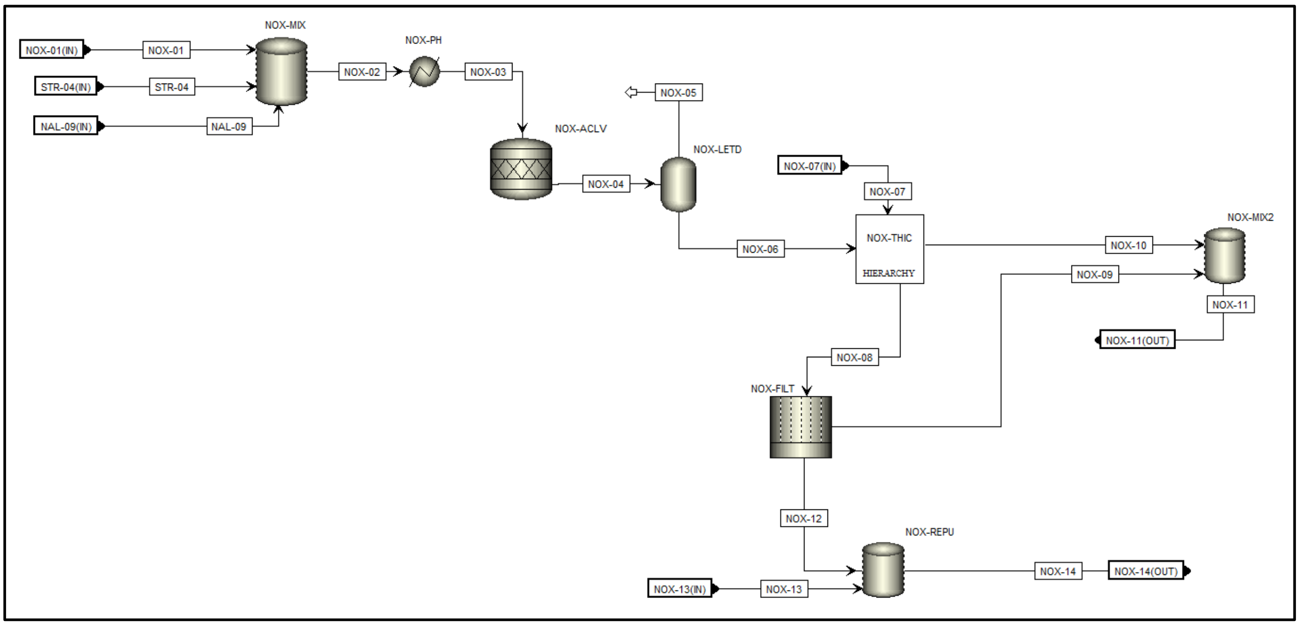

Figure 3.17: Aspen Plus RBMR nickel non-oxidizing leach section flowsheet

The nickel non-oxidizing leach section is modelled using numerous Aspen Plus user models, and are given in Table 3.5.

Table 3.5: RBMR nickel non-oxidizing leach unit operations

Equipment Name	Modelling Purpose and details
NOX-MIX	Models a mixing tank that mixes the incoming feed streams (NOX-01, STR-04, NAL-09) to the nickel non-oxidizing leach section
NOX-PH	Models a heat exchanger that pre-heats the feed to the autoclave to 155˚C. NOX-PH operates at 600 kPa gauge pressure (NOX-ACLV)
NOX-ACLV	Models the non-oxidizing leach autoclave. Two main design specifications need to be met with the autoclave discharge slurry: 1. The copper to nickel ratio in the slurry residue must be between 6 and 8 (Bryson *et al.*, 2008) 2. The acid leached to nickel leached molar ratio is specified to be 0.35 (Anglo American, 2012) Due to the many reactions present a type of feed forward algorithm was written to compute the conversions of the remaining reactions based on a simplified version of their reactivity. Thousands of “leaching rounds” are simulated whereby each mineral receives an amount of copper ions that can be reacted with based on a weight assigned to the mineral. The “leaching rounds” are simulated until design specification (1) and (2) are met. For more detail regarding the algorithm refer to Appendix F.3.
NOX-LETD	Models a let-down tank that simulates the autoclave flash to atmospheric pressure.
NOX-THIC	Models the thickener that separates the liquids from the solids to an underflow (NOX-08) and a overflow (NOX-10).
NOX-FILT	Represents a filter that produces a filtrate (NOX-09) and a filter cake (NOX-12).
NOX-MIX2	Models a mixing tank that mixes the overflow (NOX-10) from the thickener (NOX-THIC) and the filtrate (NOX-09) from the filter (NOX-FILT)
NOX-REPU	Models a mixing tank that mixes process water (NOX-13) with the filter cake (NOX-12) to re-pulp the filter cake

More information regarding unit operating conditions and chemistry can be found in Appendix B.5.2.

3.3.6. COPPER PRESSURE LEACH SECTION

The copper pressure leach section leaches the remaining copper and nickel in the refinery with acid consuming reactions in the presence of oxygen.

The Aspen Plus copper pressure leach flowsheet is given in Figure 3.18.

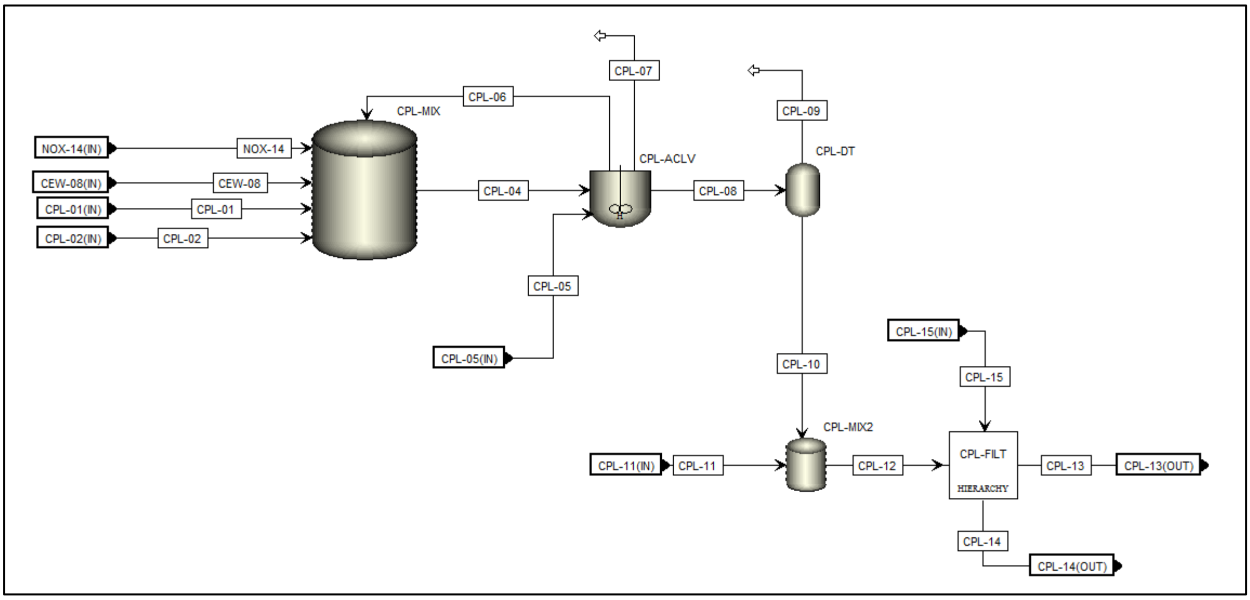

Figure 3.18: Aspen Plus RBMR copper pressure leach flowsheet

The copper pressure leach section is modelled using numerous Aspen Plus user models, and is given in Table 3.6.

Table 3.6: RBMR copper pressure leach unit operations

Equipment Name	Modelling Purpose and details
CPL-MIX	Models a mixing tank that mixes the main feed streams (NOX-14, CEW-08, CPL-01, CPL-02, CPL-06) to the copper pressure leach section
CPL-ACLV	Models an autoclave with three compartments, where the first two compartments are cooled by a recycle/flash stream and the third compartment is cooled by cooling coils. The cooling is required due to the highly exothermic reactions taking place in the reactors. Pure gaseous oxygen (CPL-05) is also fed to the autoclave to create the oxygen environment needed for the acid consuming reactions. The first two compartments have a bleed at the end where 60% of the liquid are de-pressurized to atmospheric pressure. The split is

Equipment Name	Modelling Purpose and details
	optimized to keep the first two compartments at a temperature of just below 140°C. A cooling coil is installed in compartment 3 where cooling water is used to keep the compartment temperature at 145°C.
CPL-DT	Models a let-down tank where the autoclave contents are depressurized to atmospheric pressure
CPL-MIX2	Models a mixing tank where the slurry from the let-down tank (CPL-10) is diluted to create a copper concentration in CPL-14 of 93 g/l.
CPL-FILT	Represents a filter with a multi-wash system where the solids are separated from the slurry and washed with process water (CPL-15) to produce a filtrate (CPL-13) and filter cake (CPL-14). The algorithm for the filter and washer is given in Appendix F.2.

Additional chemistry and operating conditions are available in Appendix B.6.2.

3.3.7. SE/TE REMOVAL SECTION

The selenium/tellurium removal section is the section of the refinery where the Se/Te impurities are removed from the process due to electrowinning problems caused by the impurities.

The Aspen Plus selenium/tellurium removal flowsheet is given in Figure 3.19.

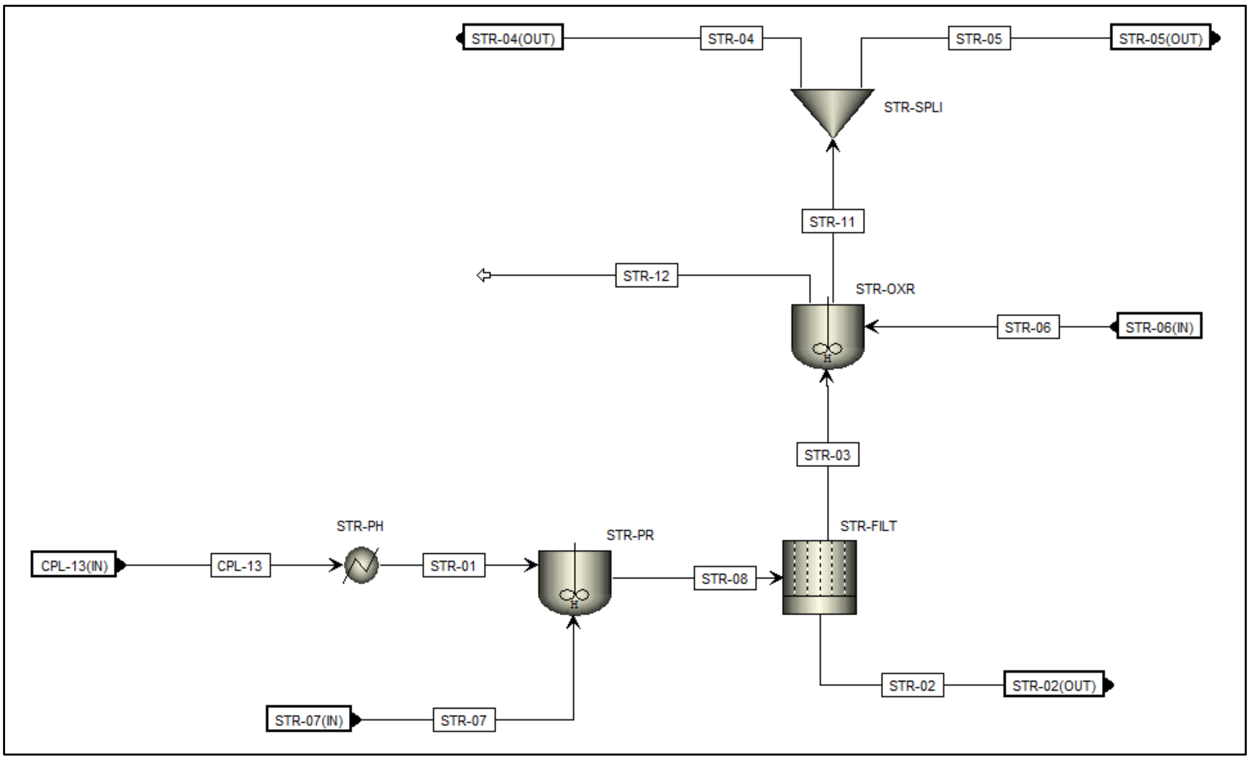

Figure 3.19: Aspen Plus RBMR selenium/tellurium removal section flowsheet

The selenium/tellurium removal section is modelled using numerous Aspen Plus user models, and are given in Table 3.7.

Table 3.7: RBMR selenium/tellurium removal section unit operations

Equipment Name	Modelling Purpose and details
STR-PH	Models a pre-heater that heats the incoming solution stream (CPL-13) to a temperature of 90°C before entering the precipitation reactor (STR-PR). The motive for the pre-heating is to achieve the desired reactivity of the reactions in reactor STR-PR.
STR-PR	Models a precipitation reactor that uses sodium sulphite solution (STR-07) to convert Cu^{2+} ions to Cu^{+} ions. The Cu^{+} ions in turn react with dissolved selenium and tellurium species to create insoluble species that precipitates out of the solution.
STR-FILT	Models the filter that produces a selenium/tellurium filter cake (STR-02) and a filtrate (STR-03)
STR-OXR	Models a mixing reactor that uses air (STR-06) to oxidize Cu^{+} ions to Cu^{2+} ions
STR-SPLI	Models a stream splitter that splits STR-11 into two streams: 1. STR-04 – recycle stream to the nickel non-oxidizing section 2. STR-05 – Recycle stream to the copper electrowinning section

Additional details regarding unit operation operating conditions and chemistry can be found in Appendix B.7.2.

3.3.8. COPPER ELECTROWINNING SECTION

The copper electrowinning section is where the dissolved copper is electroplated on cathodes to produce a high purity copper product. In this section acid is also produced which is used as leaching agent in the nickel atmospheric leach section and the copper pressure leach section.

The Aspen Plus copper electrowinning section flowsheet is given in Figure 3.20

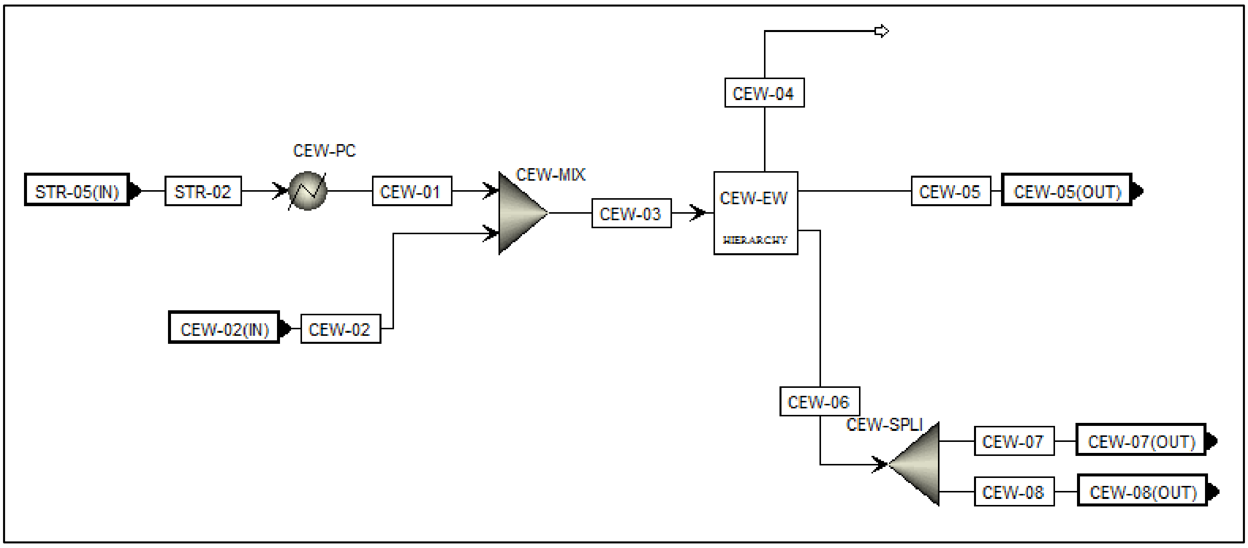

Figure 3.20: Aspen Plus RBMR copper electrowinning section flowsheet

The copper electrowinning section is modelled using numerous Aspen Plus user models, and are given in Table 3.8.

Table 3.8: RBMR copper electrowinning section unit operations

Equipment Name	Modelling Purpose and details
CEW-PC	Models a heat exchanger that cools the feed stream to the electrowinning section (STR-02) to 54°C.
CEW-MIX	Models a mixing tank that mixes water (CEW-02) and the cooled copper rich solution (CEW-01) to reduce the copper concentration to 88g/l.
CEW-EW	Models an electrowinning system that produces the spent electrolyte (CEW-06), cathodes (CEW-05) and gas (CEW-04) due to gas generation and water evaporation.
CEW-SPLI	Models a stream splitter that splits the spent electrolyte stream (CEW-06) into two streams: 1. CEW-07 is recycled to the nickel atmospheric leach section 2. CEW-08 is recycled to the copper pressure leach section

The chemistry and unit operations operating conditions of the copper electrowinning circuit can be found in Appendix B.8.2.

3.3.9. LEAD REMOVAL SECTION

The lead removal section is where the dissolved lead is precipitated out of the solution by making use of barium hydroxide. The lead causes problems in the production of nickel and thus needs to be removed.

The Aspen Plus lead removal section flowsheet is given in Figure 3.21.

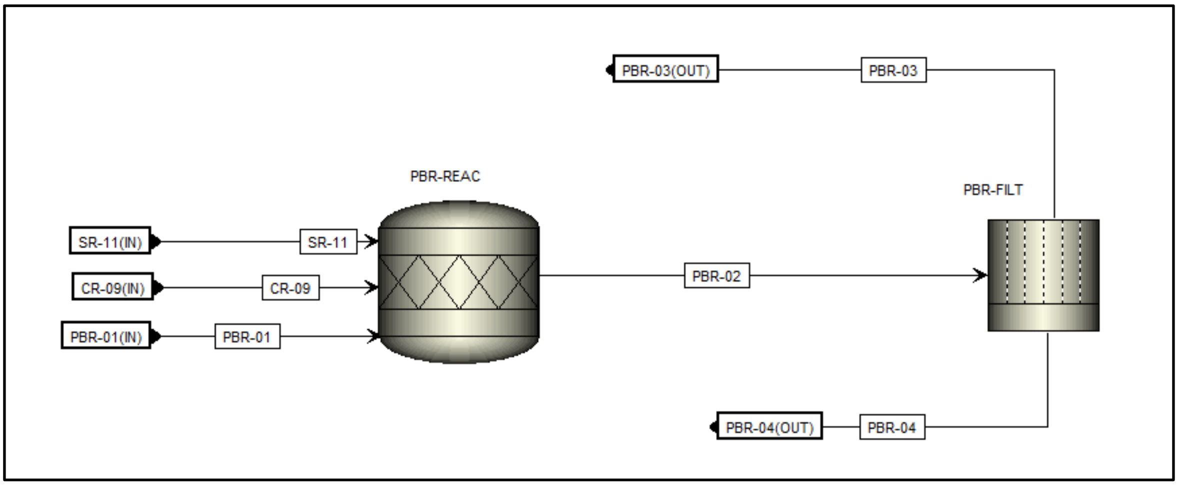

Figure 3.21: Aspen Plus RBMR lead removal section flowsheet

The lead removal section is modelled using numerous Aspen Plus user models, and are given in Table 3.9.

Table 3.9: RBMR lead removal section unit operations

Equipment Name	Modelling Purpose and details
PBR-REACT	Models a pipe reactor that uses barium hydroxide solution (PBR-01) to precipitate the lead in solution
PBR-FILT	Models a filter that produces a lead filter cake (PBR-03) and a nickel rich filtrate (PBR-04)

The unit operation operating conditions and chemistry for the lead removal section can be found in Appendix B.9.2.

3.3.10. COBALT REMOVAL SECTION

The cobalt removal section is where the dissolved cobalt is precipitated out of the solution by making use of $Ni(OH)_3$ which is produced in-house. The cobalt causes problems in the production of nickel and thus needs to be removed. The separated cobalt is a valuable commodity that is further purified in the cobalt production plant.

The cobalt removal section also contains the evaporation and pH adjustment circuits where the nickel concentration and pH of the nickel electrowinning feed is adjusted appropriately.

The Aspen Plus cobalt removal section flowsheet is given in Figure 3.22.

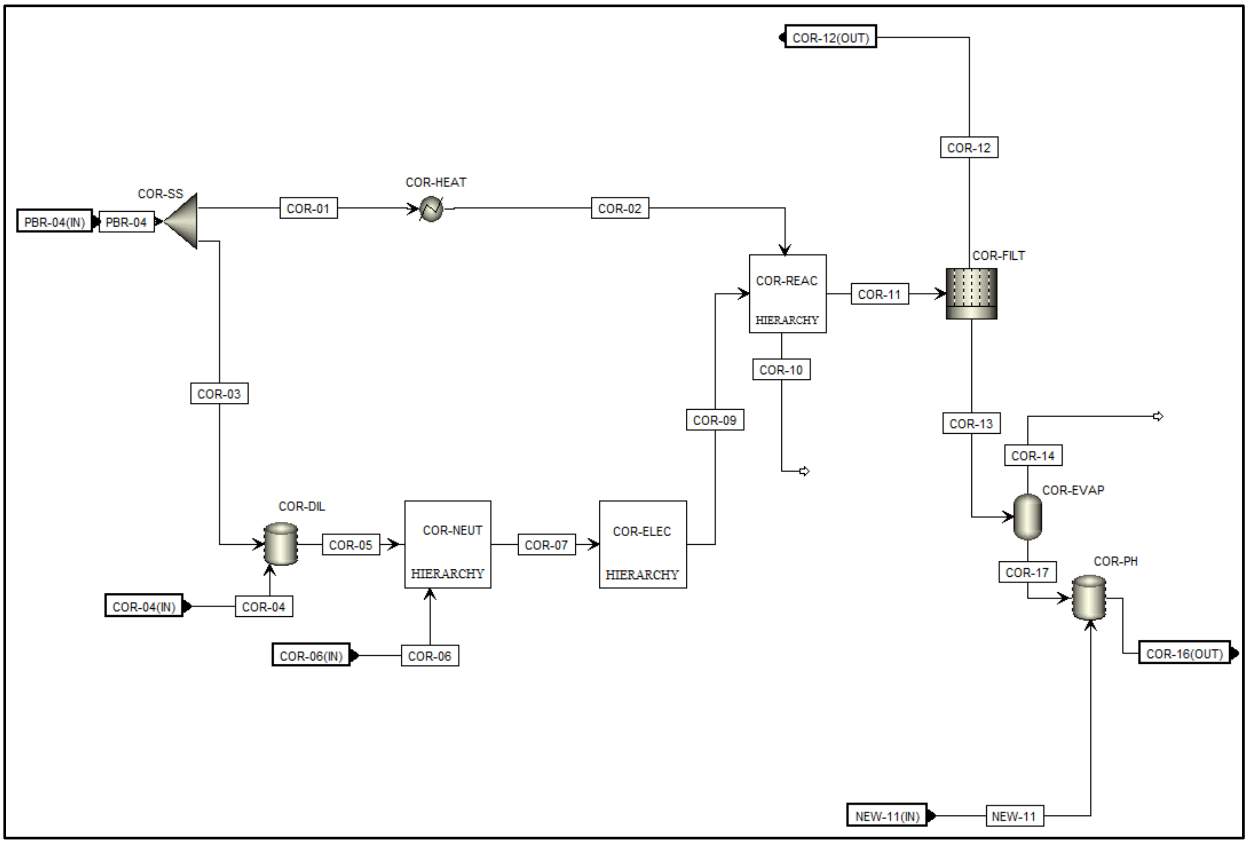

Figure 3.22: Aspen Plus RBMR cobalt removal section flowsheet

The cobalt removal section is modelled using numerous Aspen Plus user models, and are given in Table 3.10.

Table 3.10: RBMR cobalt removal section unit operations

Equipment Name	Modelling Purpose and details
COR-SS	Models a stream splitter that splits the incoming stream (PBR-04) into a stream that is used for nickelic production (COR-03) and the main nickel containing liquor (COR-01)
COR-HEAT	Models a heat exchanger that heats the nickel rich solution (COR-01)
COR-REACT	Models a mixing reactor where the nickelic reagent (COR-09) is reacted with the heated nickel rich solution (COR-02) to precipitate the cobalt out of solution.
COR-DIL	Models a mixing tank that mixes process water (COR-04) with the nickel rich liquor to dilute the nickel concentration to 21g/l.
COR-NEUT	Represents a mixing reactor where caustic soda (COR-06) is used to

Equipment Name	Modelling Purpose and details
	produce nickel hydroxide.
COR-ELEC	Models an electrolytic reactor where nickel hydroxide (COR-07) is converted to nickelic hydroxide
COR-FILT	Represents a filter that produces a cobalt filter cake (COR-12) and a nickel rich filtrate product (COR-13).
COR-EVAP	Models an evaporator that evaporates water to increase the nickel concentration to 89 g/l in stream COR-17. The evaporator model is a flash model that flashes the water, thus no energy optimization or heat recovery is present the evaporator model. Thus the duty of the evaporator will not be accurate,
COR-PH	Models a mixing tank that mixes the spent electrolyte recycle stream (NEW-11) with the product (COR-17) from the evaporator to reduce the pH to 3.5.

Detailed information on the chemistry and unit operation operating conditions can be found in Appendix B.10.2.

3.3.11. NICKEL ELECTROWINNING SECTION

The nickel electrowinning section is where the dissolved nickel is refined to a pure nickel cathode in an electrowinning process. During the electrowinning process acid is produced as a by-product and the acid is used as leaching agent in the leaching section of the process.

The Aspen Plus nickel electrowinning section flowsheet is given in Figure 3.23.

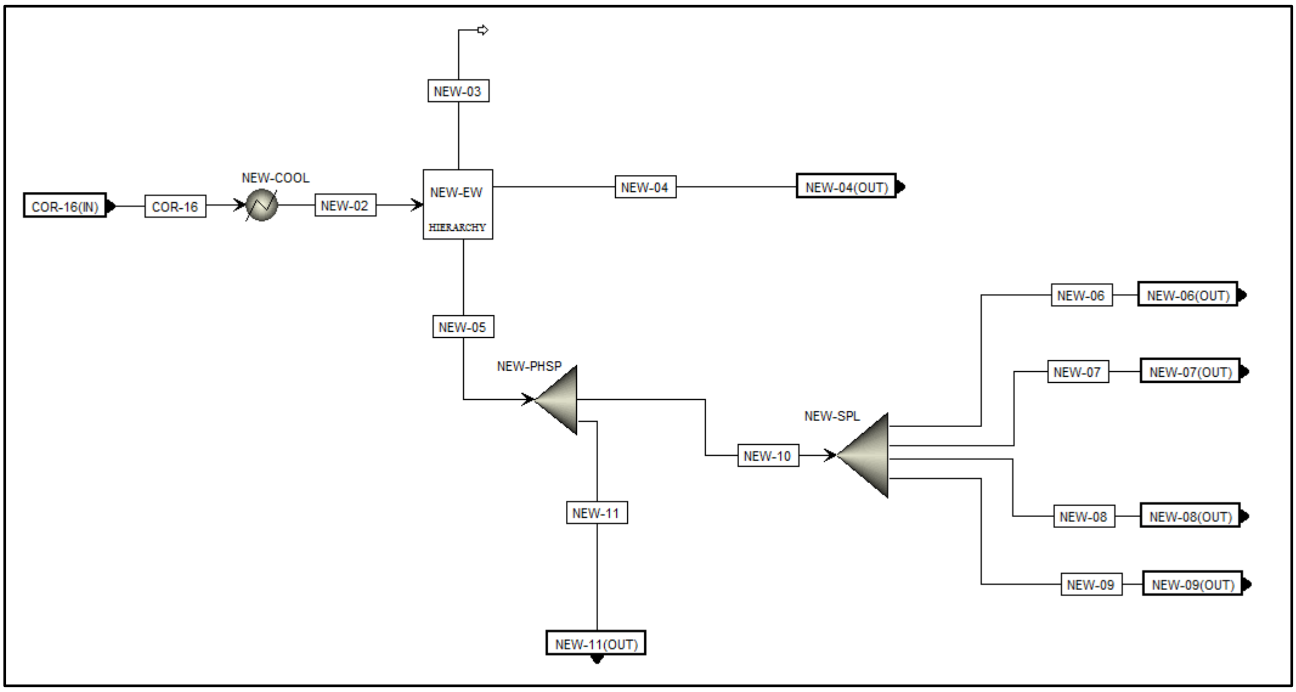

Figure 3.23: Aspen Plus RBMR nickel electrowinning section flowsheet

The nickel electrowinning section is modelled using four Aspen Plus user models, and is discussed in Table 3.11.

Table 3.11: RBMR nickel electrowinning section unit operations

Equipment Name	Modelling Purpose and details
NEW-COOL	Models a heat exchanger that cools the nickel rich liquor (COR-16) to 60°C.
NEW-EW	Models a nickel electrowinning tank-house where nickel cathodes (NEW-04), spent nickel electrolyte (NEW-05) and a vent containing water and hydrogen (NEW-03) is produced.
NEW-PHSP	Represents a stream splitter that produces the following two streams: 1. NEW-11 – Cobalt removal recycle stream for pH control 2. NEW-10 – Main spent electrolyte stream
NEW-SPL	Models a stream splitter the produces the following four streams: 1. NEW-06 – Cobalt production plant spent electrolyte feed 2. NEW-07 – Sulphur removal neutralization feed 3. NEW-08 – Sulphur removal dissolution feed 4. NEW-09 – Recycle stream to nickel atmospheric leach stage for leaching lixiviant

The unit operation operational parameters as well as the chemical reactions can be found in Appendix B.11.2.

3.3.12. SULPHUR REMOVAL SECTION

The sulphur removal section is where the excess sulphur generated in the system due to leaching and electrowinning is removed. Sulphur is present in the form of sulphate molecules. Some of the sulphates are acid bound whereas other are metal bound.

The Aspen Plus sulphur removal section flowsheet is given in Figure 3.24.

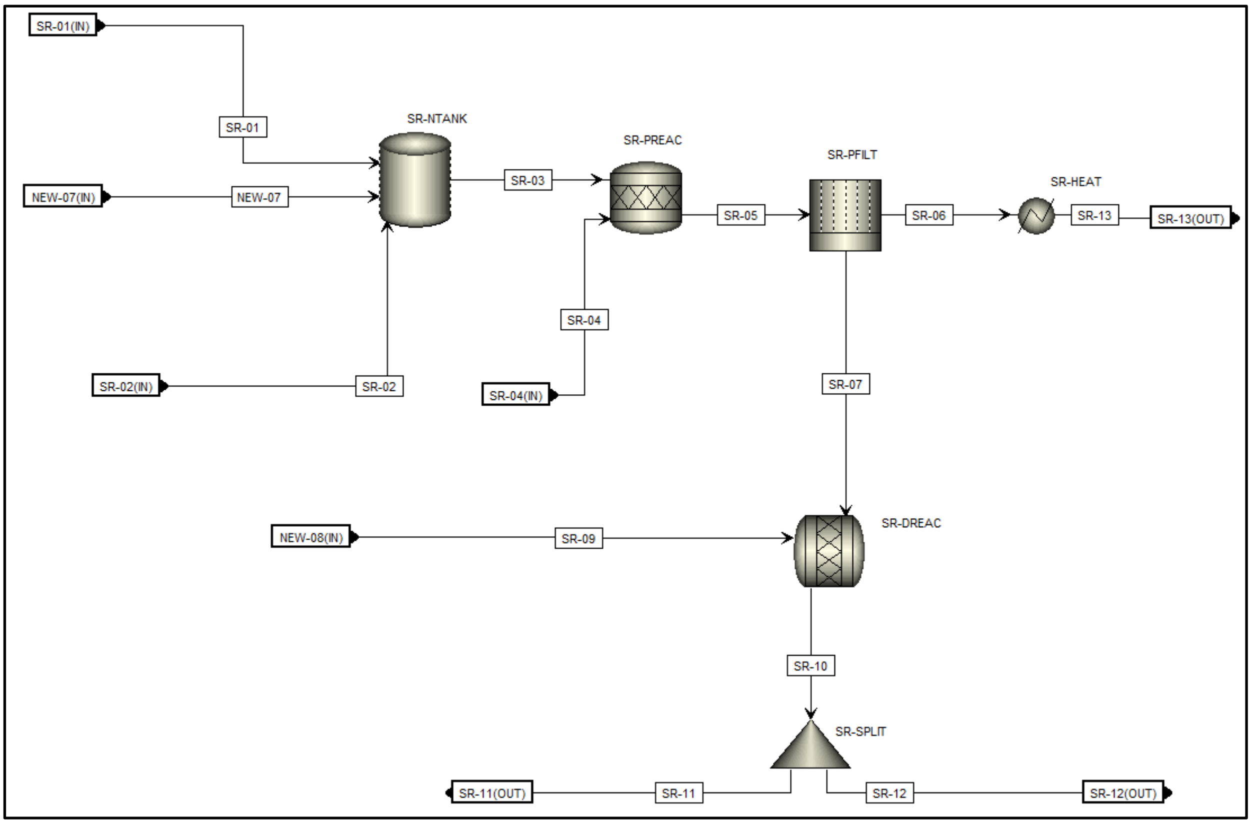

Figure 3.24: Aspen Plus RBMR sulphur removal section flowsheet

The sulphur removal section is modelled using six Aspen Plus user models, and is discussed in Table 3.12.

Table 3.12: RBMR sulphur removal section unit operations

Equipment Name	Modelling Purpose and details
SR-NTANK	Models a series of mixing tanks that mixes the main incoming feed streams to the sulphur removal section (SR-01, NEW-07 and SR-02). The caustic soda (SR-02) is used to neutralize the mixed solutions to a pH of 5.7.
SR-PREAC	Models a series of stirring reactors which precipitates dissolved nickel

Equipment Name	Modelling Purpose and details
	as nickel hydroxide. The reactor operates at a pH of 10 by adding caustic soda (SR-04).
SR-PFILT	Models the three-step process of filtration and polishing steps to produce a sodium sulphate filtrate product (SR-06) and a nickel hydroxide slurry (SR-07).
SR-HEAT	Represents a heat exchanger that heats the filtrate (SR-06) to a temperature of 72°C. The heating prepares the filtrate for the sodium sulphate crystallization process.
SR-DREAC	Models a series of stirring reactors that dissolves the nickel hydroxide (SR-07) with spent nickel electrolyte (SR-09) from the nickel electrowinning section. To achieve the optimal split of stream NEW-07 and NEW-08 in the nickel electrowinning section (to neutralize all of the acid while using as little caustic as possible) a feed forward algorithm is used in the splitter (NEW-SPL) of the nickel electrowinning section. The optimal split is calculated before the streams are split and then the split value is used to divide the dissolution stream (NEW-08) and the neutralization stream (NEW-07) into their respective flow rates. For an in-detail explanation of the algorithm refer to Appendix F.4.
SR-SPLIT	Represents a stream splitter that splits SR-10 into the following two streams: 1. SR-11 – nickel sulphate recycle stream to lead removal section 2. SR-12 – nickel sulphate recycle stream to copper removal section

For in-depth detail regarding unit operation operating conditions and chemical reactions refer to Appendix B.12.2.

