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WATER MINIMISATION AT SKORPION ZINC

**A Thesis Submitted to the
UNIVERSITY OF CAPE TOWN
In Fulfilment of the Requirements for the Degree
MASTER OF SCIENCE IN CHEMICAL ENGINEERING**

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May 2009

Plagiarism declaration

I know the meaning of plagiarism and declare that all the work in the document, save for that which is properly acknowledged, is my own.

Harshad Bhikha

Signed by candidate

Acknowledgements

I would like to thank my supervisors, Professor Alison E Lewis and Professor David A Deglon for your supervision during this project. I would also like to thank Herman Fuls and Jurgen Gnoinski at Skorpion Zinc for your assistance during this project.

Thank you to the Minerals to Metals Research Initiative for your assistance and funding of this project.

Thanks also to the members of the Crystallisation and Precipitation Unit, for making the past 2 years a really enjoyable experience.

A special thanks to Dr Mike Dry for all your assistance with the Aspen simulation, it was greatly appreciated.

Finally, thanks to the National Research Foundation for providing the funding for this project.

On a personal note, thank you to my parents and sister for all your support during my studies, as well as all my friends for making the past 6 years a truly unforgettable experience at UCT.

SYNOPSIS

The minerals processing industry has recognised that the need for the minimisation of water usage is important. This is especially true for regions of water scarcity. Special focus has been given to optimising existing processes with regards to sustainability objectives to meet stricter environmental guidelines.

This work proposes a systemic optimisation of the water balance of the Skorpion Zinc refinery, the case study selected for this work. The Skorpion process is located in Rosh Pinah in Namibia and was selected due to its location in an ecologically sensitive region where water is scarce. The project proposes that process optimisation cannot occur through focus on unit operations in isolation, but rather to use the interactions between the different operations to optimise the process systemically. The key questions for this project are as follow:

- How do water, co-extracted metals and impurities report to the various streams in the process?
- How must the water balance be optimised to minimise water consumption?
- Can different system configurations be applied to minimise the water balance?

In order to gain a deeper understanding of the process, a simulation was performed using the Aspen Plus® simulation package. The simulation process was critical given that water affects the threshold concentrations throughout the process, which if exceeded, could prevent the process from operating properly. The aim of the simulation was to develop a working mass balance of the process, from which different operating scenarios could be investigated, as dictated by the key questions. Aspen Plus® is well suited to process simulation and optimisation and is used in industry for various steady-state modelling applications.

A number of water minimisation scenarios were presented, as informed by process design heuristics. These included unit operation changes and circuit configuration changes and were formulated with the aim of retaining water in the process. Unit operation changes focused on units that could be made more efficient through the

use of new technologies (e.g. gravity thickening versus conventional thickening) or through the combination of unit operations (e.g. adding an extra filtration step) to improve the overall efficiency of a process stage. Circuit configuration changes focused on the addition of recycle streams to reuse water, thereby minimising the fresh water required and waste water produced.

Simulation results were compared to data obtained from the plant in order to validate the simulation and showed good agreement. From the various operating scenarios investigated, the following conclusions were drawn:

- The reduction of process water into the refinery is not sufficient to optimise the water balance, since a steady build-up of salts in the process will be detrimental to the product purity.
- Improving the efficiencies in solid-liquid separation steps has a negligible effect on the production rate and water flows and merely results in a shift in the water balance between the output streams.
- Supplementation of demineralised fresh water with demineralised effluent water results in a 14% reduction in fresh water required.
- Supplementation of gland seal water with fully treated effluent product water results in a 19% reduction in fresh water required.

The findings suggest that the Skorpion process already features a highly optimised water balance, with unit operation changes merely resulting in a shift in the water balance. The limiting factor in the scenarios investigated is the build-up of impurities, which will need to be investigated in more detail. The only effective water balance optimisation is thus through the recovery and re-use of effluent water to supplement the fresh water input.

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Chapter 1 – Introduction

1.1 Project Statement

Existing mineral processing plant designs are often conservative in their design, sticking to tried-and-tested process operations. Even for well-designed plants, the process may have to be changed over time, due to changes in feed mineralogy and to meet market demand. Plants therefore require optimisation in terms of a number of variables (Huband et al. 2006).

This project proposes that process optimisation cannot occur through focus only on specialist areas of the minerals beneficiation chain, as is currently the case. The process should rather be considered systemically as opposed to a series of individual unit operations. Alva-Argaez et al. (1998) showed that many localised optimisation problems can be avoided through simultaneous optimisation of the entire process, which is the approach that this project takes. Currently, the output from one unit operation is not necessarily the optimum input for the next operation and thus the issues arising at the interface of the various unit operations in the process need to be researched. In addition, the sustainable use of water as a raw material needs to be investigated. The Skorpion Zinc refinery in Namibia was selected as the case study for this work.

Water is probably the most widely used raw material in the process industry (Alva-Argaez et al. 1998) and the scarcity of good quality industrial-grade water and the costs involved are strong motivators to minimise and optimise its use. The minerals industry has to cope with increasing environmental and social demands being placed on it (Sudholter et al. 1996); which is especially true for the Skorpion Zinc process due to its location in an environmentally sensitive and arid region, where water minimisation is particularly necessary. This project aims to show how process simulation, when approached from a systemic view, can be used to optimise and minimise the water use of a given process.

The core of this project involved the development of a process simulation of the Skorpion plant. During the process of simulation, a number of issues were investigated, such as how simplified a view can be taken of the plant in simulation,

whilst still obtaining meaningful results. The deportment of water, co-extracted metals and impurities to the various streams was also analysed. This project therefore focuses on improving the existing process as much as possible, rather than a complete overhaul of the process.

1.2 Skorpion Zinc

The Skorpion Zinc refinery is situated in Rosh Pinah in Southern Namibia and falls under the Anglo American consortium. The refinery and mine were officially opened in September 2003 following the first production of metal in May 2003 (Bachmann 2004). The process currently produces some of the highest quality zinc at amongst the lowest operating costs in the world – it produces a 99.995% Special High Grade (SHG) zinc product (Fuls et al. 2005), using a zinc oxide concentrate due to the oxidised ore reserves present in the region. This means that the concentrate cannot be treated via conventional zinc processing methods, which are based on a zinc sulphide concentrate feed.

The Skorpion Zinc process is therefore unique due to its unconventional zinc oxide ore body as well as the application of solvent extraction for concentration upgrading for electrowinning. This is a revolutionary departure from conventional zinc processes, which feature a purification step involving precipitation.

The oxide ore body was found to consist of approximately 21 000 megatons of high-grade ore at an average of 11% zinc by mass. In addition, the rapid leaching kinetics observed by the plant mean that only coarse crushing and grinding is required before leaching, which cuts costs. A major environmental benefit of the process is that most of the waste produced is inert and unlikely to produce any acid mine drainage, which allows for simple disposal practices (Bachmann 2004). The operation was approved to produce 150 kilotons per annum SHG zinc, which translates into approximately 17000 kg/hr.

The refinery and mine are also situated on the same site, eliminating costly transport charges. Most conventional zinc processing operations import a concentrate from the mine, which is situated off-site.

1.3 Brief Process Summary

Figure 1 shows a simplified Block Flow Diagram of the Skorpion Zinc process.

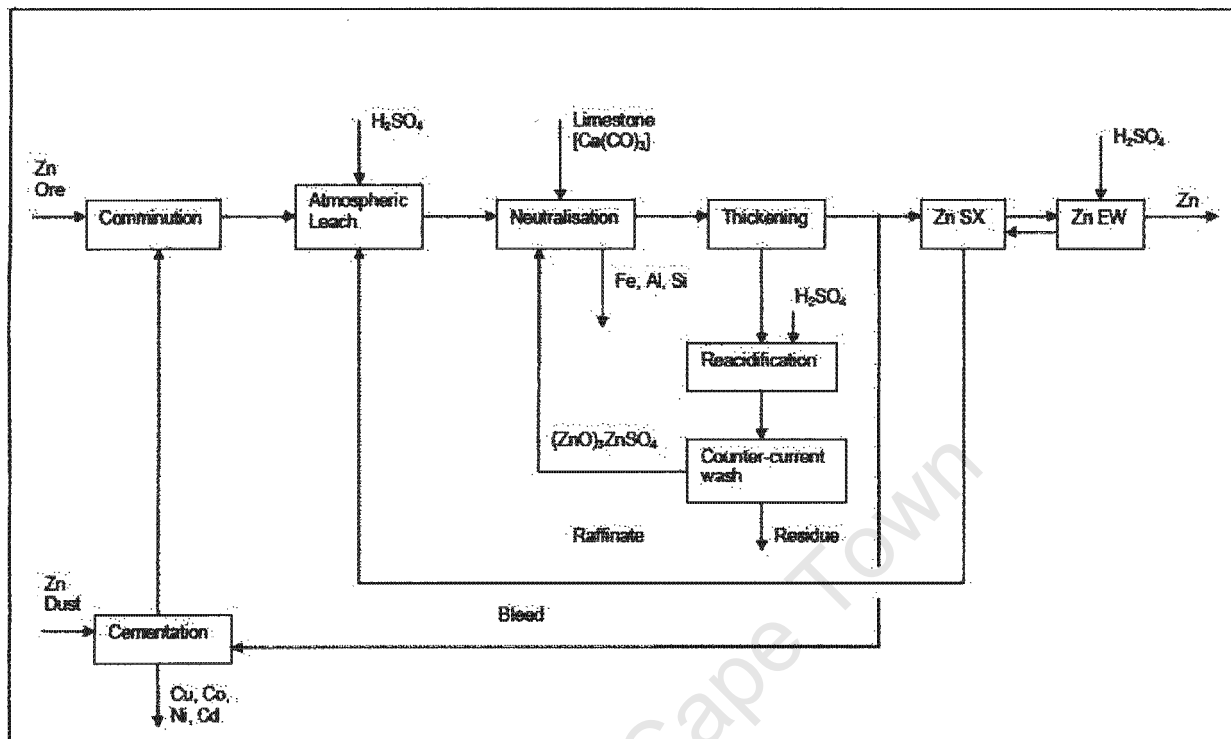


Figure 1: Simplified Block Flow Diagram of the Skorpion Zinc Process

The ore, consisting of sauconite ($\text{Na}_{0.33}\text{Zn}_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), smithsonite (ZnCO_3) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$), undergoes a 3-stage crushing process following its extraction from the mine, where it is reduced to a size suitable for leaching, with a d_{80} of $180\mu\text{m}$. The reduced ore is then leached at atmospheric pressure with sulphuric acid to form a sulphate solution. This solution, known as the pregnant leach solution (PLS) then undergoes neutralisation, where certain impurities such as iron, aluminium and silica are precipitated from solution.

The clarified PLS proceeds to the solvent extraction step, where it is purified using the organic solvent D2EHPA (di(2-ethylhexyl) phosphoric acid). The raffinate is recycled back to the leaching step and any metals that co-extract with zinc are removed via cementation with zinc dust. The purified and upgraded solvent extraction product is then sent to electrowinning for the formation of the SHG product.

1.4 Objectives

At the core of this project lies a simulation of the Skorpion Zinc process using the Aspen Plus® simulation package that will be used to answer a number of process-related questions. In developing this simulation, a deeper understanding of the process was obtained. The validity of the simulation was tested by measuring key output variables and comparing the results to the data obtained from the plant. The key questions that arose from the process are listed below.

1.4.1 Key questions

- How do water, co-extracted metals and impurities report to the various streams in the process?
- How must the water balance be optimised to minimise water consumption?
- Can different system configurations be applied to minimise the water balance?

1.5 Scope and Limitations

The movement of the zinc compounds is well understood, since zinc is the desired product, but little is known about the behaviour of the other material. Therefore, the simulation was used to trace water, co-extracted metals and impurities through the circuit. The focus is therefore not as much on the zinc but rather on how the other material moves through the process. This is important since the concentrations of trace impurities in the process affect the final zinc product purity. The main area that was investigated was the movement of water in the process.

In determining how simplified a view of the process could be obtained, the detailed block flow diagram was used in each case as the basis. Various levels of assumptions were then made to get a number of working simulations, going from crude, basic assumptions to more complex ones. This included starting the simulation by modelling the various processes as simple mixer-separators to achieve the results observed in the plant data, to more detailed, complex combinations of units to approximate the process as closely as possible. Once this had occurred, the simulation was used to answer various questions and test various

operating scenarios. The process operates at steady state; therefore the simulation was performed at steady state.

1.6 Thesis outline

The report begins at Chapter 1 with a brief introduction and background of the Skorpion operation. This is followed by a brief process summary and the objectives of the project. The areas covered by the project are outlined in the scope and limitations.

Chapter 2 contains a summary of the literature relevant to the project. The main areas of interest are covered, namely the systemic approach to process optimisation, the various sustainability issues involved with particular reference to water minimisation, and the use of the simulation package Aspen Plus®.

A more detailed description of the process is covered in Chapter 3, with the areas of interest in the process for the plant also discussed here. This is followed by the project methodology in Chapter 4.

In Chapter 5, the various simulations achieved are summarised. The simulations are ordered from the simplest initial simulation to the final realistic simulation. This chapter contains a detailed look at how each level of simulation was approached, looking at each unit operation. Chapter 6 follows with a look at the technical considerations made while simulating using Aspen Plus®. This includes configuring the package before simulation and the various input requirements of the simulation.

In Chapter 7 the results obtained from the simulation are presented, with the simulation being validated against plant data. The results from the various water minimisation scenarios are presented and discussed, including unit operational changes and circuit configuration changes. In Chapter 8, the conclusions drawn from the various scenarios are presented, with recommendations for implementation being drawn.

Chapter 2 – Literature Review and Theory

2.1 Zinc refining

2.1.1 Background

Southern Africa is one of the world's most important mining areas in terms of variety and amount of minerals produced. The mining industry in South Africa is one of the largest contributors to the economy, accounting for 6.5% of the country's gross domestic product (GDP) (Mbendi Information Services 2007). Zinc production in this region is centred on 2 major refineries, namely Zincor in South Africa and Skorpion Zinc in Namibia.

In observing the zinc trends in reserves found versus production, there are historically more known reserves than zinc mined, as shown in the graph below, sourced from the International Zinc Association website (International Zinc Association 2008). The challenge lies in the form, or mineralogy, in which the zinc is available. The main ore mineral of zinc is sphalerite (Zn,FeS), however numerous other forms are available, requiring different processing methods.

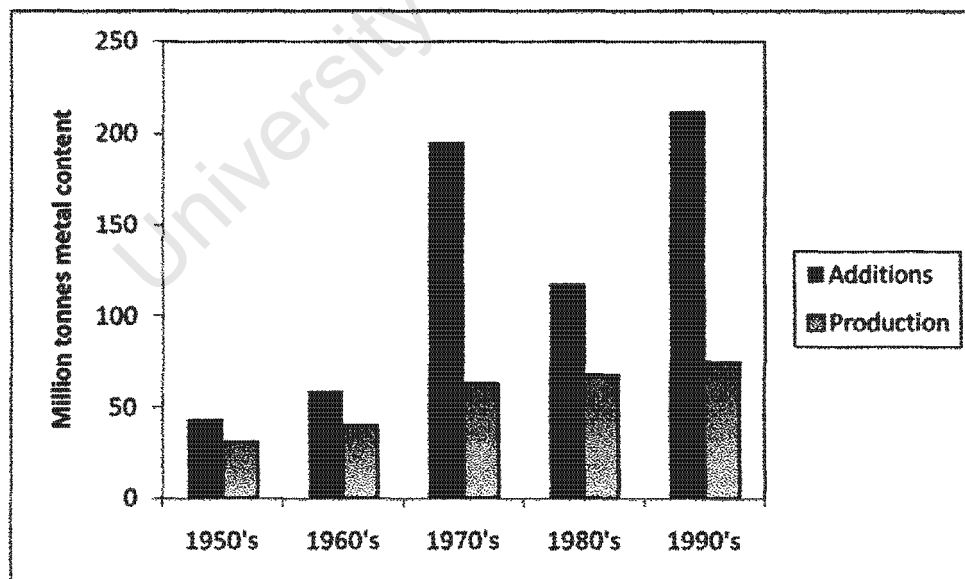


Figure 2: Zinc Reserves versus Production (Mbendi Information Services 2000)

The major end use of zinc is in the galvanising of steel, which accounts for 40% of zinc used (Mbendi Information Services 2000). Other uses include the production of various alloys and in brass manufacturing.

2.1.2 Zinc processing options and circuit configurations

There are a number of processing routes in practice for the production of zinc. These depend mostly on the condition in which the ore is available. The Zincor process makes use of a predominantly zinc sulphide concentrate (van Dyk 2006). At Zincor, the sulphide concentrate is roasted at high temperatures to form sulphur dioxide (which is used to produce sulphuric acid) and zinc oxide, which then undergoes an atmospheric leach to form zinc sulphate. The sulphate is then purified and proceeds to electrowinning, to form the final zinc product.

The Skorpion process differs from the Zincor process in a number of ways. Firstly, the refinery and mine are situated on the same site, whereas at Zincor, a concentrate is purchased from local and foreign mines and imported to the refinery. As mentioned in Section 1.2, the ore body is also unique in that it consists of an oxide ore, necessitating in a different processing route.

These two operations demonstrate that a number of different processing options are available to produce the same product. The processing route chosen is dependent on a number of variables, such as feed mineralogy and operating limitations. In this thesis, different system configurations will be investigated with the aim of optimising the water balance.

2.1.3 Market trends – the need for efficient processes

The demand for zinc is constantly growing, as the following graphs will show. This further supports the need to obtain as efficient a refining process as possible.

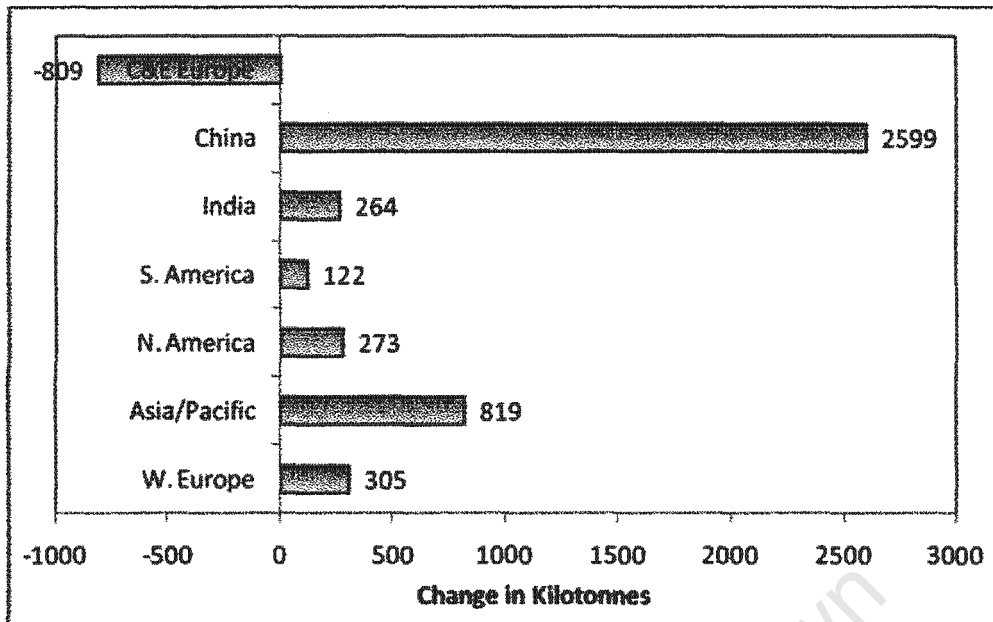


Figure 3: Changes in World Refined Zinc Demand (1985-2005) (International Zinc Association 2008)

Figure 3 shows that due to China's explosive industrial growth over the past decade, it is currently the world's largest consumer of zinc products, with demand decreasing in Central and Eastern Europe. The consumption rate of zinc world-wide is also constantly increasing, as shown in Figure 4.

As developing countries such as China and India continue to modernise, the demand for zinc will grow with prices increasing due to supply shortfalls (Hsia and Hommel 2005). This is evident with the zinc market price experiencing exponential growth over the past 5 years before the financial crisis of 2009, as shown in Figure 5. Despite the drop in price observed in 2009, the demand for zinc has continued to increase as shown in Figure 4. An increased demand for zinc therefore further motivates the need for a zinc production process that is running optimally. The financial benefits are quite evident with the historically increasing zinc selling price.

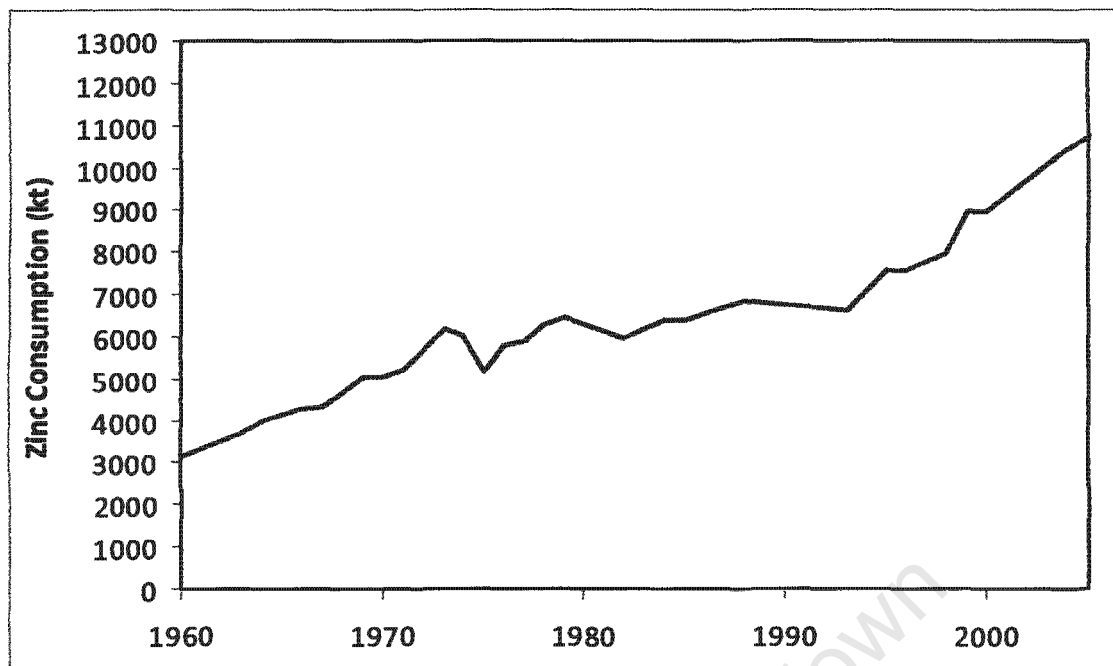


Figure 4: World Refined Zinc Demand 1960-2009 (International Lead and Zinc Study Group 2009)

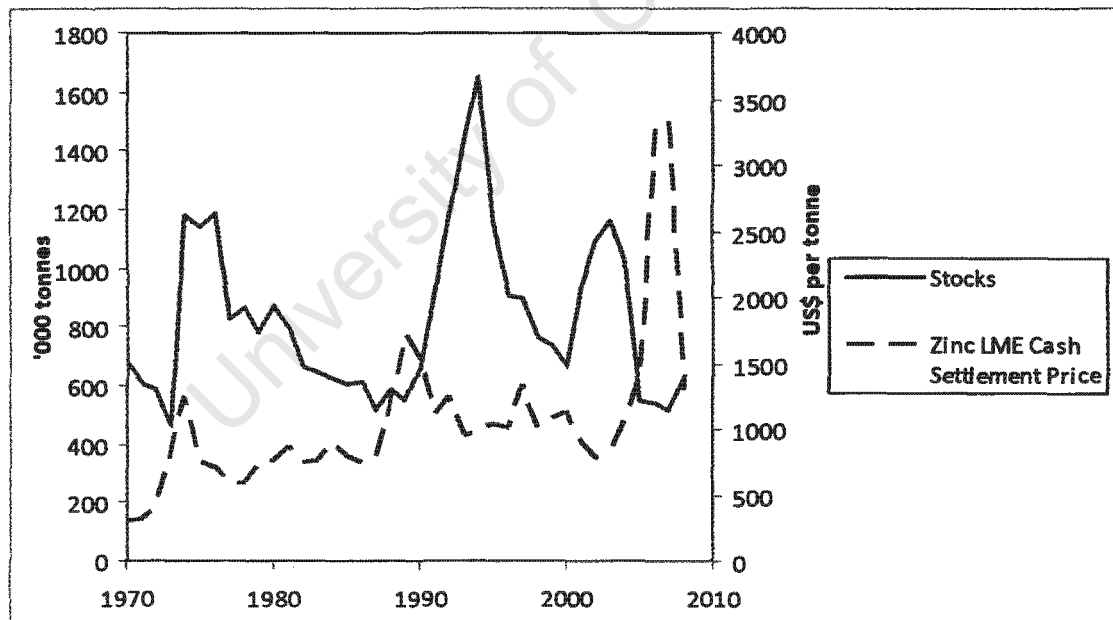


Figure 5: Zinc Stocks and Prices (International Lead and Zinc Study Group 2009)

2.2 Sustainability issues

2.2.1 *Environmental issues in the mining industry*

The minerals processing industry has historically been associated with many environmental problems, including insufficient waste management, poor rehabilitation of mine sites and the prioritisation of metal production over environmental issues (Filho & Butorina 2002), (Mudd 2007). Fresh water usage in the minerals processing industry is substantial, due to the various hydrometallurgical and separation unit operations (Norgate & Lovel 2004). In addition, a large number of wetlands, lakes and streams have been damaged due to waste-water emissions, therefore sustainable water management practices are necessary to minimise environmental impact.

Due to public concern over environmental impacts of the minerals processing industry and the greater awareness of sustainability, the minerals processing industry has shifted towards a more sustainable context (Mudd 2007). The minerals processing industry is now focused on sustainable development issues and these have become a guiding factor in process design and implementation (van Berkel 2007). A balance therefore has to be obtained between environmental issues and economic risks arising from the implementation of sustainability practices (Mudd 2007), (Yang & Shi 2000).

Sustainability issues of global interest include minimisation of water, energy, chemical consumption and pollutant emissions (Mudd 2007), as well as the reduction of greenhouse gas emissions. A major issue regarding waste water treatment is maximising the reuse and recycling of water throughout the process. This is usually coupled with the use of technologies to remove trace metal impurities to prevent build-up in the process (Nedved & Jansz 2006).

A method to significantly reduce the water requirement for a given process is through the use of dry processing. This is a new area of research and involves the use of water-free technologies to substitute existing hydrometallurgical unit operations. This is an effective technique for areas where water is scarce; however the major issue for concern is the generation of large volumes of dust (Norgate & Lovel 2004).

This could have serious environmental implications which are difficult to quantify, possibly even more severe than those associated with water usage.

2.2.2 Sustainability and Skorpion Zinc

The Skorpion Zinc plant is situated in an ecologically sensitive area where water is scarce. Its operational practices are therefore important to ensure minimal impact on the environment. Skorpion currently sources all of its fresh water from the Orange River. It is also situated close to the town of Rosh Pinah, which means that it has to ensure that the operation of the plant does not negatively impact on the community.

A major reason for the consumption of water in the Skorpion process and many other processes (Alva-Argaez et al. 1998), is to maintain the concentration of certain species at a desirable level, to minimise the level of contaminants in the final product. This project therefore aims to obtain the optimum process operation variables to minimise the demand for fresh water, with minimal impact on the final product. This will in turn lead to a minimisation of waste water produced.

A number of sustainability-related questions are raised when looking at a process Sudholter et al. (1996). These are affected by the varying compositions of the raw materials. It is therefore true that there is no generic optimal route for the production of zinc; however for a given process in a specific location, a closest approximation can be made for its unique situation. In the case of the Skorpion process, extensive research was performed on the ore deposits in the region and the process was commissioned based on this.

2.2.3 Flow sheet heuristics

Green chemistry literature provides a number of sustainability-related flow sheet heuristics. These are especially useful in the commissioning phases of a plant, where the process can be designed with sustainability issues in mind. It also serves as a guide for optimising a process with regards to sustainability. The heuristics are focused on waste prevention, energy, material and water minimisation and the use of degradable chemical products, to name a few. Process design heuristics are well-

established (Botha 2003), (Alva-Argaez et al. 1998), (Mariano-Romero et al. 2007), (Van Berkel 2007), (Stewart & Petrie 2006) and will inform the scenarios for optimisation in this project.

Botha (2003) has reviewed a collection of sustainability heuristics as they relate to bio-processing circuits. Although the focus is on bio-processing circuits, the heuristics nevertheless give an idea of the types of sustainability-related heuristics available. The heuristics reviewed are mostly design-type heuristics used in the commissioning of a new plant and would have been used when the Skorpion process was designed.

Water balance optimisation has traditionally occurred through the use of water pinch technology (Mariano-Romero et al. 2007). Water pinch technology is useful when designing new processes or retrofitting existing processes, since it provides an optimised water network. This approach however, requires highly detailed calculations. The benefit of using a simulation for optimisation is that it allows for a greater understanding of the movement of trace impurities. Water pinch technology does however provide a 3 stage method of optimising processes, namely analysis, synthesis and retrofit. These steps were adapted from (Mariano-Romero et al. 2007) and are detailed below:

1. Analysis: identifying the minimum fresh-water consumption and wastewater generation in all water-using operations.
2. Synthesis: water re-use, regeneration and recycle to meet fresh-water and wastewater requirements.
3. Retrofit: modification of the existing water network through process changes to maximise water reuse and minimise wastewater generation.

Once the optimisation procedure has been obtained, the key variables for investigation need to be identified. These include key flow rates and concentrations of contaminants that could be detrimental to production (Alva-Argaez et al. 1998). The actual optimisation will thus be divided into the following steps, as informed by the optimisation heuristics:

1. Unit operation changes: investigating water-using units and water-treatment units in the process (Alva-Argaez et al. 1998). The focus is therefore centred on units that can be made more efficient through the use of new technologies or through the combination of units to improve the overall efficiency of the processing step. This mainly applies to solid-liquid separation units, which have the largest capacity for improvement.
2. Circuit configuration changes: retrofitting the existing process to optimise the water balance (Alva-Argaez et al. 1998) and (Mariano-Romero et al. 2007). This will be focused on improving the water-retention of the process through addition of recycle streams (Norgate & Lovel 2004), thereby minimising the fresh water requirement as well as the waste water produced.

It can be seen that although there are 3 steps for circuit optimisation proposed by water pinch technology, there are only 2 sets of scenarios presented for the purposes of this project. This is due to the fact that the “analysis” step of the heuristics would have been applied in the design phase of the process and is therefore not applicable in this context, since the process already exists. The two sets of scenarios presented above both have elements of “synthesis” and “retrofit”, thereby satisfying the procedure recommended by (Mariano-Romero et al. 2007).

Before the optimisation procedure can be applied, the process needs to be checked to determine whether it is currently operating sub-optimally. This may be informed by comparing the process to other similar processes in the world in terms of water usage, to obtain an average estimate of what should be possible. An empirical equation has been formulated by (Norgate & Lovel 2004) by analysing a number of different minerals operations around the world. The equation is presented below:

$$W = 167.7 G^{-0.9039} \quad (1)$$

Where W = “cradle to gate” water consumption (m^3/ton refined metal)

G = grade of ore (% metal)

Since this equation is based solely on the grade of the ore, it does not take the type of metal into account. Nevertheless, it provides an estimate of the typical water consumption for the refining of an ore with a certain grade. Using this equation, a graph for different feed grades and their effect on the water balance can be plotted. This graph is presented in Figure 6.

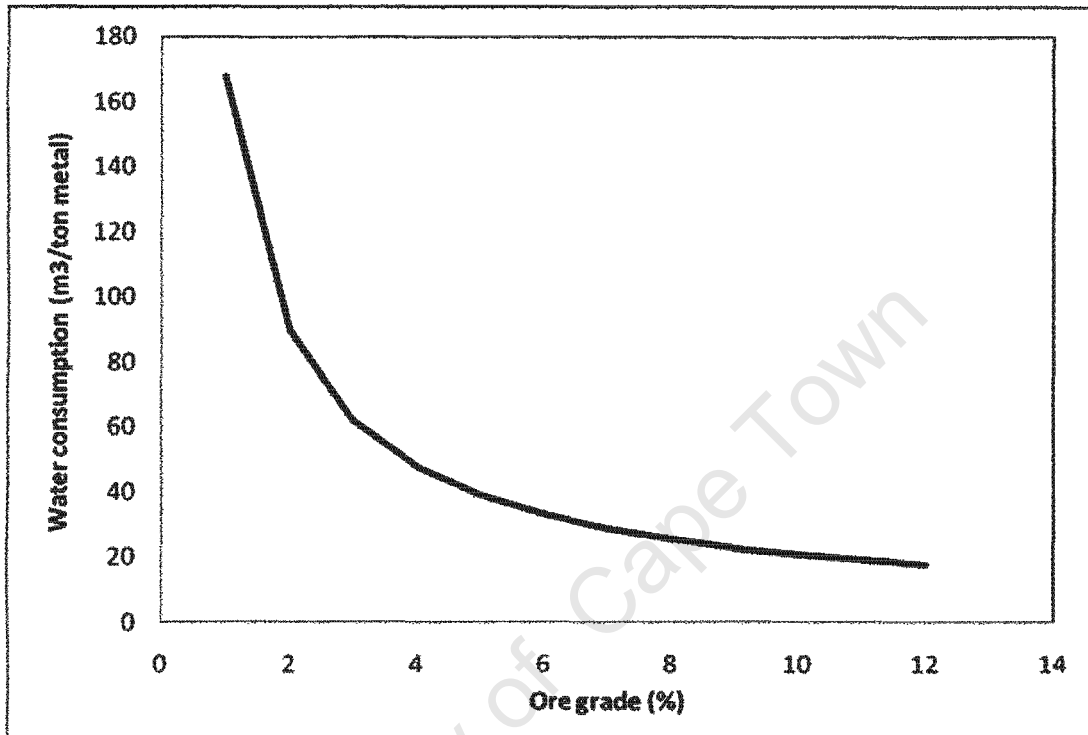


Figure 6: Effect of Feed Grade on Water Consumption

Figure 6 shows that as the feed grade decreases, the water usage increases exponentially. Due to the steady decline in ore grades across all mineral processing fields, this increased water requirement is of great concern. It shows that, over the life of a mine and refinery, the water requirement will increase substantially (Mudd 2007), necessitating the implementation of sustainable water practices from the outset to reduce the environmental impact of the process of the life over the mine.