3.4. VALIDATION OF SIMULATION

In Section 3.3, the RBMR process was simulated using Aspen Plus. The question should be asked, how valid is the model, and how descriptive is the model of reality? To answer the question, mass balance data from Anglo American (2012) were obtained and used to validate the Aspen Plus simulation. It was found that the four most important mass balance results for the simulation are (1) the total mass flow, (2) the total volume flow, (3) the liquid nickel concentration and (4) the liquid copper concentration. The results for key process streams are given in Table 3.13.

Table 3.13 shows the mass balance results of the Aspen Plus simulation and Anglo American (2012) are similar in comparison. The metal concentrations as well as the mass flow and volume flows are within 10% of Anglo American (2012) results. An explanation for stream flow differences are the water balance – more dilution water is used in the particular process areas compared to those of Anglo American (2012) results.

It can thus be concluded from the results in Table 3.13 that the Aspen Plus RBMR simulation is validated due to high similarities when compared to the data given by Anglo American (2012).

Table 3.13: Validation of RBMR Simulation with Anglo American (2012)

Stream Name	Stream Description	Aspen Plus				Anglo American				Mass Flow Difference (%)
		Mass Flow	Volume Flow	[Ni]	[Cu]	Mass Flow	Volume Flow	[Ni]	[Cu]	
		kg/hr	m^3/hr	g/l	g/l	kg/hr	m^3/hr	g/l	g/l	
CR-08	Copper removal thickener underflow	16878	6.96	96.25	0.00	16675	8.34	100	0	1.20
NAL-08	Ni atm leach thickener overflow	59458	44.57	101.43	11.89	56235	41.9	110	11.89	5.42
IR-13	Iron free solution to copper removal section	56397	40.98	110.52	13.03	53098	39.5	120	13.43	5.85
NAL-09	Ni atm leach thickener underflow	14418	5.99	98.69	11.57	14209	7.1	110	11.89	1.45
NOX-11	Ni non-oxidizing leach product solution	41676	32.03	78.82	34.70	39668	30.5	89	28.1	4.82
NOX-14	Repulped Ni non-oxidizing leach residue	12962	5.39	40.25	17.72	12545	6.42	45.7	14.4	3.22
STR-04	Copper advance electrolyte to nickel non-oxidizing leach	29673	22.57	29.22	91.54	26857	20.7	32.1	94.6	9.49
CPL-13	Copper pressure leach residue	87872	66.20	29.65	93.00	81335	63	31.2	92.6	7.44
STR-05	Copper advance electrolyte to copper electrowinning	58640	44.60	29.22	91.54	53029	40.9	32.1	94.6	9.57
CEW-08	Copper spent electrolyte to copper pressure leach	49955	43.16	26.74	40.00	45307	36.6	31.4	40.4	9.30
CR-09	Copper removal thickener overflow	100580	75.10	97.97	0.00	94753	71.8	100	0	5.79
PBR-04	Pb free solution to Co removal	213602	160.76	88.59	0.00	199977	152	88.14	0	6.38
COR-16	pH adjusted Ni advance electrolyte to Ni electrowinning	211643	160.56	88.68	0.00	204900	159	84.1	0	3.19
SR-11	Nickel rich acid free solution to lead removal section	112630	85.27	80.75	0.00	105273	80.42	77.8	0	6.53
SR-12	Nickel rich acid free solution to copper removal	41552	31.46	80.75	0.00	38836	29.67	77.8	0	6.54
NEW-05	Spent Ni electrolyte from Ni electrowinning	205795	166.01	62.69	0.00	191687	149	62.7	0	6.86

3.5. CONCLUDING REMARKS

In Chapter 3 the RBMR process was described in detail, and the RBMR was successfully simulated according to the process design criteria's as given by Anglo American (2012). Section 3.1 gave an introduction to the RBMR process, and public available literature that describes the RBMR process. Section 3.2 covered an in-depth literature study regarding the RBMR process with the applicable chemistry. Design criteria's were also defined for the RBMR process according to the literature study. Section 3.3 gave the ideology behind the Aspen Plus RBMR simulation with detailed discussions surrounding the process flow and unit operation designs. Finally, section 3.4 validated the RBMR simulation with data given by Anglo American (2012).

In conclusion the RBMR process was successfully described, simulated and validated.

4. SIMULATION OF RBMR-NF

Overview

The purpose of this chapter is to design a new RBMR-NF process, simulate the process and run different case studies to study the process-wide implications of using different types of membranes.

Section 4.1 gives a literature study on NF. Section 4.2 discusses the development of the RBMR-NF process. Section 4.3 discusses the RBMR-NF simulation together with the unit operations used and the process flow involved. Section 4.4 gives the results of different RBMR-NF case studies with a conclusion on the type of membrane characteristics required for the RBMR-NF process to work.

4.1. INTRODUCTION

The current RBMR as operated by Anglo American has a process section known as the sulphur removal process. The sulphur removal process uses caustic soda to neutralize free acid, and precipitate nickel as nickel hydroxide. The nickel hydroxide is then filtered from the slurry to produce a sodium sulphate rich stream which is processed in a crystallizer to precipitate sodium sulphate crystals. Thus in a molecular sense, excess sulphur is removed from the process.

From an operating cost point of view, the sulphur removal process is expensive in terms of reagents consumptions. Table 4.1 gives the main product (sodium sulphate) and reagent (caustic soda) operating costs according to the RBMR simulation.

Table 4.1: Simplified operating expenditures for RBMR sulphur removal process

Reagent/product	Usage/Production tons/annum	Price $/ton	Income (million $/annum)
NaOH	45 825	500[2]	-20.04
Na_2SO_4	65 000[1]	127[3]	8.3
			-11.74

1 Actual potential Na_2SO_4 production is 87 000 tons/annum. The current crystallizer can do 65 000 tons/annum and thus it is used as the upper limit.
2 ISISpricing, 2011
3 USGS, 2011

As can be seen from Table 4.1, the net reagent and product income sits at a negative of 11.7 million dollars. Other expenditures such as electricity consumption, labour and maintenance has not been incorporated and thus it is expected that the 11.7 million dollar figure will be much higher. Thus the need for an alternative process to remove sulphur in the form of sulphuric acid is clear. The focus of this study is to look at NF as an alternative technology to remove sulphur from the nickel spent electrolyte in the form of sulphuric acid.

4.1.1. NANOFILTRATION

NF separation is a pressure driven process, where the membranes are considered to be loose reverse osmosis membranes since their performance lies in between that of reverse osmosis and ultrafiltration membranes. Most of the NF membranes are thin-film composites, manufactured by making use of synthetic polymers. The synthetic polymers contain charged groups which affects the performance of the membranes, making them more selective to ions with different valences. This effect is also known as the Donnan effect. Thus NF membranes are ideal for the removal of heavy metal ions from solutions (Garcia-Aleman & Dickson, 2004).

The inner workings of a NF membrane are complex and the separation of solutes in the NF range depends on the micro hydrodynamics as well as the interfacial events occurring at the membrane surface and inside the membrane. Rejection may be caused by a combination of effects such as steric, transport and dielectric (Bowen *et al.,* 2004).

In the context of acid separation in aqueous metal containing solutions, NF is expected to achieve acid passage and metal rejection. By that is meant the acid will pass through the membrane, whereas the metal ions will be retained. The expected performance of NF is illustrated is Figure 4.1.

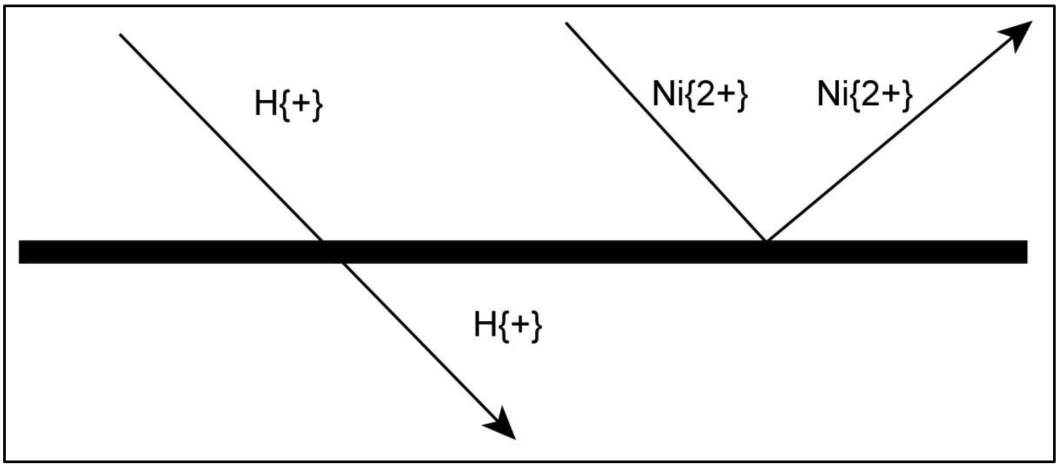

Figure 4.1: NF Illustration

The question if NF can achieve acid passage and nickel rejection will be investigated with a broad literature study in the following paragraphs. The application of NF membranes under acidic conditions has been reported by several authors as summarised in Table 4.2.

Table 4.2: Nanofiltration separation in acid/metal systems literature

Source	Research
Mehiguene *et al.* (1998)	Influence of operating conditions on the retention of copper and cadmium in aqueous solution by nanofiltration
Nyström *et al.* (2000)	Separation of metal sulphates and nitrates from their acid using nanofiltration
Taleb-Ahmed *et al.* (2002)	The influence of physic-chemistry on the retention of chromium ions during nanofiltration
Tanninen & Nystrom (2002)	Separation of ions in acidic conditions using NF
Tanninen *et al.* (2006)	Acid separation with nanofiltration — effect of electrolyte strength and Donnan forces
Tanninen *et al.* (2006 (2))	Nanofiltration of concentrated acidic copper sulphate solutions

Source	**Research**
Stolp (2006)	Nickel recovery from spent electrolyte by nanofiltration
Balanya, T. *et al.* (2009)	Separation of metal ions and chelating agents by nanofiltration
Al-Rashdi, B.A.M. *et al*. (2013)	Removal of heavy metal ions by nanofiltration

Mehiguene *et al.* (1998) reported the influence of the applied pressure, nature of the anions and pH on the retention of copper and cadmium salts by NF. Retentions of greater than 90% were achieved for copper sulphates, and it was found that any metal sulphate system gives superior rejections compared to chloride and nitrate systems. The end result of the study concluded that the solute retention depends greatly on the solute type (charge valence and hydration energy) as well as the pH and membrane pressure.

Nyström *et al.* (2000) explored the separation of nickel sulphates from sulphuric acid and nitric acid in either a single salt solution or a system of salts in solution. The study showed that NF can operate at very low pH ranges. Ni^{2+} ion rejections of between 90% and 99.5% were obtainable depending on the type of membrane that was used. The study done by Nyström *et al.* (2000) is a very good indication that NF can be used for acid separation in the RBMR sulphur removal process.

Taleb-Ahmed *et al.* (2002) did a study on the treatment of chromium salt solution using NF. Chromium retention of between 38 and 99% were obtained depending on the composition of the solution and the operating conditions. Cr^{3+} retention were found to give better retention in an acid medium at an optimal pressure of 5 bars. The influence of salts in solution was not found to have a substantial effect on the retention of Cr^{3+}. Cr^{4+} ions on the other hand were strongly dependant on the form (speciation) in which the Cr^{4+} ions were present. Higher concentrations of chromium caused the phenomena of repulsion to become less effective and thus the chromium ions were less retained.

Tanninen & Nystrom (2002) reported the retention of Na^{+} and Mg^{2+} ions in their nitrate solution in the pH range between 0.5 – 7. Mg^{2+} was retained very well at 97.5% to 99.5% whereas Na^{+} ions varied between 40 – 80%. The nitric acid permeated freely through the nanofiltration membrane. It was determined that the concentration of the nitric acid in the permeate is dependent on the ratio of H^{+} ions to rejected metal ions in the feed.

Tanninen *et al.* (2006) did a study on the separation of sulphuric acid and Cu^{2+} ions by making use of three different NF membranes (NF45, NF270 and Desal-5DK). Cu^{2+} ions were retained at 96 – 98% at $CuSO_4$ concentrations of 25 g/l and sulphuric acid concentrations of 8% weight percentage. The sulphuric acid rejection varied greatly depending on the sulphuric acid concentrations. Rejection values of between -75% and 30% were obtained at sulphuric acid concentrations of between close to zero to 100 g/l.

Tanninen *et al.* (2006 (2)) reported that NF is very suitable for the treatment of acidic waste and process streams, where a need exists to separate acid from salts.

Balanya, T. *et al.* (2009) explored the feasibility of nanofiltration for separating chelating agents from heavy metals. It was found that the more citrate that is added, the less the Cu^{2+} ions are retained. It was also found that in spite of the similar molecular sizes of citrate and Cu^{2+} ions, the Cu^{2+} ions can be efficiently separated from citrate at very low pH (1.5 – 2.5).

Al-Rashdi, B.A.M. *et al*. (2013) did a study on the effect of feed pH, pressure and metal concentration on the metal rejections and permeate fluxes on a commercial nanofiltration membrane (NF270). The experiments were done at low pressures (4 bar) and low concentrations of metal specie (in the area of 1000 mg/l). The pH investigated was in the order of 1.5 – 6. Metal ion (Cd^{2+}, As^{3+}, Cu^{2+}, Mn^{2+} and Pb^{3+}) rejections were found to be heavily dependent on metal ion concentrations, where the rejection of Cu^{2+} reduced from 99.9% to 58% as the concentration increased from close to 0 mg/l to 2500 mg/l. As^{3+} caused fouling on the membrane decreasing the flux. Cd^{2+}, Mn^{2+} and Pb^{3+} rejections were 99%, 89% and 74% respectively at a pH of 1.5 and a pressure of 4 bar, which show that the charge of the ion as well as the size of the molecule has as great effect on the rejection characteristics.

Stolp (2006) did a study on the spent nickel electrolyte (as present in the RBMR process) on the separation of nickel sulphate and sulphuric acid. The membrane used is called the FILMTEC NF-2540 membrane. The Ni^{2+} concentration was varied between 30 and 50 g/l, the pH between 1 and 2 and the pressure between 20 and 50 bar. Ni^{2+} rejections greater than 97.5% and permeate flux of between 20 and 50 $kg.m^2.hr^{-1}$ were achieved depending on the concentrations of the solution and the operating conditions. Using industrial $NiSO_4$ improved the fluid flux which indicated that even better fluxes can be achieved when used for industrial applications. An enormous problem picked up by Stolp (2006) is that Na_2SO_4 concentrations greatly inhibited the flux of the membrane by up to 90% at a sodium concentration of 37g/l.

It is therefore clear from the aforementioned studies as summarised in Table 4.2 that NF is a potential viable alternative to develop a new process to separate nickel from sulphuric acid.

4.2. DEVELOPMENT OF RBMR-NF

Section 4.1 concluded that NF is a potential technology which can be used to recover acid in an aqueous solution containing metal ions and high concentrations of acid. In this section a conceptual high-level design of the RBMR-NF process will be prepared by using NF as well as other relevant technologies. Section 4.2.1 covers the pre-treatment of the nickel spent electrolyte to produce an ideal liquor for the NF membranes, whereas Section 4.2.2 covers the NF process.

Both Section 4.2.1 and Section 4.2.2 are structured by starting out with an introduction to the process, and then following to the description of the proposed process.

4.2.1. NICKEL SPENT ELECTROLYTE TREATMENT

4.2.1.1. Introduction

If impurities are present in the feed stream to the membrane plant, pre-treatment needs to be installed to remove most of the impurities due to fouling that will decrease the flux, increase cleaning requirements as well as decrease the lifetime of the membrane. Thus the more impurities in the feeds stream, the larger the membrane and the shorter the life-span of the membrane system (Schäfer *et al*., 2005:242).

The main impurity present in the feed stream according to Stolp (2006) is sodium sulphate. Although the reasons for this inorganic compound causing problems is unclear, it might be due to the single positive charge of sodium, as well as the molecular size that is too large to be fully permeated and too small to be fully rejected, blocking the pores of the membrane. The presence of this impurity can be to a very large extent. According to the RBMR simulation any concentration of sodium sulphate between 100 – 300g/l can be expected. It is also necessary for the sodium sulphate in the spent nickel electrolyte to be at a minimum of 120g/l according to Hofirek & Halton (1990), although this can potentially be lowered to 100g/l (Anglo American, 2013).

Thus it can also be seen that the following conditions needs to be adhered to:

- Sodium needs to be removed from the membrane feed to as low a level as possible.
- The sodium sulphate concentration in the electrowinning feed stream must be at least 100 g/l

Since the nickel spent electrolyte is a mixture of sodium sulphate, acid and nickel sulphate, it is very difficult to selectively remove sodium sulphate without introducing the original RBMR process which neutralizes the acid and selectively precipitates the nickel out of the solution.

A potential solution to selectively remove sodium sulphate from the process can be deducted by a careful study of the solubility curves of nickel sulphate and sodium sulphate. A unique thermodynamic characteristic of this system is shown in the solubility curves as given in Figure 4.2.

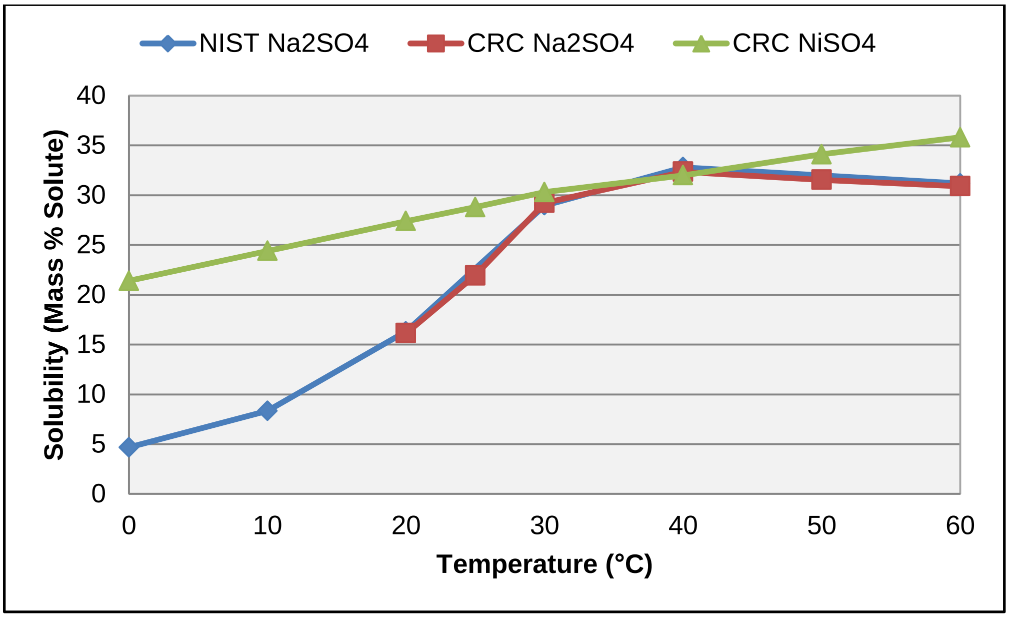

Figure 4.2: Solubility curves of Na_2SO_4 and $NiSO_4$ (NIST, 2012 & Lide, 2008:8-116)

Solubility data for sodium sulphate was obtained from NIST (2012) as well as Lide (2008:8-116). Solubility data for nickel sulphate was obtained from Lide (2008:8-116).

It is clear from Figure 4.2 that the solubility of sodium sulphate is reduced to 5g/100g H_2O at a temperature of 0°C whereas the solubility of nickel sulphate is at 21.4g/100g H_2O.

Thus the potential exist to reduce the concentration of sodium sulphate by cooling the spent nickel electrolyte while maintaining the nickel sulphate in the solution. High capital costs and energy requirements are expected, but the membrane system cannot function appropriately with high concentrations of sodium sulphate thus it is of vital importance to remove it in any way possible.

Vaessen *et al.* (2003) did a study on a scraped cooled wall crystallizer, where salts and water are separated by means of cooling and even freezing the liquid to produce ice and water. Thus such applications are in use today and quite popular where solubility is highly correlated with temperature.

If the feed pre-treatment is found to be uneconomical it will be worthwhile to investigate membranes which can selectively remove sodium sulphate. To the knowledge of the author no open literature is available on the separation of sodium with membranes and it is thus recommended for further studies to investigate this potential.

4.2.1.2. Process Description

The proposed process flow diagram for the feed treatment of the RBMR-NF sulphur removal section is illustrated in Figure 4.3.

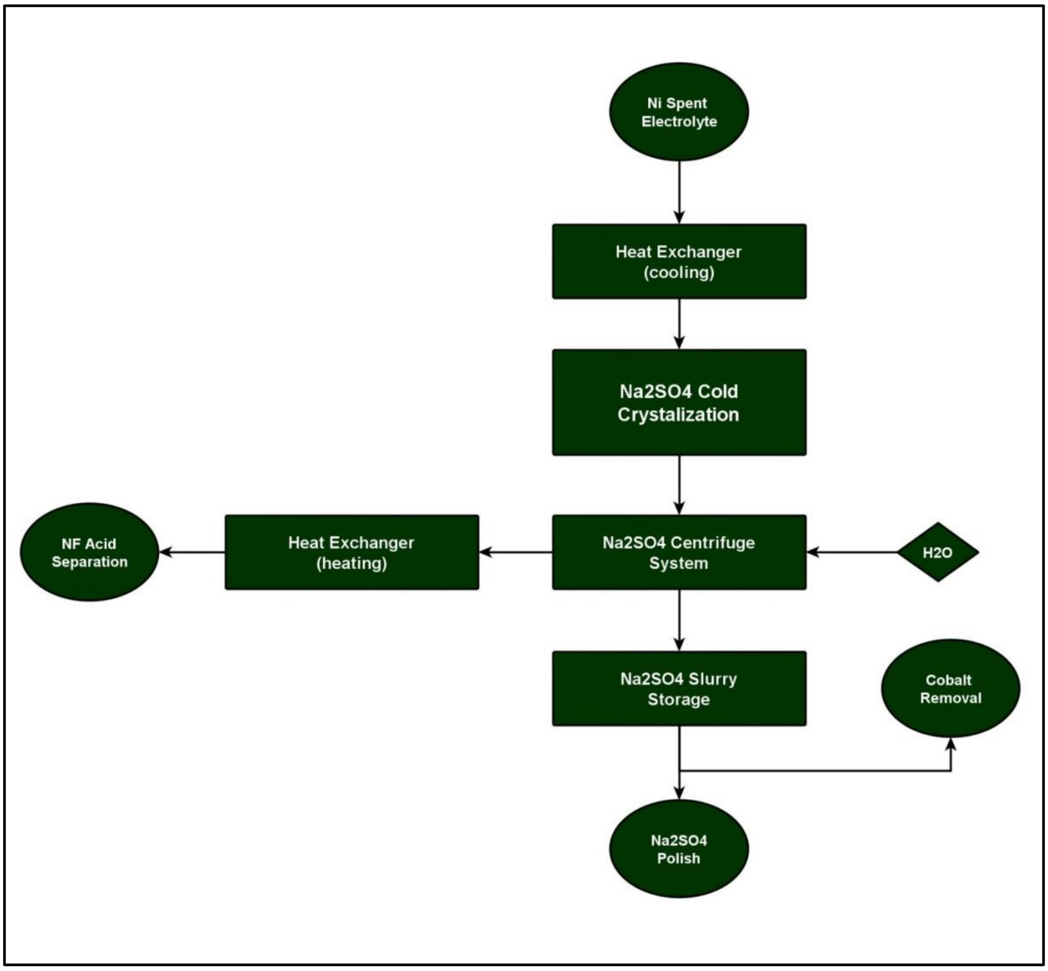

Figure 4.3: RBMR-NF sulphur removal feed treatment

The spent electrolyte stream from the nickel electrowinning section is directed to a heat exchanger which cools the liquor to 40˚C to effectively recover energy as well as reduce the duty of the crystallizer. The product from the heat exchanger is then fed to the cold crystallization equipment where sodium sulphate is selectively precipitated. The slurry stream is then centrifuged and washed where the sodium sulphate crystals are separated from the nickel/acid rich solution. A fraction of the centrifuge solids product which contains the sodium sulphate crystals are fed to the cobalt removal section to produce a 100g/l sodium sulphate concentration. The rest of the filter cake is sent to the sodium sulphate polishing plant. The centrifuge liquid product which contains the nickel and acid is fed to a heat exchanger which heats up the liquor to 20˚C to create a liquor stream that is compatible with the NF system. The product from the heat exchanger is then fed to the NF plant for nickel-sulphur separation.

A small modification to the cobalt removal process is necessary to produce a cobalt free filtrate that is compatible with the nickel electrowinning section. Figure 4.4 illustrates the modified cobalt removal process.

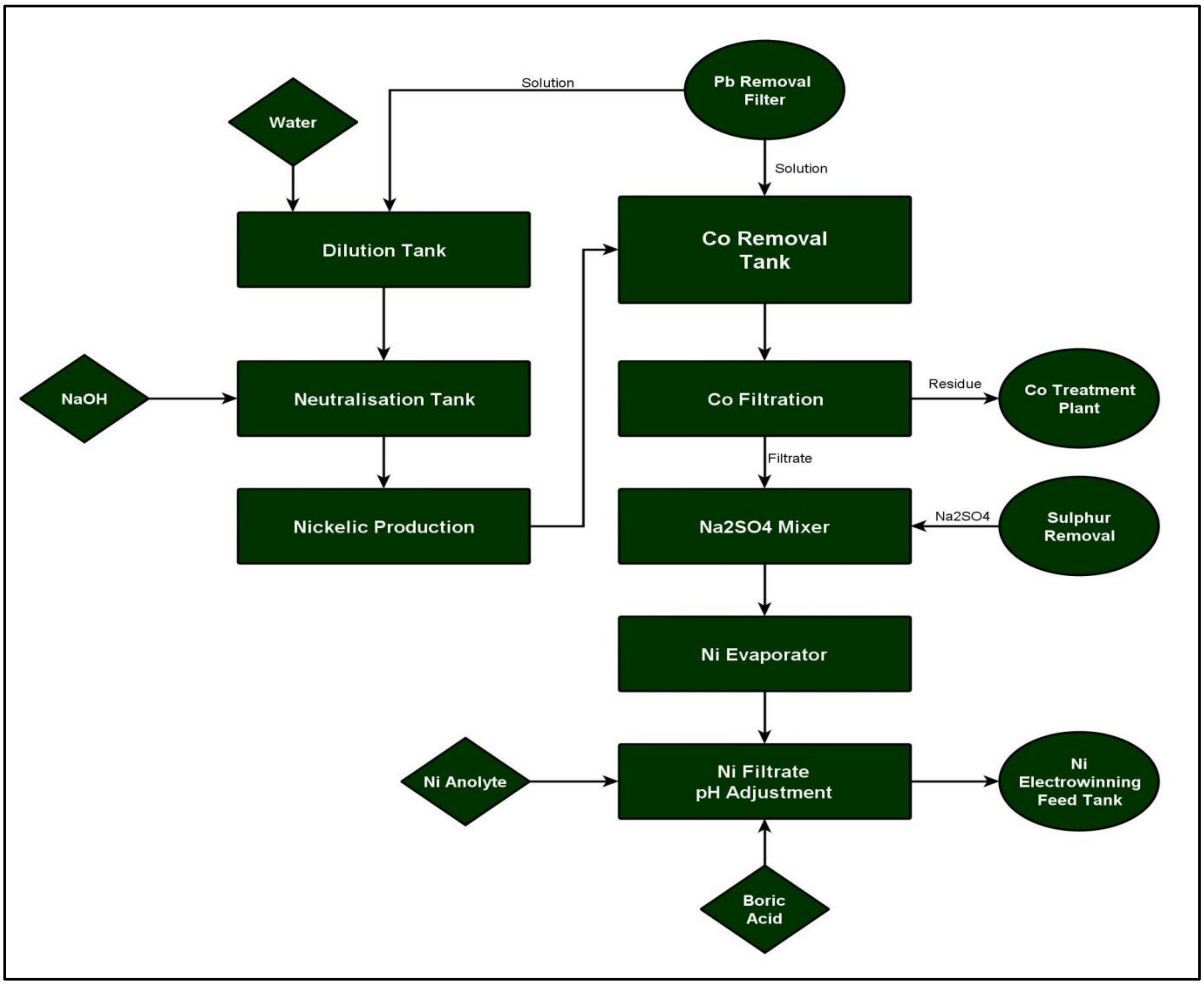

Figure 4.4: RBMR-NF Cobalt removal section

The modification to the cobalt removal process is the mixing tank which mixes recycled sodium sulphate with the cobalt filtrate to produce a liquor stream with sodium sulphate concentration of 100g/l. It should be noted that the modification causes higher evaporation duties to remove the excess water added due to the sodium sulphate recycle stream.

The products produced by the nickel electrowinning section are changed slightly to produce the required stream that is fed to the sulphur removal process. Figure 4.5 illustrates the nickel electrowinning process.

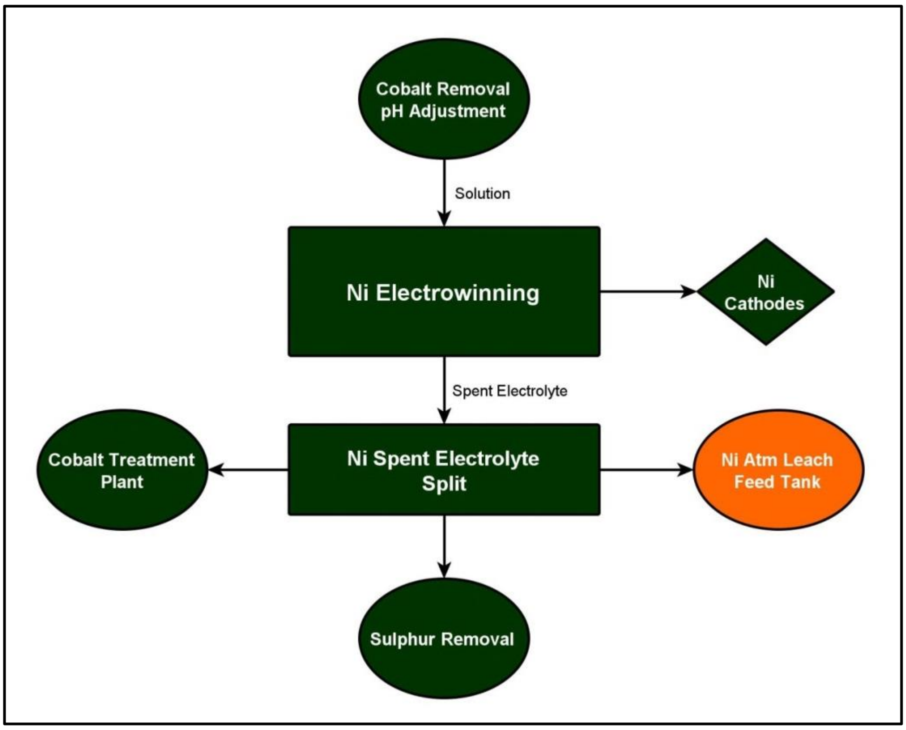

Figure 4.5: RBMR-NF nickel electrowinning section

In the RBMR process, the spent electrolyte is split into four streams, where two of the streams were fed to the sulphur removal process. In the RBMR-NF process, the spent electrolyte is split into three streams due to the sulphur removal process that only needs a single spent electrolyte stream.

4.2.2. NANOFILTRATION ACID-NICKEL SEPARATION

4.2.2.1. Introduction

To develop a NF acid-nickel separation process, the different modes of NF operation as well as operating conditions needs to be investigated.

The literature study done in Section 4.1.1 shows the nickel concentration needs to be maintained at minor levels while separating the acid; a high Ni^{2+} concentration will need high pressures to break the osmotic pressure barrier. High concentrations of ions also reduce the metal ion rejections, which will cause the system to lose nickel. Since the nickel spent electrolyte Ni^{2+} concentration is already in the area of 60g/l, it will have to sustain that level while the acid is being permeated through the membrane. Thus a NF design is required where the retentate is constantly diluted to keep the Ni^{2+} concentration at a level (+- 60g/l) that ensures proper permeation flux as well as good Ni^{2+} rejection.

Different types of NF membrane arrangements and techniques will be looked at to achieve the required results.

The basis of a membrane separation system is the arrangement of the membrane modules and the types of membrane modules used. Since this study is not interested in micro-design, only the arrangements of the modules which are assumed to be black boxes will be investigated.

Two main categories of modes of operation were identified, namely cross-flow and dead end operation (Mulder, 1996:474-479). Cross-flow is the most popular method of building membrane systems for NF whereas dead-end is a not so attractive concept in NF due to concentration polarization and fouling.

Membrane modules are usually arranged in particular arrangements to optimize the capital and running costs of the plant. The four most distinct ways in which membrane modules can be arranged are (1) series, (2) parallel, (3) tapered cascade and (4) diafiltration.

(1) Membrane systems in series configuration

Figure 4.6 represents an example of a membrane system in series.

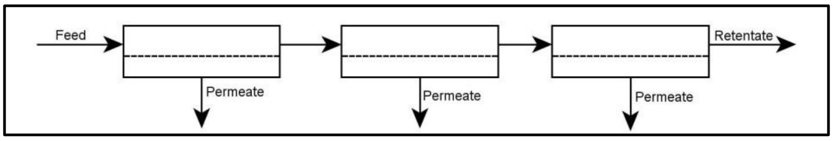

Figure 4.6: Membrane system in as given in a series configuration (adapted from Schäfer *et al.* (2005:84))

This configuration is the most simple cascade operation and does not add any additional benefits over using one big membrane unit, except potential savings on capital costs.

(2) Membrane systems in parallel configuration

Figure 4.7 represents an example of a membrane system using a parallel configuration.

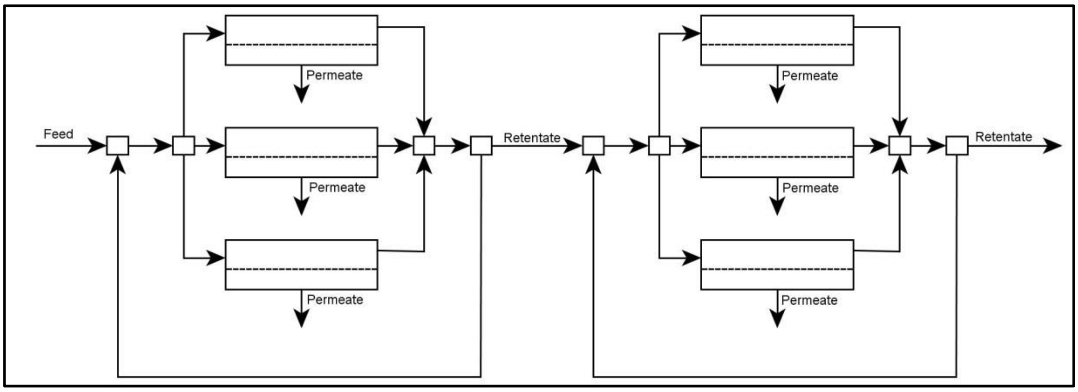

Figure 4.7: Membrane system in parallel configuration (adapted from Schäfer et al. (2005:84))

This cascade operation gets more complex and the degrees of freedom available are large. Different recycles can be added to different parallel membrane systems hooked up in series.

The possibilities are endless and it is up to the designer to come up with the best configuration for the design specification requirements.

(3) Membrane systems in tapered cascade configuration

Figure 4.8 represents an example of a tapered cascade configuration.