2.3 Systemic approach

2.3.1 Systems theory

Systems theory is the study of the relationship between a number of mutually dependent components that work together to accomplish a goal (Winston & Goldberg 2004). It recognises that the interactions between these activities and how

they impact on the system as a whole is more important than studying the activities in isolation (Batterham 2006). It therefore recognises that the interactions between the unit operations need to be used to optimise the process as a whole, as opposed to focusing on optimising the unit operations on their own.

Numerical Methods provide a means to optimise systems where the activities, such as process conditions, are assigned numerical variables and optimised using a variety of different mathematical formulae. Due to the large number of variables and operating conditions and the complexity of the Skorpion process; as well as the nature of the simulation program which already has built-in numerical methods to solve simulations iteratively, using external numerical methods to optimise the process is not a viable option in this case.

Nevertheless, systems theory does provide some important guidelines on using simulations to optimise processes, which will be outlined below.

2.3.2 Simulation as an investigative tool

The computer simulation of complex industrial systems is probably the most widely used and highly acclaimed technique of operations research (Lilienfeld 1978). The simulation is a computer representation of a specific system or process, which can be used to investigate the impact of a variety of changes on the system. It is a more cost-effective and safer method of investigation than actually implementing the changes on a real process. The simulation can therefore be seen as conducting a sampling campaign on the real system, with the results obtained being sample points (Winston & Goldberg 2004).

2.3.2.1 The benefits of simulation

A computer simulation has a number of uses (Reitman 1971). It can aid in problem definition: certain problems only become apparent once the simulation has been performed. It also helps in relating a number of factors and their impact on the overall system, since the interactions between units and their influence on each other might only be understood during the process of simulation. The simulation can

provide insight into the sensitivity of the process with respect to a number of variables. Finally, the simulation provides guidance in predicting system performance.

2.3.2.2 The simulation process

Literature provides us with a systematic approach to the simulation process. The following figure was adapted from (Winston & Goldberg 2004). It shows the major logical steps required to simulate a process. The simulation process will be discussed below.

University of Cape Town

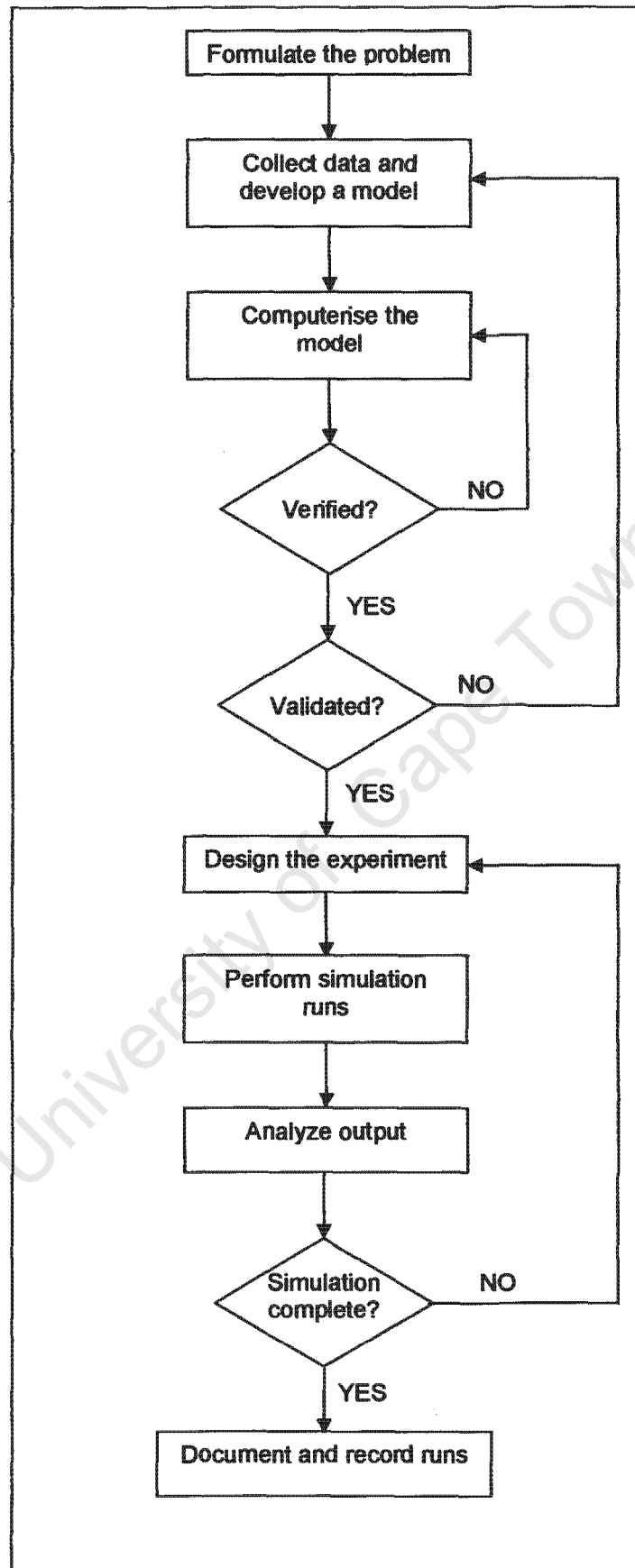


Figure 7: The Simulation Process (Winston & Goldberg 2004)

The first step in any scientific study is to formulate the problem (Winston & Goldberg 2004). This requires a detailed understanding of the objectives of the problem. A simulation would therefore aid in developing a better understanding of the process, including the gaining of knowledge on how the various species move throughout the process.

Once the problem is correctly formulated, the data acquisition phase can begin. Wherever data is not available, reasonable estimates must be made. The problem is then computerised, through the use of a simulation package for example. It should be noted that for this project, the “model” shown in Figure 7 refers to the simulation and the “simulation” refers to the optimisation scenarios. The development of the simulation is probably the most critical aspect of the simulation process. The approach employed by most experts is to start with a simple model and add more detail and complexity once more knowledge is gained about the process (Winston & Goldberg 2004). However, caution should be exercised when increasing the complexity of the simulation, as this results in an increase in modelling complexity, simulation difficulty and convergence time (Subawalla et al. 2004).

After the problem has been verified against process operation to determine if the trends observed make sense, it is validated against actual plant data to ensure that the results obtained are realistic and that the simulation is an accurate representation of the process. The simulation can then be calibrated using actual operating conditions and best approximations to reaction chemistry. Once the simulation is judged to be a good representation of the process, it can be used to investigate various scenarios with confidence.

This is the point at which investigative procedures such as process optimisation and sensitivity analyses can be performed, since one of the main purposes of a simulation is to predict system behaviour (Reitman 1971).

2.3.3 Important simulation considerations

In performing a simulation, there are a number of factors to keep in mind (Reitman 1971). These will be discussed below.

2.3.3.1 Degree of detail

In the case of this project, the simulation needs to be sufficiently detailed to obtain meaningful results, but not too detailed to a point where the model becomes too complex and computing time becomes prohibitive. This means that fixed conversions based on plant operation are favoured over reaction kinetics. The use of kinetics would increase the complexity of the simulation significantly due to the number of reactions occurring in the various units.

This simplification does not negatively affect the quality of the findings, since the conversions observed on the plant do not fluctuate to a large extent and are thus relatively stable, making this a reasonable simplification. In addition, a level of uniformity in the simulation of the various units needs to be maintained. This means that the same level of complexity should run throughout the system, and a highly detailed reaction process will detract from the systemic approach of this project.

2.3.3.2 Constraints or bounds

A simulation can only be an accurate representation of reality if the constraints imposed on it are realistic (Padulo & Arbib 1974). For example, if the reactor operating conditions can only operate in a specific range due to energy costs or reaction kinetics, it does not make sense to perform an optimisation investigation on conditions outside this range. In the case of a complex flow sheet, there are as many constraints as there are unit operations, if not more. It is therefore essential that the correct combination of operating conditions is chosen that satisfies all of the constraints of the system.

2.3.3.3 Interactions between models in the simulation

In certain cases, simulating a process resulted in problems arising in the interactions between various unit operations (Reitman 1971). This is especially true when a number of detailed models of unit operations were performed separately. The output from one unit operation may not be in the correct form for the next operation. This is not a problem in Aspen Plus®, since the model interactions occur automatically due to the user-friendly graphical user interface (GUI). The challenge in this case is to

maintain a level of parity in complexity across the entire system, that is, to not go into too much detail in one unit operation at the possible expense of another.

2.3.4 Past work

Previously in the minerals processing industry, the focus has always been on making sure that each unit is running as optimally as possible, at the possible expense of the optimal operation of the process as a whole. This is due to the fact that optimising a process on a unit-by-unit basis results in a local optimum around a given unit, which might not be the optimal solution for the entire plant.

This is reflected by Subawalla et al. (2004), who noted that when optimisation tools were used in industry, they were focused on the optimisation of individual unit operations and rarely used for an entire process. They found that this method of thinking was not useful when considering the wide range of operating conditions usually experienced by a process.

Subawalla et al. (2004) investigated energy and waste minimisation using a multivariable optimisation (MVO) technique. MVO is a numerical programming technique used to optimise processes. This is one of the techniques implemented in Aspen Plus® through sequential quadratic programming (SQP). MVO is described as the “steady-state optimisation of a process flow sheet using predictive unit operation models” (Subawalla et al. 2004). Aspen Plus® as a simulation package uses models for the various unit operations and links them to form a flow sheet.

This is in contrast with traditional optimisation techniques that work on a unit-by-unit basis. One such example is optimisation through retrofitting of minerals circuits, using computer simulation (Connolly & Prince 2000). Connolly & Prince (2000) used a computer flow sheet design system to produce economically viable flow sheets for a base metal concentrator. The flow sheets were built up gradually, and decisions made on whether to recycle unassigned streams or reuse them, as they are added. The problem with this method is that this could give an optimal solution that might not actually be the optimal solution for the entire process. In fact, this method could

yield an “optimal” solution for a specific region of the process that is actually quite far from optimum for the process.

This is due to the fact that if optimisation on a process occurs on a unit-by-unit basis as it is built up, the process becomes increasingly constrained to a point where there might be only one possible solution that satisfies all the previous optimisations or no solution at all. This method also means that it would be very difficult to investigate different optima according to changing requirements, since the optimisation procedure is built into the flow sheet.

Systemic thinking has, however, been applied to other industries. Karuppiiah and Grossmann (2006) used a systemic approach in optimising integrated water systems in chemical processes. In their paper, water-using processes and water treatment operations were combined into a single network and optimised so that the cost of obtaining fresh water for water-using operations and the cost of treating wastewater was globally minimised.

In this case, mathematical models such as non-linear programming were used to optimise the process. Using Aspen Plus, optimisation can be achieved by using built-in mathematical models incorporating the physical and thermodynamic properties of the components to arrive at a solution iteratively. Karuppiiah and Grossmann (2006) illustrate that it is possible to optimise the process as a whole as opposed to focusing on specific areas.

An area in which the systemic approach to optimisation using simulations has been applied successfully is the brewing industry (Trelea et al. 2001). In their paper, a model of the brewing process was made at 3 different levels of complexity. Only the two most relevant ones, namely the “fundamental” approach and the “black-box” approach, will be discussed.

The fundamental model was based on biological knowledge of the brewing process, set up using rate equations and kinetics. This method is the most accurate since it accounts for the physical processes involved in the reactions; however it is also the most time-consuming. This is not an option however, if reaction kinetic data is not available. It is clearly preferable to use this information if it is available, since it

creates a more realistic model, but it can introduce a greater level of complexity and drastically increase simulation time, when compared to a purely black-box approach. It was found that the black box approach, if suitable data is available, can be a much easier way to obtain a reliable model than the fundamental approach.

Another application of systemic thinking is to simultaneously optimise process operations and financial decisions (Guillen et al. 2006). Their paper addresses the integrated planning and scheduling of chemical supply chains taking into account financial management issues. It demonstrates that by considering both production and financial factors, an overall optimisation of a process can be achieved. This is more of a financial application of the systemic approach as opposed to a process application, but shows its relevance to a variety of different areas.

These papers demonstrate the next step forward in sustainable operation in the chemical engineering industry and show the benefit of the systemic approach to process optimisation in order to meet sustainability objectives. This is especially useful where systemic thinking is used to effectively optimise a process and minimise water consumption, where a focused, individual unit optimisation would not prove effective.

2.4 Mineral processing and optimisation

2.4.1 Minerals process simulations

Although the systemic approach to optimisation is fairly new to the minerals industry, process simulation has been used extensively. Simulation for process design and optimisation is an established technique (Napier-Munn & Lynch 1992). Processes containing solids especially, present a specific challenge. This is discussed by (Toebermann et al. 2000) and (Reimers et al. 2008), where the more complex stream information required makes simulating these processes more difficult than fluid processes.

A major application of simulation is in the design or retrofit of a process for which the flow sheet has already been constructed (Sikdar & El-Halwagi 2001). A base case

flow sheet is developed and then a process simulator is constructed. Aspen Plus® is considered to be a modular-type simulator, since the equations in the different unit operations (or modules) can be used in isolation from the rest of the flow sheet. Modular simulations have pre-programmed unit operation modules, which makes them easier to use, due to the user-friendly graphical user interface (GUI). It also allows for easy addition and deletion of units in the flow sheet. However, due to the sequential nature of the modular approach, a certain solution order may be required. This is not a problem in Aspen Plus®, since tear streams can be used to specify convergence order. Tear streams are discussed in more detail later.

2.4.2 Circuit optimisation

In general terms, optimisation refers to running a process in the best possible manner in order to meet a certain objective. For cost optimisation this involves maximising profit or minimising losses for a given process. Optimisation basically entails finding the combination of variables that yields the best value of the optimisation criterion (Sikdar & El-Halwagi 2001). Sikdar & El-Halwagi (2001) propose six steps for solving optimisation problems. These are shown in Figure 8 below.

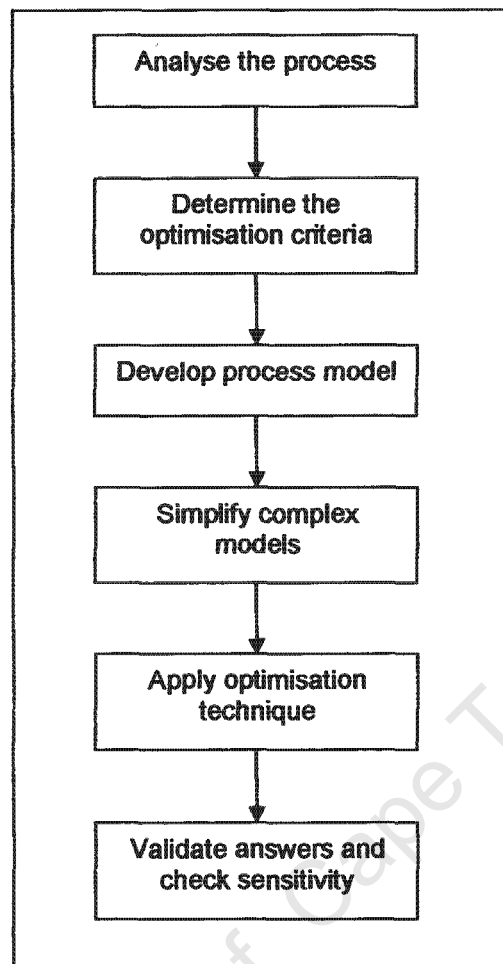


Figure 8: Six Steps to Solving Optimisation Problems

The first step is to analyse the process and determine what the purpose of the optimisation would be. The choices for optimisation criteria would therefore be cost optimisation, or process optimisation with regards to sustainability issues or production rate. Once a clear objective of the optimisation is obtained, the process simulation is performed. Complex models are simplified through the use of justified assumptions, which make the simulation process easier. The optimisation technique is then applied, which can be investigating a number of different operating scenarios to satisfy a certain criterion, for which the simulation is used to predict trends in the process. The results then need to be checked to determine if they make sense in the context of plant operation.

The main challenge is therefore to obtain an accurate model, while understanding that the model is merely being used as a tool to investigate the systemic approach

and not the main output of the project. Many examples of optimising chemical processes are proposed by Sikdar & El-Halwagi (2001).

2.4.2.1 Global optimisation theory

Global optimisation methods can be divided into 2 main categories, namely exact methods, which involve numerical, mathematical solutions and heuristic methods, which use a set of heuristics to arrive at a solution. The heuristics are generally formulated as rules of thumb based on experience. Heuristic methods are not always guaranteed to find the best possible solution, but they are easier to use than numerical methods, which sometimes require specialist knowledge. The other drawback of a numerical method approach is that it could require a large amount of computational time.

2.4.2.2 Technical challenges to process optimisation

The optimisation of a process with regards to sustainability objectives is a multi-variable optimisation, where the environmental objectives have to be balanced against other process requirements. In general, a trade-off needs to be reached between economic and environmental objectives (Cano-Ruiz & McCrae 1998). An improvement in one area of the plant may lead to a worsening in another; therefore a detailed understanding of the entire process is necessary.

A major method of optimisation is through the use of new technologies. The most important problems arising from the implementation of new technologies are capital cost, the risk of committing capital to new and unproven technologies and implementing these technologies into the current process (Moors et al. 2005). The more radical the departure of the new technology from the current norm, the less likely is it to be implemented in industry, with industry preferring to stick with tried and tested technologies.

Technological changes are divided by (Moors et al. 2005) as follows, with increasing departure from the norm: auxiliary technologies which involve a change to process control and monitoring, end-of-pipe technology which involves treatment steps added

to the end of the existing process to mitigate environmental impact, in-process technology where the changes are made to existing operations within the process, and breakthrough technology in which a complete redesign of the process occurs with focus on new technologies.

Given the economic risks associated with breakthrough technologies, the safest area for improvement in a process in terms of environmental issues is through the use of waste and water treatment and re-use (end-of-pipe), as well as improving existing operations in the process (in-process).

One of the major uses of water in industrial processes is to control the concentrations of various species in the process (Alva-Argaez et al. 1998), (Norgate & Lovel 2004). An optimisation scenario may therefore lead to the build-up of certain impurities, resulting in the need for a purge stream. This is especially true when recycle streams are considered.

However, this may not be necessary if the contaminants leave the process via an exit stream, such as entrained moisture in a filter cake. A detailed understanding of the process therefore prevents the addition of an unnecessary purge stream. Of special note is that a process may well be able to operate at higher-than-recommended levels of impurities (Norgate & Lovel 2004) however this is not ideal since it may place strain on the process, especially if there are hydraulic or chemical loading limits on equipment.

In addition, environmental regulations governing the levels of contaminants need to be adhered to before streams can be disposed of to the environment. An optimisation scenario may push the levels of contaminants in a certain exit stream beyond the allowed values, thereby necessitating a further treatment step.

2.4.3 Past work

It was mentioned earlier that many optimisation techniques exist that make use of numerical methods, such as MINLP (Mixed Integer Non-Linear Programming), which is beyond the scope of this project and will not be discussed. In this context, these

techniques would assume that a valid flow sheet exists before the optimisation technique is performed.

Subawala et al. (2004) proposed a method for optimising a process flow sheet. In their paper, a 3 step procedure for developing a MVO (Multi-Variable Optimisation) process in Aspen Plus® is proposed. Figure 9 below shows this procedure graphically and the technique will be discussed in more detail.

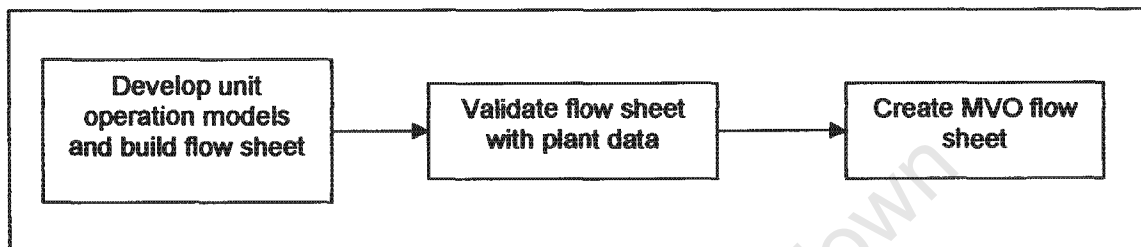


Figure 9: MVO Optimisation Technique

The first step was to develop a process flow sheet with simple models that can be substituted with more complex ones once the process is better understood. This step creates an accurate representation of the process as it currently operates.

The procedure taken for the validation step was that the process was simulated using a known set of data and then calibrated and adjusted to obtain values that matched the actual plant operation. Subawalla et al. (2006) found that their simulation matched plant data within 5%, which was deemed a good fit.

Once the simulation was judged to accurately represent the actual plant operation, the MVO flow sheet was created. This involves the development of an optimised flow sheet of the process. In this step, the variables of interest, their ranges and constraints were defined. Two common optimisation variables are flow rates and recycle rates. The simulation was then performed to obtain the optimum operating conditions. A key consideration in the MVO flow sheet is the incorporation of sustainability objectives in the generation of flow sheet design alternatives. A balance between economic variables and environmental issues can be obtained, in this project's case production rate and product purity, and water minimisation respectively (Yang & Shi 2000), (Mudd 2007), (Huband et al. 2006).

It was found by Subawalla et al. (2006) that MVO can be a highly useful tool when used by an engineer with intimate knowledge of the process. It is therefore necessary to obtain as much operations input as possible, since this will ensure that the simulation represents the process as accurately as possible and that the results from the optimisation procedure are accepted by industry. Process simulation and environmental considerations are thus a powerful combination in MVO (Yang & Shi 2000).

The easiest method of optimisation for this project would be a heuristic-based methodology, which details a step-by-step process on how to optimise mineral processes. Most literature focuses on numerical method optimisation, as can be seen from the literature above; however process design heuristics are well-established and will be used to inform the various optimisation scenarios.

2.5 Applicability of Aspen Plus® for simulation

Aspen Plus is used for a number of steady-state modelling applications. Simulation with Aspen Plus allows the prediction of the behaviour of a process based on mass and energy balances and allows for the tracking of trace impurities.

Aspen Plus is used in industry to simulate processes and can be used to optimise them. A good example of such an application is the process simulation of a copper solvent extraction plant (Dry 2005). In this simulation, a copper-rich stream enters the extraction step where it is contacted counter-currently with a copper-selective organic. The loaded organic then enters a stripping stage where the loaded copper is removed and sent to electrowinning and the copper-lean process stream is recycled back into the system as the raffinate. The copper-free organic is then recycled back to the extraction step in a closed loop. The electrowinning stage then produces the final copper product. The level of detail observed in this simulation is similar to that which would be encountered in an industrial process simulation. The simulation is very useful due to the similarities between zinc and copper processes in terms of solvent extraction and electrowinning.

Aspen Plus is used across a number of different industries and processes. Cimini et al. (2005) simulated a waste incineration plant using Aspen Plus. This involved solving the mass and energy balance for the plant, optimising the process to choose the best operational parameters and evaluating the system behaviour for a variety of operating conditions.

It was found that the Aspen Plus results were in good agreement with the actual data from the plant. It was also demonstrated that the model developed using Aspen Plus could be a reliable instrument in the control and retrofitting of existing plants, and in the design and planning of new plants.

Aspen Plus is particularly useful in solving complex energy balance problems that would otherwise prove very difficult and time-consuming. This was demonstrated when it was used to simulate a cogeneration plant, which produces both electricity and steam or hot water, (Zheng and Furimsky 2003) and in determining the optimum operating conditions for a combined power and cooling thermodynamic cycle (Sadrameli and Goswami 2007).

Zheng and Furimsky (2003) simulated a natural gas-fed cogeneration plant to show its benefits over coal-fed plants. The plant produces electricity which is supplied to the electricity grid and produces steam for local heating purposes. It was found that the results (operating conditions such as flow rates, temperatures and pressures) from the simulation compared well to those obtained from the plant. It was therefore concluded that Aspen Plus is a useful tool for preparing the operating strategy of the plant, since the impact of various parameters on the process can be predicted well using the simulation.

Sadrameli and Goswami (2007) used Aspen Plus to simulate the combined production of thermal power and cooling. It was found that a trade-off exists between cooling and work production and thus the optimum combination of operating conditions was determined using the simulation.

In trying to optimise water usage, the product purity was affected due to the accumulation of impurities in the process as well as the change in concentrations. It

was found that the results (flow rates and compositions) obtained from the simulation compared well with those obtained experimentally from the cycle and the optimum operating conditions for the combined cooling and power optimisation were predicted.

These papers show that Aspen Plus can be a very useful tool in accurately predicting the impact of various parameters on the operability of a process and can prove very useful in process optimisation. It also allows for problems to be solved that might otherwise prove too difficult or complex on a spreadsheet package. It is particularly useful in that optimum conditions obtained from the simulation can be implemented on the actual plant.

Chapter 3 – Process Information

3.1 Detailed Process Description for Simulation

Figure 10 below shows the detailed block flow diagram of the Skorpion Zinc process that will be used for the simulation (Bachmann 2004).

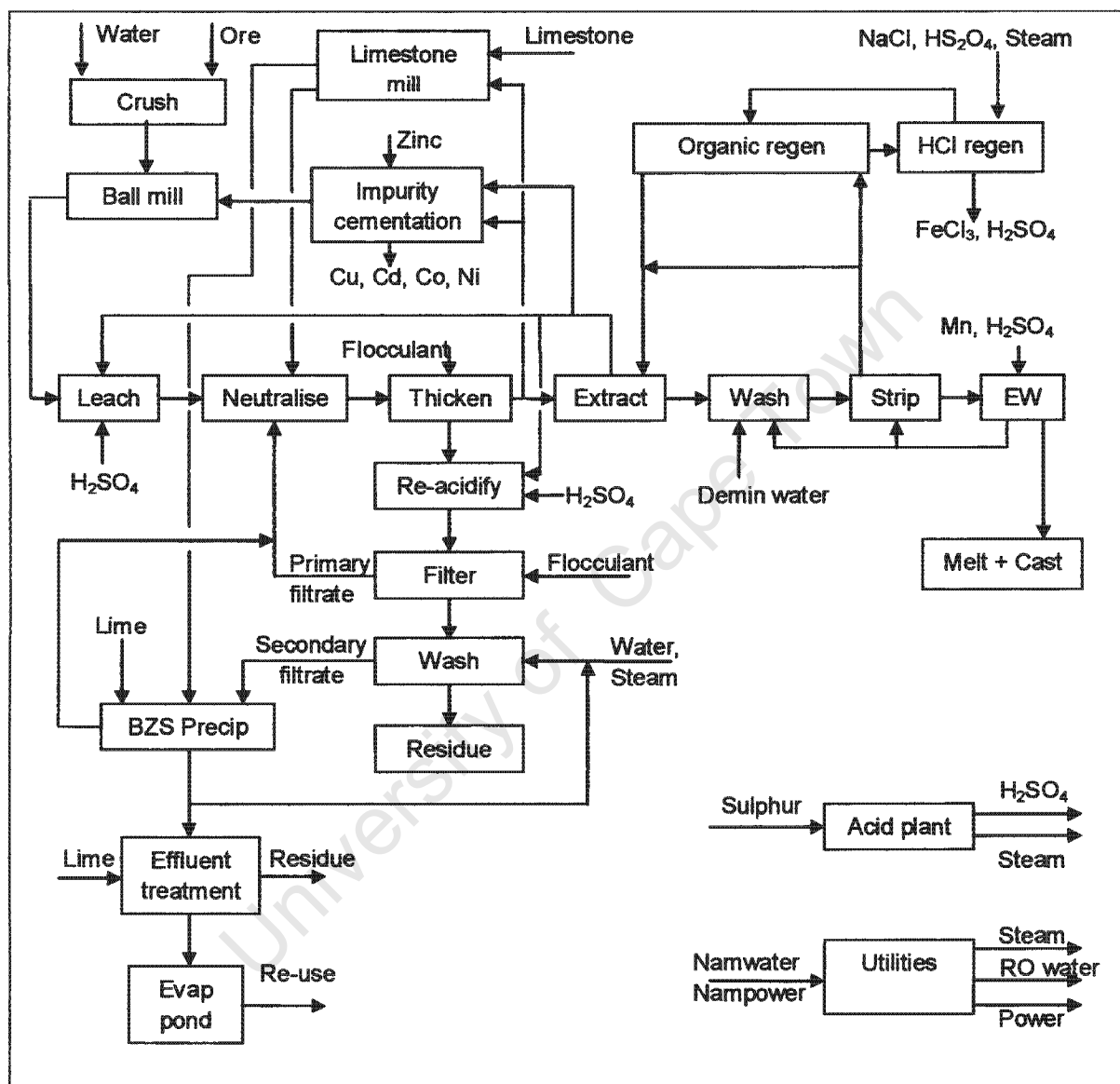


Figure 10: Detailed Block Flow Diagram for Simulation

3.1.1 Comminution

The comminution step consists of a 3-stage crushing process followed by homogenising in a stacker-reclaimer to form a uniform plant feed. The ore is then

milled in a closed-circuit wet ball mill to produce the atmospheric leach feed slurry, with a top size of 500 μ m and a d_{80} of 180 μ m.

3.1.2 Atmospheric leach and neutralisation

The leaching step facilitates the dissolution of the complex zinc oxide ore. The leach kinetics are rapid, therefore around 95% of the zinc in the feed slurry is leached. The atmospheric leach is facilitated in a series of agitated vessels at 50°C. This product then proceeds on to neutralisation, where limestone is used as a neutralising agent to precipitate the iron, aluminium and silica impurities.

The neutralisation step also precipitates a small amount of zinc in the form of basic zinc sulphate (BZS, formula: $(\text{ZnO})_3\text{ZnSO}_4$). The leaching and neutralisation steps are carefully pH controlled to ensure that undesirable silica gel does not form, which could result in crud formation which would drastically affect the solvent extraction step (Banza et al. 2002).

3.1.3 Reacidification, filtration and effluent treatment

The neutralisation slurry undergoes reacidification to recover any precipitated basic zinc sulphate. The majority of this zinc is recycled back to neutralisation, with the remainder undergoing filtration and washing to remove impurities. The plant uses a wash ratio of 1 with a wash efficiency of 80%. This means that the wash water added displaces an equal amount of impure solution from the stream in question, removing 80% of the impurities.

The BZS plant then precipitates any remaining zinc in the stream using limestone and recycles it back to the neutralisation section. The impurity-rich solution then proceeds on to effluent treatment. The effluent treatment step makes use of a lime stream to precipitate out the remaining impurities (Mn^{2+} and Mg^{2+}), which are then removed from the process.

3.1.4 Impurity cementation

The neutralisation step allows for the precipitation of certain impurities such as iron, aluminium and silica, which leave in the solid residue, but impurities that co-precipitate with zinc, such as copper, cobalt, nickel and cadmium need a dedicated treatment step. The impurity bleed following the thickening step proceeds to impurity cementation, where the impurity sulphates are cemented with zinc dust and removed. The stream is then recycled to the milling step, where it is used as the mill solution instead of pure water, to maintain the water balance and ensure water reduction.

3.1.5 Solvent extraction and electrowinning

The solvent extraction stage follows a thickening step which removes unwanted solid impurities. This novel approach is used due to the prevalence of halides and silica in the ore, as noted by Fuls et al. (2005), which means that it cannot be treated via conventional zinc processing routes.

The solvent extraction step comprises 3 extraction, 3 washing and 2 strip stages in a conventional mixer-settler design. The extraction stages are where the main solvent extraction occurs. Physically entrained impurities are removed in the first 2 washing stages and spent electrolyte from electrowinning is used in the 3rd washing stage to remove co-extracted impurities from the loaded organic phase. Spent electrolyte is also used as the strip liquor.

The use of D2EHPA (di(2-ethylhexyl) phosphoric acid) as the extraction agent is due to its selectivity for zinc over the other base metal impurities. This is important, since electrowinning can only tolerate trace amounts of these impurities ($\mu\text{g/L}$), so a high-purity, high-clarity feed is required.

The solvent extraction step upgrades the pregnant leach solution (PLS) from a 30g/L zinc concentration to 105g/L, which is required by electrowinning. The leach step produces such a dilute PLS due to the high silica content (26%) of the ore. The dilution ensures that soluble losses of zinc are avoided and that problematic silica gel is not formed.

3.1.6 Reagent preparation and utilities

Sulphuric acid is prepared in the acid plant using imported sulphur. Limestone is milled to prepare it for use in the process in the limestone milling section. Water and electricity for the utilities plant are sourced from municipal services, named Namwater and Nampower respectively.

3.2 Areas of Interest for Plant

On the first plant visit to Skorpion Zinc a number of issues were raised that would be of interest to investigate. These are explored below.

3.2.1 Change in ore

It was found during a sampling campaign that, when mining deeper into the ore body past the oxide ore, a sulphide ore is obtained. This means that in the future, the process will have to be changed to accommodate the change in ore characteristics.