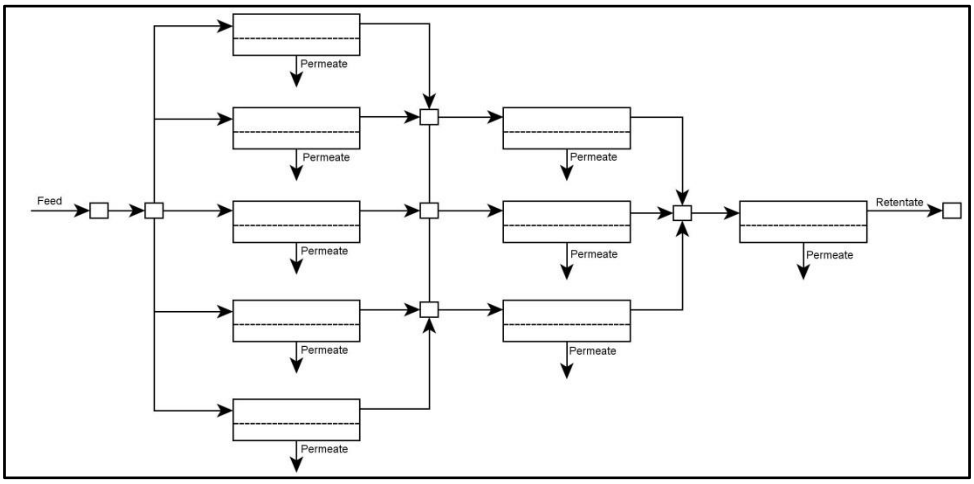

Figure 4.8: Membrane system in tapered cascade configuration (adapted from Schäfer et al. (2005:84))

As the volume flow inside the retentate stream is reduced, the flow velocity also decreases. To counter the reduction in volume flow the volume available for the retentate to flow in is reduced by decreasing the amount of membranes in series.

Tapered cascade membranes are used when flow velocities are a problem, or when large fluxes are required which reduces the retentate stream by a considerable fraction.

(4) Membrane systems in diafiltration configuration

Although diafiltration is not necessarily a new "configuration", it does have unique characteristics to be discussed apart from series, parallel and tapered configurations.

Figure 4.9 represents an example of a diafiltration configuration.

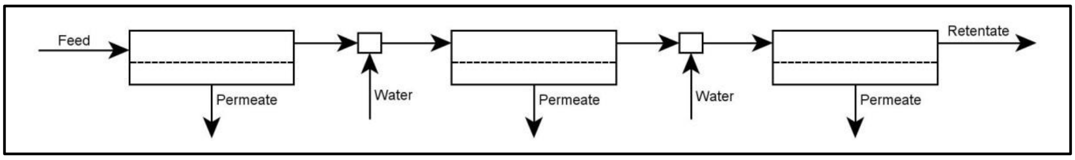

Figure 4.9: Membrane system in diafiltration configuration

The diafiltration technique is where fresh water is added to the system to improve the "wash out" of a membrane permeable species. This strategy is particularly useful for fractionation processes where a specie needs to be retained whereas another needs to be removed. Since

NF has good fractionation characteristics, diafiltration is usually used as a NF separation configuration (Schäfer et al., 2005:86).

Mulder (1996:491) also states that a complete separation between high and low molecular solutes is impossible to achieve with normal cascade designs such as series and parallel. The retentate needs to be diluted with water through a series of membrane separation stages until all of the undesired solute is washed out of the retentate. Complete separation is achieved with the concept of diafiltration, and is very applicable to the scenario at hand.

Thus from the different configuration that were looked at, diafiltration is the only configuration that will make complete acid separation possible. For this reason the diafiltration configuration is chosen as the basis of the NF design.

4.2.2.2. Process Description

The proposed nickel-sulphur separation circuit which mainly includes NF is illustrated in Figure 4.10.

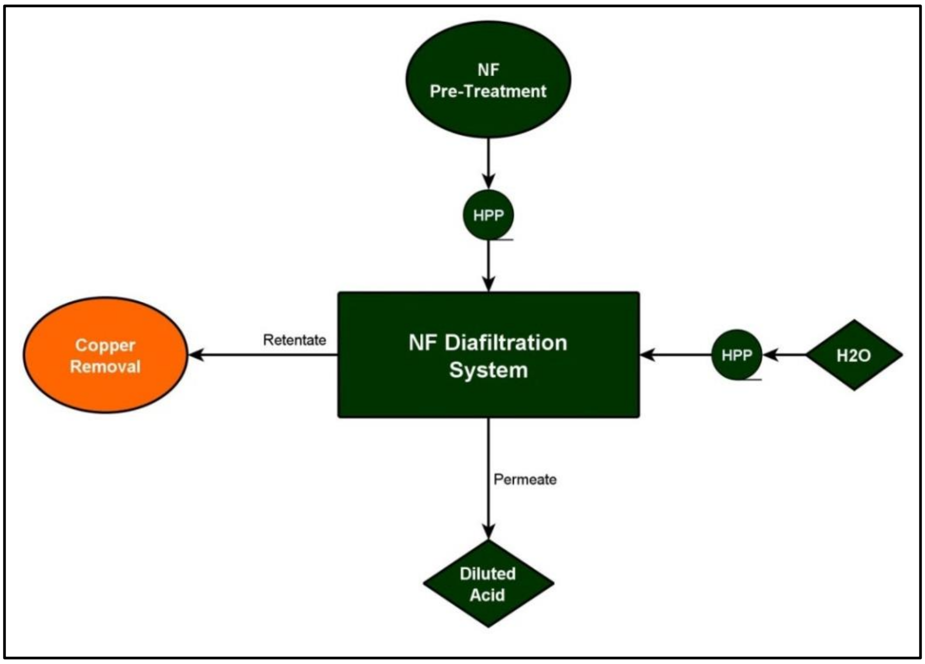

Figure 4.10: Nickel-sulphur separation process

The product from the feed treatment (to remove sodium sulphate) is fed to a high pressure pump (HPP), which increases the pressure to 50 bar. The operating pressure was decided upon the tests done by Stolp (2006) who determined that very high pressures of up to 50 bar is required for realistic flux. The pressurized liquor is then introduced into a NF diafiltration system, together with pressurized water. The products from the NF diafiltration system are the retentate stream which is fed to the copper removal circuit, and the permeate stream which contains medium concentrations of acid and low concentrations of nickel.

A more detailed illustration of the nickel-sulphur separation process is illustrated in Figure 4.11.

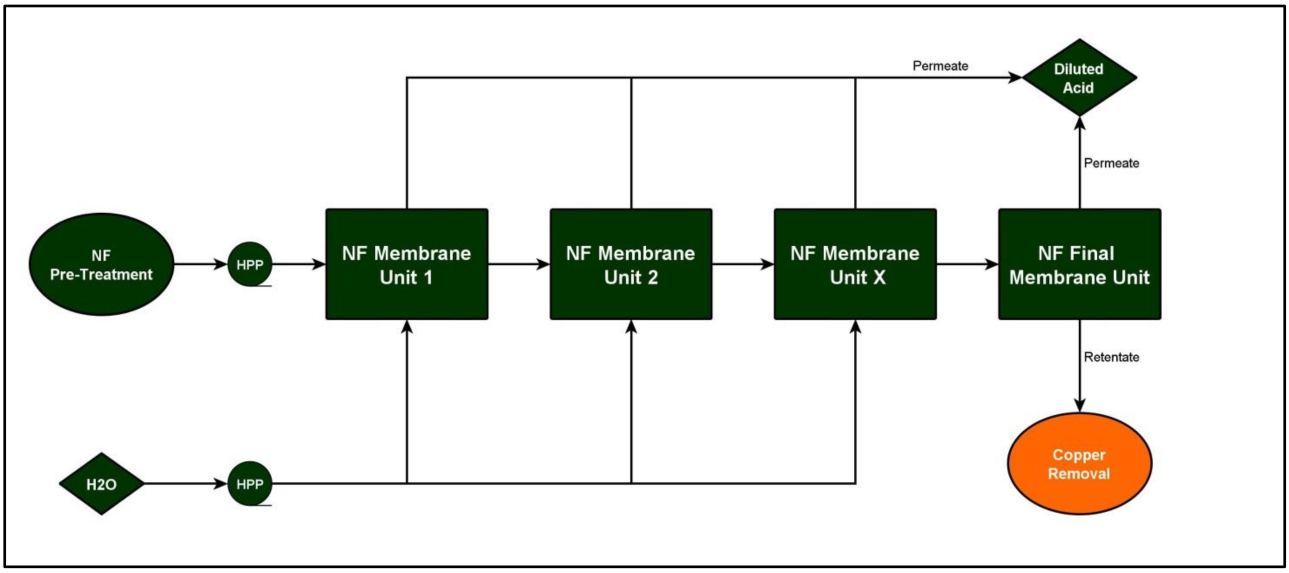

Figure 4.11: Nickel-sulphur detailed separation process

The NF diafiltration system is illustrated more clearly in Figure 4.11. The amount of membranes used depends on the property of the membrane itself as well as the feed to the membrane plant. For illustration purposes four membranes are shown.

An intermediate NF permeate concentration is assumed to be 65 g/l.

According to Taute & George (2010) the product nickel sulphate stream from the sulphur removal process is at a pH of 3.2. To increase the pH to 3.2 with a NF system will be costly, and thus a limit is set at 2/gl of sulphuric acid, which equates to a pH of about 2.6 depending on the sulphate concentrations. Due to a decrease in pH more acid will be reported to the copper removal section, which will result in more heazlewoodite being leached. Anglo American (2006) reports that the Ni^{2+} concentration is 77g/l, and thus a final retentate Ni^{2+} concentration of 80g/l is specified.

4.2.3. RBMR-NF DEVELOPMENT CONCLUSION

In Section 4.2 the RBMR-NF process was developed by using NF and other relevant technologies. A Cold crystallization circuit is required for the pre-treatment of the spent nickel electrolyte, whereas the NF plant needs to operate in diafiltration mode to achieve close to 100% acid separation. Small modifications in the electrowinning as well as cobalt section is required to maintain overall process stability in the electrowinning circuit.

4.3. SIMULATION OF RBMR-NF

4.3.1. INTRODUCTION

The Aspen Plus RBMR-NF flowsheet were developed by modelling the RBMR-NF as discussed in Chapter 4.2. The flow sheet is based on a hierarchal design where each section is built into a hierarchy with relevant inputs and outputs. The global view of the Aspen Plus flowsheet with the respective hierarchies can be seen Figure 4.12. All of the hierarchy inputs are viewed whereas only the most important outputs are specified in the global flow sheet.

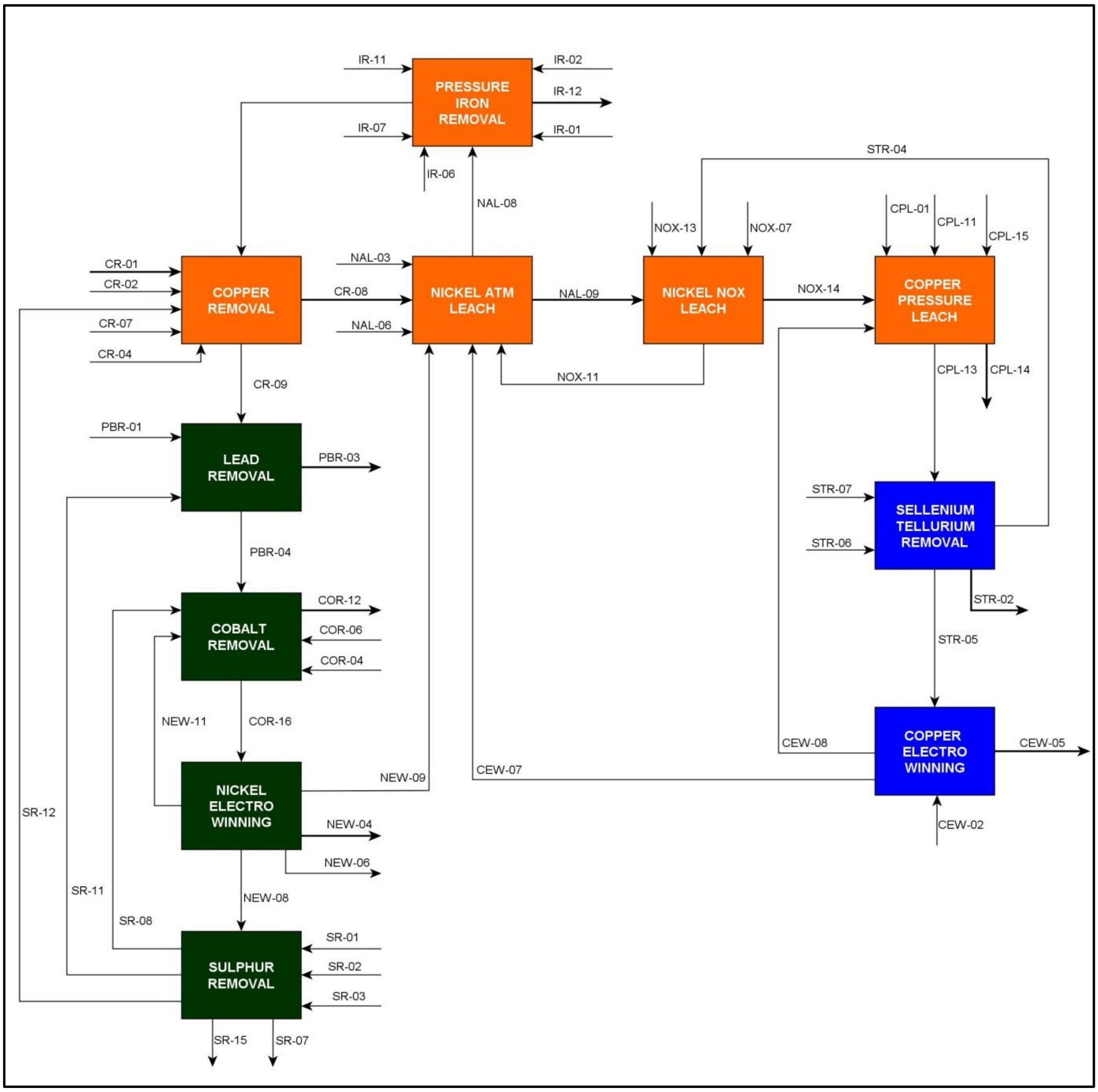

Figure 4.12: Hierarchal view of RBMR-NF Aspen Plus Flowsheet

Compared to the RBMR case, no new chemicals or reagents are used, and thus the chemicals and reagents are specified in Appendix A. The new sections as well as the modified sections compared to RBMR will be described in detail. The Aspen Plus equipment used, as well as the design specifications are available in Appendix D. Stream tables containing the results of the simulation is available in Appendix E. Algorithms used in Aspen Plus can be found in Appendix F.

4.3.2. COBALT REMOVAL SECTION

The modifications in the cobalt removal section will be discussed. For more information about the cobalt removal section refer to Section 3.3.10. The modified cobalt removal section Aspen Plus flowsheet is given in Figure 4.13.

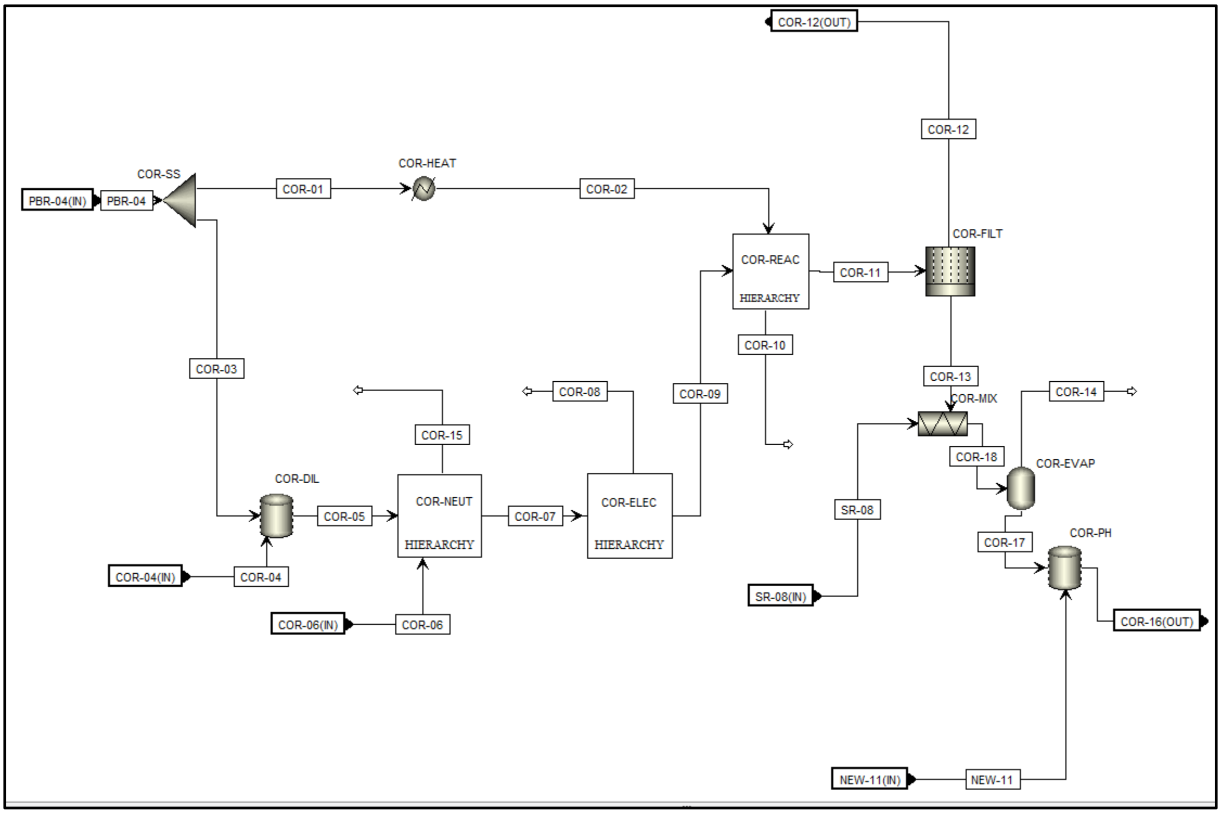

Figure 4.13: Aspen Plus RBMR-NF copper flowsheet

The additional unit operations added to the cobalt removal section can be seen in Table 4.3.

Table 4.3: RMBR-NF cobalt removal additional unit operations

Equipment Name	Modelling Purpose and details
COR-MIX	Additional mixing tank that mixes the sodium sulphate recycle stream (SR-08) and the filter filtrate (COR-13). The extra mixer is due to the recycled sodium sulphate from the nickel-sulphur separation process to produce a 100 g/l sodium sulphate solution to electrowinning

For in-depth detail regarding unit operation operating conditions refer to Appendix D.1.

4.3.3. NICKEL ELECTROWINNING SECTION

The modifications in the nickel electrowinning will be discussed. For more information detailed information about the nickel electrowinning flowsheet refer to Section 3.3.11. The modified nickel electrowinning Aspen Plus flowsheet is given in Figure 4.14.

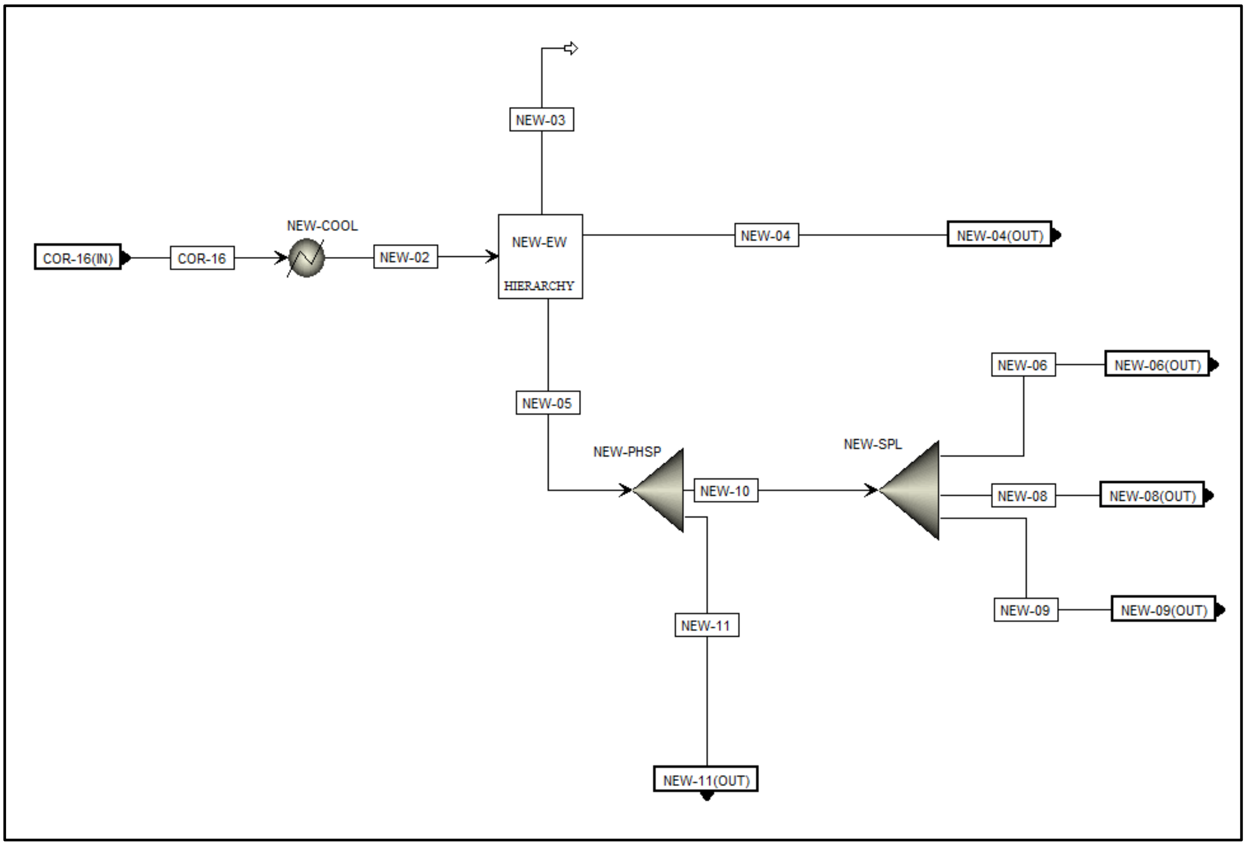

Figure 4.14: Aspen Plus RBMR-NF nickel electrowinning section flowsheet

The only modification in the nickel electrowinning section is the modification of the spent electrolyte stream splitter (NEW-SPL). The spent nickel electrolyte (NEW-10) is fed to the stream splitter (NEW-SPL). NEW-08 is sent to the sulphur removal section, whereas NEW-06 is sent to the cobalt production plant. NEW-09 is recycled to the nickel atmospheric leach stage to act as leaching agent. The reason for the small modification is due to the new sulphur removal process that receives the spent electrolyte stream as a total. The RBMR sulphur removal process received the spent electrolyte in two separate streams.

Detailed specifics of the RBMR-NF nickel electrowinning section can be seen in Appendix D.2.

4.3.4. SULPHUR REMOVAL SECTION

The RBMR-NF sulphur removal section removes sulphates from the process by separating nickel sulphate from sulphuric acid using NF technology. The RBMR-NF sulphur removal section Aspen Plus flowsheet is given in Figure 4.15.

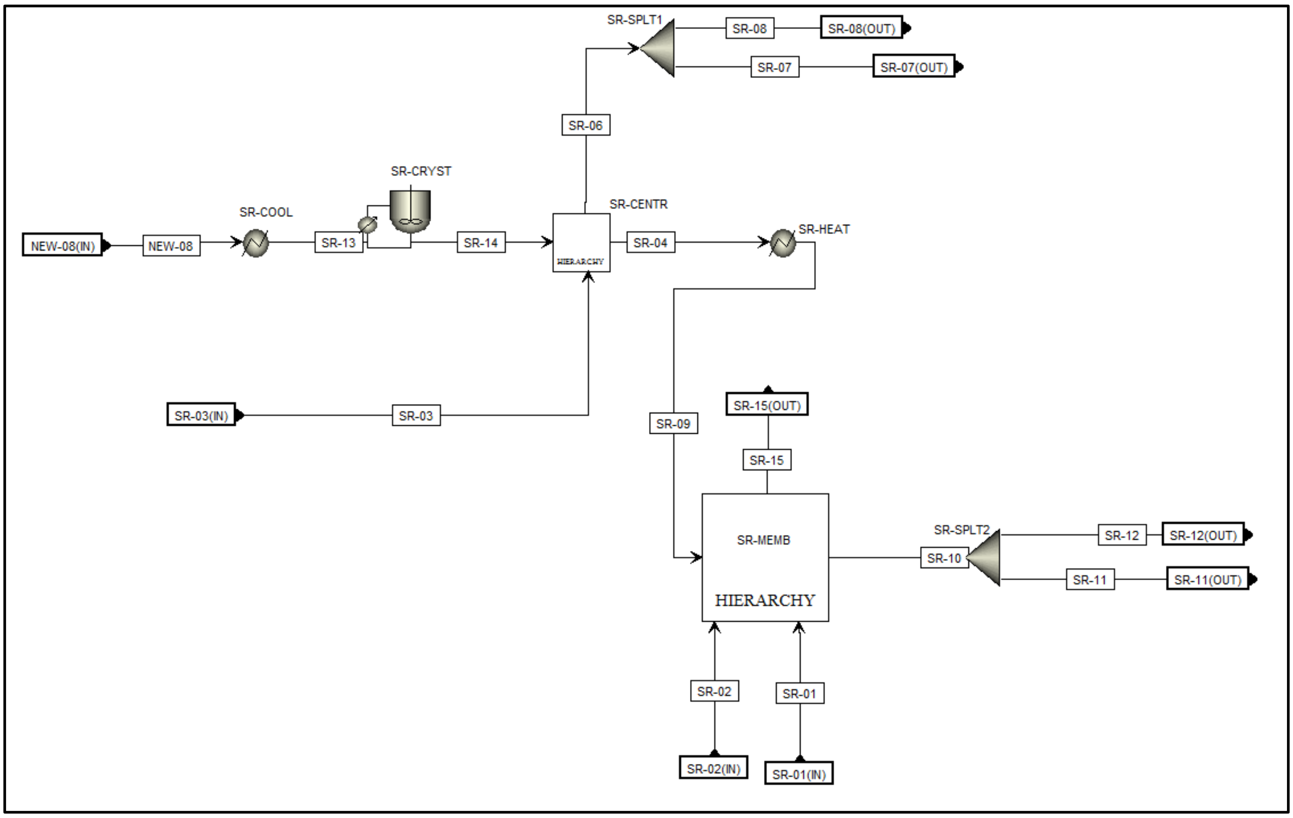

Figure 4.15: Aspen Plus RBMR-NF sulphur removal section flowsheet

Detailed specifics of the RBMR-NF sulphur removal section can be seen in Appendix D.3. The sulphur removal process is modelled using seven unit operations as given in Table 4.4.

Table 4.4: RMBR-NF sulphur removal unit operations

Equipment Name	Modelling Purpose and details
SR-COOL	Models a cooling heat exchanger. The nickel spent electrolyte is fed to the cooling heat exchanger to reduce the heat duty required by the crystallizer (SR-CRYST).
SR-CRYST	Models the cold crystallizer. The cold crystallizer cools the liquor and crystalizes the sodium as sodium sulphate crystals.
SR-CENTR	Models a system of centrifuges. The system is modelled using the filter and wash algorithm as reviewed in Appendix F.2.
SR-SPLT1	Models a stream splitter that splits the solids product (SR-06) from the centrifuge into two streams (SR-08, SR-07).

Equipment Name	Modelling Purpose and details
SR-HEAT	Models a heater that heats the he liquid stream (SR-04) from the centrifuge system. The heat exchanger heats the liquid to appropriate levels (20˚C) suitable for the NF system.
SR-SPLT2	Models a stream splitter where the acid-free liquor (SR-10) is split into two streams (SR-11 and SR12).
SR-MEBM	The NF system is modelled using a hierarchy containing membrane systems, mixers, stream splitters and pumps. The NF system, although consisting of separate unit operations, is seen as a single unit. SR-MEBM is explained in detail in Section 4.3.4.1.

4.3.4.1. SR-MEBM: NF System

A detailed view of the NF system (SR-MEMB) is given in Figure 4.16.

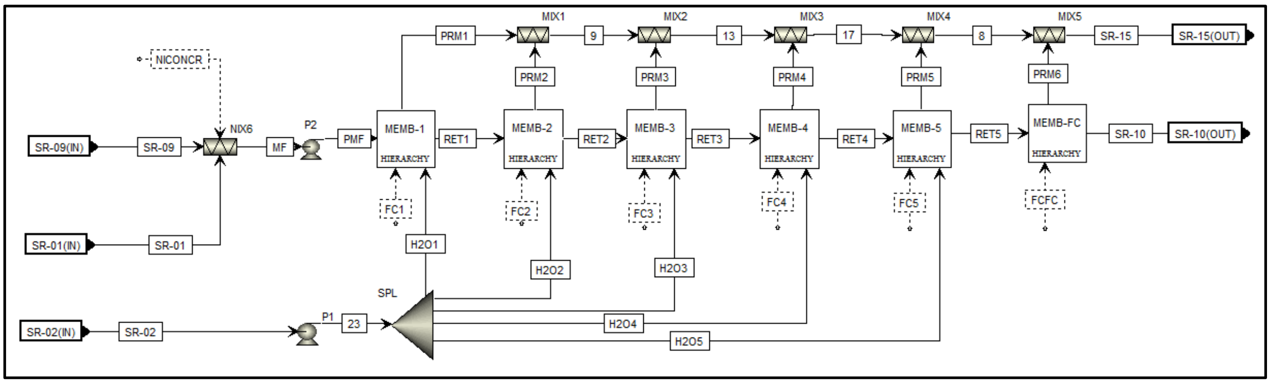

Figure 4.16: Aspen Plus RBMR-NF sulphur removal section NF system flowsheet

The product from the heating heat exchanger (SR-09) as well as two water streams (SR-01 and SR-02) is fed to the NF system. The NF system consists of high pressure pumps, mixers, and NF unit operations.

A total of six NF modules in series (MEMB-1, MEMB-2, MEMB-3, MEMB-4, MEMB5 and MEMB-FC) make up the NF system. The amount of NF modules needed to optimize the operating expenditures is dependent on the type of membrane used and the feed composition. Thus to simplify the matter six membranes were considered to be a good average to use.

A NF unit operation works with four parameters to predict the permeate and retentate product compositions and flow rates:

- Flux
- Nickel rejection
- Sodium rejection

- Sulphuric acid rejection

Thus different membrane characteristics can be an input to the NF unit operations to predict the performance of the membrane system. The NF unit operation algorithm is given in Appendix F.5.

The dotted streams (NICONCR, FC1, FC2, FC3, FC4, FC5 and FCFC) are dummy streams which provide control inputs to the design specifications as well as algorithms used to model the NF system.

The intermediate permeate streams (PRM1, PRM2, PRM3, PRM4, PRM5, PRM6) are all combined to form one permeate stream (SR-15). The retentate streams (RET1, RET2, RET3, RET4, RET5) increases in PH in following order as the acid is washed out of the permeate stream.

The two final products from the NF system are the retentate product (SR-10) as well as the permeate product (SR-15). The retentate product is fed to the stream splitter (SR-SPLT2) whereas the permeate product is fed to permeate product treatment to recover nickel and further refine the acid.

4.3.5. SIMULATION CONCLUSION

In Section 4.3, the RBMR-NF process was successfully simulated in Aspen Plus. The RBMR-NF Aspen Plus simulation can now be used to study the RBMR-NF process, as well as investigate different types of membranes in terms of acid, nickel and sodium rejection and flux.

4.4. RBMR-NF CASE STUDIES

4.4.1. INTRODUCTION

In this chapter case studies will be performed on the RBMR-NF process to ascertain the feasibility of applying NF technology in a BMR.

The NF unit operations in the RBMR-NF simulation are compatible with correlations for nickel rejection, sodium rejection, acid rejection and flux. Thus the four mentioned parameters can be calculated with any algebraic correlation.

One of the objectives of this study is to determine the type of membrane required to produce technically sound results in the RBMR-NF. To achieve this objective, different scenarios (otherwise known as case studies) will be investigated to determine the effect of different membrane characteristics on the RBMR-NF process by varying the membrane parameters.

4.4.2. MANIPULATED VARIABLES

To determine the effect of different membrane characteristics on the RBMR-NF process, acid, nickel and sodium rejection parameters need to be varied. In this section the to-be varied parameters will be discussed.

Parameter variations as applied in this study are based on the experimental results obtained by Stolp (2006). Stolp (2006) investigated several parameters as summarized in Table 4.5:

Table 4.5: NF manipulated variable and results ranges (Stolp, 2006)

Manipulated Variable		Ni^{2+} Rejection (%)	H_3O^+ Rejection (%)	Flux ($kg.hr^{-1}.m^{-2}$)
[P: 20 – 40 bar] [Ni:30g/l] [pH: 1]	Upper	99	-7	85
	Lower	97.8	-15	27
[P: 25 – 50 bar] [Ni:40g/l] [pH: 1]	Upper	98.5	-16.97	74
	Lower	97.8	-38.04	25
[P: 25 – 55 bar] [Ni:50g/l] [pH: 1]	Upper	97.95	-4.7	59
	Lower	97.5	-34.9	29

Manipulated Variable		Ni^{2+} Rejection (%)	H_3O^+ Rejection (%)	Flux ($kg.hr^{-1}.m^{-2}$)
[P: 20 – 40 bar] [Ni:30g/l] [pH: 2]	Upper	98.9	-75.8	95
	Lower	98.7	-84	40
[P: 20 – 40 bar] [Ni:40g/l] [pH: 2]	Upper	99.2	-77	59
	Lower	99	-108	31
[P: 20 – 50 bar] [Ni:50g/l] [pH: 2]	Upper	98.9	-62	66
	Lower	98.3	-72	30

The results obtained by Stolp (2006) show the operating pressure influences the flux to a great extent. It can also be seen that the nickel rejection across all experiments are on average in the area of 98%, whereas the acid rejection differs greatly as the pressure, pH and nickel concentration changes.

It should be noted that Stolp (2006) did not include any sodium sulphate in the experiments shown in Table 4.6, although Stolp (2006) did report in a separate experiment that sodium sulphate addition at 100g/l reduces the flux ten-fold. Stolp (2006) also reported that sodium rejections of 50-60% were obtainable. Although the RBMR-NF pre-treatment process removes most of the Na_2SO_4, a noticeable amount (in the area of 10 g/l) is still in solution and thus lower fluxes as reported by Stolp (2006) are expected. Also of importance is the nickel rejections reported by Stolp (2006). Nickel rejections in the area of 98% were observed at feed conditions which contained at most 50 g/l of nickel. The RBMR-NF operates at nickel concentrations up to 80 g/l. Taleb-Ahmed et al. (2002) and Al-Rashdi, B.A.M. *et al*. (2013) both reported that high reductions in metal rejection is expected as the metal concentration increases, thus it can be expected that the average nickel rejection for the RBMR-NF will be much lower than 98%.

In this study three main categories of case studies are completed to ascertain the feasibility of applying NF technology in a BMR. The three categories are the manipulation of acid rejection, manipulation of sodium rejection and manipulation of nickel rejection. In all three categories the operating pressure is assumed to be 50 bar whereas the flux is a conservative 20 $kg.hr^{-1}.m^{-2}$.

4.4.2.1. Varied Parameter 1: NF Acid Rejection

The case studies for studying the effect of acid rejection variations are given in Table 4.7:

Table 4.7: NF Acid Rejection Case Studies

Case	Ni^{2+} Rejection %	Na^{+} Rejection %	H_3O^{+} Rejection %	Flux @ 50 bar $kg.hr^{-1}.m^{-2}$
1	98	50	-100	20
2	98	50	-80	20
3	98	50	-60	20
4	98	50	-40	20
5	98	50	-30	20
6	98	50	-20	20
7	98	50	0	20

The effect of acid rejection on the RBMR-NF will be determined by the case studies as given in Table 4.7. The acid rejection is varied from -100% to 0%, whereas the average sodium and nickel rejections are kept at 50% and 98%.

4.4.2.2. Varied Parameter 2: NF Sodium Rejection

The case studies for studying the effect of sodium rejection variations are given in Table 4.8

Table 4.8: Sodium Rejection Case Studies

Case	Ni^{2+} Rejection %	Na^{+} Rejection %	H_3O^{+} Rejection %	Flux @ 50 bar $kg.hr^{-1}.m^{-2}$
8	98	30	-40	20
9	98	40	-40	20
10	98	50	-40	20
11	98	60	-40	20
12	98	70	-40	20

The case studies as given in Table 4.8 will determine the effect sodium rejection has on the RBMR-NF process. The acid rejection is kept at an average of -40% and the nickel rejection at 98%.

4.4.2.3. Varied Parameter 3: NF Nickel Rejection

The case studies for studying the effect of nickel rejection variations are given in Table 4.9

Table 4.9: Nickel Rejection Case Studies

Case	Ni^{2+} Rejection %	Na^+ Rejection %	H_3O^+ Rejection %	Flux @ 50 bar $kg.hr^{-1}.m^{-2}$
13	90	50	-40	20
14	92	50	-40	20
15	94	50	-40	20
16	96	50	-40	20
17	97	50	-40	20
18	98	50	-40	20
19	99	50	-40	20
20	99.5	50	-40	20

Table 4.9 shows the different case studies to study the effect nickel rejection has on the RBMR-NF concentration. The acid rejection is kept at an average of -40% and the sodium rejection at 50%.

4.4.3. REPORTED VARIABLES

The process variables that will be evaluated for each case study are given in Table 4.10

Table 4.10: Parameter variations results variables

Variable	Units	Type
Stream SR-09 (NF system feed)		1
Mass Flow	t/hr	
Volume Flow	m^3/hr	
Ni^{2+} Concentration	g/l	
Na^+ Concentration	g/l	
H_2SO_4 Concentration	g/l	
Stream SR-15 (final permeate)		1
Mass Flow	t/hr	
Volume Flow	m^3/hr	
Ni^{2+} Concentration	g/l	
Na^+ Concentration	g/l	
H_2SO_4 Concentration	g/l	
Stream SR-10 (final retentate)		1
Mass Flow	t/hr	
Volume Flow	m^3/hr	
Ni^{2+} Concentration	g/l	
Na^+ Concentration	g/l	
H_2SO_4 Concentration	g/l	
% Nickel Permeated	%	2
% Acid Permeated	%	2

Variable	Units	Type
% Sodium Permeated	%	2
Total Pump Power	kW	3
Total Membrane Area	m^2	3
Total Membrane Water Usage	t/hr	3
Evaporator Duty	GW	4
Na_2SO_4 Production	kg/hr	4
Nickel Cathode Production	kg/hr	4

The process variables as given in Table 4.10 can be divided into four types:

1) **NF system stream information**

   Stream information consists of mass flows, volume flows and specie concentrations. Note stream SR-09 is the feed to the NF system, and not the feed to the actual NF membrane. The total feed into the membrane system will be the sum of stream SR-09 and the membrane water usage.

2) **NF system permeation**

   Total permeation of nickel, acid and sodium are reported in the system permeation variables.

3) **NF system performance**

   System performance variables consists of the total duty of all the pumps used, the total membrane area as well as the dilution water used in the NF system.

4) **Plant miscellaneous**

   Variables termed “miscellaneous” are variables outside of the NF system, although important to report. The evaporator duty is the duty of the evaporator used in the cobalt section to prepare the solution for electrowinning. The evaporator duty variable is reported due to the NF system that influences the evaporator duty (hydrous sodium sulphate is recycled back to the cobalt section). Sodium sulphate production is reported due to the NF system that also influences the amount of sodium sulphate lost in the permeate stream. Nickel cathode production is reported due to nickel lost in the permeate stream – thus the performance of the NF membrane directly affects the amount of nickel lost in the permeate stream.

4.4.4. RESULTS & DISCUSSION

The results for the different case studies in regards to the three groups of parameter variations are given in this section. Detail results of the different cases are summarized in Appendix G.

4.4.4.1. Parameter 1: Effect of acid rejection

The effect of the acid rejection on the RBMR-NF process will be discussed in this section. Detailed results of the different cases can be found in Appendix G.1.

Three figures are used to visually illustrate the performance of the NF system for the related cases:

- The effect of acid rejection on the NF system feed mass flow rate, the retentate mass flow rate and permeate mass flow rate(Figure 4.17)
- The effect of acid rejection on the permeation of Ni^{2+}, Na^{+} and H_2SO_4 (Figure 4.18)
- The effect of acid rejection on the total membrane size (Figure 4.19)

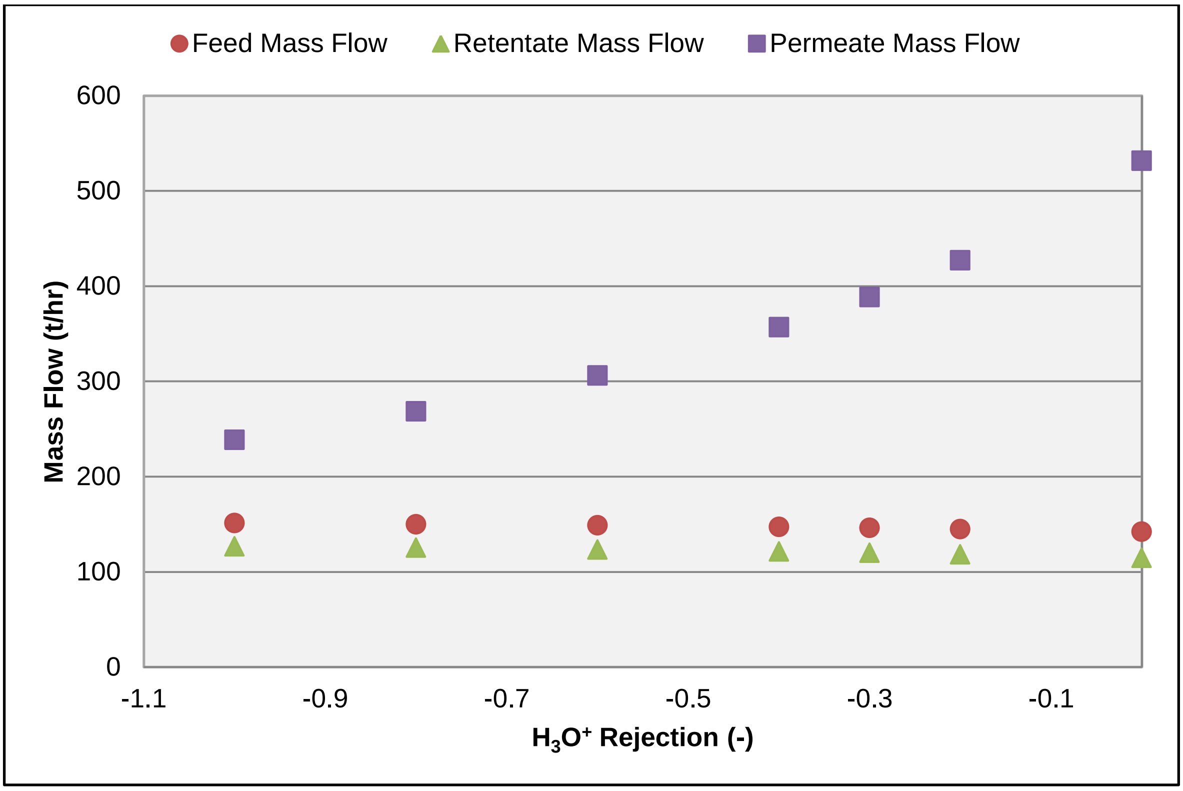

Figure 4.17: NF mass flows against acid rejection

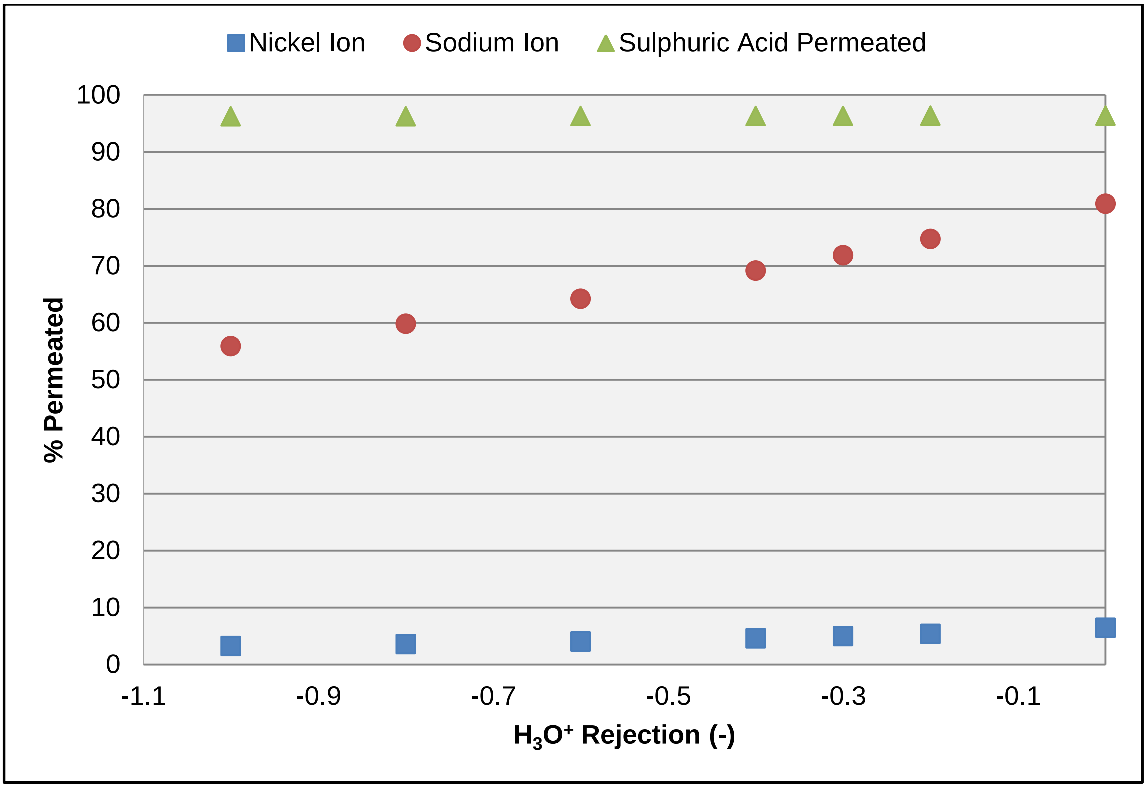

Figure 4.18: Permeated specie percentage versus acid rejection

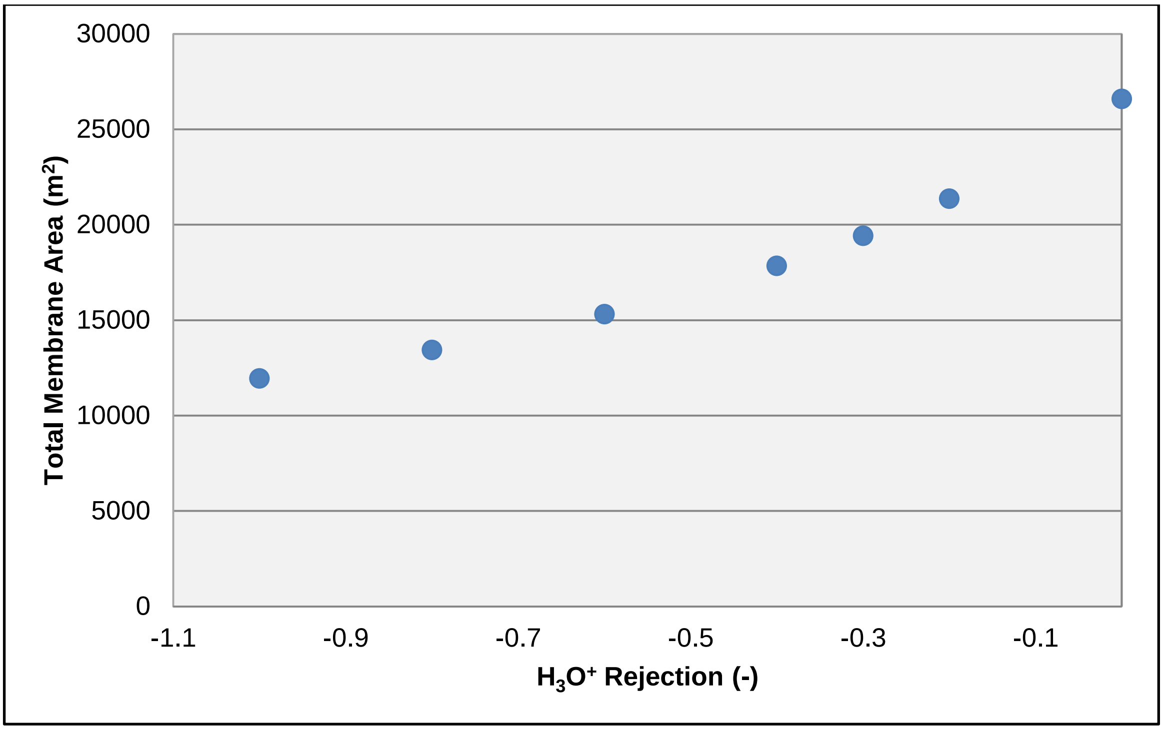

Figure 4.19: Total membrane area versus acid rejection

Figure 4.17, Figure 4.18 and Figure 4.19 shows the smaller the acid rejection, the more economically feasible the RBMR-NF process becomes. The statement can be made due to the permeate stream that reduces in size as the acid rejection decreases; consequently as the permeate stream decreases, the membrane size also decreases due to less volumes of liquid that needs to permeate through the membrane.

From Figure 4.18 can be seen that both the sodium and nickel permeation increases as the acid rejection increases. This phenomena is attributed to more wash water required to flush the sulphuric out of the system; a larger volume of water that passes through the membrane takes more sodium and nickel with it, consequently causing sodium and nickel to be lost in the permeate stream. Also clear is the sodium permeation incremental increase with increase in acid rejection which is greater compared to the nickel permeation incremental increase. The reason for the bigger incremental sodium permeation is due to smaller sodium rejection (50%) compared to nickel rejection (98%).

Figure 4.19 shows an exponential distribution of the data (exponential increase of membrane size), which states the importance of the acid rejection performance of the membrane. It is difficult to give an indication of the cut-off point for a viable process due to the lack of an economic study; although from a technical point of view the acid rejection should be less than -100% to minimize nickel losses to the permeate stream.

4.4.4.2. Parameter 2: Effect of sodium rejection

The effect of Na^{+} rejection NF characteristics on the RBMR-NF process will be discussed in this this section. Detailed tabulated data can be seen in Appendix G.2.

The performance of the NF system for the related cases to sodium rejection is illustrated in the following five figures:

- The effect of sodium rejection on NF system feed, retentate and permeate mass flows (Figure 4.20)
- The effect of sodium rejection on Specie permeations (Figure 4.21)
- The effect of sodium rejection on Total membrane area (Figure 4.22)
- The effect of sodium rejection on Evaporator duty 9Figure 4.23)
- The effect of sodium rejection on Anhydrous sodium sulphate production (Figure 4.24)

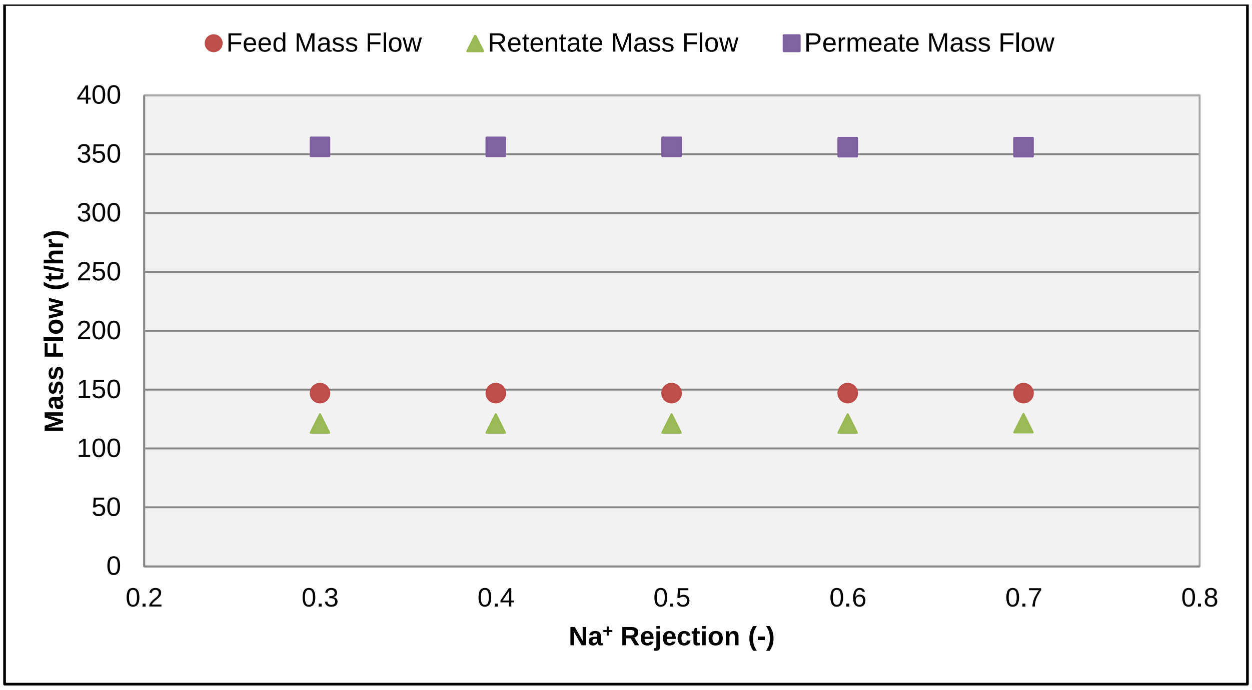

Figure 4.20: NF mass flows versus sodium rejection

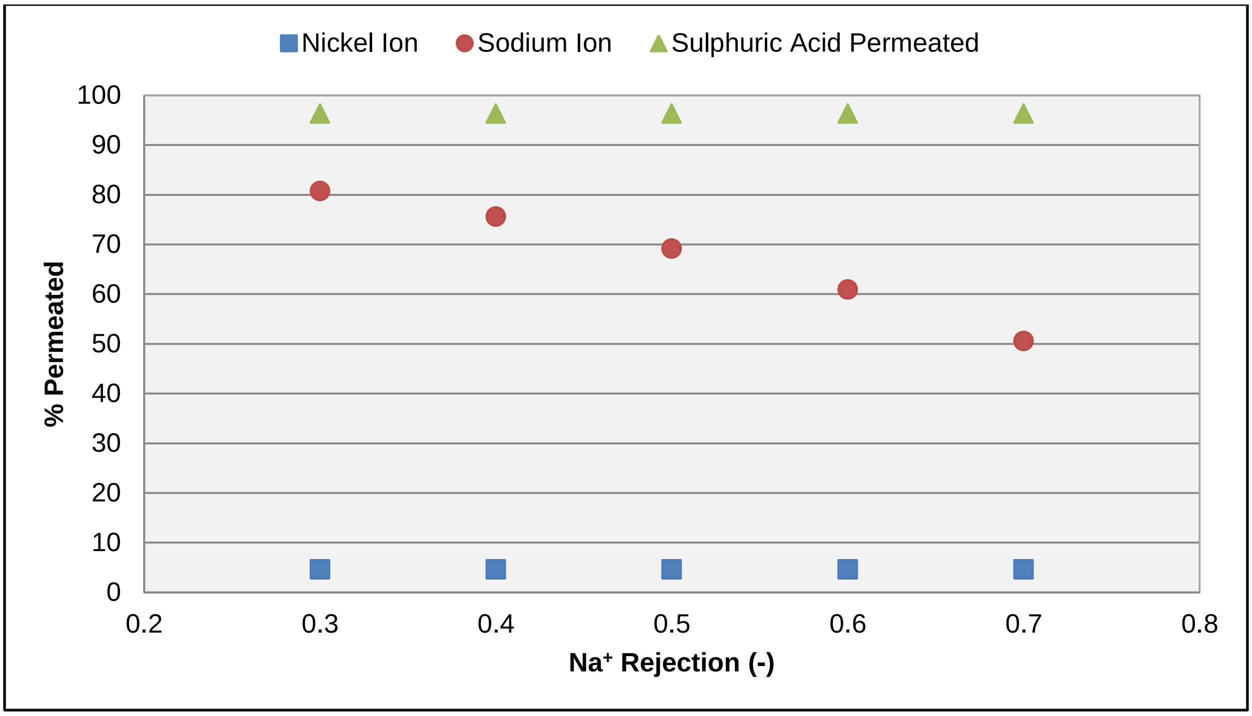

Figure 4.21: Percentage specie permeation versus sodium rejection

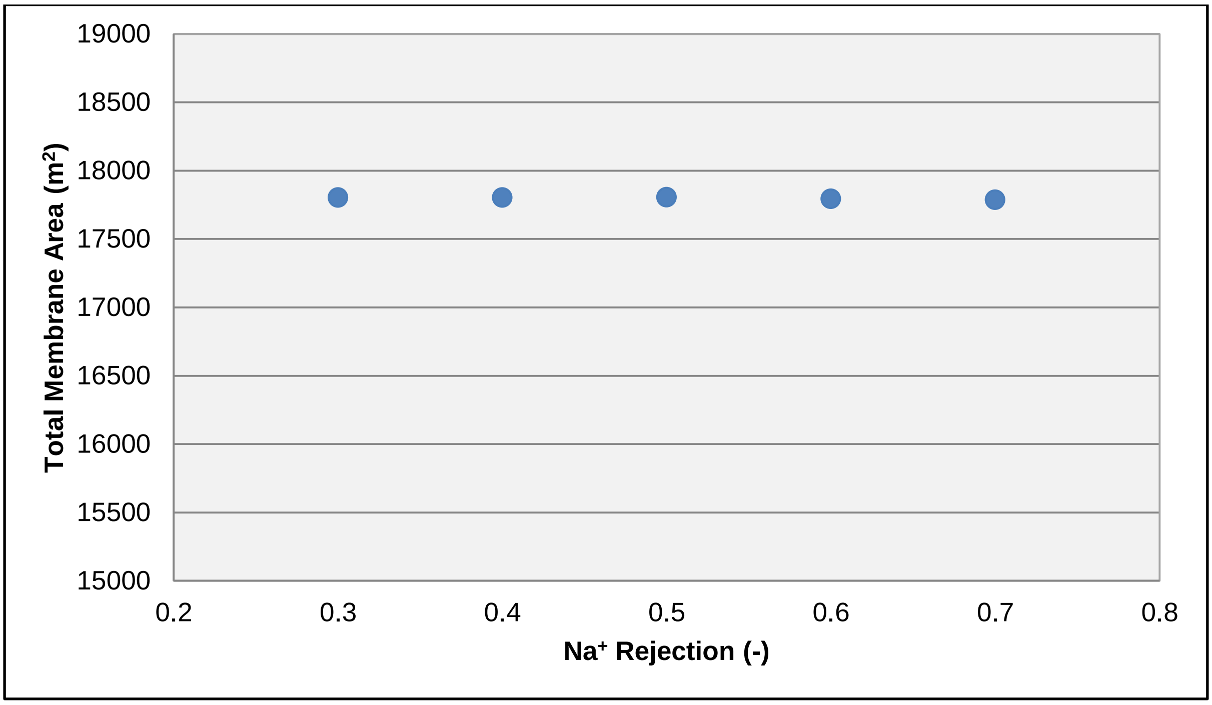

Figure 4.22: Total membrane area versus sodium rejection

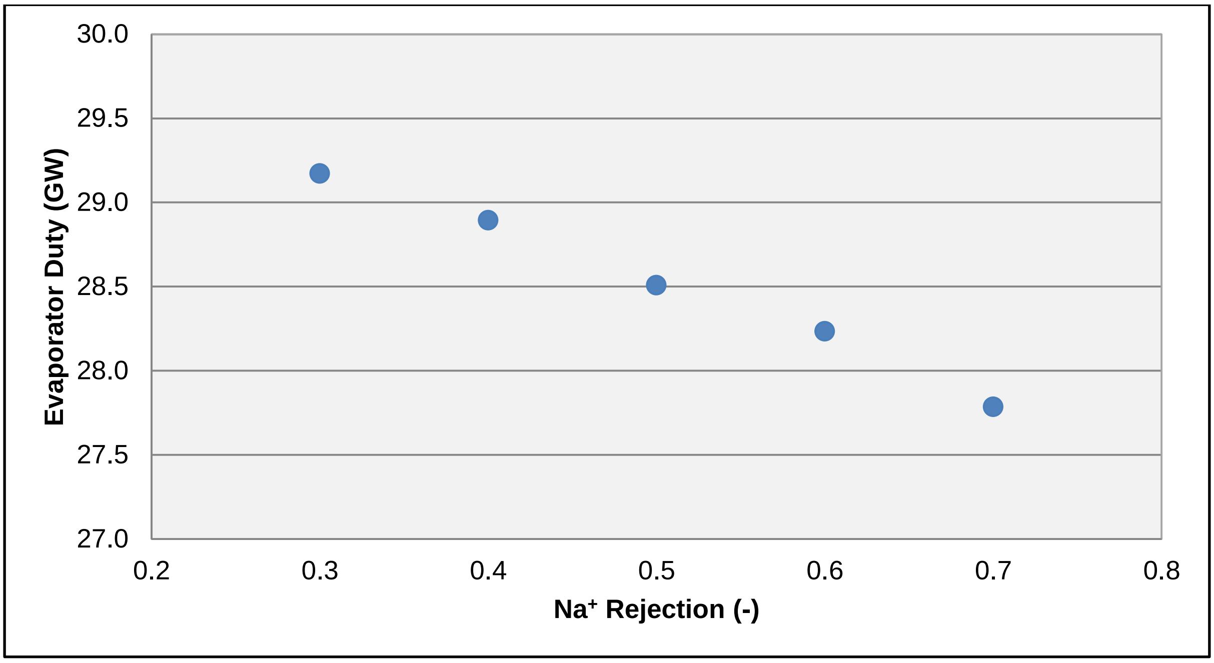

Figure 4.23: Evaporator duty versus sodium rejection

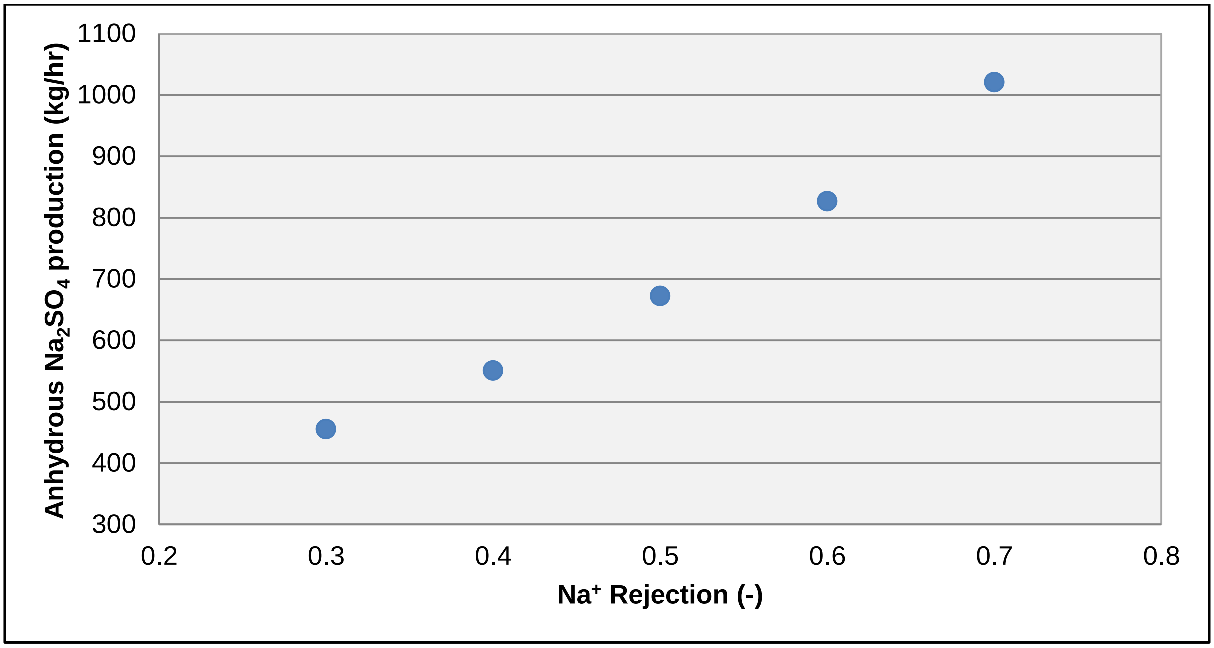

Figure 4.24: Anhydrous sodium sulphate production versus sodium rejection

It can be seen from Figure 4.20 and Figure 4.22 that sodium rejection does not have a major impact on the flow rates of the NF system feed, permeate and retentate streams (flow rates affects membrane size). This is due to the sodium sulphate concentration that is relatively minor (5 g/l) in the NF system feed stream as well as no process control being present on the sodium sulphate concentration. In contrast to the acid rejection, a strict control is placed on the retentate acid concentration and thus the acid rejection greatly influences the stream flows of the permeate and retentate streams.

Figure 4.21 is clear to show that only the sodium permeation increases with a decrease in sodium rejection.

Figure 4.23 and Figure 4.24 shows how the sodium rejection influences the evaporator duty as well as the production of sodium sulphate. An increase in sodium sulphate production from 450 kg/hr to 1020 kg/hr is observed, whereas a reduction in evaporator duty from 29MW to 28MW is observed. This shows how an increase in sodium rejection is beneficial to the economic viability of the RBMR-NF due to a reduction in operating costs and an increase in sodium sulphate production.

4.4.4.3. Parameter 3: Effect of nickel rejection

The effect of Ni^{2+} rejection NF characteristics on the RBMR-NF process will be discussed in this this section. Detailed tabulated data can be seen in Appendix G.3.