3.2.2 High copper content in ore

It was also found during this sampling campaign that the copper content in the ore can reach up to 2%. This can impact negatively on the circuit, since copper is co-extracted with zinc. If the copper is not removed from the process in the cementation step, it can contaminate the solvent extraction circuit. This will have a negative impact on the product purity, since electrowinning requires a high-purity feed free of contaminants to produce a high-purity product.

3.2.3 Water minimisation

The plant sources its raw water from the Orange River. Due to the location of the plant in the desert, water is a scarce commodity and water minimisation practices are in place. It is also true however, that if too much water is reused, a build-up of impurities occurs which affects the final product. Therefore, there exists a trade-off between water minimisation and desired operation of the process.

3.2.4 Solvent extraction circuit optimisation

The plant is investigating other diluents for use in organic regeneration to reduce cost. A cost saving could also be achieved by using less organic compound i.e. increasing its loading, but it has been found that if the organic loading is increased above 35g/L, the viscosity of the organic increases. There is therefore a physical constraint on how little organic can be used. Another problem is that impurities have been found to build up in the organic over time, which reduces its efficacy.

3.2.5 BZS plant optimisation

It was noted that, in practice, the precipitation of BZS does not occur very efficiently. An area of interest is that the BZS plant is currently operating at lower-than-design limestone reactivity. This is due to an effect known as armoring, where coating around the limestone prevents dissolution. The BZS plant is therefore very sensitive to limestone reactivity (quality), which has a possible negative impact in that it leads to crud formation since BZS liquor is recycled back to neutralisation.

The BZS circuit therefore impacts the PLS due to the impurities present in the recycled water stream (BZS liquor) which is used to supplement the raw water in the washing stage. If only raw water were used, it would greatly improve the efficiency of the washing stage and thus the PLS quality. The observed crud formation could therefore be as a result of recycling BZS water to satisfy environmental and water minimisation requirements.

3.2.6 Cementation plant optimisation

The plant produces 1000-1500tpa copper cake in the cementation process. However, there is a problem of cadmium contamination in the cake, which means that the copper cake is not obtained as a high-value product. The plant is investigating possibilities to obtain copper as a high-purity value product. One such possibility is the use of a copper electrowinning circuit.

Chapter 4 – Research Approach and Methodology

The first step in this project was to conduct an extensive literature review and identify relevant papers. This included identifying kinetics and mechanisms for the various reactions occurring in the process. Thermodynamic and physical data not included in the Aspen Plus simulation package had to be found from literature. This provided a “microscopic” view of the process in terms of the analysis of the different unit operations. The benefit of the systemic approach in optimising a process was investigated. Due to confidentiality issues, there was very little information available in open literature; therefore the majority of the data came from the plant.

The main part of the project involved performing a simulation of the Skorpion Zinc process. This produced a “macroscopic” view of the process and allowed for a deeper understanding of how the various operations in the process interacted with each other (Batterham 2006). The data needed to calibrate the simulation was obtained from the plant. In producing the simulation, the range in which operating conditions are likely to exist was needed before the simulation could be carried out. In this project, the operating conditions that were not known had to be estimated using typical values from literature. Certain operating variables such as flow splits and solids contents therefore had to be manually adjusted until the same trends and concentrations observed in the plant data became apparent in the simulation.

Due to the complexity of the Skorpion process, it could not be simulated exactly as it is with all the unit operations such as pumps and heat exchangers, but rather the simulation would focus on the major unit operational steps. This is justified since the interest in this project is not in the minor unit operations. The method used to simplify the process was the “black-box” approach. Using this approach, a group of similar unit operations are grouped together as a single “box”. For example, in the case of leaching, the plant has a number of leaching tanks, each with its own conversion. In the simulation, these tanks were all grouped together to form a leaching unit, with the same conversion as the overall conversion of the train of leach reactors on the plant. If a specific reagent is split between a number of reactors on the plant, such as sulphuric acid for the leach, the sulphuric acid input in the simulation will be the total reagent used over the train of reactors.

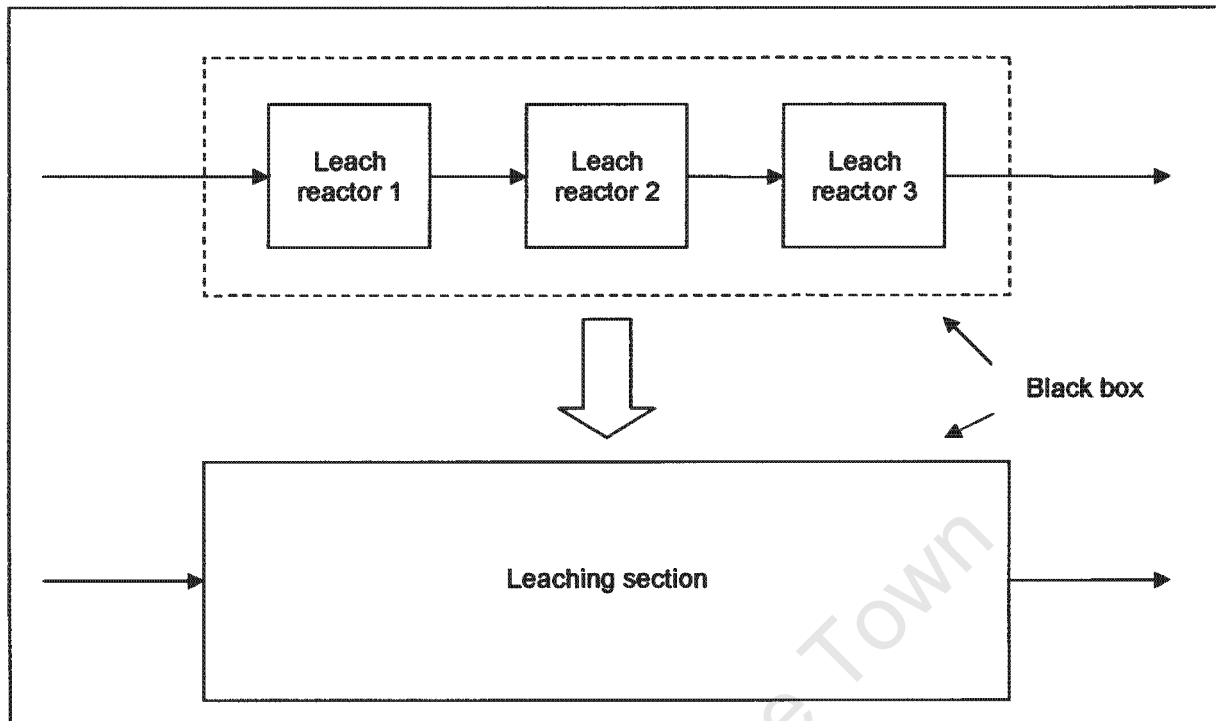


Figure 11: The Black Box Approach

The Skorpion Zinc operation has a mixture of solids and fluid streams. For this project however, the problems encountered when simulating solids processes were avoided by not taking the particle size distribution (PSD) of the solids into account. This was to save simulation time as well as due to the lack of information about the grindability indices of the various minerals. It was also due to the fact that in a real process, the particle size distribution has an impact on the leaching kinetics and extent of reaction. Due to the fact that reaction kinetics were not used, but rather fixed stoichiometric conversions based on plant data, the PSD would have no influence on the extent of reaction in the simulation and would merely serve to increase the simulation time.

In the case of the Skorpion process, which has large internal recycles and loops, including the flow rates of minor components occurring in parts-per-million concentrations was necessary to obtain an understanding of the trace impurities, however this impacted significantly on computing time.

The main fact to keep in mind was that when simulating the process, the simulation had to be built up gradually. This ensured that if a problem occurred, it was easier to

isolate. For example, if an error occurred after adding a certain unit operation, the error had to be associated with that unit if the simulation ran properly beforehand. This became complicated when recycle streams were involved, since it became much more difficult to isolate the cause of the problem. In this case, the recycle loops were disconnected and the simulation was run again to determine the cause of the problem.

Once a final, satisfactory simulation was obtained, it was used to answer the key questions outlined above by investigating the influence of different variables on the process. The main focus was to optimise the water balance; therefore operating scenarios were formulated and tested to achieve this objective. These included unit operation changes and circuit configuration changes. The simulation was then drawn on to formulate recommendations for operational practices.

Chapter 5 – Process Simulation Summary

The core of this project involves a process simulation of the Skorpion Zinc operation. Due to the complexity of the Skorpion process, with numerous recycles and variables, a number of simulations were performed. Each simulation increased in complexity from the previous one, until a final, working simulation was obtained which modelled the operating conditions of the plant as closely as possible.

As mentioned earlier, the simulation package used was Aspen Plus ®. A detailed summary of the final simulation will be discussed below, with special focus on reactions and operating conditions.

5.1 Feed

The composition of the minerals was calculated from the elemental analysis of the ore. An elemental assay of the ore was used to construct the mineralogy line with plant data. It was initially assumed that the ore mainly composed of simple oxides; however it became apparent that this approach would not work, since the assay did not add up to 100%. It was therefore decided that the metal oxides would be changed to carbonates in order to achieve a total assay of 100%. It was also assumed that the hydrated silicate $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ would represent all the silicates as well as the remaining, unreactable gangue material in the ore.

The feed composition was obtained using Premium Solver, which is included in the Microsoft® Excel® 2007 package. The mass percentages of the major elements in the feed were entered into Excel and the minor component percentages were assumed. The Least-Squares method was then used to obtain the corresponding mass percentages of the minerals for the given elemental mass percentages.

The sum of the error squared was defined as the sum of the input mass percentages minus the mass percentages obtained from Solver, squared. Solver was then used to vary the mineral mass percentages subject to the constraints of the input mass percentages. This resulted in a best possible approximation of the feed mineralogy in absence of actual data.

The main zinc-bearing mineral in the ore is sauconite ($\text{Na}_{0.33}\text{Zn}_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), with smithsonite (ZnCO_3) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) occurring to a lesser degree. The least-squares method was used to obtain the mass percentage of the feed, using the actual mineralogy of the zinc-bearing minerals.

Table 1: Feed Assay for Actual Feed Mineralogy

Mineral	Composition
	Mass %
CaCO_3	2.11
Al_2O_3	2.21
Fe_2O_3	1.86
CdCO_3	0.15
MgCO_3	1.73
$\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	61.70
Sauconite	20.56
Smithsonite	0.27
Hemimorphite	7.93
CuO	0.09
CoO	0.13
NiO	0.03
MnO	0.76
ZnCl_2	0.19
ZnF_2	0.27
Total	100

5.2 Leach

For the leaching step, industrial grade 98% H_2SO_4 was used. H_2SO_4 does not actually exist as a compound in the process, rather it exists as $\text{SO}_4^{2-} + \text{H}_3\text{O}^+$. The leach dissolution reactions are as follows, with the conversion of the zinc leaching reactions set at 95% in accordance with plant data and the conversions of the other species adjusted to obtain the concentrations observed in the process:





In addition, the following dissociation reaction of sulphuric acid was included, with full conversion. This was due to the fact that the product HSO_4^- is merely an intermediate and does not exist in the process. The pH of the leach reactor was set to 2 by controlling the amount of H_2SO_4 added. In addition, a vent was placed after the leach reactor in order to remove the CO_2 formed in the various leach reactions.



The temperature in the reactor was set at 50°C and the pressure at atmospheric.

5.3 Neutralisation

For the neutralisation step, limestone was added as a 40% CaCO_3 slurry with water. The neutralisation reactions are as follows:



Where $\text{Zn}_2\text{SO}_6\text{H}_2$ is actually $\text{ZnSO}_4 \cdot \text{Zn}(\text{OH})_2$ an approximation to basic zinc sulphate (BZS).

The final zinc reaction goes to 5%, the CaCO_3 reaction proceeds to completion and the Fe^{3+} and Al^{3+} reactions have a conversion of 99.9% to ensure that some of these ions remain in the process. This is due to the fact that although the conversion is high for these reactions, it is not perfect and some ions will remain in solution. This results in the simulation reflecting the plant operation more accurately. The reason for the low BZS-formation conversion is that the purpose of neutralisation is to precipitate out the impurities and not the zinc. One would therefore expect the zinc precipitation reaction to have a very low conversion.

The reactions occur in series, therefore the BZS dissolution reaction occurs first, since this is the dissolution of the BZS recovered from BZS precipitation. The BZS formation reaction is therefore not cancelled out by the BZS dissolution reaction. The amount of limestone entering the neutralisation step is controlled to maintain the pH at 5.5. A vent was once again placed after the neutralisation reactor to remove any gases formed.

5.4 Thickening

The thickener was modelled as a perfect solid separator, with all the solids proceeding to the underflow. The amount of liquid proceeding to the underflow was adjusted to achieve 33% solids in the underflow. This was due to the fact that of the solid-liquid separators available, a thickener will have the highest liquid content, since it is merely a settling tank. The purpose of a thickener is to separate solids from the liquid, whereas the purpose of a filter is to obtain a concentrated solid cake, with minimal liquid. Therefore, in this process, the thickener underflow will have a higher liquid content than the filter cake from filtration.

5.5 Reacidification

For reacidification, a 98% H_2SO_4 stream was used, with the flow rate controlled to maintain a pH of 4. The reactions are as follows:



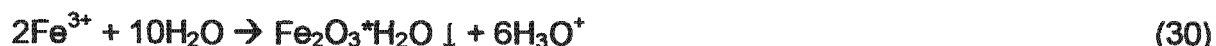
Since the purpose of reacidification is to re-dissolve any zinc that precipitated out, the zinc reaction conversion was set to 95%, with the $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ reactions set to 5%. The sulphuric acid reactions once again proceed to completion.

5.6 Washing and filtration

The process consists of a 2 stage filtration process, with the primary filtrate from the first filtration step being sent back to the neutralisation step and the secondary filtrate proceeding to BZS precipitation. In the washing step, the amount of wash water entering this step was adjusted to achieve a wash ratio of 1 with a displacement efficiency of 80%. The solids content of the 2 filter cakes was set at 65% in accordance with plant operation since the solids content from the filters have to be higher than that from the thickener.

5.7 BZS precipitation

A lime slurry of 40% CaCO_3 was added and controlled to give a pH of 5.5. The precipitated solids were then sent back to neutralisation.



Where $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is goethite.

The BZS formation reaction has a conversion of 95%, which is expected since the purpose of this step is to recover as much zinc as possible. The remaining reactions proceed to completion.

5.8 Effluent treatment

The purpose of effluent treatment is to remove any impurities that are still in the stream so that the water can be re-used in the process. This is achieved through the addition of a 40% Ca(OH)_2 slurry to obtain a pH of 10. Lime was used since limestone will not achieve the high pH required. At this stage of the process, the only impurities remaining are Mg^{2+} and Mn^{2+} . The reactions are therefore as follows:



Both reactions proceed to completion.

5.9 Impurity cementation

50% of the thickener overflow is sent to the cementation section. Zinc dust is added at an excess of 50% to remove all the Cu, Cd, Co and Ni from the stream. The amount of liquid leaving with the cement cake is adjusted to achieve a solids content of 60%. The reactions are as follows and all proceed to completion:



5.10 Solvent extraction

Due to the fact that Aspen ® does not contain any data for the organic D2EHPA; all data had to be manually entered into the databanks. Since the organic in the SX step forms a closed loop, the chemistry involved was very important. It was found that in

initially simulating SX as an open system, with an organic input and exit step, a good approximation to the flows in this closed loop could be obtained. These values could then be entered as initial guesses into the tear streams once the loop was closed. The SX step consists of 3 stages: extraction, washing and stripping. Wash water was added in line with operational data, therefore only extraction and stripping will be discussed below.

5.10.1 Extraction

The organic used was D2EHPA. The extraction reactions are as follows:



Where DH is the organic D2EHPA with the molecular formula $\text{C}_{16}\text{H}_{35}\text{O}_4\text{P}_1$

D4ZN is the organic loaded with zinc, formula $\text{C}_{64}\text{H}_{138}\text{O}_{16}\text{P}_4\text{Zn}_1$

D6Fe is the organic loaded with iron, formula $\text{C}_{96}\text{H}_{207}\text{O}_{24}\text{P}_6\text{Fe}_1$

D6Al is the organic loaded with aluminium, formula $\text{C}_{96}\text{H}_{207}\text{O}_{24}\text{P}_6\text{Al}_1$

The zinc reaction conversion was varied to achieve a zinc concentration of 13g/L in the raffinate and the other reactions proceeded to completion. The organic was added at an O:A ratio of 1.5, by varying the amount of diluent in the organic stream. The amount of aqueous phase entrained in the organic stream proceeding to washing was set at $0.01 \text{ m}^3/\text{hr}$. This low value is due to the fact that a very low carryover of impurities between stages is observed on the plant.

5.10.2 Stripping

The strip step is merely the opposite of the extraction step. The reactions are therefore:



The reason for the sulphuric acid dissociation reactions is that spent electrolyte is recycled from the electrowinning circuit. The D4Zn reaction was set to 100% conversion, since the purpose of the strip is to recover the zinc ions.

5.11 Organic regeneration

The organic is treated with 6M HCl to separate the loaded ions. The regenerated organic then re-enters the SX circuit at the extraction step. The reactions are therefore:



All of the reactions proceed to completion. In addition, the mass flow of the HCl stream entering this step was adjusted to obtain an O:A ratio of 56.

5.12 Electrowinning

An overall reaction where the half-reactions were combined was used for the electrowinning reaction.



The conversion of this reaction was varied to achieve the desired concentration of 50g/L Zn in the spent electrolyte. In addition, the amount of acid added was varied to obtain 180g/L H_2SO_4 in the spent electrolyte.

Chapter 6 – Development of the Aspen Plus ® Simulation

The simulation package Aspen Plus ® is widely used in the petrochemical industry to simulate processes, however its use in the minerals industry, especially hydrometallurgical processes, is fairly limited (Dry 2007). In this section, the method of simulating this process will be explained in detail.

6.1 Configuring Aspen Plus®

Before the actual simulation work could be started, a number of settings in the program had to be configured. This ensured the optimal operation of the program for the needs of the simulation.

Aspen Plus® uses an iterative approach to solving the mass balance. To do this, it makes use of a number of different numerical convergence methods, including Wegstein, Secant, Broyden, Direct Substitution and Newton methods. The main two are the Wegstein and Secant methods. A brief outline of these methods will be discussed below.

6.1.1 Tear streams

In order to solve complex flow sheets such as the Skorpion process, with its numerous recycle streams, Aspen Plus® makes use of “tear” streams. Tearing results in a decoupling of connections between modules in the simulation so that the simulation can be solved sequentially (Sikdar 2001). This prevents a build-up of information in recycle streams. This means that certain streams are “torn”, that is, they are split in half and an initial guess is used for the first part of that stream. The entire simulation then performs a single iteration and a value is obtained for the second half of the torn stream. This new value is then entered into the first half as the new initial guess. The simulation finally converges if both halves of the tear stream are the same. This is known as successive substitution. The procedure is better illustrated in Figure 12 below, adapted from Sikdar (2001).

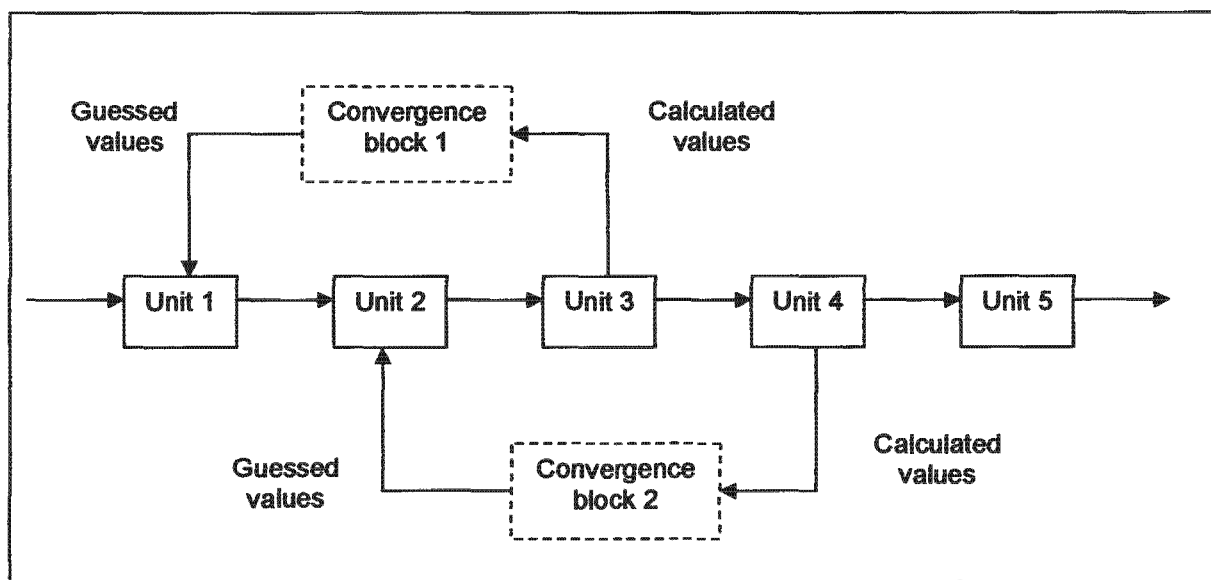


Figure 12: Stream Tear Procedure

Initial guesses, which are generally user-defined, are used for both recycle streams. The flow sheet then undergoes an iteration and the calculated value is compared to the initial guess in the convergence block. Tear streams are usually, but not limited to, the recycle streams in a process. Problems arise in complex flow sheets where the issue of “nested” recycles occurs. “Nesting” refers to recycle streams that are present within other recycles and this make it necessary for tear streams to be solved simultaneously. In this case, the selection of tear streams was very important, since the objective was to choose appropriate tears so as to minimise the total number of tear streams. This minimised computing time and made the simulation easier to debug when problems arose.

6.1.2 Wegstein convergence method

Aspen Plus® uses this method to converge its tear streams simultaneously, since it is a fairly rapid method. It is an extension of the Direct Substitution iteration. The main areas of interest in the Wegstein options were the “Maximum flow sheet evaluations” and the “Wegstein acceleration parameters”. The flow sheet evaluations determined how many iterations the simulation would go through to converge the flow sheet. This value can be adjusted freely, if it appears from the convergence history that the simulation needs more iterations.

The acceleration parameter determines how aggressive an approach the simulation will take in order to converge. The acceleration parameter q is calculated for each tear stream as follows:

$$q = \frac{s}{(s-1)} \quad (51)$$

$$s = \frac{G(X_k) - G(X_{k-1})}{X_k - X_{k-1}} \quad (52)$$

Where X = Estimate of the tear stream variable

$G(X)$ = Calculated value of the variable

k = Iteration number

The new estimate calculated is therefore:

$$X_{k+1} = X_k + (1 - q)(G(X_k) - X_k) \quad (53)$$

If q is left unbounded, a large amount of oscillation or divergence can be observed. Limits are therefore set as upper and lower bounds for q . If the bounds are set to negative values, the convergence method is accelerative. The more negative the values are, the more aggressive and accelerative the convergence will be. This also means that the convergence will be fairly "noisy", with a large amount of oscillation. If the bounds are positive, the more dampening the convergence will be. This means that the simulation can take much longer to converge, since it is not as accelerative.

It is generally sufficient to leave the acceleration parameter bounds at their default values, unless it is observed that there is too much oscillation, which was found in this simulation. In order to solve this problem, the lower and upper bounds of the acceleration parameter were changed to 0.25 and 0.75 respectively (Dry 2007). Because the values are fairly close to zero, the dampening effect is not too overpowering and the simulation did not converge excessively slowly.

6.1.3 Secant convergence method

For convergence of design specifications and calculator blocks, Aspen Plus uses the Secant method as default. This is a fairly rapid method, however the Broyden method is also sometimes used, since it is faster. The Broyden method is an extension of the Secant method into more than one dimension. For most cases however, the Secant method is sufficient. The Secant method is described by the following equation:

$$X_{n+1} = X_n - \frac{X_n - X_{n-1}}{f(X_n) - f(X_{n-1})} \cdot f(X_n) \quad (54)$$

Where X = Estimate of the variable

$f(X)$ = Calculated value of the variable

n = Iteration number

The method is converged when X_{n-1} and X_n lie sufficiently close to X_{n+1} , the root. This is achieved iteratively by bounding the root with the previous two solutions, X_{n-1} and X_n , with each iteration. To ensure that the Secant method operated correctly, the bracketing was set to check the bounds. This ensured that in the simulation, when a sign change did not occur, the upper and lower bounds were checked again to force the solution to be bounded. This prevented the simulation from stopping its convergence should the sign fail to change.

6.1.4 Convergence history

Viewing the convergence history of the tear streams is the best way to determine if the simulation would or would not converge. The graph of error/tolerance should gradually approach zero until the simulation is converged. If the trend of the graph is to tend away from zero, it could mean that there is an accumulation of species in the process. This could be remedied by introducing a purge stream. If the general trend of the graph is to approach zero, however at regular intervals there is a sharp jump away from this trend, it could mean that a design specification or calculator block needs to be changed. If the convergence trend is correct and the simulation ended, it could merely mean that the simulation needs more iterations.

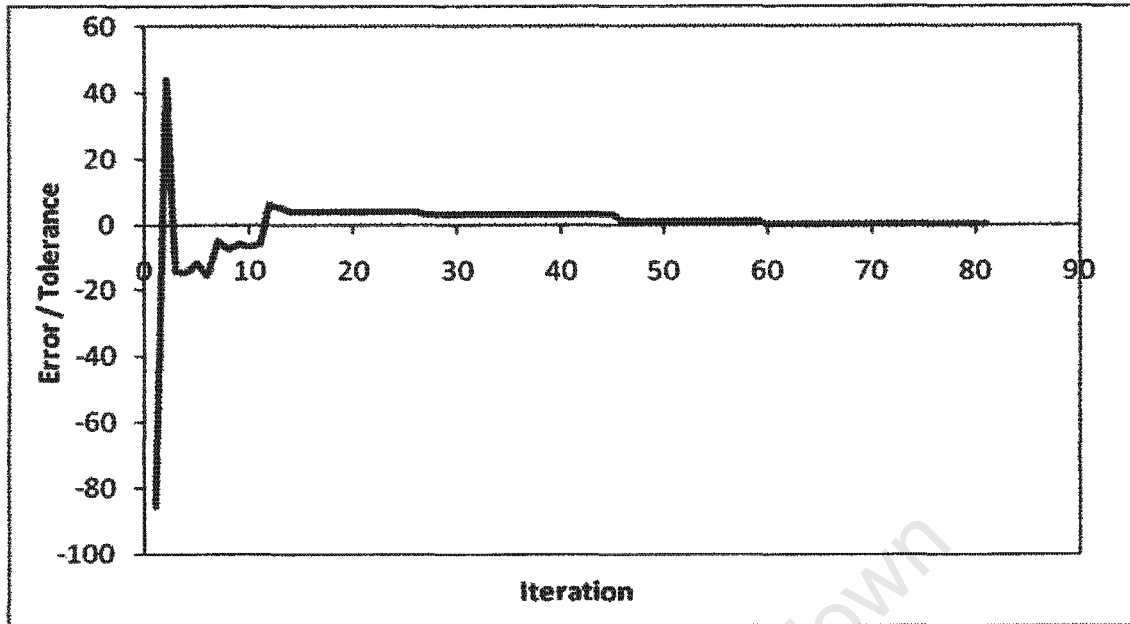


Figure 13: Graph of Good Convergence

Figure 13 above is an example of a good convergence history, since the graph gradually approaches zero. The simulation corresponding to this graph took 81 iterations to converge, as shown on the x-axis.

However, it can be seen in Figure 14 below that the graph does not converge to zero. This is an example of a bad convergence history, with a very “noisy” plot with a large amount of oscillation. This trend is due to the fact that there is a build-up of impurities in the system, meaning that the simulation would never converge.

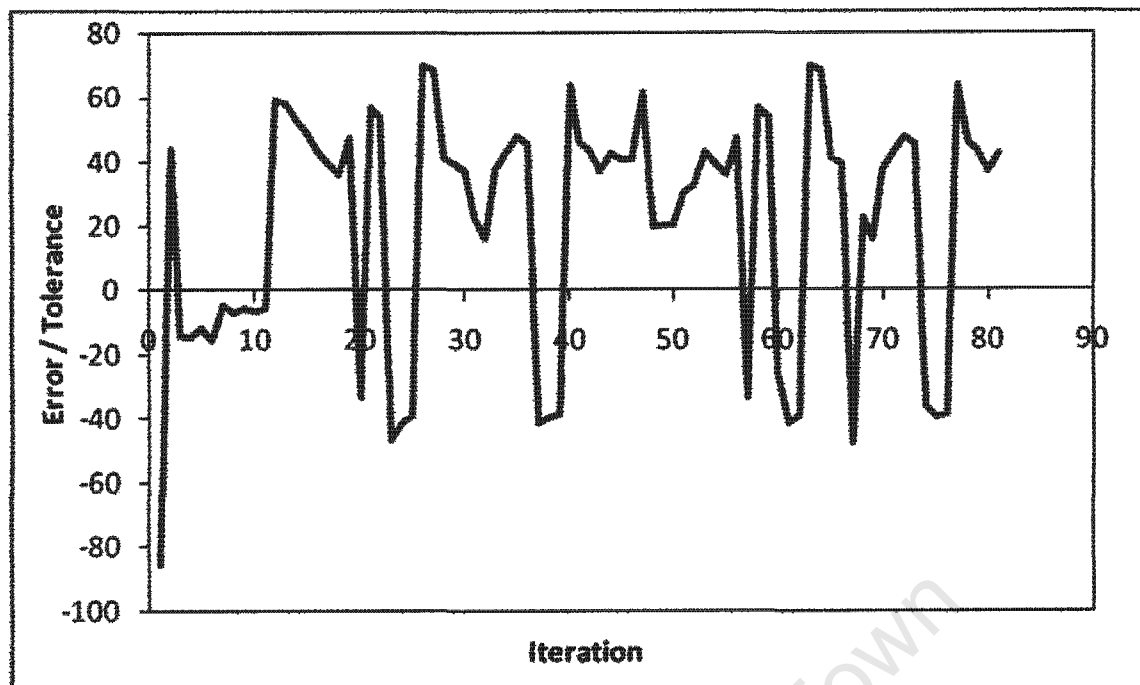


Figure 14: Graph of Bad Convergence

6.1.5 Calculation sequence

This is a very important area to check when the simulation does not converge. The main point to note is that the tear streams should always converge on the outermost loop. The main purpose of a design specification or calculator is to manipulate a certain variable to obtain a desired outcome. If a tear stream converges inside a design specification or calculator loop, it means that every time the design specification changes the variable, the tear stream would have to re-converge. This makes it almost impossible for the simulation to converge, since the design specification would always have to change its variable to account for the changed tear stream. When a tear stream converges on the outside; all the design specifications converge fully, followed by the tear streams.

6.1.6 Tolerance

The last area to investigate is the tolerances of the design specifications. Relaxing the tolerance on a certain design specification could result in the simulation converging since it is less constrained, but this has to be exercised with caution. Having the same level of tight tolerance on all the design specifications is ideal, since there is less room for error. For example, relaxing the tolerance on one design

specification could result in another design specification not being met, since it might be dependent on the first one. A flow rate, for example, could have a more relaxed tolerance since flow rates change on a daily basis in a real process.

6.2 Simulating the process

The steps taken to simulate this process, as well as the problems encountered, will be discussed below.

6.2.1 Feed

In order to obtain the feed assay shown in Table 1, it was necessary to make a number of assumptions. It was known from plant data that the zinc-bearing minerals were sauconite ($\text{Na}_{0.3}\text{Zn}_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), smithsonite (ZnCO_3) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$), with sauconite as the main component. It was also known from the elemental analysis that the overall zinc content of the ore was 11.4%.

Using this information, a mineral assay was constructed. This involved assuming the relative compositions of the 3 zinc-bearing minerals. It was also known from correspondence with the plant that the ore consisted of a significant amount of oxides, namely iron oxides such as goethite (FeOOH) and magnetite (Fe_3O_4). Calcium and magnesium –bearing carbonates were also present. The gangue was mainly comprised of silicates and thus all gangue material was grouped together as $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ for simplification. Halides were also present in small quantities and were assumed to be in the form of ZnF_2 and ZnCl_2 .

6.2.2 Component specifications

For hydrometallurgical operations, all 3 phases are involved in the process. The simulation therefore had to take into account the liquid, gas and solid phases. This ensured that Aspen Plus ® recognised compounds correctly for any dissociation chemistry that might occur.

Aspen Plus ® has an extensive component database built into it; however certain compounds, especially the ore minerals, were not included. For this reason, it was necessary to manually enter certain components and their properties, or if this data was not available, “approximate” the component using another component with similar attributes. This was found to be true with the zinc-bearing minerals sauconite and hemimorphite. In order to obtain a working simulation, these compounds were approximated as paragonite ($\text{NaAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$) and $\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 5\text{H}_2\text{O}$ respectively. These compounds are similar in appearance to the actual mineral, so it was expected that they would have similar physical and thermodynamic properties.

Although the two minerals sauconite and hemimorphite were approximated as other compounds already present in the database, the actual molecular structure for these compounds had to be entered. If this was not done, the mass balance would not hold, since the reactions are all based on the actual mineralogy and not the approximate component.

Vapour-liquid equilibria were calculated using Henry’s Law for all gases that were involved in the process. This ensured that an accurate model of the dissolved gas’s behaviour was obtained.