Three figures are used to graphically illustrate the performance of the case studies related to nickel rejection:

- The effect of nickel rejection on NF system feed, retentate and permeate mass flows (Figure 4.25)
- The effect of nickel rejection on specie percentage permeation (Figure 4.26)
- The effect of nickel rejection on total membrane area (Figure 4.27)

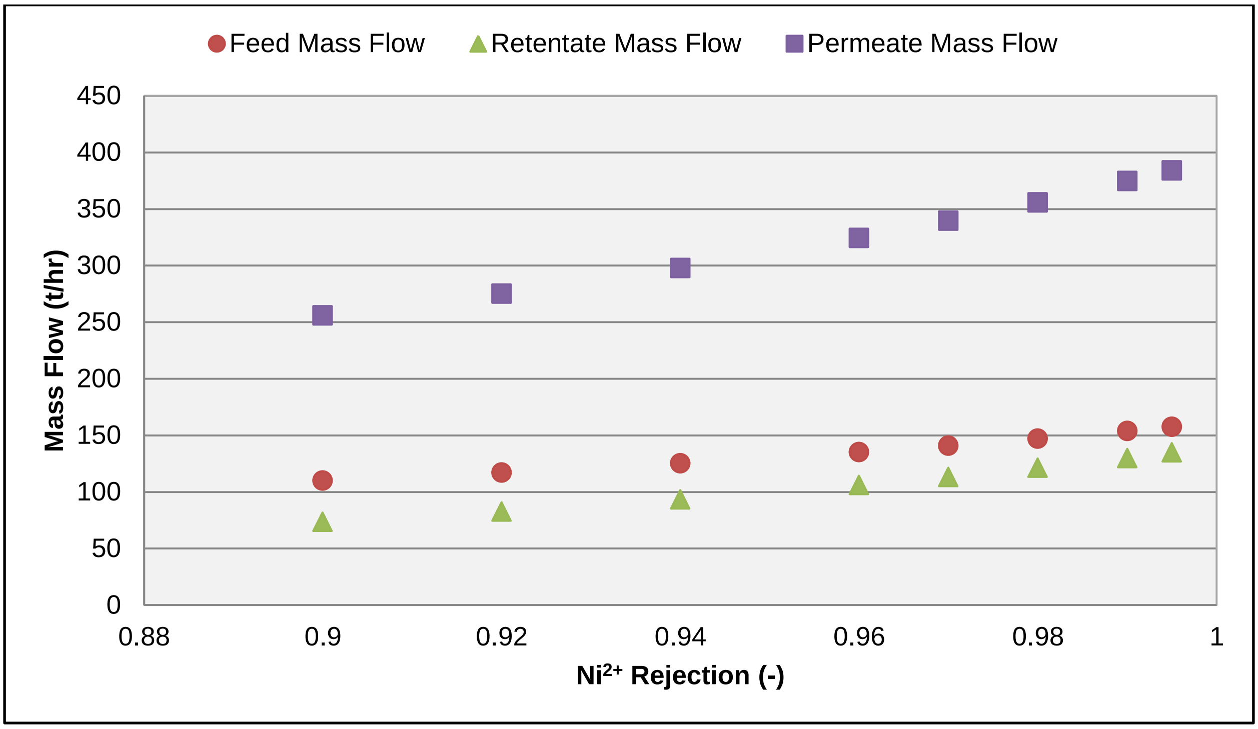

Figure 4.25: NF feed mass flow versus nickel rejection

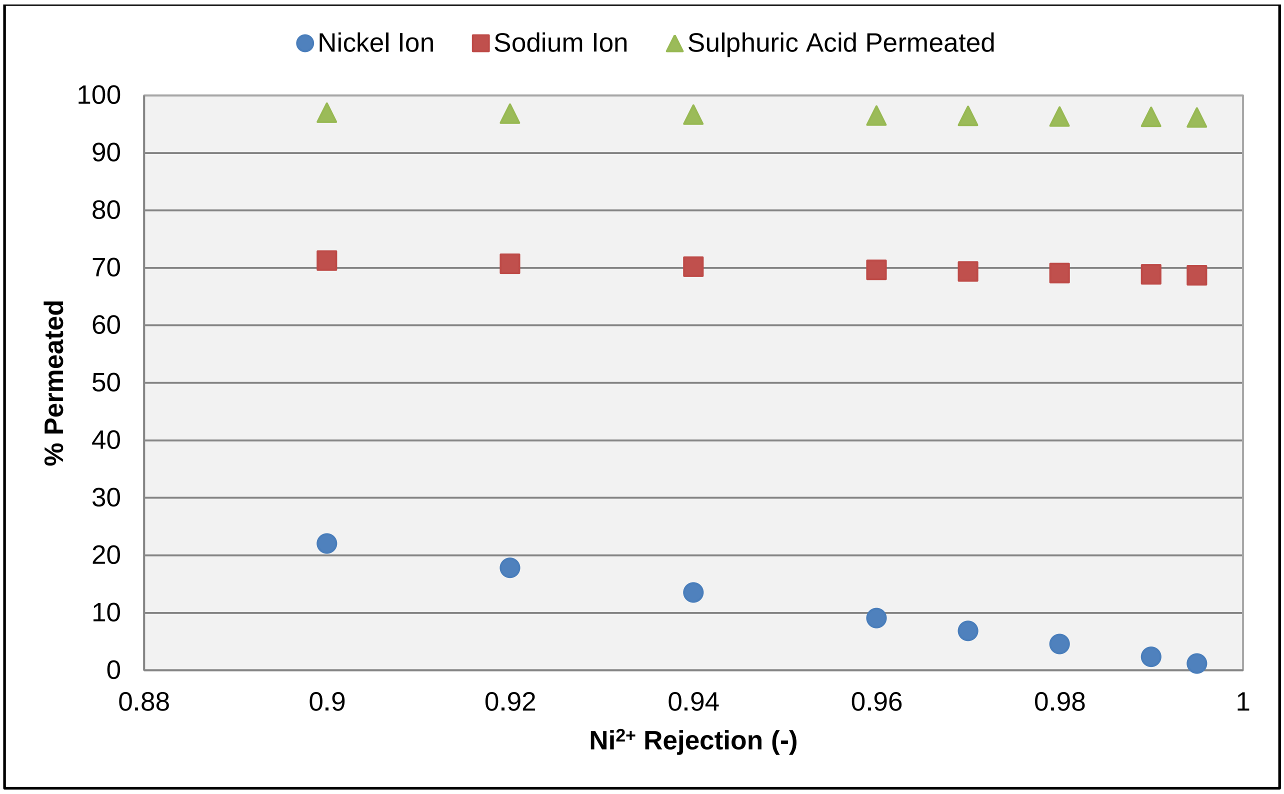

Figure 4.26: Percentage permeated versus nickel rejection

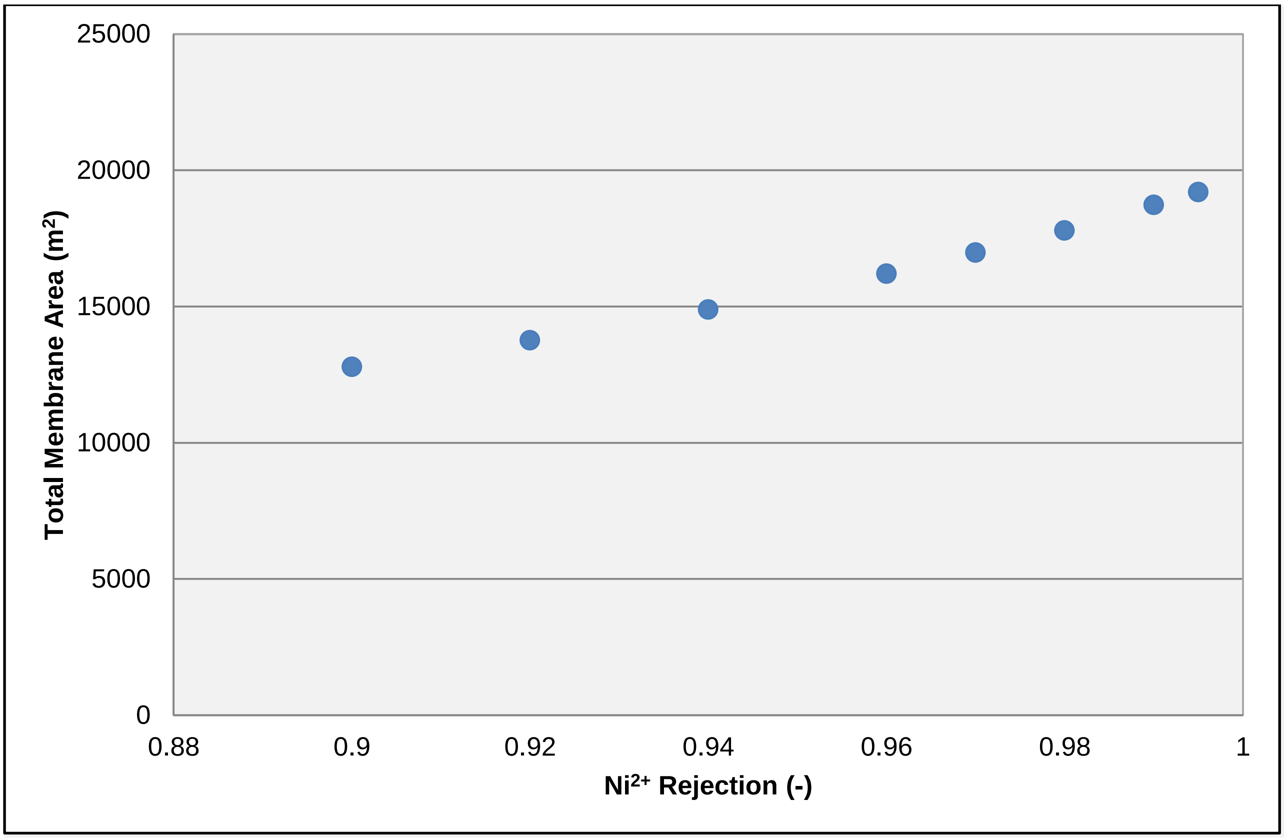

Figure 4.27: Total membrane area versus nickel rejection

Figure 4.25 shows how the retentate, permeate and feed mass flow rates increases as the nickel rejection increase. The lower the nickel rejection, the more nickel is permeated through the membrane and thus the less volume is required to maintain the specified nickel concentrations in the RBMR process. Thus the feed to the NF system is reduced with a reduction nickel rejection.

Ion permeation through the membrane is indicated in Figure 4.26, and shows how the sulphuric acid permeation and sodium ion permeation stays relatively constant. The sodium permeation average is 70%, whereas the sulphuric acid permeation is 96.5%. The nickel permeation is reduced from 22% to 1.2% as the Ni^{2+} rejection decreases from 90% to 99.5%. The results show that Ni^{2+} rejection greatly affects the viability of the NF system due to nickel losses through the membrane.

Figure 4.27 show how a higher Ni^{2+} rejection increases the total membrane area. The phenomena are attributed to the fact that a lower Ni^{2+} rejection causes nickel losses, and thus a decrease in the flow rate to the NF plant.

Nickel rejection is thus an important characteristic of the membrane due to nickel that potentially leaks through the membrane. It is important for the membrane to be characteristic of nickel rejections high in the 90% region, at least 98%, so that minor amount of nickel permeates through the membrane which can be recovered again in a secondary process.

4.4.5. CONCLUSION FROM CASE STUDIES

In this section the RBMR-NF simulation was used to execute different case studies, by varying the acid, nickel and sodium rejection parameters of the membrane.

It was found that the acid rejection has a key influence on the total size of the membrane needed, the amount of dilution water needed as well as the concentration of the acid in the permeate stream. Thus it is of importance for the NF membrane to consist of low acid rejection characteristics (in the order of -100%) to minimize the amount of water used as well as the total size of the membranes.

The sodium rejection does not have a big impact on the overall viability of the RBMR-NF process due to the low amounts of sodium present in the NF system feed stream. Although the impact is minimal, it can still be seen that a higher sodium rejection is beneficial to the overall economics due to an increase in Na_2SO_4 production as well as a reduction in evaporator duty.

Nickel rejection directly impacts the heart of the process – nickel is the primary product of the RBMR process and thus it is unacceptable to lose nickel through permeation in the NF system.

It is thus of great importance that the nickel rejection should be at least 98% to minimize the amount of nickel that permeates through the membrane. Even at a rejection of 99.5% a decent amount of nickel (114 kg/hr) still permeates through (depending on the acid rejection as well), and thus a secondary process will be required to recover the lost nickel.

Overall from a technical point of view, the RBMR-NF process is technically viable for the range of membrane characteristics tested (all case studies). It is however required for an economic study on the RBMR-NF to investigate the economic viability of the process.

4.5. CONCLUDING REMARKS

In this chapter the RBMR-NF process was investigated, developed, simulated and tested.

A literature study was done on the application of NF for acid separation in metal containing solution. It was found that NF can separate acid from metal ions in aqueous solution. To what extent the separation took place depended highly on the type of membrane as well as the metal and acid concentrations.

The RBMR-NF process was developed by combining literature studies with process design. It was found that a complex spent electrolyte treatment was necessary to remove sodium sulphate which fouls the membrane and in turn reduces the flux, consisting of cold crystallization and centrifugation. Small modifications such as a sodium sulphate recycle to the cobalt removal section had to be made to ensure the overall stability of the process.

Three membrane parameter variations were investigated on the nickel-sulphur removal process consisting of NF modules. The parameters were the sodium, nickel and sulphuric acid rejection. The acid and nickel rejection were found to affect the technical and economic viability of the RBMR-NF process, whereas the sodium rejection to a lesser extent due to low concentrations of sodium sulphate in the feed stream.

5. CONCLUSIONS & RECOMMENDATIONS

Overview

In this study, a conceptual process was developed to separate acid from metal containing solution in a base metals refinery. In this Chapter, conclusions and recommendations made from the study will be discussed.

This Chapter is subdivided into four sections, namely (1) the RBMR investigation and simulation, (2) the NF investigation and simulation of RBMR-NF, (3) the RBMR-NF case studies and (4) the final recommendations.

5.1. RBMR INVESTIGATION AND SIMULATION

In this study the RBMR process was successfully investigated, described, simulated and validated. Multiple literature sources were used to describe the RBMR process, develop design criteria as well as define chemistry for the process.

The information gathered as well as the simulation developed gave know-how of the RBMR process, and provided the basic tools and information needed to develop a new BMR process which includes NF as an alternative technology.

5.2. NF INVESTIGATION AND RBMR-NF SIMULATION

A literature study on NF technology was done, and it was found that NF is a suitable technology that can be used to substitute the RBMR nickel-sulphur separation process by separating acid from nickel.

A conceptual flow-sheet was then developed for the RBMR-NF, together with the applicable literature studies on the technologies used. Sodium sulphate was found to be a fouling agent who negatively influenced the flux and rejection properties of the membrane. It was thus required to provide a pre-treatment section which consisted of cold crystallization and centrifugation to remove most of the sodium sulphate in solution. Due to the removal of sodium sulphate, addition of sodium sulphate pre-electrowinning was required to meet the minimum sodium sulphate level of 100 g/l in the electrowinning section. For this reason a recycle stream from the sodium removal section was introduced to recycle a fraction of the sodium sulphate to pre-electrowinning. The NF system consists of six NF membranes in diafiltration configuration. Diafiltration was used due to the necessity to separate most of the acid from the retentate stream; diafiltration is the only technique that can achieve almost perfect acid separation by keeping the nickel concentration below osmotic pressure with the addition of dilution water.

A NF sulphur removal process was developed and simulated in Aspen Plus. The NF simulation was constructed in such a way that the nickel, sodium and acid rejection parameters as well as flux parameter can be varied with a constant or an algebraic expression for the modification of membrane performance. Thus the simulation has the ability to represent any type of membrane. The RBMR-NF conceptual flowsheet was simulated in Aspen Plus by combining the RBMR process with a simulation of the NF sulphur-removal process. The RBMR-NF simulation therefore provided a useful tool to predict process variabilities as a result of plant modifications.

5.3. RBMR-NF CASE STUDIES

The RBMR-NF simulation was used to study the effect of different NF membrane characteristics on the RBMR-NF process. The literature study on NF provided a range of parameters for acid, sodium and nickel rejection as well as flux. The different case studies were grouped according to the variation of a parameter; either acid, sodium or nickel rejection.

The case studies concluded that acid rejection of the membrane is an important characteristic which influences the technical and economic viability of the RBMR-NF process due to an exponential increase in membrane size, dilution water consumption and permeate product with an increase in acid rejection. Thus the acid rejection is favourable in the area of -100% to decrease operating and capital expenditures.

Sodium sulphate rejection was found to be of little importance due to low concentrations (5 g/l sodium) of sodium sulphate present in the NF system feed. Regardless of this, it was observed that a reduction in sodium rejection was beneficial to the operating expenditures due to an increase in sodium sulphate production as well as a decrease in evaporator duty.

Nickel rejection was found to be important to the RBMR-NF process due to nickel permeation through the membrane with a decrease in nickel rejection; nickel production decreases with a decrease in nickel rejection. Any nickel losses is unacceptable due to nickel being the primary product of the BMR. Thus it is required that nickel rejection be as high as possible to block the nickel from permeating through the membrane. The lower limit for realistic performance from a technical point of view (for later recovery of nickel in the permeate stream) is in the area of 98%, to produce a nickel concentration in the permeate at 1 g/l.

5.4. RECOMMENDATIONS

This study contributed the following information for the potential application of NF in a BMR:

- The RBMR-NF process is technically feasible for any kind of membrane characteristics tested, although not necessarily economically feasible
- Applying NF in a BMR to completely separate acid from metal containing solution is not a simple endeavour.
- Pre-treatment of the spent electrolyte is required to remove most of the sodium in solution due to NF performance degradations caused by the sodium – the process is energy intensive and possibly expensive
- Large volumes (relative to the feed volume) of water for dilution is required to separate all of the acid from the membrane

- The NF membrane used need to be able to achieve very low acid rejections (-100%) and very high nickel rejections (98%)
- With low acid rejections of up to -100%, the acid in the permeate stream is diluted at 42 g/l. Thus the acid cannot be used in an acid plant in the condition that it is in – concentration of the acid is required
- With high nickel rejections of up to 99.5%, a significant amount of nickel (114 kg/hr) is lost in the permeate stream – thus a secondary process to recover the nickel is required
- A large membrane surface area is required: 10 000m^2 and greater for this study

The following recommendations are made for future studies regarding the implementation of NF for the complete separation of acid from metal ions:

- Find a NF membrane that can potentially reject close to 98% of the nickel, and rejection close to -100% of the acid. This will enable minimum additional water usage for dilution purposes, and minimize the amount of nickel that permeates through the membrane
- The membrane will need to reject sodium to a large extent (greater than 90%) so that sodium does not block the membrane and cause performance degradations. If such a membrane is found then pre-treatment of the spent electrolyte might not be required and thus remove the requirement for an energy expensive cold crystallizer
- A simple and cheap process to recover nickel from the permeate needs to be developed
- A simple and cheap process to concentrate the acid in the permeate needs to be developed; this is vital in the sense that the acid needs to be concentrated to be used in an acid plant, and is thus of importance to the economics of the process. If the acid cannot be concentrated then the acid will need to be neutralized with limestone, which will further increase the operating costs of the RBMR-NF process

If the above recommendations are fulfilled in future studies then the potential of using NF to completely separate acid from metal containing solutions could become a reality.

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APPENDIX A - RBMR FEED STREAMS

Overview

Appendix A gives the raw and chemical/reagent materials and compositions used in the RBMR.

A.1. PROCESS RAW MATERIALS

A.1.1. Nickel-copper matte feed

The most important raw material feed to the base metals refinery is the nickel/copper matte feed, and the chemical analysis is given in Table A.2 (Anglo American, 2012).

Table A.1: Chemical analysis of NCM feed (dry basis)

Element		
Ni	wt%	43.8
Cu	wt%	29.3
Co	wt%	0.27
Fe	wt%	2.35
S	wt%	24.1
Si	wt%	0.02
PGM	g/t	112
Ca	g/t	56.9
Mn	g/t	8.28
Se	g/t	707
Te	g/t	251
Pb	g/t	621
Mg	g/t	16.6
Zn	g/t	23.8

From the chemical analysis in Table A.2 the following assumptions were made to calculate the mineralogy of the NCM feed:

- 50% of the iron in the matte is present as bornite (CU_5FeS_4), with the remaining iron present as troilite (FeS)
- All calcium and magnesium are present as oxides (MgO, CaO)
- Silicon is present as SiO_2
- Cobalt, manganese, lead and zinc are present as respective sulphides (Co_3S_4, MnS, PbS and ZnS)
- Selenium and tellurium are present as cuprous sellinide and telluride (Cu_2Se, Cu_2Te)
- The remaining copper is present as chalcocite (Cu_2S)
- Nickel is proportioned between metallic nickel (Ni), heazlewoodite (Ni_3S_2) and millerite (NiS) to balance the nickel and remaining sulphur

The mineralogical composition of the NCM feed can be seen in Table A.2.

Table A.2: NCM mineralogical feed composition

Mineral	Fraction
Ni	2.8189
Ni_3S_2	55.8531
Cu_2S	28.1276
Cu_5FeS_4	10.5513
Cu_2Se	0.1844
Cu_2Te	0.0502
FeS	1.8485
PbS	0.0717
SiO2	0.0443
MgO	0.0027
CaO	0.008
MnS	0.0013
ZnS	0.0035
Co_3S_4	0.4233
PGM	0.0112

A.1.2. Magnetic concentrate solution

The magnetic concentrate solution is a product from the precious metals refinery, rich in nickel and copper. The solution is introduced to the base metals refinery in the nickel non-oxidizing leach section. The composition of the solution is given in Table A.3 (Anglo American, 2012).

Table A.3: Magnetic concentrate solution composition

Property		
Rate	t/h	10.2
Temperature	°C	80.0
Solution Composition		
Ni	g/l	92.6
Cu	g/l	24.4
Fe (as Fe^{2+})	g/l	4.40
Co	g/l	1.10
H_2SO_4	g/l	11.70

A.2. PROCESS CHEMICALS/REAGENTS

Process chemical/reagents used are given in Table A.4 (Anglo American, 2012).

Table A.4: Process chemicals/reagents

Chemical/Reagent		
Air		
Pressure	atm	1
Temperature	°C	25
Gaseous oxygen		
Pressure	kPa	1400
Temperature	°C	25
Purity	wt%	99.5
Sodium hydroxide		
Temperature		25
Concentration	g/l	755
Sodium sulphite		
Temperature	°C	25
Concentration	g/l	150
Ferrous sulphite		
Temperature	°C	25
Concentration	g/l	272

APPENDIX B - RBMR DESCRIPTION & SIMULATION

Overview

Appendix B identifies and reports the chemistry of the RBMR process. It also gives the chemistry, equipment and design specifications as used in the Aspen Plus simulation for the different unit operations.

B.1. RBMR PROCESS

B.1.1. RBMR Global Chemistry

Chemistry exists that is valid across the entire refinery, such as the water dissociation reaction and the equilibrium between sulphuric acid and hydrogen sulphate. The global chemical reactions as used in the simulation of the process are given in Table B.1.

Table B.1: Global chemical reactions

Reaction	Reaction number
Equilibrium reactions	
$H_2SO_4 + H_2O \leftrightarrow H_3O^+ + HSO_4^-$	R-B.1
$HSO_4^- + H_2O \leftrightarrow H_3O^+ + SO_4^{2-}$	R-B.2
$2H_2O \leftrightarrow OH^- + H_3O^+$	R-B.3
Salt forming reactions	
$NaOH \leftrightarrow OH^- + Na^+$	R-B.4
$Na_2SO_4 \leftrightarrow 2Na^+ + SO_4^{2-}$	R-B.5

As seen from Table B.1 equilibrium as well as salt forming reactions are present. The salt forming reactions is the equilibrium between caustic soda and hydroxide/sodium ions (R-B.4), and the equilibrium between sodium sulphate and sodium/sulphate ions. The equilibrium reactions are the dissociation of sulphuric acid, of hydrogen sulphate, and the water dissociation reaction.

R-B.1 – R-B.5 are used throughout the simulation of the RBMR and will not be mentioned again.

B.1.2. NCM Leaching Mineral Reactivity

A brief overview of the general chemistry and reactivity of mineral compounds present in the leaching circuit will be given in this section, whereas in-detail chemical reactions will follow in the following sections where each unit of the process will be described. The reason for the literature study about the leaching circuit minerals is to get a better understanding of the leaching behaviour of the minerals to make accurate assumptions in the reaction presence and conversion in the leaching circuit.

The leaching circuit chemistry is described in detail by many sources as listed in Table B.2.

Table B.2: Leaching Chemistry Literature Sources

Source	**Research**
Hofirek & Kerfoot (1992)	The chemistry of the Ni-Cu matte leach and its application to process control and optimisation
Fugleberg *et al.(1995)*	The development of the Hartley Platinum leaching process
Rademan *et al.* (1999)	The leaching characteristics of Ni-Cu matte in the acid-oxygen pressure leach process at Impala Platinum
Provis *et al.* (2003)	A kinetic model for the acid-oxygen pressure leaching of Ni-Cu matte
Bryson *et al.* (2008)	Review of new matte leaching developments at Anglo Platinum's Base Metal Refinery
McDonald & Whittington (2008)	Review on acid leaching of nickel laterites by sulphuric acid
Büyükakinci & Topkaya (2009)	Extraction of nickel from lateritic ores at atmospheric pressure with agitation leaching
Lamya & Lorenzen (2009)	A semi-empirical kinetic model for the atmospheric leaching of Ni-Cu matte in copper sulphate-sulphuric acid
Chuan-Lin *et al.* (2010)	Kinetic of acid-oxygen leaching of low-sulphur Ni-Cu matte at atmospheric pressure

The main goal of the leaching circuit is the selective dissolution of copper and nickel. Selective dissolution of copper and nickel is possible due to the reactivity of copper sulphides being more stable than nickel sulphides (Fugleberg *et al.1995).*

Another factor contributing to the selective leaching is that while leaching heazlewoodite, copper ions are precipitated as chalcocite in a substitution reaction which releases nickel ions into the solution. Thus the presence of heazlewoodite ensures that nickel will be dissolved selectively (Rademan *et al.*, 1999).

Hofirek and Kerfoot (1992) showed that three main leaching steps can be identified within distinct pH ranges:

- Metathesis of copper (also known as cementation) is present up to a pH of 2.5. The formation of djurleite (which is very close to chalcocite), millerite and godlevskite is present within this pH range.

- Hydrolysis of iron in the pH range of 2.5 – 4.5. Ferric hydroxide ($Fe(OH)_3.xH_2$) or basic ferric sulphate ($Fe(OH)SO_4$) is formed in this stage.

- Antlerite formation in the pH range of 4.5 – 6

The concentrations of individual species as well as the availability of reactants play a large role in the chemistry. The early stages of the leach are predominantly driven by the leaching of the metal elements by sulphuric acid. Iron and copper is removed by means of hydrolysis with an increase in pH. The different leaching stages are accompanied by different sets of chemical reactions that occur in parallel (Lamya & Lorenzen, 2009; Hofirek & Kerfoot, 1992)

Reactivity of metal sulphides

Hartley (1995) leached different nickel materials in acid copper sulphate solutions to determine the reactivity of different feed materials in oxidative acid leaching. It was found that the metallic phase is the most reactive, followed by heazlewoodite. The most stable metal sulphide is chalcocite.

According to Rademan *et al.* (1999) the mineral with the most symmetry regarding to the molecular structure will comprise of the lowest free energy of formation and therefore the highest resistance to further leaching. The crystal structure for the major minerals present can be seen in Table B.3.

Table B.3: Crystal Structure of Minerals

Mineral	Mineral Name	Crystal Structure
Ni	Nickel Alloy	Cubic
Nickel Sulphides		
Ni_3S_4	Polydymite	Cubic
NiS	Millerite	Hexagonal
Ni_3S_2	Heazlewoodite	Hexagonal
Ni_7S_6	-	Orthorhombic
Copper Sulphides		
$Cu(Ni,Co)_2S_4$	Fletcherite	Cubic
Cu_9S_5	Digenite	Hexagonal
CuS	Covelite	Hexagonal
Cu_2S	Chalcocite	Orthorhombic

According to Rademan *et al.* (1999) the order of symmetry from high to low is cubic, tetragonal, hexagonal, orthorhombic, monoclinic and triclinic. Thus for nickel sulphides polydymite will be the least reactive, whereas heazlewoodite is expected to be the most reactive followed by millerite. Since Ni_7S_6 is an intermediary mineral it is expected to have the highest reactivity (Hofirek and Kerfoot, 1992)

For the copper sulphides fletcherite is the least reactive, followed by digenite, covelite and chalcocite.

What seems to happen is the more sulphur is present in the mineral, the more symmetrical it is. Thus reactivity of the mineral is directly related to the density and sulphur content of the mineral itself.

B.2. COPPER REMOVAL

B.2.1. Chemistry

The chemistry for the copper removal section is given in Table B.4.

Table B.4: Copper removal section chemistry

Chemical Reaction	Reaction number	Reference
Acid consuming		
$2Ni + 4H^{+} + O_2 \rightarrow 4NiS + 2Ni^{2+} + 2H_2O$	R-B.6	(1)
$2Ni_3S_2 + 4H^{+} + O_2 \rightarrow 4NiS + 2Ni^{2+} + 2H_2O$	R-B.7	(1)
Hydrolytic reactions		
$4Fe^{2+} + 4H^{+} + O_2 \rightarrow 4Fe^{3+} + 2H_2O$	R-B.8	(1)
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+}$	R-B.9	(1)
$Fe^{3+} + HSO_4^{-} + H_2O \rightarrow Fe(OH)SO_4 + 2H^{+}$	R-B.10	(1)
$Fe(OH)SO_4 + 2H_2O \rightarrow Fe(OH)_3 + H^{+} + HSO_4^{-}$	R-B.11	(1)
Copper Hydrolysis		
$3Cu^{2+} + HSO_4^{-} + 4H_2O \rightarrow Cu_3(OH)_4SO_4 + 5H^{+}$	R-B.12	(1)

(1) Hofirek and Kerfoot (1992)

As seen from Table B.4, three categories of chemical reactions take place. The first is the acid consuming reactions, where metallic nickel (R-B.6) and heazlewoodite (R-B.7) are reacted with hydrogen and oxygen to produce millerite and water.

The second category is the hydrolytic reactions, which occur above pH levels of 2 – 2.5. The ferrous ion is oxidised to ferric by the reaction of ferrous with oxygen and acid as illustrated in R-B.8. Above a pH of 3.5 the ferric ions become unstable and the result is R-B.9 and R-B.10 where the ferric ion is hydrolysed to basic ferric sulphate or ferric hydroxide. It is also possible for $Fe(OH)SO_4$ to be converted to $Fe(OH)_3$ as depicted in R-B.11. An iron concentration of below 0.1 g/l causes the pH to rise above the stability of the cupric ion, which results in the cupric ion being hydrolysed to form basic cupric sulphate $Cu_3(OH)_4SO_4$, also known as antlerite (Hofirek & Kerfoot, 1992). The reaction is depicted in R-B.12

R-B.12 releases acid into the solution, and the acid is consumed by R-B.6 and R-B.7 (unreacted heazlewoodite and metallic nickel consumes the acid).

At a residual copper concentration of 0.05 g/l in the solution the acid production due to the hydrogen ion production by hydrolysis becomes slower. Thus more acid is removed than produced and the pH rises to a maximum level of 6.5 – 6.7, where nickel sulphates may start to precipitate (Hofirek & Kerfoot, 1992).

B.2.2. Process Equipment

The process equipment for the copper removal section with their respective operating conditions and assumptions are given in Table B.5.

Table B.5: Copper removal process equipment

Equipment		
Feed stream mixer (CR-MIX)		
Pressure	kPa	88.24
Mixing reactor system (CR-REACT)		
Pressure	kPa	88.24
Temperature	°C	80
Vent evaporation rate	$kg.hr^{-1}$	1507
Reactions (in series)	Conversion	
X1 (R-B.12)		1
X3 (R-B.8)		1
X4 (R-B.11)		1
X5 (R-B.6)		1
X6 (R-B.7)		Design Spec CR1
Thickener (CR-THICK)		
Pressure	kPa	88.24
Vent evaporation rate	$kg.hr^{-1}$	1319
Overflow		
Solid fraction		0
Underflow		
Solid fraction		0.45

B.2.3. Design specifications

Design specification CR1

A design specification is set on the conversion of heazlewoodite in R-B.7 to satisfy a solution discharge from the reactor system (CR-REACT) pH of 4.

B.3. NICKEL ATMOSPHERIC LEACH

B.3.1. Chemistry

The chemistry for the nickel atmospheric leach section is given in Table B.6.

Table B.6: Nickel atmospheric leach section chemistry

Chemical Reaction	Reaction number	Reference
Feed preparation		
$Cu_3(OH)_4SO_4 + 5H^+ \rightarrow 3Cu^{2+} + HSO_4^- + 4H_2O$	R-B.13	(2)
$Ni_3(OH)_4SO_4 + 5H^+ \rightarrow 3Ni^{2+} + HSO_4^- + 4H_2O$	R-B.14	(2)
$Fe(OH)SO_4 + 2H^+ \rightarrow Fe^{3+} + HSO_4^- + H_2O$	R-B.15	(1)
$Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O$	R-B.16	(1)
$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+}$	R-B.17	(1)
$2Ni_3S_2 + 4H^+ + O_2 \rightarrow 4NiS + 2Ni^{2+} + 2H_2O$	R-B.7	(1)
$Ni_3S_2 + 2Fe^{3+} \rightarrow 2Fe^{2+} + 2NiS + Ni^{2+}$	R-B.18	(1)
Non-oxidizing leach (Reactors in series)		
$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+}$	R-B.17	(1)
$NiS + Cu^{2+} \rightarrow CuS + Ni^{2+}$	R-B.19	(3)
$FeS + Cu^{2+} \rightarrow CuS + Fe^{2+}$	R-B.20	(2)
Oxidizing leach (Reactors in series)		
$Ni_3S_2 + 2Fe^{3+} \rightarrow 2Fe^{2+} + 2NiS + Ni^{2+}$	R-B.18	(1)
$2FeS + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2S^o + 2H_2O$	R-B.20	(3)
$FeS + 2O_2 \rightarrow Fe^{2+} + SO_4^{2-}$	R-B.21	(2)
$2Ni_3S_2 + 4H^+ + O_2 \rightarrow 4NiS + 2Ni^{2+} + 2H_2O$	R-B.7	(1)
$8NiS + 4H^+ + O_2 \rightarrow 2Ni_3S_4 + 2Ni^{2+} + 2H_2O$	R-B.22	(2)
$10Cu_2S + 4H^+ + O_2 \rightarrow 2Cu_9S_5 + 2Cu^{2+} + 2H_2O$	R-B.23	(3)

(1) Hofirek and Kerfoot (1992)

(2) Taute & George (2010)

(3) Bryson *et al.* (2008)

As seen from Table B.6 chemical reactions takes place in the feed preparation (where the feed streams are mixed), the non-oxidizing leach section of the stirring reactors as well as the oxidizing leach section of the stirring reactors.

Feed Preparation

The contact of the copper removal residue with the spent electrolytes and nickel non oxidizing solution immediately starts the dissolution process of sulphates such as $Cu_3(OH)_4SO_4$ as given in R-B.13 to R-B.16.

Due to the high acid content (low pH) the cementation reaction as well as the decomposition of heazlewoodite takes place in R-B.17 and R-B.7. The reduction of ferric with heazlewoodite is also possible according to Reaction R-B.18.

Non-oxidizing leach

The non-oxidizing environment causes the leaching of heazlewoodite through metathesis reaction of copper ions as depicted in R-B.17.

Millerite formed in R-B.17 is also reacted through metathesis with copper ions as illustrated by R-B.19.

Troilite is known to react with copper ions via a metathesis reaction as given by R-B.20.

Oxidizing leach

The dissolved ferric is reduced in the oxidative leaching of heazlewoodite according to R-B.18.

One of the main goals of the nickel atmospheric leach is to consume a significant portion of the produced acid that comes from the nickel non-oxidizing leach stage. The acid is used for the continual leaching of nickel and iron under oxidizing conditions. Iron is leached according to R-B.20 and R-B.21.

Heazlewoodite is converted to millerite and millerite in turn is again converted to polydymite (R-B.7, R-B.22).

Some of the more reactive copper sulphides can also react to form digenite as given in R-B.23.

B.3.2. Process equipment

The process equipment for the copper removal section with their respective operating conditions and assumptions are given in Table B.7.

Table B.7: Nickel atmospheric leach section process equipment

Equipment		
Feed stream mixer (NAL-MIX)		
Pressure	kPa	88.24
Reactions (in series)	Conversion	
X2 (R-B.16)		1
X3 (R-B.18)		0.5
X4 (R-B.13)		1
Mixing reactor system (CR-REACT)		
Pressure	kPa	88.24
Vent evaporation rate	$kg.hr^{-1}$	1231
Non-oxidizing reactions (in series)	Conversion	
X1 (R-B.17)		Design Spec NAL-01
Oxidizing reactions (in series)	Conversion	
X2 (R-B.20)		1
X3 (R-B.21)		0.6
X4 (R-B.18)		Algorithm
X5 (R-B.7)		Algorithm
X6 (R-B.23)		Algorithm
Thickener (CR-THICK)		
Pressure	kPa	88.24
Vent evaporation rate	$kg.hr^{-1}$	1200
Overflow		
Solid fraction		0
Underflow		
Solid fraction		0.45

B.3.3. Design specifications

Design specification NAL1

A design specification is put R-B.17 to meet a copper concentration of 11.9 g/l in the nickel atmospheric leach product solution (NAL-09). The design specification manipulates the conversion of R-B.17 until the copper concentration is met.

B.4. PRESSURE IRON REMOVAL

B.4.1. Chemistry

The chemistry for the pressure iron removal section is given in Table B.8.

Table B.8: Pressure iron removal section chemistry

Chemical Reaction	Reaction number	Reference
Feed Tank		
$Ni(OH)_2 + 2H^+ \rightarrow Ni^{2+} + 2H_2O$	R-B.24	(2)
$Fe(OH)SO_4 + 2H^+ \rightarrow Fe^{3+} + HSO_4^- + H_2O$	R-B.15	(2)
Autoclave		
$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$	R-B.25	(2)
$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$	R-B.26	(1)
$12Fe^{2+} + 4Na^+ + 18H_2O + 8HSO_4^- + 3O_2 \rightarrow 4NaFe_3(OH)_6(SO_4)_2 + 20H^+$	R-B.27	(2)
$3Fe^{3+} + Na^+ + 6H_2O + 2HSO_4^- \rightarrow NaFe_3(OH)_6(SO_4)_2 + 8H^+$	R-B.28	(2)
$4Fe^{2+} + 6HSO_4^- + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O + 2H^+$	R-B.29	(2)

(1) Hofirek and Kerfoot (1992)

(2) Taute & George (2010)

As seen from Table B.8 chemical reactions are present in the feed tank and in the autoclave.

Feed Tank

Due to acid in the feed tank, sulphates and hydroxides are dissolved, as for example given by R-B.24 and R-B.15.

Autoclave

The pH levels inside the autoclave are controlled to ensure that iron is precipitated predominantly as hematite, since hematite removes many of the other impurities such as arsenic, tellurium and ruthenium. Hematite is also known to produces smaller quantities of solids.

Hematite is produced according to R-B.25 and R-B.26, whereas jarosite is formed according to R-B.27 and R-B.28.

It is also possible for the ferrous to be oxidized to ferric and precipitate as ferric sulphate as given in R-B.29.

B.4.2. Process Equipment

The process equipment for the pressure iron removal section with their respective operating conditions and assumptions are given in Table B.9.