6.2.3 Property specifications

To ensure that calculations were carried out properly, the properties of the components had to be specified. The most important part of this was in the selection of an appropriate base method. For hydrometallurgical operations, the electrolytic NRTL (non-random two-liquid) method is used. This method makes use of the Redlich-Kwong equation of state for vapour-phase calculations and is the most versatile electrolyte method, due to its ability to handle very high and very low concentrations. It can describe vapour-liquid and liquid-liquid equilibria of strongly non-ideal solutions, such as those found in mineral processes. It can also model any combination of polar and non-polar compounds, making it the most suited to this process.

The Redlich-Kwong equation of state (EOS) is used for vapour phase properties. Due to the fact that this system runs at atmospheric pressure, the Redlich-Kwong EOS is used since it is applicable at low pressures where non-ideal behaviour in the vapour phase is limited. The equation is as follows:

$$p = \frac{R.T}{V_m - b} - \frac{a}{T^{0.5} \cdot V_m(V_m + b)} \quad (55)$$

$$a = 0.427 \frac{R^2 \cdot T_c^{2.5}}{P_c} \quad (56)$$

$$b = 0.0866 \frac{R \cdot T_c}{P_c} \quad (57)$$

Where T_c = critical temperature

P_c = critical pressure

V_m = molar volume

R = ideal gas constant

The ideal gas equation:

$$P.V = n.R.T \quad (58)$$

The Redlich-Kwong EOS (55) is a modification of the ideal gas equation (58), taking into account the real properties of the gas as described by constants a and b . It therefore provides a more accurate calculation of the vapour phase thermodynamics.

6.2.4 Reactions

When specifying conversions for reactions as in this case, the reactions were labelled as occurring in series. This causes the simulation package to read the reactions as occurring in the order in which they are entered. This ensured that the reactions did not “compete” for the reagent if they were to occur simultaneously. It also enables the specification of which reactions are more important by placing them higher up on the list.

This was found to be especially important when reagents such as sulphuric acid, which fully dissociate, were added. It was discussed earlier that the intermediate HSO_4^- does not exist in the process. If the sulphuric acid dissociation reactions were allowed to occur simultaneously, this ion will be present in solution. By specifying that the HSO_4^- formation reaction occurs before the HSO_4^- dissociation reaction when the reactions occur in series, this problem is eliminated.

6.2.5 Unit operation and stream specifications

The operating conditions for most of the units were obtained from plant data; those that could not be obtained were assumed, to mimic plant operation. Because Aspen Plus® is an iterative package; it works best when the closest possible initial inputs are entered. The plant data was therefore used to obtain the best approximations for the input streams, which decreased the simulation period.

6.2.6 Design specifications and calculator blocks

A design specification is used to determine the value of a variable required to meet a certain specification. For example, if it was known that a certain temperature or pH requirement had to be met in a unit, a design specification was used to determine how much reagent or utility needed to be added to meet that specification. A calculator block is a more powerful and customisable version of a design specification, which allows for programming using Microsoft Excel or Fortran. Design specifications and calculator blocks were used to constrain the system according to certain key variables. For this simulation, a number of design specifications and calculator blocks were employed. These will be discussed below.

6.2.6.1 PLS Concentration

The concentration of the PLS solution entering the SX step had to be maintained at 35g/L Zn^{++} . This is in line with the plant data. If this value is too low, the amount of organic required in SX will increase. If it is too high, the organic becomes overloaded. This concentration was achieved by varying the amount of ore entering the process, in line with plant operation.

6.2.6.2 Solids contents

In a real process, the solids and liquids do not split perfectly- there is always a certain amount of liquid that proceeds with the solids. The solid-liquid separators in the simulation were modelled with a realistic solids percentage. As explained in Simulation 5, the thickener, filter and cement cake solids percentages were set at 33%, 65% and 60% respectively.

6.2.6.3 SX extraction step O:A ratio

A design specification was set up to obtain the desired O:A ratio of 1.5 in the extraction step. This was achieved by varying the amount of diluent in the organic stream.

6.2.6.4 Scrub O:A ratio

The scrub O:A ratio was set to 56 by varying the amount of HCl added.

6.2.6.5 SX extraction step organic flow

The amount of organic was set to 40% of the stream in accordance with Fuls et al. (2005), given that the stream comprises of diluent, fresh organic and aluminium and iron -loaded organic.

6.2.6.6 Filter wash ratio and efficiency

The desired wash ratio and filter efficiency were set at 1 and 0.8 respectively, according to plant data. The filtration and washing steps were set up to recover as much of the zinc as possible whilst removing as many of the impurities as possible. The wash solution in this case was effluent solution.

The split of solution to the tailings dam and the split of liquid proceeding to the BZS plant were adjusted so that when the wash water was added, the wash efficiency was 80% and the amount of liquid added was the same as the amount of liquid displaced. This is due to the fact that the purpose of the wash is to wash the impurities out of the cake and replace the original, impure filtrate with pure water.

That is, the wash displaces the impurity-laden solution with purer water, thereby purifying the stream.

6.2.6.7 Charge imbalance

It was found that charge imbalances arose during the process of simulation due to the various separation steps. This is an artefact of the simulation due to the separation blocks and is not something that would be encountered in the real process. As such, calculator blocks were set up to balance the charges in the affected streams. This was done by calculating the cation and anion flow rates in the affected stream and then calculating the imbalance. If it was found that the anion flow rate was larger than the cation flow, the H_3O^+ flow rate was adjusted to make up the balance. Similarly, if the cation flow rate was found to be higher, the OH^- flow rate was adjusted.

Chapter 7 – Simulation Results and Discussion

The results obtained from the simulation of the Skorpion Zinc process are now presented and discussed. The first set of results presented show parity charts of simulated versus plant values, which were used to validate the simulation. This step was necessary before investigating the various minimisation scenarios, which are subsequently presented. These scenarios included unit operational changes and circuit configuration changes. The benefit of the simulation is that it allows for tracking of critical concentrations. Due to confidentiality issues, certain values have been removed from the graphs. It should be noted that the water minimisation scenarios explored do not completely reflect the plant operational philosophy, which is to control zinc concentrations, but rather the Skorpion Zinc circuit is used as a case study for investigating water minimisation scenarios.

7.1 Simulation validation

In order to validate the process, key flow rates were compared to actual plant data. Only the major flow rates were considered, since these would determine how accurately the simulation matched the process.

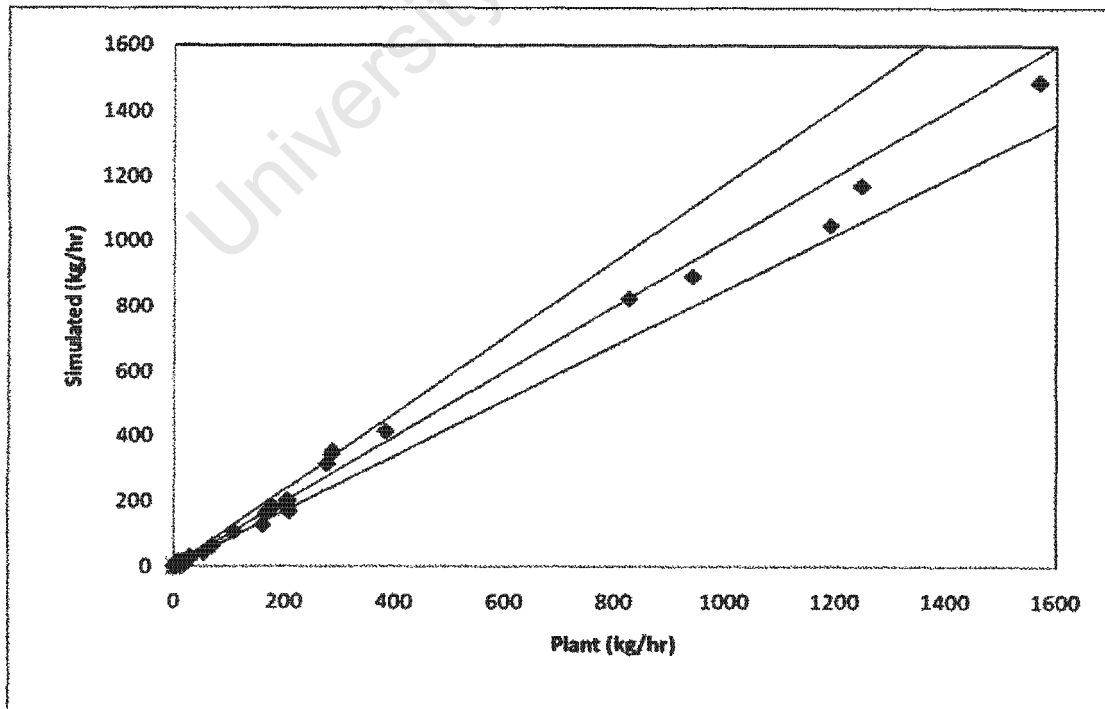


Figure 15: Parity Chart for Simulation Results – Flow Rates

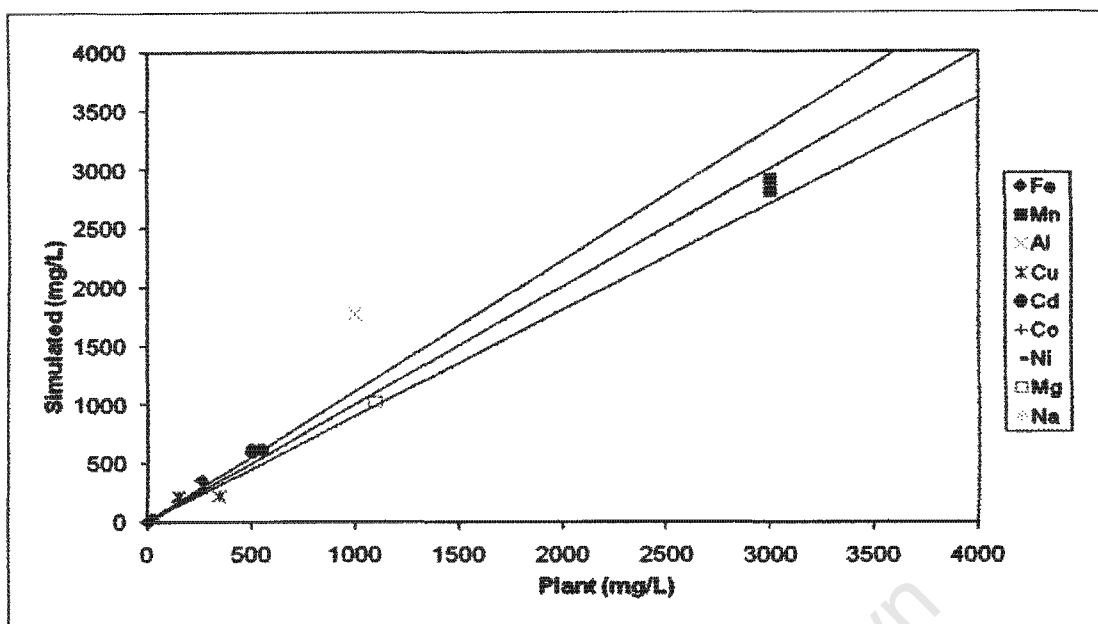


Figure 16: Parity Chart for Simulation Results – Concentrations

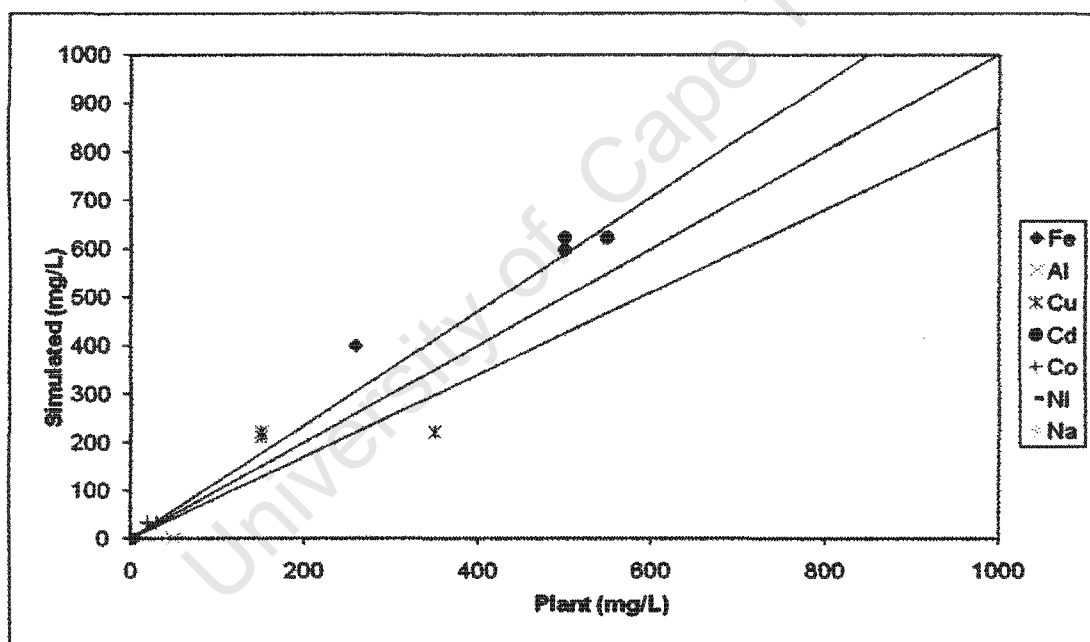


Figure 17: Expanded Parity Chart for Simulation Results – Concentrations

Results show a good agreement between simulated and plant values for flow rates, as displayed in Figure 15 above. It can be seen that scatter is evident at the upper range of the graph. These data points are from the internal flow rates in the process. For the purposes of this study, where the water inputs and outputs are being investigated, it was judged more important to gain good parity in the input and output flows. These flows appear on the lower range of the graph and show good

agreement. Nevertheless, the scattered points do fall within a 10-15% range that was judged acceptable for such a complex process.

Figure 16 shows the key concentrations throughout the process. Figure 17 shows the expanded view of the lower range of Figure 16. It can be seen that the agreement is good, with some outliers. The outliers, however, do not detract from the trends observed in the process and were judged acceptable. The critical concentrations, namely Mg^{2+} and Mn^{2+} were found to be in good agreement. It should be noted that due to the fact that Skorpion is a zinc process, the zinc concentrations had to be completely accurate. This was found to be the case, as shown in Figure 18 below.

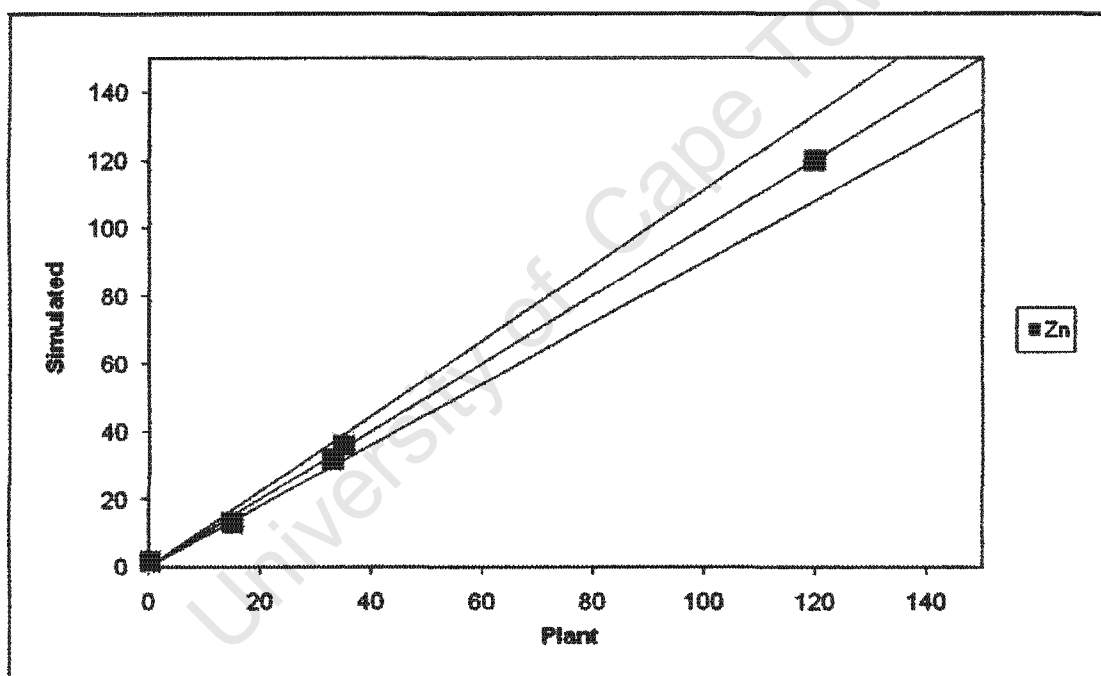


Figure 18: Parity Chart for Zinc Concentrations

It was therefore judged that the simulation accurately represented the process for the purposes of this project and could be used to predict trends for a number of operating scenarios. This concluded the simulation process presented in Figure 7 in section 2.3.2.2: The simulation process, and starts at the 5th step of applying the optimisation technique presented in Figure 8 in section 2.4.2: Circuit optimisation. The optimisation techniques in this case are the various operating scenarios presented below.