Table B.9: Pressure iron removal section process equipment

Equipment		
Feed stream mixer (IR-MIX)		
Pressure	kPa	88.24
pH		3.5
Feed pre-heater (IR-PH)		
Pressure	kpa	688
Temperature	°C	150
Autoclave (IR-AUTOC)		
Pressure	kPa	688
pH		4.5
Reactions (in series)	Conversion	
X1 (R-B.25)		1
Pressure Let-down (IR-LETDO)		
Pressure	kPa	88.24
Filter & wash (IR-FILT)		
Pressure	kPa	88.24
Cake		
Solids fraction		0.65
Filtrate		
Solids Fraction		0
Washing Efficiency 1		0.5
Washing Efficiency 2		0.95
Washing cycles		2

B.4.3. Design specifications

Design specification IR1

A design specification is set on the discharge stream (IR-04) from the feed mixer (IR-MIX). The design specification sets the flow rate of the caustic feed (IR-01) to the mixer (IR-MIX) so that the discharge stream (IR-04) from the mixer has a pH of 3.5. This pH is required for optimal iron precipitation inside the autoclave.

Design specification IR2

A design specification is set on the discharge stream (IR-08) of the autoclave (IR-AUTOC). The design specification sets the flow rate of the caustic soda to the autoclave to produce a solution with a pH of 4.5 in the discharge stream (IR-08).

B.5. NICKEL NON-OXIDIZING LEACH

B.5.1. Chemistry

The chemistry for the nickel non-oxidizing leach section is given in Table B.10.

Table B.10: Nickel non-oxidizing leach section chemistry

Chemical Reaction	Reaction number	Reference
Non-acid producing metathesis reactions (autoclave)		
$Cu_5FeS_4 + Cu^{2+} \rightarrow 2Cu_2S + 2CuS + Fe^{2+}$	R-B.30	(2)
$Ni_3S_4 + Cu^{2+} \rightarrow CuNi_2S_4 + Ni^{2+}$	R-B.31	(2)
$5NiS + 2Cu^{2+} \rightarrow Cu_2S + Ni_3S_4 + 2Ni^{2+}$	R-B.32	(2)
$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+}$	R-B.17	(2)
$NiS + Cu^{2+} \rightarrow CuS + Ni^{2+}$	R-B.19	(2)
$FeS + Cu^{2+} \rightarrow CuS + Fe^{2+}$	R-B.20	(1)
Acid producing metathesis reactions (autoclave)		
$5Ni_3S_2 + 18Cu^{2+} + 4H_2O \rightarrow 9Cu_2S + 15Ni^{2+} + 7H^+ + HSO_4^-$	R-B.33	(2)
$6NiS + 9Cu^{2+} + 4H_2O \rightarrow Cu_9S_5 + 6Ni^{2+} + 7H^+ + HSO_4^-$	R-B.34	(2)
$8Ni_3S_4 + 45Cu^{2+} + 28H_2O \rightarrow 5Cu_9S_5 + 24Ni^{2+} + 49H^+ + 7HSO_4^-$	R-B.35	(2)
$8CuNi_2S_4 + 37Cu^{2+} + 28H_2O \rightarrow 5Cu_9S_5 + 16Ni^{2+} + 49H^+ + 7HSO_4^-$	R-B.36	(2)
$CuNi_2S_4 + 5Cu^{2+} + 4H_2O \rightarrow 3Cu_2S + 2Ni^{2+} + 7H^+ + HSO_4^-$	R-B.37	(2)
$6CuS + 3Cu^{2+} + 4H_2O \rightarrow Cu_9S_5 + 7H^+ + 2HSO_4^-$	R-B.38	(2)
$5CuS + 3Cu^{2+} + 4H_2O \rightarrow 4Cu_2S + 7H^+ + HSO_4^-$	R-B.39	(2)

(1) Taute & George (2010)

(2) Bryson *et al.* (2008)

As seen from Table B.10 the nickel non-oxidizing autoclave consist of two reaction types, namely non-acid producing reactions and acid producing reactions.

Non-acid producing metathesis reactions

By the end of the nickel atmospheric leach it is expected to have only trace amounts of millerite and troilite, although studies done by Bryson *et al.* (2008) suggest that heazlewoodite, polydymite and millerite are present in the residue.

The major iron compound expected is bornite, and it is dissolved according to R-B.30.

Polydymite is also expected to dissolve, and based on mineralogical analysis done by Bryson *et al.* (2008) it was found that the copper-nickel-sulphide product mineral is present as fletcherite. The reaction is presented in R-B.31

Millerite reacts with copper ions to form chalcocite and polydymite as represented by R-B.32. Any remaining heazlewoodite, millerite or troilite is converted to chalcocite or covelite according to R-B.17, R-B.19 and R-B.20.

Acid producing metathesis reactions

The major nickel sulphides at this stage is expected to be polydymite as well as fletcherite with little heazlewoodite and millerite present. Nickel containing sulphur compounds react with copper to form acid in R-B.33 – R-B.37

As leaching progresses and the remaining nickel sulphides are in minority, copper sulphates may react according to R-B.38 and R-B.39.

B.5.2. Process Equipment

The process equipment for the nickel non-oxidizing leach section with their respective operating conditions and assumptions are given in Table B.11.

Table B.11: Nickel non-oxidizing leach section process equipment

Equipment		
Feed stream mixer (NOX-MIX)		
Pressure	kPa	88.24
Feed pre-heater (NOX-PH)		
Pressure	kpa	688
Temperature	°C	155
Autoclave (NOX-ACLV)		
Pressure	kPa	688

Reactions (in series)	Conversion	
X3 (R-B.30)		0.8
X4 (R-B.17)		Algorithm
X5 (R-B.33)		Algorithm
X6 (R-B.19)		Algorithm
X7 (R-B.34)		Algorithm
X8 (R-B.35)		Algorithm
X9 (R-B.31)		Algorithm
X10 (R-B.37)		Algorithm
X11 (R-B.39)		1
Pressure Let-down (NOX-LETD)		
Pressure	kPa	88.24
Thickener (NOX-THIC)		
Pressure	kPa	88.24
Vent evaporation rate	$kg.hr^{-1}$	600
Overflow		
Solids fraction		0
Underflow		
Solids fraction		0.45
Filter (NOX-FILT)		
Pressure	kPa	88.24
Filtrate		
Solid fraction		0
Cake		
Solid fraction		0.65
Repulp Mixer (NOX-REPU)		
Pressure	kPa	88.24
Product solids fraction		0.52
Leach Solution Mixer (NOX-MIX2)		
Pressure	kPa	88.24

B.5.3. Design specifications

NOX-RES

The product from the repulp mixer (NOX-REPU) needs to have a 52% solids content. The water flow to the mixer is calculated to produce the required 52% solids content.

B.6. COPPER PRESSURE LEACH

B.6.1. Chemistry

The chemistry for copper pressure leach section is given in Table B.12.

Table B.12: Copper pressure leach section chemistry

Chemical Reaction	Reaction number	Reference
Autoclave(all three compartments)		
$2Cu_2S + 4H^+ + O_2 \rightarrow 2CuS + 2Cu^{2+} + 2H_2O$	R-B.23	(1)
$Cu_9S_5 + 8H^+ + 2O_2 \rightarrow 5CuS + 4Cu^{2+} + 4H_2O$	R-B.40	(1)
$4Cu_5FeS_4 + 20H^+ + 5O_2 \rightarrow 16CuS + 4Cu^{2+} + 10H_2O + 4Fe^{3+}$	R-B.41	(2)
$Cu_2Se + 4H^+ + 2O_2 \rightarrow 2Cu^{2+} + H_2SeO_3 + H_2O$	R-B.42	(2)
$Cu_2Te + 4H^+ + 2O_2 \rightarrow 2Cu^{2+} + H_2TeO_3 + H_2O$	R-B.43	(2)
$CuS + 2O_2 \rightarrow Cu^{2+} + SO_4^{2-}$	R-B.44	(1)
$2CuNi_2S_4 + 2H_2O + 15O_2 \rightarrow 2Cu^{2+} + 4Ni^{2+} + 4H^+ + 8SO_4^-$	R-B.45	(2)
$2Ni_3S_4 + 15O_2 + 2H_2O \rightarrow 6Ni^{2+} + 4H^+ + 8SO_4^{2-}$	R-B.46	(1)
$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O$	R-B.8	(1)
$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$	R-B.26	(2)
$2CuS + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2\ S^0 + 2H_2O$	R-B.47	(1)
$8NiS + 4H^+ + O_2 \rightarrow 2Ni_3S_4 + 2Ni^{2+} + 2H_2O$	R-B.23	(1)
$Ni_3S_4 + 6O_2 \rightarrow 3Ni^{2+} + 3SO_4^{2-} + S^0$	R-B.48	(1)
$2CuNi_2S_4 + 6O_2 \rightarrow 2Ni^{2+} + Cu^{2+} + 3SO_4^{2-} + S^0$	R-B.49	(2)
$2H_2SeO_3 + O_2 \rightarrow 2H_2SeO_4$	R-B.50	(2)
$PbS + H^+ + 2O_2 \rightarrow Pb^{2+} + HSO_4^-$	R-B.51	(2)
$2Co_3S_4 + 15O_2 + 2H_2O \rightarrow 6Co^{2+} + 2H^+ + 2HSO_4^- + 6SO_4^-$	R-B.52	(2)

(1) Hofirek and Kerfoot (1992)

(2) Taute & George (2010)

As seen from Table B.12 various chemical reactions are present in the autoclave. Although the chemistry has been given as a whole, the autoclave is in reality divided into three compartments, where different reactions take place in compartment 1 & 2 and compartment 3. The overall chemistry will be explained first, and then the chemistry present in the first & second compartment as well as the chemistry in the third compartment will be given. Assumptions were made regarding the chemical reactions in the different compartments with help from Anglo American (2006) since the actual chemistry is not described in its entirety in public literature. The different chemical reactions are attributed to the difference in temperature and the mineral composition of the slurry.

Overall

Chalcocite, digenite, and bornite react with free acid and oxygen to form covelite according to R-B.23, R-B.40 and R-B.41.

Any selenium or tellurium compounds can react with acid to form aqueous acids as given by R-B.41 and R-B.43. The selenous and telluric acid formed are dissociated in water to form the hydrogen selenite and hydrogen tellurite ion.

The next phase of the leach involves oxidation of the sulphide sulphur to sulphate and the dissolution of the associated metals according to R-B.44 – R-B.46.

During the course of the leach ferrous reacts with acid and oxygen to form ferric in R-B.8. Ferric in turn reacts with water to form hematite and acid in R-B.26.

If excessive acid is added to the system elemental sulphur will form according to R-B.47. Even with no excessive acid, elemental sulphur can also form according to R-B.48 and R-B.49. In low acid environments copper and iron will start to precipitate which is undesirable thus a low pH of below 4 is required in the discharge leach solution stream.

The selenium compounds are dissolved during the course of the leaching. Selenate is formed as the solids are dissolved. As the oxidation of the sulphides approach completion, the selenate is reduced to selenite as illustrated in R-B.50.

Due to the harsh conditions in the copper pressure leach, any cobalt and lead present is dissolved due to the reactivity of the acid and oxygen. The lead dissolution reaction is illustrated in R-B.51 whereas the cobalt dissolution reaction is illustrated in R-B.52.

First & second compartment

The following reactions occur in the first and second compartment of the autoclave:

R-B.41, R-B.8, R-B.26, R-B.22, R-B.51, R-B.52, R-B.46, R-B.45, R-B.23, R-B.40 and R-B.44.

Third compartment

The following reactions occur in the third compartment of the autoclave:

R-B.41, R-B.26, R-B.42, R-B.43, R-B.50, R-B.47 and R-B.44.

B.6.2. Process Equipment

The process equipment for the copper pressure leach section with their respective operating conditions and assumptions are given in Table B.13.

Table B.13: Copper pressure leach section process equipment

Equipment		
Feed stream mixer (CPL-MIX)		
Pressure	kPa	88.24
Autoclave (CPL-ACLV)		
Pressure	kPa	688
Compartment 1 & 2 outlet flash split		0.6
Compartment 1 & 2Reactions (in series)	Conversion	
X2 (R-B.41)		0.87
X3 (R-B.8)		1
X4 (R-B.26)		0.01
X5 (R-B.22)		1
X6 (R-B.52)		0.95
X7 (R-B.48)		1
X8 (R-B.49)		1
X9 (R-B.23)		Design Spec CPL1
X10 (R-B.40)		1
X11 (R-B.47)		0.5
X12 (R-B.51)		1
Compartment 3 Reactions (in series)	Conversion	
X2 (R-B.41)		1
X3 (R-B.26)		Design Spec CPL2
X4 (R-B.42)		1
X5 (R-B.50)		0.5
X6 (R-B.43)		0.5
X7 (R-B.47)		0.01

X8 (R-B.44)		1
Pressure Letdown (CPL-DT)		
Pressure	kPa	88.24
Mixer (CPL-MIX2)		
Pressure	kPa	88.24
Filter & wash (CPL-FILT)		
Pressure	kPa	88.24
Cake		
Solids fraction		0.86
Filtrate		
Solids fraction		0
Washing efficiency 1		0.5
Washing Efficiency 2		0.95
Washing cycles		2

B.6.3. Design specifications

Design specification CPL1

A design specification is set on the reaction conversion of R-B.23 in the first two compartments of the autoclave (CPL-ACLV). The design specification changes the conversion of R-B.23 to create a mineral copper flow of 126 kg/hr in the copper pressure leach residue product stream (CPL-14).

Design specification CPL2

A design specification is set on the conversion of R-B.26 in the third compartment of the autoclave. The target is to produce a 5% mineral iron content (mass) in the copper pressure leach residue product stream (CPL-14).

Design specification CPL3

A design specification is set on the water flow to the mixer (CPL-MIX2) to create a copper concentration of 93 g/l in the copper pressure leach product solution (CPL-13).

B.7. SELENIUM/TELLURIUM REMOVAL

B.7.1. Chemistry

The chemistry for copper pressure leach section is given in Table B.14.

Table B.14: Selenium/tellurium section chemistry

Chemical Reaction	Reaction number	Reference
Reduction pipe reactor		
$Na_2SO_3 \rightarrow 2Na^+ + SO_3^{2-}$	R-B.53	(1) (2)
$SO_3^{2-} + 2Cu^{2+} + H_2O \rightarrow 2Cu^+ + SO_4^{2-} + 2H^+$	R-B.54	(1) (2)
$HSeO_3^{2-} + 8Cu^+ + 5H^+ \rightarrow Cu_2Se + 6Cu^{2+} + 3H_2O$	R-B.55	(1) (2)
$HSeO_4^{2-} + 10Cu^+ + 7H^+ \rightarrow Cu_2Se + 8Cu^{2+} + 4H_2O$	R-B.56	(1) (2)
$HTeO_3^{2-} + 8Cu^+ + 5H^+ \rightarrow Cu_2Te + 6Cu^{2+} + 3H_2O$	R-B.57	(1) (2)
$HTeO_4^{2-} + 10Cu^+ + 7H^+ \rightarrow Cu_2Te + 8Cu^{2+} + 6H_2O$	R-B.58	(1) (2)
$2Cu^{2+} \rightarrow Cu^0 + Cu^{2+}$	R-B.59	(1) (2)
Oxidation reactor		
$2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O$	R-B.60	(1) (2)
$4Cu^+ + O_2 + 4H^+ \rightarrow 4Cu^{2+} + 2H_2O$	R-B.61	(1) (2)

(2) Taute & George (2010)

(3) Bryson *et al.* (2008)

From Table B.14 it is evident that chemistry is present in the reduction pipe reactor as well as the oxidation reactor.

Reduction pipe reactor

Na_2SO_3 is introduced into the inlet stream of the reduction pipe reactor, and is the causing factor of R-B.53 – R-B.57 taking place. Cupric is reduced to cuprous according to R-B.54, and Se^{4+} and Se^{6+} is reduced to Se^{2-} according to R-B.55 and R-B.56.

The reduction and precipitation of tellurium is expected to follow similar mechanism of the selenium according to R-B.57 and R-B.58.

It is possible for the cuprous ion to react by disproportionation, which forms metallic copper as given by R-B.59.

Oxidation reactor

R-B.59 is undesired, and thus the metallic copper is re-oxidized along with copper according to R-B.60 and R-B.61 in an oxidation reactor.

B.7.2. Process equipment

The process equipment for the selenium/tellurium removal section with their respective operating conditions and assumptions are given in Table B.15.

Table B.15: Selenium/tellurium removal section process equipment

Equipment		
Feed pre-heater (STR-PH)		
Pressure	kpa	88.24
Temperature	°C	90
Pipe reactor (STR-PR)		
Pressure	kPa	88.24
Reactions (in series)	Conversion	
X1 (R-B.53)		1
X2 (R-B.54)		1
X3 (R-B.55)		1
X4 (R-B.56)		1
X5 (R-B.57)		1
Filter (STR-FILT)		
Pressure	kPa	88.24
Cake		
Solids fraction		0.85
Filtrate		
Solids fraction		0
Pipe reactor (STR-OXR)		
Pressure	kPa	88.24
Reactions (in series)	Conversion	
X2 (R-B.61)		1
Feed splitter (STR-SPLI)		
Copper electrowinning section		0.664
Nickel non-oxidizing leach section		0.336

B.8. COPPER ELECTROWINNING

B.8.1. Chemistry

The chemistry for the copper electrowinning section is given in Table B.16.

Table B.16: Copper electrowinning section chemistry

Chemical Reaction	Reaction number	Reference
Electrowinning		
$Cu^{2+} + H_2O \rightarrow Cu^0 + 2H^+ + 0.5O_2$	R-B.62	(1)
$2Fe^{3+} + Cu \rightarrow Cu^{2+} + 2Fe^{2+}$	R-B.63	(1)

(1) Taute & George (2010)

The chemistry given in Table B.16 is representative of the net electrowinning reaction (R-B.62) and the side reaction which occurs if too much iron is present (R-B.63).

B.8.2. Process equipment

The process equipment for the copper electrowinning section with their respective operating conditions and assumptions are given in Table B.17.

Table B.17: Copper electrowinning section process equipment

Equipment		
Feed pre-cooler (STR-PH)		
Pressure	kpa	88.24
Temperature	°C	90
Mixer (CEW-MIX)		
Pressure	kpa	88.24
Electrowinning (CEW-EW)		
Pressure	kPa	88.24
Temperature	°C	52
Vent evaporation rate	$kg.hr^{-1}$	2276
Reactions (in series)	Conversion	
X1 (R-B.62)		Design Spec CEW1
Feed splitter (CEW-SPLI)		
Copper pressure leach section		0.885
Nickel atmospheric leach section		0.115

B.8.3. Design specifications

Design specification CEW1

A design specification is put on the conversion of R-B.62 in the copper electrowinning model (CEW-EW) to create a copper concentration of 40g/l in the spent copper electrolyte stream (CEW-06).

Design specification CEW2

A design specification is put on the flow rate of the water stream to the feed mixer (CEW-MIX). The flow rate of the water is adapted to create a copper concentration of 88g/l in the discharge stream (CEW-03).

B.9. LEAD REMOVAL

B.9.1. Chemistry

The chemistry for the lead removal section is given in Table B.18.

Table B.18: Lead removal section chemistry

Chemical Reaction	Reaction number	Reference
Precipitation reactor		
$Ba(OH)_2 \rightarrow Ba^{2+} + 2(OH)^-$	R-B.64	(1)
$Pb^{2+} + Ba^{2+} + 2SO_4^{2-} \rightarrow BaSO_4.PbSO_4$	R-B.65	(1)
$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$	R-B.66	(1)

(1) Taute & George (2010)

The barium hydroxide is dissolved in water according to R-B.64, where the barium ion reacts with lead and sulphate ions to produce a precipitate lead specie $BaSO_4.PbSO_4$ as given in R-B.65. The remaining lead in the solution reacts with sulphate ions to produce barium sulphide (R-B.66).

B.9.2. Process equipment

The process equipment for the lead removal section with their respective operating conditions and assumptions are given in Table B.19.

Table B.19: Lead removal section process equipment

Equipment		
Lead removal reactor (PBR-REAC)		
Pressure	kPa	88.24
Reactions (in series)	Conversion	
X1, X2 (R-B.64)		1
X3 (R-B.65)		1
X4 (R-B.66)		1
Filter (STR-FILT)		
Pressure	kPa	88.24
Cake		
Solids fraction		0.42
Filtrate		
Solids fraction		0

B.10. COBALT REMOVAL

B.10.1. Chemistry

The chemistry for the cobalt removal section is given in Table B.20.

Table B.20: Cobalt removal section chemistry

Chemical Reaction	Reaction number	Reference
Nickelic production		
$Ni^{2+} + OH^- \rightarrow Ni(OH)_2$	R-B.67	(1)
$2Ni(OH)_2 + 2H_2O \rightarrow 2Ni(OH)_3 + H_2$	R-B.68	(1)
Cobalt precipitation		
$Ni(OH)_3 + Co^{2+} \rightarrow Co(OH)_3 + Ni^{2+}$	R-B.69	(1)

(1) Taute & George (2010)

From Table B.20 it is evident that the chemistry is divided into two categories, the one in the nickelic production tanks and the other in the cobalt precipitation reactor.

$Ni(OH)_3$ Production

Nickel sulphate is first converted to $Ni(OH)_2$ by reaction with caustic soda according to R-B.67. $Ni(OH)_2$ is then electrolytically converted to $Ni(OH)_3$. The overall reaction is given by R-B.68.

Cobalt Removal

$Ni(OH)_3$ reacts with cobalt to form $Co(OH)_3$ as illustrated in R-B.69. The precipitation is achieved at pH levels of 5.6 – 5.7, thus pH control with caustic soda is of extreme importance.

B.10.2. Process equipment

The process equipment for the cobalt removal section with their respective operating conditions and assumptions are given in Table B.21.

Table B.21: Cobalt removal section process equipment

Equipment		
Stream splitter (COR-SS)		
Nickelic production split		0.0102
Cobalt removal split		0.9898
Pre-heater (COR-HEAT)		
Pressure	kPa	88.24
Temperature	°C	85
Mixer (COR-DIL)		

Pressure	kPa	88.24
Neutralization Reactor		
Pressure	kPa	88.24
Reaction	Conversion	
X1 (R-B.67)		1
Nickelic production tank (COR-ELEC)		
Pressure	kPa	88.24
Reaction	Conversion	
X1 (R-B.68)		1
Precipitation Reactor (COR-REAC)		
Pressure	kPa	88.24
Reaction	Conversion	
X1 (R-B.69)		1
Filter (COR-FILT)		
Pressure	kPa	88.24
Cake		
Solids fraction		0.85
Filtrate		
Solids fraction		0
Evaporator (COR-EVAP)		
Pressure	kPa	88.24
Heat Duty	kW	Design Spec COR3
Mixer (COR-PH)		
Pressure	kPa	88.24

B.10.3. Design specifications

Design specification COR1

A design specification is put on the flow of the water stream (COR-04) to the nickelic production feed mix tank (COR-DIL). The design changes the water stream flow rate until a nickel concentration of 21 g/l is achieved in the discharge stream (COR-05).

Design specification COR2

A design specification is set on the caustic soda flow to the nickelic production neutralization reactor (COR-NEUT). The design specification changes the caustic soda flow to make sure enough caustic soda is available to precipitate all of the nickel. Thus the design specification checks the nickel flow in the discharge stream (COR-07) and makes sure the flow is zero.

Design specification COR3

A design specification is put on the heat duty of the evaporator (COR-EVAP) to create a nickel concentration of 89 g/l in the discharge stream (COR-17).

B.11. NICKEL ELECTROWINNING

B.11.1. Chemistry

The chemistry for the nickel electrowinning section is given in Table B.22.

Table B.22: Nickel electrowinning section chemistry

Chemical Reaction	Reaction number	Reference
Nickelic electrowinning		
$2Ni^{2+} + 2H_2O \rightarrow 2Ni + 4H^+ + O_2$	R-B.70	(1)

(1) Taute & George (2010)

From Table B.22 the net electrowinning reaction occurring in the electrowinning section can be seen (R-B.70). Oxygen is produced as seen in R-B.70, which bubbles up from where the water decomposes.

B.11.2. Process equipment

The process equipment for the nickel electrowinning section with their respective operating conditions and assumptions are given in Table B.23.

Table B.23: Nickel electrowinning section process equipment

Equipment		
Pre-cooler (NEW-COOL)		
Pressure	kPa	88.24
Temperature	°C	60
Nickel electrowinning (NEW-EW)		
Pressure	kPa	88.24
Vent evaporation rate fraction		0.0064
Reaction	Conversion	
X1 (R-B.70)		Design Spec NEW1
Splitter (NEW-PHSP)		
Cobalt removal section		Design spec NEW2
Nickel electrowinning section		Design spec NEW2
Splitter (NEW-SPL)		
Cobalt plant		0.043
Nickel atmospheric leach section		0.047
Sulphur removal section - neutralization		Algorithm
Sulphur removal section - dissolution		Algorithm

B.11.3. Design specifications

Design specification NEW1

A design specification is set on the spent nickel electrolyte discharge stream (NEW-05) from the electrowinning model (NEW-EW). The spent nickel electrolyte stream concentration is set to 62.7 g/l by changing the conversion of R-B.70.

Design specification NEW2

A design specification is set on the split fraction of the recycle stream to the cobalt removal section (NEW-11) in the splitter (NEW-PHSP). The design specification optimizes the flow of NEW-11 to create a pH of 3.5 in stream COR-16.

B.12. SULPHUR REMOVAL

B.12.1. Chemistry

The chemistry for the sulphur removal section is given in Table B.24.

Table B.24: Sulphur removal section chemistry

Chemical Reaction	Reaction number	Reference
Nickel precipitation reactor		
$Ni^{2+} + OH^- \rightarrow Ni(OH)_2$	R-B.71	(1)
Nickel hydroxide dissolution reactor		
$2H^+ + Ni(OH)_2 \rightarrow Ni^{2+} + 2H_2O$	R-B.72	(1)

(1) Taute & George (2010)

Acid is neutralized with caustic soda until a pH of 5.8 is achieved. From there on more caustic soda is added to precipitate nickel as nickel hydroxide according to R-B.72. The nickel hydroxide precipitation occurs from a pH of 8.8.

The nickel hydroxide precipitate has to be dissolved after separation from the sodium sulphate solution. This is done through addition of acid due to the spent nickel electrolyte stream being mixed with the nickel hydroxide stream as given in R-B.72.

B.12.2. Process equipment

The process equipment for the sulphur removal section with their respective operating conditions and assumptions are given in Table B.25.

Table B.25: Sulphur removal section process equipment

Equipment		
Mixer (SR-NTANK)		
Pressure	kPa	88.24
pH		5.8
Precipitation reactor (SR-PREAC)		
Pressure	kPa	88.24
pH		8.8
Reaction	Conversion	
X1 (R-B.66)		1
Filter System (SR-FILT)		
Pressure	kPa	88.24
Cake		

Solid fraction		0.242
Filtrate		
Solid fraction		0
Heater (SR-HEAT)		
Pressure	kPa	88.24
Temperature	°C	72
Dissolution reactor (SR-PREAC)		
Pressure	kPa	88.24
Sulphuric Acid Concentration	g/l	< 1
Reaction	Conversion	
X1 (R-B.72)		1
Stream splitter (SR-SPLIT)		
Lead removal section		0.7305
Copper removal section		0.2695

B.12.3. Design specifications

Design specification SR1

A design specification is put on the caustic soda flow rate (SR-02) to the neutralization tank. The design specification changes the flow rate of the caustic soda to create a pH of 5.7 in the discharge stream (SR-03).

Design specification SR2

A design specification is put on the caustic soda flow rate (SR-04) to the precipitation reactor. The design specification changes the flow rate of the caustic soda to create a pH of 10 in the discharge stream (SR-05).

APPENDIX C - RBMR ASPEN PLUS STREAM TABLES

Overview

The stream names and stream tables for the RBMR simulation is given in this Appendix.

C.1. STREAM NAMES

The stream names for the RBMR process are given in Table C.1.

Table C.1: RBMR stream names and descriptions

Stream Name	Stream Description
CR-01	Ni-Cu Matte Feed
CR-02	Supernatant from Co Cake Precipitation
CR-03	Cu removal feed slurry
CR-04	Air to Cu removal
CR-05	Cu removal reactors vent
CR-06	Cu removal thickener feed
CR-07	Diluted flocculant to Cu removal thickener
CR-08	Copper removal thickener underflow
CR-09	Copper removal thickener overflow
CR-10	Copper removal thickener vent
NAL-02	Ni atm leach feed slurry
NAL-03	Air to Ni atm leach
NAL-04	Ni atm leach reactors vent
NAL-05	Ni atm leach thickener feed
NAL-06	Diluted flocculant to Ni atm leach thickener
NAL-08	Ni atm leach thickener overflow
NAL-09	Ni atm leach thickener underflow
NAL-10	Ni atm leach thickener vent
IR-01	NaOH to pressure iron removal feed tank
IR-02	Co solution purification residue
IR-04	Pressure iron removal feed solution
IR-05	Heated pressure iron removal feed solution
IR-06	NaOH to pressure iron removal autoclave
IR-07	Oxygen to pressure iron removal autoclave
IR-08	Pressure iron removal autoclave discharge
IR-09	Pressure iron removal flash discharge vent
IR-10	Pressure iron removal flash discharge slurry
IR-11	Wash water to pressure iron removal filter
IR-12	Washed pressure iron removal residue
IR-13	Iron free solution to copper removal section
NOX-01	Pressure vessel leach solution
NOX-02	Ni non-oxidizing leach feed
NOX-03	Heated Ni non-oxidizing leach
NOX-04	Ni non-oxidizing leach discharge slurry
NOX-05	Flashed steam from Ni non-oxidizing leach
NOX-06	Ni non-oxidizing leach flash discharge slurry
NOX-07	Diluted flocculant to Ni non-oxidizing leach
NOX-08	Ni non-oxidizing leach thickener underflow
NOX-09	Ni non-oxidizing leach belt filter filtrate
NOX-10	Ni non-oxidizing leach thickener overflow

Stream Name	Stream Description
NOX-11	Ni non-oxidizing leach product solution
NOX-12	Ni non-oxidizing leach belt filter cake
NOX-13	Ni non-oxidizing leach repulp water
NOX-14	Repulped Ni non-oxidizing leach residue
NOX-15	Ni non-oxidizing thickener vent
CPL-01	Water to copper pressure leach
CPL-02	Ferrous sulphate additive
CPL-04	Copper pressure leach autoclave feed slurry
CPL-05	Oxygen to copper pressure leach
CPL-06	Copper pressure leach flash recycle return
CPL-07	Copper pressure leach flash recycle vent
CPL-08	Copper pressure leach autoclave discharge slurry
CPL-09	Copper pressure leach flash discharge vent
CPL-10	Copper pressure leach flash discharge slurry
CPL-11	Make-up water to copper pressure leach flash discharge slurry
CPL-12	Diluted copper pressure leach discharge slurry to filter
CPL-13	Copper pressure leach residue
CPL-14	Copper pressure leach product solution
CPL-15	Copper pressure leach residue cake wash water
STR-01	Heated feed solution to Se/Te removal
STR-02	Se/Te removal residue
STR-03	Se/Te removal product filtrate
STR-04	Copper advance electrolyte to nickel non-oxidizing leach
STR-05	Copper advance electrolyte to copper electrowinning
STR-06	Air to Se/Te removal sulphur dioxide oxidation
STR-07	Na_2SO_3 to Se/Te pipeline reactor
STR-08	Se/Te removal filter feed
STR-11	Total copper advance electrolyte
STR-12	Vent for sulphur dioxide oxidation
CEW-01	Cooled copper advance electrolyte to copper electrowinning
CEW-02	Make-up water to copper electrowinning
CEW-03	Copper electrowinning advance electrolyte feed
CEW-04	Vent from copper electrowinning
CEW-05	Copper cathode product
CEW-06	Copper electrowinning spent electrolyte discharge
CEW-07	Copper spent electrolyte to Ni atm leach
CEW-08	Copper spent electrolyte to copper pressure leach
PBR-01	$Ba(OH)_2$ slurry
PBR-02	Pb removal discharge
PBR-03	Filter cake from Pb removal
PBR-04	Pb free solution to Co removal
COR-01	Split feed to Co removal
COR-02	Heated feed to Co removal
COR-03	Feed to $Ni(OH)_3$ production
COR-04	Dilution water to $Ni(OH)_3$ production

Stream Name	Stream Description
COR-05	Diluted NiSO4 to Ni(OH)3 production
COR-06	NaOH to Ni(OH)3 production
COR-07	Neutralised NiSO4 to Ni(OH)3 production
COR-08	Ni(OH)3 production cells vent
COR-09	Ni(OH)3 feed to Co removal
COR-10	Co removal vent
COR-11	Co removal filter feed
COR-12	Co removal cake
COR-13	Co free NiSO4
COR-14	NiSO4 evaporation vent
COR-15	Ni(OH)3 production neutralization reactor vent
COR-16	pH adjusted Ni advance electrolyte to Ni electrowinning
COR-17	NiSO4 evaporator discharge
NEW-02	Cooled Ni catholyte to Ni electrowinning
NEW-03	Ni electrowinning vent
NEW-04	NI cathodes product
NEW-05	Spent Ni electrolyte from Ni electrowinning
NEW-06	Spent Ni electrolyte to Co upgrade
NEW-07	Spent Ni electrolyte to sulphur removal neutralization
NEW-08	Spent Ni electrolyte to sulphur removal dissolution
NEW-09	Spent Ni electrolyte to Ni atm leach
NEW-10	Total Ni anolyte discharge
NEW-11	Ni anolyte recycle to Co pH adjustment
SR-01	Co SX raffinate
SR-02	NaOH to sulphur removal neutralization
SR-03	Feed to Ni precipitation
SR-04	NaOH to Ni(OH)2 precipitation
SR-05	Filter system feed from Ni precipitation
SR-06	Liquids from filter system
SR-07	NI(OH)2 solids from filter system
SR-11	Neutral NiSO4 recycle to Pb removal
SR-12	Neutral NiSO4 recycle to Cu removal
SR-13	Heated Na2SO4 solution to crystallization

C.2. STREAM TABLES

The stream tables are available on the Appendix CD.

APPENDIX D - RBMR-NF PROCESS DESCRIPTION & SIMULATION

Overview

Appendix D gives the unit operations and criteria (including design specifications) used in the RBMR-NF Aspen Plus simulation.

D.1. COBALT REMOVAL

D.1.1. Process Equipment

The process equipment that are added or modified to the cobalt removal section is given in Table D.1.

Table D.1: Cobalt removal equipment additions/modifications

Equipment		
Tank with Mixer (COR-MIX) [new equipment]		
Pressure	kPa	88.24

D.1.2. Design specifications

Design specification NEW-NAC

The design specification controls the amount of sodium sulphate that is recycled to the sodium sulphate mixer (COR-MIX) to create a sodium sulphate liquor concentration of 100g/l.

D.2. NICKEL ELECTROWINNING

The process equipment that are added or modified in the nickel electrowinning section is given in Table D.2.

Table D.2: Nickel electrowinning equipment additions/modifications

Equipment	
Splitter (NEW-SPL) [modified equipment]	
Cobalt plant	0.043
Nickel atmospheric leach section	0.047
Sulphur removal section	0.91

D.3. SULPHUR REMOVAL

Since the entire sulphur removal process is new, the equipment of the entire process will be given. The equipment can be seen in Table D.3.

Table D.3: Sulphur removal section equipment

Equipment		
Heat exchanger (cooler) (SR-COOL)		
Pressure	kPa	88.24
Temperature	°C	40
Crystallizer		
Pressure	kPa	88.24
Operating Temperature	°C	5
Crystal product		$Na_2SO_4.10H_2O$
Centrifuge System (SR-CENTR)		
Liquid stream		
Solid fraction		0
Solid stream		
Solid fraction		0.7
Washing Efficiency 1		0.5
Washing Efficiency 2		0.95
Washing cycles		2
Heat exchanger (heater) (SR-HEAT)		
Pressure	kPa	88.24
Temperature	°C	20
Stream splitter (SR-SPLT1)		
Sodium sulphate polishing plant		Design specification NEW-NAC
Cobalt treatment		Design specification NEW-NAC
NF Membrane System		
Total NF Membrane Steps	#	5
Operating pressure	bar	50
Final retentate sulphuric acid concentration	g/l	2
Permeate operating pressure	bar	50
Membrane intermediate permeate product nickel	g/l	65
Membrane system final permeate product nickel	g/l	80
Stream splitter (SR-SPLT2)		
Lead removal section split		0.73

Copper rremoval section split	0.27

D.3.1. Design specifications

SR-WF1

Varies the water flow to the membrane feed stream to create a membrane system feed of 65g/l.

SR-WF2

Each membrane has an internal design specification (Mx-RC) to vary the size of the membrane to create a permeate product with a nickel concentration of 65 g/l. Coupled with this internal design specification is SR-WF2 that varies the volume flow of water to each individual membrane, to create a final sulphuric acid permeate concentration of 2 g/l, which is close to what the RBMR is operating at. Thus the membrane plant size is varied to create a specific permeate product sulphuric acid conncentration.

Mx-RC

Each membrane contains an internal design specification which varies the size of the membrane to create a specific permeate nickel concentration. In this case the concnetration is 65 g/l.

MFC-RC

The final membrane size is varied to create a permeate product of nickel concentration of 80g/l.

APPENDIX E - RBMR-NF ASPEN PLUS STREAM TABLES

Overview

The stream names and stream tables for the RBMR-NF simulation is given in this Appendix

E.1. STREAM NAMES

The stream names for the RBMR process are given in Table C.1.

Table E.1: RBMR stream names and descriptions

Stream Name	Stream Description
CR-01	Ni-Cu Matte Feed
CR-02	Supernatant from Co Cake Precipitation
CR-03	Cu removal feed slurry
CR-04	Air to Cu removal
CR-05	Cu removal reactors vent
CR-06	Cu removal thickener feed
CR-07	Diluted flocculant to Cu removal thickener
CR-08	Copper removal thickener underflow
CR-09	Copper removal thickener overflow
CR-10	Copper removal thickener vent
NAL-02	Ni atm leach feed slurry
NAL-03	Air to Ni atm leach
NAL-04	Ni atm leach reactors vent
NAL-05	Ni atm leach thickener feed
NAL-06	Diluted flocculant to Ni atm leach thickener
NAL-08	Ni atm leach thickener overflow
NAL-09	Ni atm leach thickener underflow
NAL-10	Ni atm leach thickener vent
IR-01	NaOH to pressure iron removal feed tank
IR-02	Co solution purification residue
IR-04	Pressure iron removal feed solution
IR-05	Heated pressure iron removal feed solution
IR-06	NaOH to pressure iron removal autoclave
IR-07	Oxygen to pressure iron removal autoclave
IR-08	Pressure iron removal autoclave discharge
IR-09	Pressure iron removal flash discharge vent
IR-10	Pressure iron removal flash discharge slurry
IR-11	Wash water to pressure iron removal filter
IR-12	Washed pressure iron removal residue
IR-13	Iron free solution to copper removal section
NOX-01	Pressure vessel leach solution
NOX-02	Ni non-oxidizing leach feed
NOX-03	Heated Ni non-oxidizing leach
NOX-04	Ni non-oxidizing leach discharge slurry
NOX-05	Flashed steam from Ni non-oxidizing leach
NOX-06	Ni non-oxidizing leach flash discharge slurry
NOX-07	Diluted flocculant to Ni non-oxidizing leach
NOX-08	Ni non-oxidizing leach thickener underflow
NOX-09	Ni non-oxidizing leach belt filter filtrate
NOX-10	Ni non-oxidizing leach thickener overflow

Stream Name	Stream Description
NOX-11	Ni non-oxidizing leach product solution
NOX-12	Ni non-oxidizing leach belt filter cake
NOX-13	Ni non-oxidizing leach repulp water
NOX-14	Repulped Ni non-oxidizing leach residue
NOX-15	Ni non-oxidizing thickener vent
CPL-01	Water to copper pressure leach
CPL-02	Ferrous sulphate additive
CPL-04	Copper pressure leach autoclave feed slurry
CPL-05	Oxygen to copper pressure leach
CPL-06	Copper pressure leach flash recycle return
CPL-07	Copper pressure leach flash recycle vent
CPL-08	Copper pressure leach autoclave discharge slurry
CPL-09	Copper pressure leach flash discharge vent
CPL-10	Copper pressure leach flash discharge slurry
CPL-11	Make-up water to copper pressure leach flash discharge slurry
CPL-12	Diluted copper pressure leach discharge slurry to filter
CPL-13	Copper pressure leach residue
CPL-14	Copper pressure leach product solution
CPL-15	Copper pressure leach residue cake wash water
STR-01	Heated feed solution to Se/Te removal
STR-02	Se/Te removal residue
STR-03	Se/Te removal product filtrate
STR-04	Copper advance electrolyte to nickel non-oxidizing leach
STR-05	Copper advance electrolyte to copper electrowinning
STR-06	Air to Se/Te removal sulphur dioxide oxidation
STR-07	Na2SO3 to Se/Te pipeline reactor
STR-08	Se/Te removal filter feed
STR-11	Total copper advance electrolyte
STR-12	Vent for sulphur dioxide oxidation
CEW-01	Cooled copper advance electrolyte to copper electrowinning
CEW-02	Make-up water to copper electrowinning
CEW-03	Copper electrowinning advance electrolyte feed
CEW-04	Vent from copper electrowinning
CEW-05	Copper cathode product
CEW-06	Copper electrowinning spent electrolyte discharge
CEW-07	Copper spent electrolyte to Ni atm leach
CEW-08	Copper spent electrolyte to copper pressure leach
PBR-01	Ba(OH)2 slurry
PBR-02	Pb removal discharge
PBR-03	Filter cake from Pb removal
PBR-04	Pb free solution to Co removal
COR-01	Split feed to Co removal
COR-02	Heated feed to Co removal
COR-03	Feed to Ni(OH)3 production
COR-04	Dilution water to Ni(OH)3 production

Stream Name	Stream Description
COR-05	Diluted NiSO4 to Ni(OH)3 production
COR-06	NaOH to Ni(OH)3 production
COR-07	Neutralised NiSO4 to Ni(OH)3 production
COR-08	Ni(OH)3 production cells vent
COR-09	Ni(OH)3 feed to Co removal
COR-10	Co removal vent
COR-11	Co removal filter feed
COR-12	Co removal cake
COR-13	Co free NiSO4
COR-14	NiSO4 evaporation vent
COR-15	Ni(OH)3 production neutralization reactor vent
COR-16	pH adjusted Ni advance electrolyte to Ni electrowinning
COR-17	NiSO4 evaporator discharge
COR-18	Co free NiSO4 with added Na_2SO_4
NEW-02	Cooled Ni catholyte to Ni electrowinning
NEW-03	Ni electrowinning vent
NEW-04	NI cathodes product
NEW-05	Spent Ni electrolyte from Ni electrowinning
NEW-06	Spent Ni electrolyte to Co upgrade
NEW-08	Spent Ni electrolyte to sulphur removal (NF plant)
NEW-09	Spent Ni electrolyte to Ni atm leach
NEW-10	Total Ni anolyte discharge
NEW-11	Ni anolyte recycle to Co pH adjustment
SR-01	Water feed to membrane feed dilution
SR-02	Water feed to membrane intermediary dilution
SR-03	Wash water feed to centrifuge system
SR-04	Centrifuge system liquid product
SR-06	Centrifuge system crystals product
SR-07	Crystals product to crystals polishing
SR-08	Na_2SO_4 crystals recycle to electrowinning sodium make-up
SR-09	Heated feed to NF system
SR-10	NF retentate product (nickel rich acid free solution)
SR-11	Nickel rich acid free solution to lead removal section
SR-12	Nickel rich acid free solution to copper removal
SR-15	NF permeate product (diluted acid and nickel)

E.2. STREAM TABLES

The stream tables are available on the Appendix CD.

APPENDIX F - ASPEN PLUS ALGORITHMS

Overview

Appendix C identifies and illustrates algorithms used in Aspen Plus for simulation purposes.

F.1. NICKEL ATMOSPHERIC LEACH NON-OXIDIZING LEACH CONVERSION ALGORITHM

F.1.1. Background and algorithms

The nickel atmospheric leach non-oxidizing reactor that is part of the reactor in the model NAL-REAC consists of six reactions that take place in series. The six reactions with their respective conversions are given in Table F.1. The equilibrium reaction R-B.2 is forced in the acid producing regime to convert all of the hydrogen sulphide ions to hydronium ions for simulation purposes.

Table F.1: Nickel atmospheric leach non-oxidizing leach conversion algorithm reaction conversions

Reaction Number	Algorithm Reaction Number	Conversion
R-B.2	1	1
R-B.20	2	0.6
R-B.21	3	1
R-B.18	4	1
R-B.7	5	Calculation
R-B.23	6	Calculation

A design specification needs to be implemented on the output stream (NAL-05) of the reactor. The design specification is on the nickel content of the minerals in the output stream. 54% of the nickel in the incoming matte (CR-01) to the process needs to be leached at the end of the reactor (NAL-REAC). Another design specification is that all of the iron needs to be leached. Four of the six reactions are specified with pre-defined reaction conversions as can be seen in Table F.1.

The fifth and the sixth reaction (R-B.7 and R-B.23) is the leaching of heazlewoodite and millerite. Since heazlewoodite and millerite are in abundance they will determine if the 54% leached nickel design specification is met or not. Thus R-B.7 and R-B.23 are leached (in series, first R-B.7) until 54% of the total nickel in the incoming matte is leached.

To predict the conversion a type of feed forward algorithm is applied, where R-B.2, R-B.20, R-B.21 and R-B.18 are converted according to their pre-defined conversions. The products and reagents are monitored and stored in variables after each reaction. R-B.7 and R-B.23's conversions are thereafter calculated, with the amount of nickel that can be leached as the limiting reagent.

F.1.2. Variable definitions

The variables used in the Fortran 77 algorithm are defined in Table F.2

Table F.2: Nickel atmospheric leach non-oxidizing leach conversion algorithm variable definitions

Variable	Definition
Algorithm import and export variables	
X1-X6	Reaction conversion extents for reaction 1 – 6
HSO4IN	HSO_4^- ions inlet flow rate
H3OIN	H_3O^+ ions inlet flow rate
NI3S2IN	Ni_3S_2 inlet flow rate
NISIN	NiS inlet flow rate
FESIN	Fe inlet flow rate
FEION3IN	Fe^{3+} ion inlet flow rate
Algortihm inner variables	
NiI	Nickel in matte
NiRi	Nickel in reactor inlet
NiRO	Amount of nickel in the reactor outlet
NiAvail	Amount of nickel that is available for leaching
HSO4	HSO_4^- ions outlet flow rate
H3O	H_3O^+ ions outlet flow rate
NI3S2	Ni_3S_2 outlet flow rate
NIS	NiS outlet flow rate
FES	Fe outlet flow rate
FEION3	Fe^{3+} ion outlet flow rate

F.1.3. Algorithm

The flow diagram of the conversion calculation algorithm can be seen in Figure F.1.

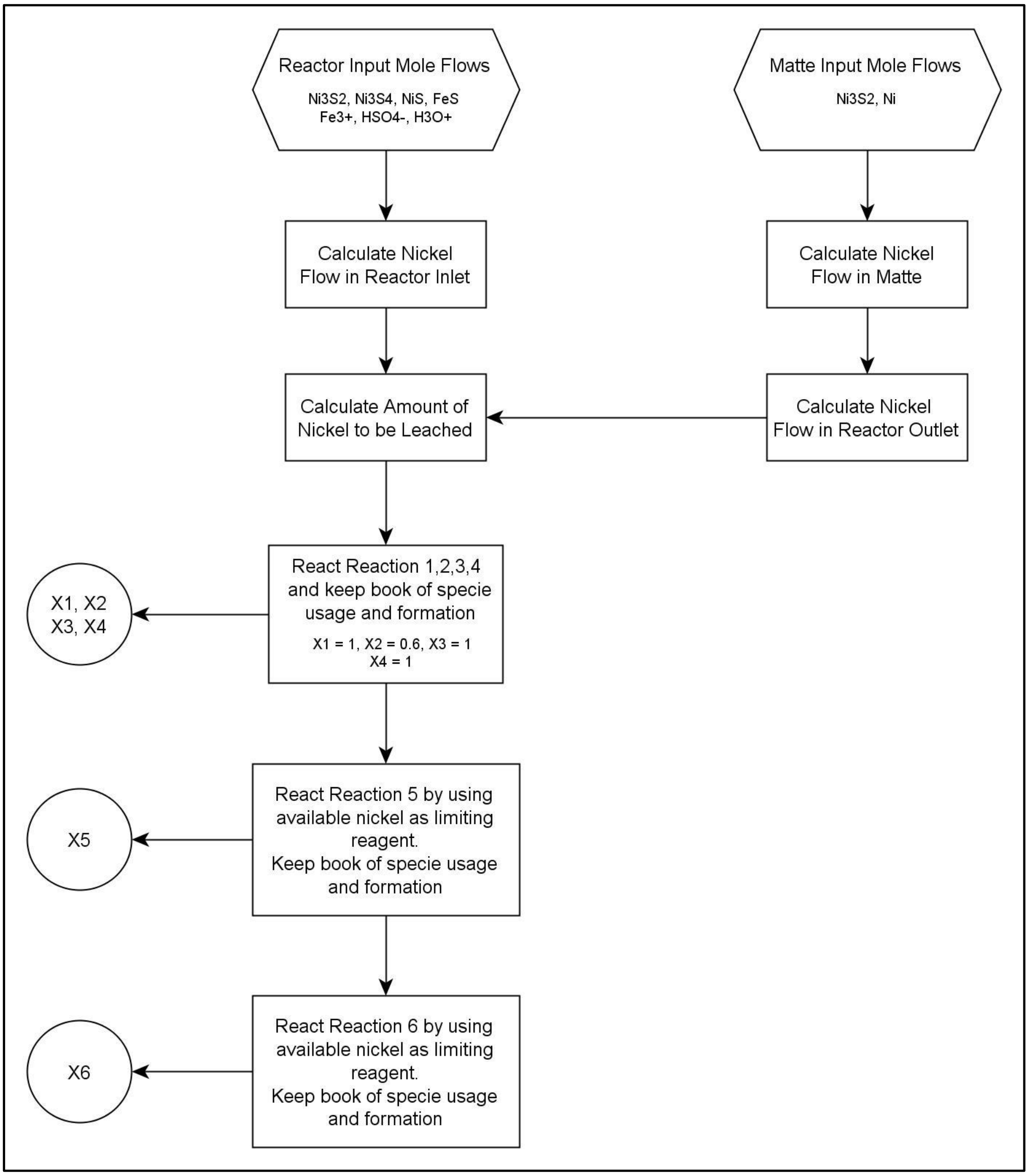

Figure F.1: Flow diagram of the nickel atmospheric leach non-oxidizing reactor conversion algorithm

F.1.4. FORTRAN 77 Code

```
C Assign initial conversions

      X1 = 1
      X2 = 0.6
      X3 = 1
      X4 = 1
      X5 = 1
      X6 = 1

C   Assign import variables to new variables

      HSO4 = HSO4IN
      H3O = H3OIN
      NI3S2 = NI3S2IN
      NIS = NISIN
      FES= FESIN
      FEION3 = FEION3IN

C   Calculate nickel in matte
      NiI = NI3S2INI*240.21*0.733 + NIINI*58.6934
C   Calculate nickel in reactor inlet
      NiRI=NI3S2IN*240.21*0.733+NISIN*90.76*0.647+NI3S4IN*304.34*0.579
C   Calculate How Much Nickel should be leached
      NiRO = 0.44 * NiI

      NiAvail = ((NiRI - NiRO) / 0.0586934)/1000

      IF (NiAvail .LT. 0) THEN
        NiAvail = 0
      END IF


C   Calculate each reaction individually

C   (1)
      H3O = H3O + HSO4 * X1
      HSO4 = HSO4 * (1 - X1)

C   (2)
      H3O = H3O - 2 * FES * X2
      FES = (1 - X2) * FES

C   (3)
      FES = (1 - X3) * FES

C   (4)
      NI3S2 = NI3S2 - FEION3 * X4 / 2
      NIS = NIS + FEION3 * X4

      NiAvail = NiAvail - FEION3*X4 / 2

      FEION3 = FEION3 * (1 - X4)

      IF (NiAvail .LT. 0) THEN
        NiAvail = 0
      END IF

C    (5)
       X5 = NiAvail / NI3S2

      IF (X5 .GT. 1) THEN
        X5 = 1
      END IF

      H3O = H3O - 2 * NI3S2 * X5
      NIS =  NIS + 2 * NI3S2 * X5

      NiAvail = NiAvail - NI3S2*X5

      NI3S2 = NI3S2 * (1 - X5)
```

```
C   (6)
    X6 = 4*NiAvail / (NIS)

    IF (X6 .GT. 1) THEN
      X6 = 1
    END IF

    H3O = H3O - 0.5 * NIS * X6
    NI3S4 = NI3S4 + 0.25*NIS*X6

    NiAvail = NiAvail - 0.25*NIS*X6

    NIS = NIS * (1 - X6)
```

F.2. FILTER WITH MULTI-STAGE WASHER ALGORITHM

F.2.1. Background and algorithms

A filter and wash unit is used in the pressure iron removal and copper pressure leach sections of the base metals refinery. A custom built filter and wash was created, and the model can be seen in Figure F.2.

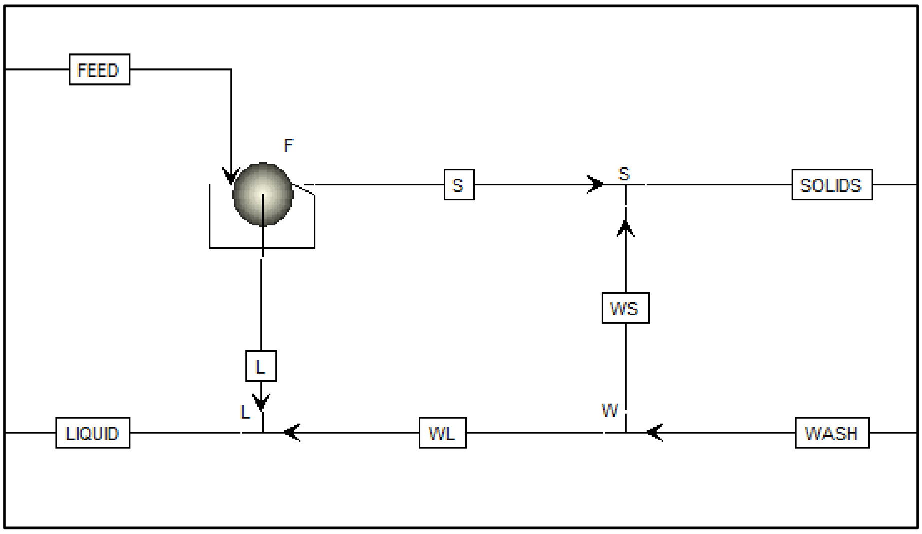

Figure F.2: Filter with multi-stage washer Aspen Plus model

The model represents the effect of a filter and wash system, and not necessarily the actual filter and wash system. Component separator F splits the solids and liquids into the results of a filter and wash system, whereas component separator W splits the incoming wash water into the fraction leaving with the solids and the fraction leaving with the liquids.

F.2.2. Variable definitions

Before the mathematics is explained, a few variable definitions need to be made that is used in the Fortran 77 algorithm, and is given in Table F.3.

Table F.3: Filter and wash algorithm variable definitions

Variable	Definition
A	Washing efficiency
E	Filter efficiency
R	Amount of washing stages
Wflow	Amount of water needed for wash
Sflow	Solid flow into the filter and wash system
Lflow	Liquid flow into the filter and wash system
X	Split fraction of liquids exiting with solids in filter and wash process
Y	Split fraction of water exiting with solids in filter and wash process

F.2.3. Mathematical model

First the total amount of water needed for the system is calculated in Equation F.2.1.

$$M_{water} = \frac{M_{solids}}{E_W}(1 - E_W)R \qquad \text{F.2.1}$$

where M_i is the total mass flow of the particular phase/specie.

Second, the split fraction of liquids exiting the system is calculated as given in Equation F.2.2.

$$X = \frac{M_{solids}(1 - E_W)}{E_W}\left(\frac{1}{M_{liquid}}\right)(1 - E_F)^2 \qquad \text{F.2.2}$$

where X is the split fraction of liquids exiting the system, E_W is the washing efficiency and E_F is the filter efficiency.

The final step is to calculate the split fraction of water exiting with the solid stream in the system, and the equation is given in Equation F.2.3.

$$Y = \frac{\frac{M_{solids}}{E_W}(1 - E_W) - X\left(M_{liquid}\right)}{M_{water}} \qquad \text{F.2.3}$$

where Y is the split fraction of water exiting with the solids stream in the system/

F.2.4. FORTRAN 77 Code

```
A = 0.5
E = 0.95
R = 2
Wflow = Sflow/A*(1-A)*R
X = Sflow/A*(1-A)/Lflow*(1-E)**R
Y = (Sflow/A*(1-A)-X*Lflow)/Wflow
```

F.3. NICKEL NON-OXIDIZING LEACH CONVERSION ALGORITHM

F.3.1. Background and algorithms

The nickel non-oxidizing leaching stage autoclave (NOX-ACLV) is where a large portion of the nickel is leached out of the nickel minerals. The reaction system is very complex since nine reactions were specified to take place inside the reactor. To complicate things even more two design specifications needs to be met on the outlet stream (NOX-04) of the reactor:

- The acid generated in the system divided by the nickel leached out of the ore needs to be 0.35
- The copper to nickel ratio in the residue needs to be between 6 and 8

The reactions convert inside the stoichiometric reactor in series according to the reactions specified in Table F.4 with their respective conversions. The reactions occur in series according to their specified order.

Table F.4: Nickel non-oxidizing leach conversion algorithm reaction conversions

Reaction Number	Algorithm Reaction Number	Conversion
R-B.30	3	0.8
R-B.17	4	Calculation
R-B.33	5	Calculation
R-B.19	6	Calculation
R-B.34	7	Calculation
R-B.35	8	Calculation
R-B.31	9	Calculation
R-B.37	10	Calculation
R-B.39	11	1

The reactions can be divided into two groups, acid forming and non-acid forming reactions. To build an algorithm where nine reactions can be leached simultaneously, two while loops are used, one for each design specification, and weights are assigned to each reaction in the inner loop, while a single variable iterated in the outer loop changes the weights of the non-acid producing reactions. These weights give each reaction the amount of copper ions that it can react with. After each round the loop is repeated until the design specification is met. Reaction R-B.30 and R-B.39 have predefined conversion of 80% and 100% respectively and thus is not contained in the inner while loop of the algorithm.

This method is thus a brute-force method to find a solution to the two design specifications while trying to take a simple version of reactivity of each mineral into account. The flow diagram of the algorithm can be seen in Figure F.3.

F.3.2. Variable definitions

To better understand the FORTRAN 77 code Table F.5 is provided as an explanation for the important variables used in the code.

Table F.5: Nickel non-oxidizing leach reaction algorithm code variable definitions

Variable	Definition
Algorithm import and export variables	
NI3S2I	Ni_3S_2 mole flow
NI3S4I	Ni_3S_4 mole flow
NISI	NiS mole flow
CU5FES4I	Cu_5FeS_4 mole flow
CUSI	CuS mole flow
CU2SI	Cu_2S mole flow
CU9S5I	Cu_9S_5 mole flow
CUNI2S4I	$CuNi_2S_4$ mole flow
CUION2I	Cu^{2+} mole flow
X3,X4,X5,X6,X7,X8,X9,X10,X11	Conversion of reaction 3 to 11
Algorithm inner variables	
ActoNi	The acid produced to Ni leached ratio.
AGenW	The value which is used to multiply the weights of the non-acid producing reactions with. This value is increased after each outer while loop until a solution to the design specification is found.
NiLchd	The amount of Ni ions leached in moles.

CuNiR	The ratio of Cu to Ni in the residue
CuRd	Cu in the residue in kg
NiRd	Ni in the residue in kg
MCUMolx	The amount of copper ions in mole available to be leached for the individual reaction in total.
Mx	The amount of copper ion moles used during the inner loop per each individual reaction.
Wx	The weight of the respective reaction. This is used to assign a number of copper ions (in mole) to the reaction.

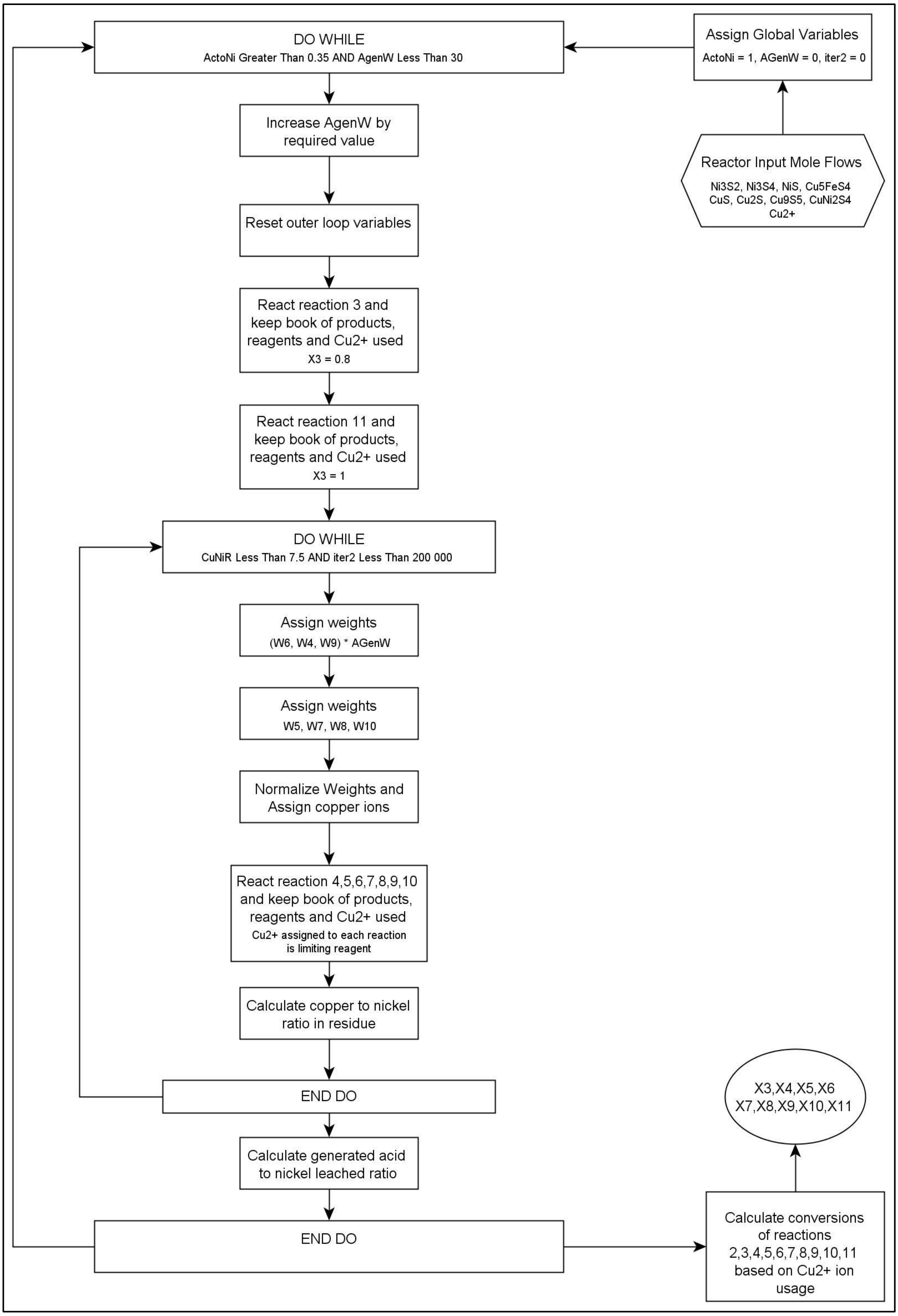

Figure F.3: Flow diagram of the nickel non-oxidizing leach autoclave reactions algorithm

F.3.3. FORTRAN 77 Code

```
C    Initialize globally used variables
      ActoNi = 1
      AGenW = 0
      iter2 = 0

C     Outer loop of the algorithm.
C     Checks for the acid generated divided by the nickel leached
C     Loop iterates the AGenW variable to modify the inner loop
       DO WHILE (ActoNi.GT.0.35.AND.AGenW.LT.30)

C         Iterates the AGenW variable
         AGenW = AGenW + 0.2

C        Reassigns the initial component flows
         NI3S2 = NI3S2I
         NI3S4 = NI3S4I
         NIS = NISI
         CUION2 = CUION2I
         CU5FES4 = CU5FES4I
         CUS = CUSI
         CUNI2S4 = CUNI2S4I
         CU2S = CU2SI
         CU9S5 = CU9S5I

C        Resets variables used internally
         AcidGen = 0
         NiLchd = 0
         iter2 = 0

         CuNiR = 0
         CuRd = 0
         NIRd = 0

         MU3 = 0
         MU4 = 0
         MU5 = 0
         MU6 = 0
         MU7 = 0
         MU8 = 0
         MU9 = 0
         MU10 = 0
         MU11 = 0

C       Reactions 3 and 11 and reacted outside of the inner loop

C (3)
         X3 = 0.8
         CUION2 = CUION2 - CU5FES4 * X3
         CUS = CUS + 2*CU5FES4 * X3
         CU2S = CU2S + 2*CU5FES4 * X3
         MU3 = MU3 + CU5FES4 * X3
         CU5FES4 = CU5FES4 * (1 - X3)



C (11)
         X11 = 1
         CUION2 = CUION2 - 0.6 * CUS * X11
         CU2S = CU2S + 0.8* CUS * X11
         AcidGen = AcidGen + (CUS * X11 * 1.6 / 2)
         MU11 = MU11 + CUS * X11
         CUS = CUS * (1 - X11)


C       The inner loop where the copper to nickel ratio is checked

         DO WHILE (CuNiR.LT.7.5.AND.iter2.LT.200000)


C           Iterates an iterator to check to exit the loop if
C           solution does not converge after 200 000 iterations
            iter2 = iter2 + 1
```

```
C          Assigns weights to each reaction
C          W6, W4 and W9 are non-acid generating reactions
C         and thus AGenW is a multiplier
          W6 = (0.4 / 22.725) * 20 * AGenW
          W4 = (2 / 22.725) * 10 * AGenW
          W9 = (1 / 22.725) * 1 * AGenW

C         W5, W7, W8 and W10 are the weights for the acid
C         generating reactions
          W5 = 3.6 / 22.725 * 10
          W7 = 1.5 / 22.725 * 10
          W8 = (5.625 / 22.725) * 0.001
          W10 = (5 / 22.725) * 0.001


C         The weights are normalized
          WTotal = W4 + W5 + W6 + W7 + W8 + W9 + W10
          W4 = W4 / WTotal
          W5 = W5 / WTotal
          W6 = W6 / WTotal
          W7 = W7 / WTotal
          W8 = W8 / WTotal
          W9 = W9 / WTotal
          W10 = W10 / WTotal

C         Copper ions that can be reacted with are assigned to
C         each reaction
          MCUMol4 = W4 * CUION2 * (0.01)
          MCUMol5 = W5 * CUION2 * (0.01)
          MCUMol6 = W6 * CUION2 * (0.01)
          MCUMol7 = W7 * CUION2 * (0.01)
          MCUMol8 = W8 * CUION2 * (0.01)
          MCUMol9 = W9 * CUION2 * (0.01)
          MCUMol10 = W10 * CUION2 * (0.01)

C          The reactions of 4 - 10 are reacted according to the
C          available copper ions assigned to them

C (4)
          IF ((2 * NI3S2).GE.MCUMol4) THEN
            X4 = MCUMol4 / (NI3S2 * 2)
          ELSE IF ((2 * NI3S2).LT.MCUMol4) THEN
            X4 = 1
          END IF

          CUION2 = CUION2 - 2 * NI3S2 * X4
          NIS = NIS + NI3S2 * X4
          CU2S = CU2S + NI3S2 * X4
          NiLchd = NiLchd + NI3S2 * X4 * 2
          MU4 = MU4 + NI3S2 * X4

          NI3S2 = NI3S2 * (1 - X4)

C (5)
          IF ((3.6 * NI3S2).GE.MCUMol5) THEN
            X5 = MCUMol5 / (NI3S2 * 3.6)
          ELSE IF ((3.6 * NI3S2).LT.MCUMol5) THEN
            X5 = 1
          END IF

          CUION2 = CUION2 - 3.6 * NI3S2 * X5
          CU2S = CU2S + 1.8 * NI3S2 * X5
          AcidGen = AcidGen + (NI3S2 * X5 * 1.6 / 2)
          NiLchd = NiLchd + NI3S2 * X5 * 3
          MU5 = MU5 + NI3S2 * X5

          NI3S2 = NI3S2 * (1 - X5)

C (6)
          IF ((0.4 * NIS).GE.MCUMol6) THEN
            X6 = MCUMol6 / (NIS * 0.4)
          ELSE IF ((0.4 * NIS).LT.MCUMol6) THEN
            X6 = 1
```

```
        END IF

        CUION2 = CUION2 - 0.4 * NIS * X6
        NI3S4 = NI3S4 + 0.2 * NIS * X6
        CU2S = CU2S + 0.2 * NIS * X6
        NiLchd = NiLchd + NIS * X6  *0.4
        MU6 = MU6 + NIS * X6

        NIS = NIS * (1 - X6)

C (7)
        IF ((1.5 * NIS).GE.MCUMol7) THEN
          X7 = MCUMol7 / (NIS * 1.5)
        ELSE IF ((1.5 * NIS).LT.MCUMol7) THEN
          X7 = 1
        END IF

        CUION2 = CUION2 - 1.5 * NIS * X7
        CU9S5 = CU9S5 + 0.16667 * NIS * X7
        AcidGen = AcidGen + (NIS * X7 * 1.33333 / 2)
        NiLchd = NiLchd + NIS * X7 * 1
        MU7 = MU7 + NIS * X7

        NIS = NIS * (1 - X7)

C (8)
        IF ((5.625 * NI3S4).GE.MCUMol8) THEN
          X8 = MCUMol8 / (NI3S4 * 5.625)
        ELSE IF ((5.625 * NI3S4).LT.MCUMol8) THEN
          X8 = 1
        END IF

        CUION2 = CUION2 - 5.625 * NI3S4 * X8
        CU9S5 = CU9S5 + 0.625 * NI3S4 * X8
        AcidGen = AcidGen + (NI3S4 * X8 * 7 / 2)
        NiLchd = NiLchd + NI3S4 * X8 * 3
        MU8 = MU8 + NI3S4 * X8

        NI3S4 = NI3S4 * (1 - X8)

C (9)
        IF (NI3S4 .GE. MCUMol9) THEN
          X9 = MCUMol9 / NI3S4
        ELSE IF (NI3S4 .LT. MCUMol9) THEN
          X9 = 1
        END IF

        CUION2 = CUION2 - NI3S4 * X9
        CUNI2S4 = CUNI2S4 + NI3S4 * X9
        NiLchd = NiLchd + NI3S4 * X9
        MU9 = MU9 + NI3S4 * X9

        NI3S4 = NI3S4 * (1 - X9)

C (10)
        IF ((5 * CUNI2S4).GE.MCUMol10) THEN
          X10 = MCUMol10 / (CUNI2S4 * 5)
        ELSE IF ((5 * CUNI2S4).LT.MCUMol10) THEN
          X10 = 1
        END IF

        CUION2 = CUION2 - 5 * CUNI2S4 * X10
        CU2S = CU2S + 3 * CUNI2S4 * X10
        AcidGen = AcidGen + (CUNI2S4 * X10 * 8 / 2)
        NiLchd = NiLchd + CUNI2S4 * X10 * 2
        MU10 = MU10 + CUNI2S4 * X10

        CUNI2S4 = CUNI2S4 * (1 - X10)


C       Updates the nickel to copper ratio variable
        NIRd = NIS*90.76*0.6467+NI3S2*240.21*0.733
        NIRd = NIRd + NI3S4*304.34*0.5785+CUNI2S4*309.19*0.38
```

```
          CURd = CUS*95.611*0.665+CU2S*159.16*0.7985
          CURd = CURd + CU9S5*732.24*0.781+CUNI2S4*309.19*0.205
          CURd = CURd + CU5FES4*501.8387*0.6331

          CuNiR = CURd / NIRd

        END DO


C         The acid to nickel variable is updated to the new value
        ActoNi = AcidGen / NiLchd

      END DO


C     Assign the final flows to the initial incoming flows
      NI3S4F = NI3S4I
      NI3S2F = NI3S2I
      NISF = NISI
      CUION2F = CUION2I
      H2SEO4F = H2SEO4I
      CU5FES4F = CU5FES4I
      CUNI2S4F = CUNI2S4I
      CUSF = CUSI



C      Calculate the conversion of each reaction
C      based on the moles used

C (3)
      IF (CU5FES4F .EQ. 0) THEN
        X3 = 0
      ELSE
        X3 = MU3 / CU5FES4F
      END IF

      CUSF = CUSF + 2*MU3
      CU5FES4F = CU5FES4F - MU3

C (4)
      IF (NI3S2F .EQ. 0) THEN
        X4 = 0
      ELSE
        X4 = MU4 / NI3S2F
      END IF

      NI3S2F = NI3S2F - MU4
      NISF = NISF + MU4


C (5)
      IF (NI3S2F .EQ. 0) THEN
        X5 = 0
      ELSE
        X5 = MU5 / NI3S2F
      END IF

      NI3S2F = NI3S2F - MU5


C (6)
      IF (NISF .EQ. 0) THEN
        X6 = 0
      ELSE
        X6 = MU6 / NISF
      END IF

      NI3S4F = NI3S4F + MU6 * 0.2
      NISF = NISF - MU6

C (7)
      IF (NISF .EQ. 0) THEN
        X7 = 0
```

```
    ELSE
      X7 = MU7 / NISF
    END IF

    NISF = NISF - MU7

C (8)
    IF (NI3S4F .EQ. 0) THEN
      X8 = 0
    ELSE
      X8 = MU8 / NI3S4F
    END IF

    NI3S4F = NI3S4F - MU8

C (9)
    IF (NI3S4F .EQ. 0) THEN
      X9 = 0
    ELSE
      X9 = MU9 / NI3S4F
    END IF

    NI3S4F = NI3S4F - MU9
    CUNI2S4F = CUNI2S4F + MU9



C (10)
    IF (CUNI2S4F .EQ. 0) THEN
      X10 = 0
    ELSE
      X10 = MU10 / CUNI2S4F
    END IF

    CUNI2S4F = CUNI2S4F - MU10

C (11)
    IF (CUSF .EQ. 0) THEN
      X11 = 0
    ELSE
      X11 = MU11 / CUSF
    END IF

    CUSF = CUSF - MU11
```

F.4. SULPHUR REMOVAL NEUTRALIZATION AND DISSOLUTION STREAM FLOW RATE

F.4.1. Background and algorithm

The sulphur removal section is where the excess sulphur in the process is removed. A process where acid is neutralized and nickel is precipitated as $Ni(OH)_2$ is used as detailed in Section X.

Two of the four streams from the stream splitter (NEW-SPL) in the nickel electrowinning section are used in the sulphur removal section, one to be neutralized (NEW-07) and the other to dissolve precipitated $Ni(OH)_{2.}$ An optimal ratio between the two streams exists, and an algorithm is used to calculate the split fraction of the two streams.

In the FORTRAN 77 code SPL1 and SPL4 are the split fractions of streams not sent to the sulphur removal section, whereas SPL2 is the split fraction for the neutralization stream (NEW-07) and SPL3 is the split fraction for the dissolution stream (NEW-08).

F.4.2. Variable definitions

Variables used with respective definitions in the algorithm are given in Table F.6.

Table F.6: Sulphur removal neutralization and dissolution flow rate algorithm variable definitions

Variable	Definition
Algorithm import and export variables	
HSO4F	HSO_4^- mole flow rate
H3OF	H_3O^+ mole flow rate
NIF	Ni^{2+} mole flow rate
SPL1	Split fraction for stream NEW-06
SPL3	Split fraction for stream NEW-08
SPL4	Split fraction for stream NEW-09
Algorithm inner variables	
ACIDF	Total moles of $H3O^+$
NIF2	Ni^{2+} mole flow rate after NEW-06 and NEW-09 Ni^{2+} flow rates are subtracted
ACIDF2	H_3O^+ mole flow rate after NEW-06 and NEW-09 H_3O^+ flow rates are subtracted

F.4.3. Algorithm

The flow diagram for the algorithm can be seen in Figure F.4.

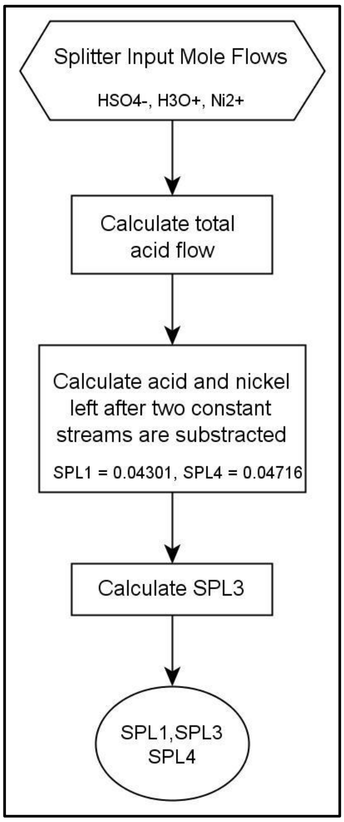

Figure F.4: Algorithm Flow diagram for sulphur removal neutralization and dissolution streams split fractions

F.4.4. FORTRAN 77 Code

```
C     Calculate the total acid flow
       ACIDF = HSO4F + H3OF

C     Pre-defined split values for two of the four streams being split

      SPL1 = 0.04301
      SPL4 = 0.04716

C     Calculate acid flow after the two streams (1 and 4)
C     are subtracted
      ACIDF2 = ACIDF - ACIDF*SPL1 - ACIDF*SPL4

C     Calculate nickel flow after the two streams(1 and 4)
C     are subtracted
      NIF2 = NIF - NIF*SPL1 - NIF*SPL4

C     Calculate the split fraction for SPL3
C     Split fraction for SPL2 is automatically calculated in
C     block NEW-SPL
C     A factor of 1.125 is multiplied in the SPL3 ratio to cater
C     for excess acid due to the filter removing solution with Ni(OH)2


      SPL3 = 2*ACIDF2 / (2*ACIDF2 + NIF2) * 1.125
```

```
C     Put bounds on the split so that convergence does not overshoot
       IF (SPL3.LT.0.64) THEN
         SPL3 = 0.64
      END IF

      IF (SPL3.GT.0.68) THEN
         SPL3 = 0.68
      END IF
```

F.5. NF UNIT OPERATION

F.5.1. Background

The NF unit operation is the core model used in the RBMR-NF simulation. Figure F.5 illustrates the NF unit operation inner workings as constructed in Aspen Plus.

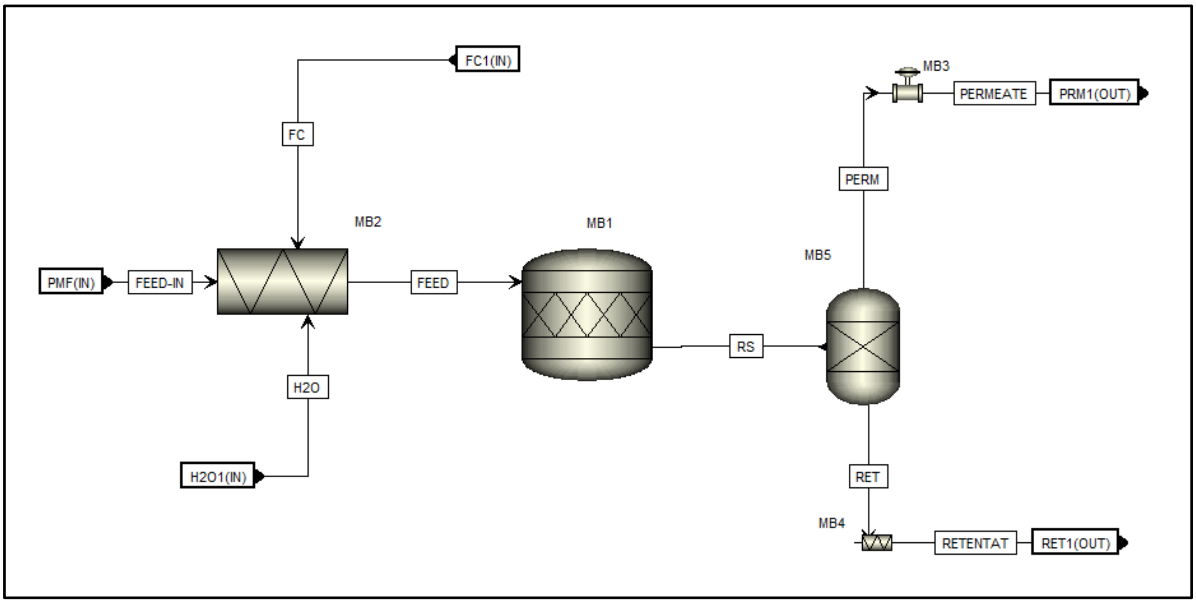

Figure F.5: NF membrane Aspen Plus model

Mixer MB2 mixes the incoming feed (FEED-IN), water (H2O) and dummy stream (FC). The water stream is used for dilution of the membrane feed, and the dummy stream is used as a variable storage mechanism to control the size of the membrane. The reactor (MB1) converts all HSO_4^- ions to H_3O^+ form so that an accurate transfer of acid can be achieved through the membrane. The component separator (MB5) splits the water and ions into their respective permeate and retentate streams according to the calculations of the algorithm. The valve (MB3) releases the pressure to atmospheric pressure and also restores equilibrium to the permeate stream. The mixer (MB4) activates the global chemistry so that equilibrium can be restored in the retentate stream.

F.5.2. Variable definitions

Before the mathematics and algorithm can be explained, few variable definitions need to be made that is used in the algorithm, and is given is

Table F.7: NF unit operation variable definitions

Variable	Definition
Algorithm import and export variables	
NIF	Stream RS Ni^{2+} mass flow rate

Variable	Definition
NAF	Stream RS Na^+ mass flow rate
H3OF	Stream RS H_3O^+ mass flow rate
SO4F	Stream RS SO_4^{2-} mass flow rate
H2OF	Stream RS H2O mass flow rate
MF	Stream RS total mass flow rate
SO4PAC	Permeate SO_4^{2-} mass flow rate
H3OPAC	Permeate H_3O^+ mass flow rate
NIPAC	Permeate Ni^{2+} mass flow rate
H2OPAC	Permeate H_2O mass flow rate
NAPAC	Permeate Na^+ mass flow rate
TOTAREA	Total area of NF membrane
NIRR	Imported Ni^{2+} rejection
NARR	Imported Na^+ rejection
ACIDRR	Imported H_3O^+ rejection
Algorithm inner variables	
NIR	Mass flow rate of Ni^{2+} in retentate
NAR	Mass flow rate of Na^+ in retentate
H3OR	Mass flow rate of H_3O^+ in retentate
SO4R	Mass flow rate of SO_4^{2-} in retentate
H2OR	Mass flow rate of H2O in retentate
NICF	Ni^{2+} concentration in membrane feed
NACF	Na^+ concentration in membrane feed
H3OCF	H_3O^+ concentration in membrane feed
SO4CF	SO_4^{2-} concentration in membrane feed
H2OCF	H_2O concentration in membrane feed
H2SO4CF	H_2SO_4 concentration in membrane feed
NA2SO4CF	Na_2SO_4 concentration in membrane feed
NICP	Ni^{2+} concentration in permeate
NACP	Na^+ concentration in permeate
H3OCP	H_3O^+ concentration in permeate
NICR	Ni^{2+} concentration in retentate
NACR	Na^+ concentration in retentate
H3OCR	H_3O^+ concentration in retentate
SO4CR	SO_4^{2-} concentration in retentate
H2OCR	H_2O concentration in retentate

Variable	Definition
NIMW	Ni^{2+} molecular weight
NAMW	Na^{+} molecular weight
SO4MW	SO_4^{2-} molecular weight
H2OMW	H_2O molecular weight
H3OMW	H_3O^{+} molecular weight
VF	Feed volume flow rate
VP	Permeate volume flow rate
VR	Retentate volume flow rate
MP	Permeate mass flow rate
MR	Retentate mass flow rate
NIRE	Ni^{2+} rejection
NARE	Na^{+} rejection
H3ORE	H_3O^{+} rejection
Area	Incremental area of membrane
Flux	Flux of membrane
H2SO4	General variable to store H_2SO_4 mass flow rate
NA2SO4	General variable to store Na_2SO_4 mass flow rate
NISO4	General variable to store $NiSO_4$ mass flow rate
H2O	General variable to store H_2O mass flow rate
TOTFLOW	General variable to store total mass flow rate
FH2SO4	General variable to store H_2SO_4 mass fraction
FNA2SO4	General variable to store Na_2SO_4 mass fraction
FNISO4	General variable to store $NiSO_4$ mass fraction
FH2O	General variable to store H_2O mass fraction
RHOF	Membrane feed stream density
RHOP	Membrane permeate stream density
RHOR	Membrane retentate stream density
NIP	Ni^{2+} Mass flow rate
NAP	Na^{+} Mass flow rate
H3OP	H_3O^{+} Mass flow rate
SO4P	SO_4^{2-} Mass flow rate
H2OP	H_2O Mass flow rate

F.5.3. Mathematical and numerical model

The idea behind the membrane unit operation algorithm is to use simple mathematical correlations that relate permeate and retentate concentrations to the rejection parameter of each specie in solution. Since the flow of liquid through a membrane can be seen as plug flow where the specie concentration of the liquid inside the membrane and the permeate constantly changes, the numerical method where the membrane is divided into many smaller membranes to approximate plug flow can be used.

The rejection of specific specie i in the membrane is given by Equation F.5.1:

$$R_i = 1 - \frac{C_{P,i}}{C_{R,i}} \tag{F.5.1}$$

where R_i is the rejection of specie i, $C_{p,i}$ is the concentration of specie i in the permeate and $C_{R,i}$ is the concentration of specie i in the retentate. Thus from Equation F.5.1 can be seen that the rejection of a specie is a function of the permeate and retentate concentration.

Furthermore the flux of the membrane is given by Equation F.5.2:

$$J_M = \frac{M_p}{A} \tag{F.5.2}$$

where J_M is the flux of the membrane, M_P is the mass flow of the permeate and A is the area of the membrane. The concentration of specie i can also be related to its mass flow and total volume flow and is given in Equation F.5.3:

$$C_i = \frac{M_i}{V} \tag{F.5.3}$$

where c_i is the concentration of specie i, M_i is the mass flow of specie i, and V is the volume flow. The volume flow of the permeate, retentate or feed can be related to density and mass flow by Equation F.5.4:

$$V = \frac{M}{\rho} \tag{F.5.4}$$

where M is the total mass flow rate and ρ is the total density. For accurate concentration prediction, density data at different NiSO4, Na_2SO4 and H_2SO_4 concentrations were generated from Aspen Plus. The data were fitted using machine learning methods to create the density correlation as given in F.5.5:

$$\rho = -919.9 + 4883 \times MF_{NiSO4} + 2953 \times MF_{Na_2SO_4} + 4233 \times MF_{H_2SO_4} - 9124 \times MF_{H_2SO_4} MF_{NiSO_4} - 5648 MF_{H_2SO_4} MF_{Na_2SO_4} + 1676 MF_{Na_2SO_4} MF_{H_2O} + 1920\left(MF_{H_2O}\right)^2 \quad \text{(F.5.5)}$$

where MF is the mass fraction of the specific specie.

Additional discussion regarding the machine learning method used is outside the scope.

Equation F.5.1 – Equation F.5.5 is used in conjunction with the numerical integration approximation technique to create the NF membrane algorithm. The main parameters to the membrane are the flux, nickel rejection, sodium rejection and acid rejection. Each of the four parameters can either be calculated with correlations, or can be constant values.

F.5.4. Algorithm

The algorithm for the NF unit operation is given in Figure F.6.

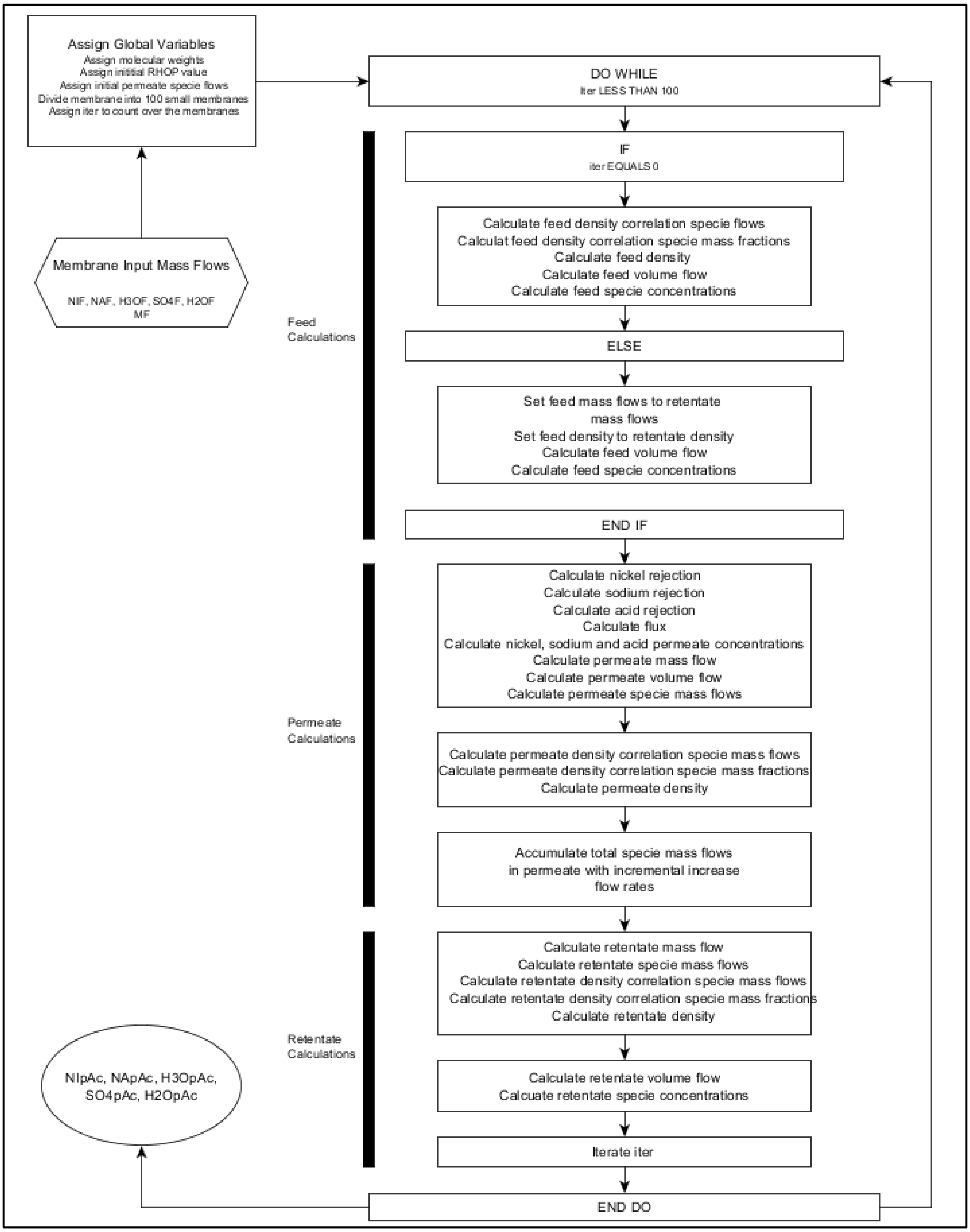

Figure F.6: NF membrane algorithm

F.5.5. FORTRAN 77 Code

```
C Unit conversion
      TotArea = TotArea * 10000


C ASSIGN VARIABLES

      NiMW = 58.6889
      NaMW = 22.98922
      SO4MW = 96.0647
      H2OMW = 18.01528
      H3OMW = 19.02267

      NIpAc = 0
      NApAc = 0
      H3OpAc = 0
      SO4pAc = 0
      H2OpAc = 0

      RHOP = 1054

C Divide the membrane into 100 small membranes
      Area = TotArea / 100

      Iter = 0


      IF (Area.GT.0) THEN

      DO WHILE (Iter .LT. 100)


C FEED CALCULATIONS

      IF (Iter .EQ. 0) THEN


        H2SO4 = H3Of * 0.052985 / 0.020553634
        Na2SO4 = NAf / 0.323701
        NiSO4 = NIf / 0.37926
        H2O = H2Of
        TotFlow = H2SO4 + Na2SO4 + NiSO4 + H2O
        FH2SO4 = H2SO4 / TotFlow
        FNa2SO4 = Na2SO4 / TotFlow
        FNiSO4 = NiSO4 / TotFlow
        FH2O = H2O / TotFlow
        RHOf = -919.9 + 4883*FNiSO4 + 2953*FNa2SO4 + 4233*FH2SO4
        RHOf = Rhof -9124*FH2SO4*FNiSO4 -5648*FH2SO4*FNa2SO4
        RHOf = Rhof + 1676*FH2O*FNa2SO4 + 1920*FH2O*FH2O

        Vf = Mf / Rhof
        NICf = NIf / Vf
        NACf = NAf / Vf
        Na2SO4Cf = (NAf/0.323701) / Vf
        H3OCf = H3Of / Vf
        H2SO4Cf = (H3Of * 0.052985 / 0.020553634) / Vf
        SO4Cf = SO4f / Vf
        H2OCf = H2Of / Vf


      ELSE

        Mf = Mr
        Nif = Nir
        Naf = Nar
        H3Of = H3Or
        SO4f = SO4r
        H2Of = H2Or

        RHOf = RHOr



        Vf = Mf / Rhof
```

```
      NICf = NIf / Vf
      NACf = NAf / Vf
      H3OCf = H3Of / Vf
      SO4Cf = SO4f / Vf
      H2OCf = H2Of / Vf

    END IF

C PERMEATE CALCULATIONS

    NiRe=NIRR
    NaRe=NARR
    H3ORe = ACIDRR

     Flux = 20

    NICp = -NICf * (NIRe - 1)
    NACp = -NACf * (NARe - 1)
    H3OCp = -H3OCf * (H3ORe - 1)

    Mp = Flux * Area

    Vp = Mp / RHOP
    NIp = NICp * Vp
    NAp = NACp * Vp
    H3Op = H3OCp * Vp
    SO4p = NIp/NiMW + NAp/(NaMW*2) + H3Op/(H3OMW*2)
    SO4p = SO4p * SO4MW
    H2Op = Mp - NIp - NAp - H3Op - SO4p

    H2SO4 = H3Op * 0.052985 / 0.020553634
    Na2SO4 = NAp / 0.323701
    NiSO4 = NIp / 0.37926
    H2O = H2Op
    TotFlow = H2SO4 + Na2SO4 + NiSO4 + H2O
    IF (TotFlow .GT. 0) THEN
    FH2SO4 = H2SO4 / TotFlow
    FNa2SO4 = Na2SO4 / TotFlow
    FNiSO4 = NiSO4 / TotFlow
    FH2O = H2O / TotFlow
    RHOp = -919.9 + 4883*FNiSO4 + 2953*FNa2SO4 + 4233*FH2SO4
    RHOp = Rhop -9124*FH2SO4*FNiSO4 -5648*FH2SO4*FNa2SO4
    RHOp = Rhop + 1676*FH2O*FNa2SO4 + 1920*FH2O*FH2O
    END IF

    NIpAc = NIpAc + NIp
    NApAc = NApAc + NAp
    H3OpAc = H3OpAc + H3Op
    SO4pAc = SO4pAc +  SO4p
    H2OpAc = H2OpAc + H2Op

C RETENTATE CALCULATIONS

    Mr = Mf - Mp

    SO4r = SO4f - SO4p
    NIr = NIf - NIp
    NAr = NAf - NAp
    H3Or = H3Of - H3Op
```

```
H2Or = H2Of - H2Op


H2SO4 = H3Or * 0.052985 / 0.020553634
Na2SO4 = NAr / 0.323701
NiSO4 = NIr / 0.37926
H2O = H2Or
TotFlow = H2SO4 + Na2SO4 + NiSO4 + H2O
IF (TotFlow .GT. 0) THEN
FH2SO4 = H2SO4 / TotFlow
FNa2SO4 = Na2SO4 / TotFlow
FNiSO4 = NiSO4 / TotFlow
FH2O = H2O / TotFlow
RHOr = -919.9 + 4883*FNiSO4 + 2953*FNa2SO4 + 4233*FH2SO4
RHOr = Rhor -9124*FH2SO4*FNiSO4 -5648*FH2SO4*FNa2SO4
RHOr = Rhor + 1676*FH2O*FNa2SO4 + 1920*FH2O*FH2O
END IF


Vr = Mr / RHOR
SO4Cr = SO4r / Vr
NICr = NIr / Vr
NACr = NAr / Vr
H3OCr = H3Or / Vr
H2OCr = H2Or / Vr


Iter = Iter + 1


END DO

ELSE

C If the membrane size is zero, the permeate flow will also be zero.  A water flow of 1 kg/hr is given to the permeate  stream to
ensure that no Aspen Plus errors are thrown due to no water that is present
NIpAc = 0
NApAc = 0
H3OpAc = 0
SO4pAc = 0
H2OpAc = 1

 END IF
```

APPENDIX G - RBMR-NF CASE STUDIES

Overview

Appendix G reports the results as generated by the RBMR-NF case studies.

G.1. EFFECT OF ACID REJECTION

The results for the acid rejection parameter variation case studies are given in Table G.1.

Table G.1: Acid rejection variation case study results

Variable	Units	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7
Parameters								
Ni^{2+} Rejection		0.98	0.98	0.98	0.98	0.98	0.98	0.98
Na^{+} Rejection		0.5	0.5	0.5	0.5	0.5	0.5	0.5
$H3O^{+}$ Rejection		-1	-0.8	-0.6	-0.4	-0.3	-0.2	0
Stream SR-09 (NF system feed)								
Mass Flow	t/hr	151.0	149.9	148.6	146.9	145.9	144.8	141.9
Volume Flow	m^3/hr	127	126	125	123	122	121	119
Ni^{2+} Concentration	g/l	66.7	66.7	66.6	66.6	66.6	66.6	66.6
Na^{+} Concentration	g/l	4.9	4.9	4.9	4.9	4.9	4.9	4.9
H_2SO_4 Concentration	g/l	42.8	42.8	42.8	42.7	42.7	42.7	42.7
Stream SR-15 (final permeate)								
Mass Flow	t/hr	238.6	268.5	306.1	356.8	388.3	427.1	531.7
Volume Flow	m^3/hr	235	265	302	353	385	423	528
Ni^{2+} Concentration	g/l	1.2	1.1	1.1	1.1	1.0	1.0	1.0
Na^{+} Concentration	g/l	1.5	1.4	1.3	1.2	1.1	1.1	0.9
H_2SO_4 Concentration	g/l	22.2	19.5	17.0	14.4	13.1	11.8	9.3
Stream SR-10 (final retentate)								
Mass Flow	t/hr	126.6	125.1	123.3	121.2	119.8	118.3	114.5
Volume Flow	m^3/hr	102.1	100.9	99.6	97.9	96.8	95.6	92.6
Ni^{2+} Concentration	g/l	80.0	80.0	80.0	79.9	80.0	80.0	80.0
Na^{+} Concentration	g/l	2.7	2.5	2.2	1.9	1.7	1.6	1.2
H_2SO_4 Concentration	g/l	2.0	2.0	2.0	2.0	2.0	2.0	2.0
% Nickel Permeated	%	3.2	3.6	4.0	4.6	4.9	5.4	6.4
% Acid Permeated	%	96.2	96.3	96.3	96.3	96.3	96.3	96.4
% Sodium Permeated	%	55.9	59.8	64.2	69.2	71.9	74.7	80.9
Total Pump Power Consumption	kW	620	666	723	800	848	906	1063
Total Membrane Area	m^2	11932	13426	15305	17839	19416	21355	26583
Total Membrane Water Usage	t/hr	214.2	243.7	280.9	331.0	362.1	400.6	504.3
Evaporator Duty	GW	29.3	29.1	28.9	28.6	28.3	28.1	27.4
Na_2SO_4 Production	kg/hr	888	821	750	672	631	590	508
Nickel Cathode Production	kg/hr	3549	3525	3495	3458	3436	3410	3346

G.2. EFFECT OF SODIUM REJECTION

The results for the sodium rejection parameter variation case studies are given in Table G.2.

Table G.2: Sodium rejection variation case study results

Variable	Units	Case 8	Case 9	Case 10	Case 11	Case 12
Parameters						
Ni^{2+} Rejection		0.98	0.98	0.98	0.98	0.98
Na^{+} Rejection		0.3	0.4	0.5	0.6	0.7
$H3O^{+}$ Rejection		-0.4	-0.4	-0.4	-0.4	-0.4
Stream SR-09 (NF system feed)						
Mass Flow	t/hr	146.9	146.9	146.9	147.0	147.0
Volume Flow	m^3/hr	123	123	123	123	123
Ni^{2+} Concentration	g/l	66.6	66.6	66.6	66.6	66.6
Na^{+} Concentration	g/l	4.9	4.9	4.9	4.9	4.9
H_2SO_4 Concentration	g/l	42.8	42.7	42.7	42.7	42.7
Stream SR-15 (final permeate)						
Mass Flow	t/hr	356.1	356.1	356.1	355.9	355.8
Volume Flow	m^3/hr	352	352	352	352	352
Ni^{2+} Concentration	g/l	1.1	1.1	1.1	1.1	1.1
Na^{+} Concentration	g/l	1.4	1.3	1.2	1.0	0.9
H_2SO_4 Concentration	g/l	14.4	14.4	14.4	14.4	14.4
Stream SR-10 (final retentate)						
Mass Flow	t/hr	121.1	121.1	121.0	121.3	121.4
Volume Flow	m^3/hr	98.0	97.9	97.8	97.9	97.9
Ni^{2+} Concentration	g/l	79.9	80.0	80.1	80.0	80.0
Na^{+} Concentration	g/l	1.2	1.5	1.9	2.4	3.1
H_2SO_4 Concentration	g/l	2.0	2.0	2.0	2.0	2.0
% Nickel Permeated	%	4.6	4.6	4.6	4.6	4.6
% Acid Permeated	%	96.3	96.3	96.3	96.3	96.3
% Sodium Permeated	%	80.7	75.6	69.1	60.9	50.6
Total Pump Power Consumption	kW	799	799	799	799	799
Total Membrane Area	m^2	17804	17804	17806	17795	17788
Total Membrane Water Usage	t/hr	330.2	330.2	330.2	330.2	330.2
Evaporator Duty	GW	29.2	28.9	28.5	28.2	27.8
Na_2SO_4 Production	kg/hr	455	551	672	827	1021
Nickel Cathode Production	kg/hr	3459	3459	3458	3459	3459

G.3. EFFECT OF NICKEL REJECTION

The results for the nickel rejection parameter variation case studies are given in Table G.3.

Table G.3: Nickel rejection variation case study results

Variable	Units	Case 13	Case 14	Case 15	Case 16	Case 17	Case 18	Case 19	Case 20
Parameters									
Ni^{2+} Rejection		0.9	0.92	0.94	0.96	0.97	0.98	0.99	0.995
Na^{+} Rejection		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$H3O^{+}$ Rejection		-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4
Stream SR-09 (NF system feed)									
Mass Flow	t/hr	109.8	116.9	125.3	135.1	140.8	147.0	153.8	157.5
Volume Flow	m^3/hr	92	98	105	113	118	123	129	132
Ni^{2+} Concentration	g/l	66.0	66.1	66.3	66.5	66.5	66.6	66.7	66.8
Na^{+} Concentration	g/l	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
H_2SO_4 Concentration	g/l	42.3	42.4	42.5	42.6	42.7	42.7	42.8	42.9
Stream SR-15 (final permeate)									
Mass Flow	t/hr	255.7	275.1	297.7	324.2	339.5	355.8	374.5	384.0
Volume Flow	m^3/hr	251	270	293	320	336	352	371	380
Ni^{2+} Concentration	g/l	5.3	4.3	3.2	2.1	1.6	1.1	0.5	0.3
Na^{+} Concentration	g/l	1.3	1.3	1.2	1.2	1.2	1.2	1.2	1.2
H_2SO_4 Concentration	g/l	15.1	14.9	14.7	14.6	14.5	14.4	14.3	14.3
Stream SR-10 (final retentate)									
Mass Flow	t/hr	73.4	82.5	93.3	106.0	113.2	121.3	129.9	134.7
Volume Flow	m^3/hr	59.2	66.7	75.4	85.6	91.4	98.0	104.9	108.8
Ni^{2+} Concentration	g/l	80.0	80.0	79.9	80.0	80.0	79.9	80.1	80.0
Na^{+} Concentration	g/l	2.2	2.1	2.0	2.0	1.9	1.9	1.9	1.9
H_2SO_4 Concentration	g/l	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
% Nickel Permeated	%	22.1	17.8	13.5	9.1	6.8	4.6	2.3	1.2
% Acid Permeated	%	97.0	96.8	96.6	96.5	96.4	96.3	96.2	96.1
% Sodium Permeated	%	71.3	70.7	70.2	69.6	69.4	69.1	68.9	68.7
Total Pump Power Consumption	kW	571	615	667	727	761	799	840	862
Total Membrane Area	m^2	12786	13755	14885	16208	16974	17788	18727	19198
Total Membrane Water Usage	t/hr	219.3	240.7	265.7	295.0	311.9	330.1	350.6	361.2
Evaporator Duty	GW	16.3	18.7	21.5	24.7	26.5	28.7	30.8	32.1
Na_2SO_4 Production	kg/hr	1008	944	870	780	729	673	610	578
Nickel Cathode Production	kg/hr	2628	2787	2973	3194	3320	3459	3612	3695