The key output variables investigated were as follows:

- Cl^- , Mn^{2+} , Mg^{2+} and Zn^{2+} ion concentrations entering solvent extraction
- Zinc production rate
- Water lost to effluent treatment
- Water lost to filter cake

These variables were judged to be the most important indicators of how well the process responded to the various operating scenarios.

7.2 Reducing process water

This scenario is the most apparent, since it merely involves reducing all water inputs to the process and investigating the impact on the key variables. This gave a good indication of how far the overall water could be reduced before problems arose. It should be noted that all of the scenarios presented below are for a fixed ore feed rate.

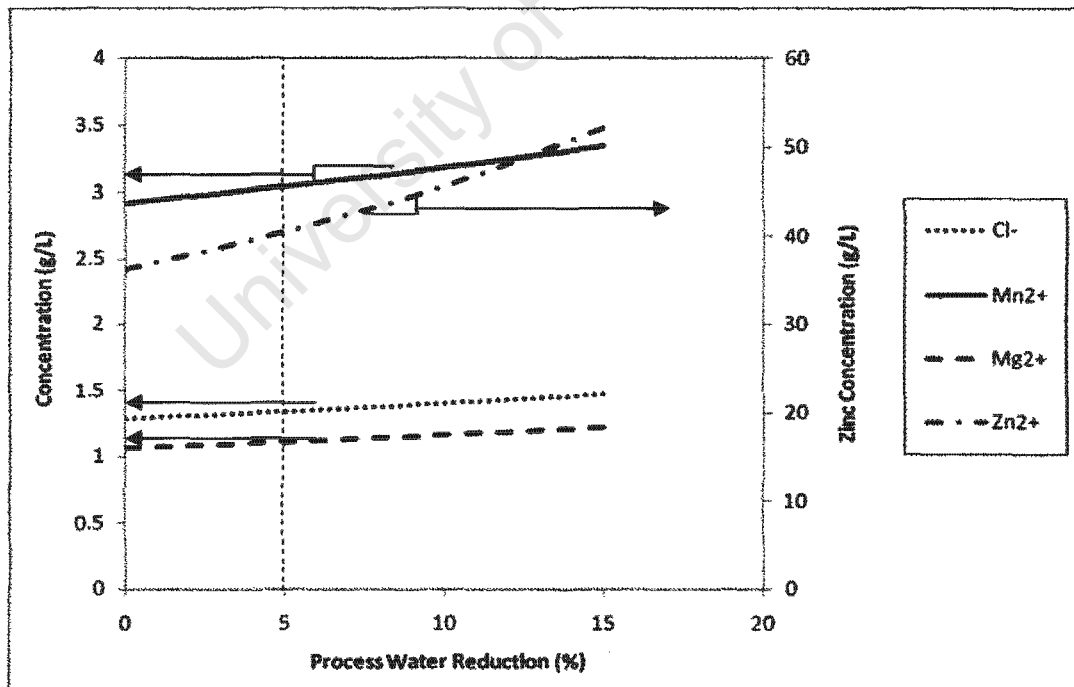


Figure 19: Effect of Reducing Process Water on Concentration

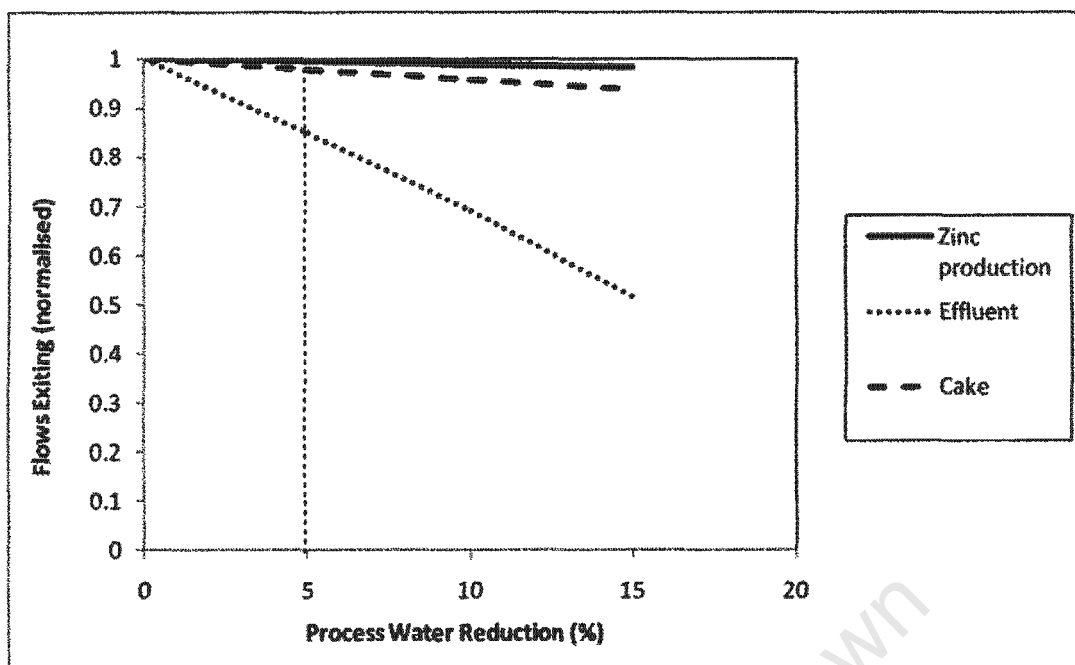


Figure 20: Effect of Reducing Process Water on Flow Rates

Figure 19 above shows that reducing process water results in an increase in the concentrations of trace minerals as expected, since there is less solution available in the process. Figure 20 shows that the water exiting the process is reduced; once again this is expected since there is less liquid in the process.

In the scenario shown by Figure 20 above, all water inputs to the process were reduced and the actual process was left unchanged. This resulted in a steady reduction in water lost, since there was less water available in the process. The water exiting via the effluent shows a more dramatic result, since the flow rate in this stream is small compared to that in the cake. When examining the actual amount reduced, the value is comparable to the reduction observed in the cake. In addition, a build-up of salts in the process was observed which reduces product purity. A compromise therefore had to be reached between zinc production, water minimisation and product purity. It was found that beyond a 5% reduction in process water, the impurities in the system pass the maximum allowable limits. Specifically, a 5% reduction in water resulted in a 10% increase in concentrations, namely Mn^{2+} , Mg^{2+} and Cl^- . A small reduction in water therefore results in a large increase in contaminants, meaning that the Skorpion process is already optimised.

It was found that although the concentration increased, the actual mass of zinc ions decreased. This is due to the fact that because there was less water available in the process, the solid-liquid equilibrium was shifted. This meant that less zinc went into solution in terms of mass, meaning that there were less zinc ions in the process. The increase in concentration was merely a consequence of the reduction in water in the process. The observed reduction in zinc production was thus attributed to the decrease in availability of solution to transport the zinc ions to solvent extraction, which is the main process step determining how much zinc will be recovered.

7.3 Unit operational changes

Changes in this respect were limited to those units operations that could be made more efficient through a combination of unit operations to improve on the overall efficiency for an operating step, or through the implementation of new technologies. In the case of Skorpion, these were the thickener underflow solids content and the solids content of the filter cake. The results of these investigations are presented below.

7.3.1 Effect of thickener underflow solids content

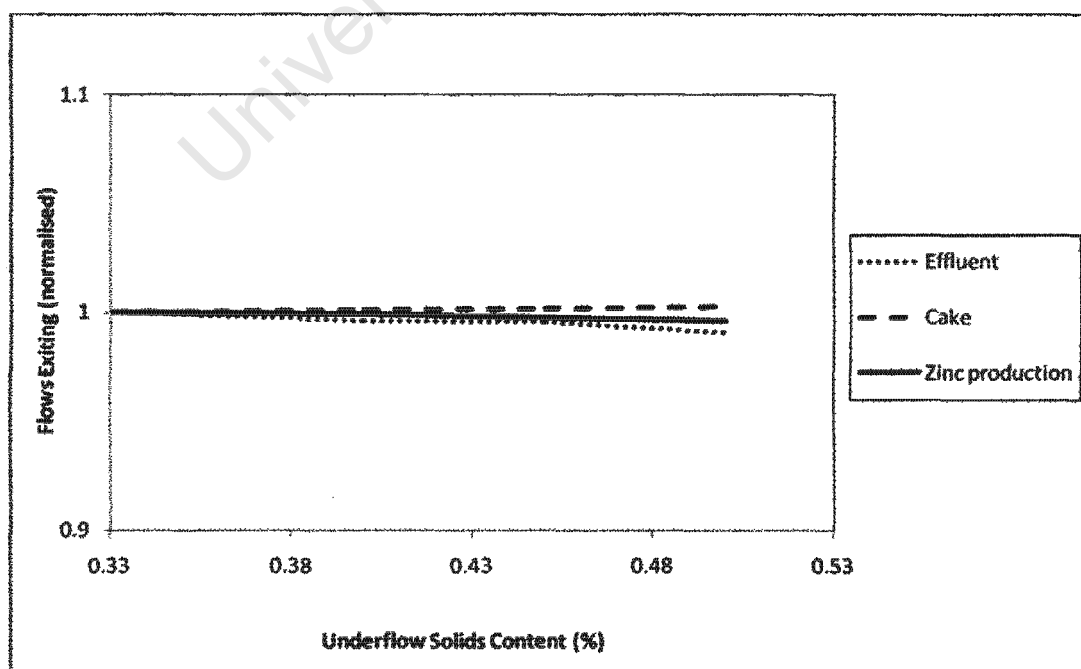


Figure 21: Effect of Thickener Underflow Solids Content on Flow Rates

Figure 21 above shows a scenario where the underflow solids content of the main thickener in the process was varied and the effect on the water balance and zinc production was investigated. An increase in the solids content in the underflow means that more liquid proceeds to the solvent extraction step. This is a result that can be achieved through a combination of thickeners and filters, thereby improving the overall efficiency of the step, or through the use of new technologies such as gravity thickening versus normal thickening.

It can be seen in this graph that the amount of water lost as well as zinc production are largely unaffected. An increase in the solids content of the thickener underflow means that less solution proceeds to BZS precipitation. This in turn results in a smaller recycle of solution to the leaching step, which results in less solution entering thickening. This causes less solution to enter solvent extraction when compared with the base case, which results in a slightly decreased production rate.

However, a decrease in solution to BZS results in a smaller amount of solids precipitating out of solution when compared to the base case. This means that in the filters, which operate on a percentage solids basis, less solution leaves with the filter cake in order to achieve the same solids percentage as the base case. The changes observed from this scenario are therefore balanced by the two effects and the net effect on the process is minimal.

7.3.2 Effect of filter cake solids content

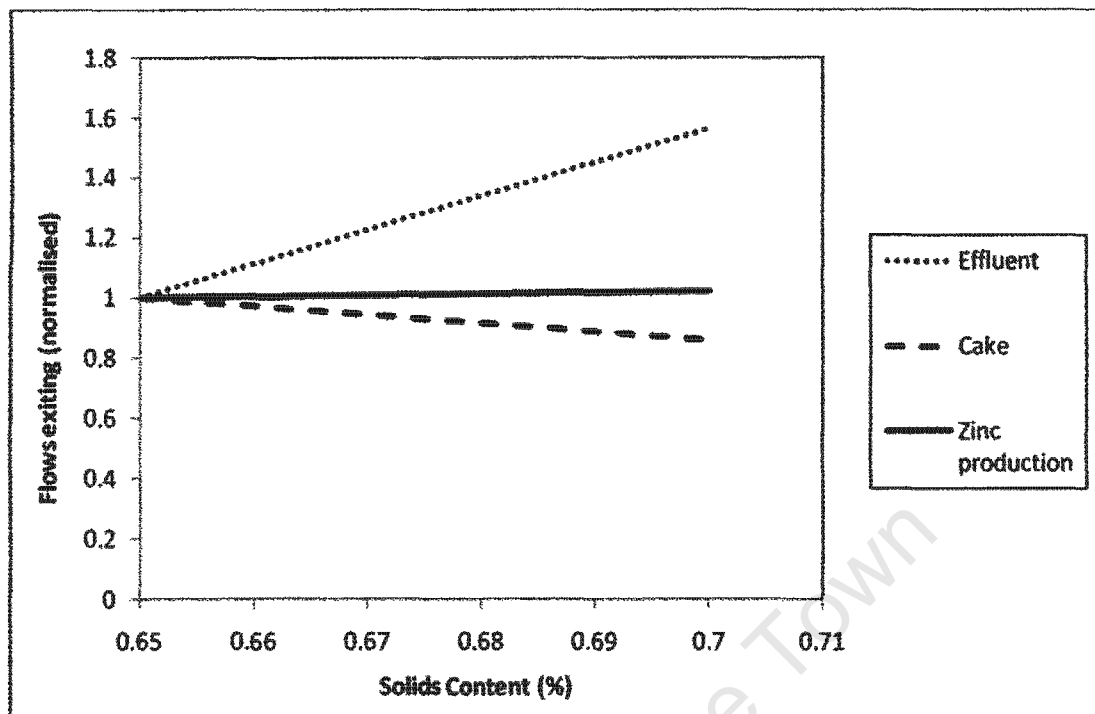


Figure 22: Effect of Filter Underflow Solids Content on Flow Rates

Due to the fact that the filters in the process already operate at a high efficiency, there was not much room for improvement in this scenario. In the scenario represented by Figure 22, the effect of improving the efficiency of the main filtration step in the process was investigated. Due to the nature of the solids, it is not possible to achieve a cake solids content of higher than 70%. The results show that an increase in filter efficiency results in a decrease in the water exiting via the filter cake, which is expected and an increase in the water exiting via the effluent. The zinc production remains largely unaffected. As mentioned for Figure 20, the effluent stream shows a more dramatic trend since the flow rate is smaller than that in the cake. The net effect of this scenario is once again minimal. Trace concentrations increase, however within acceptable limits. Unit operational changes therefore have very little effect on the overall process and merely result in a shift in the water balance.

7.4 Circuit configuration changes

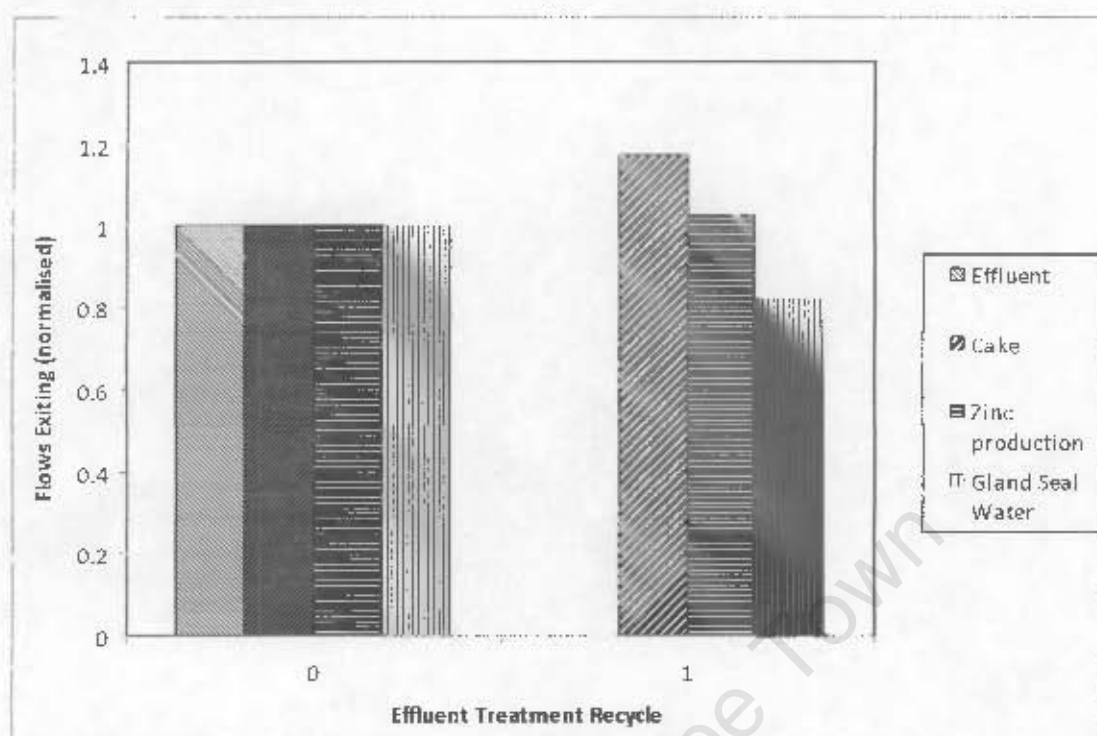


Figure 23: Effect of Full Effluent Recycle to Solvent Extraction

Figure 22 above shows the scenario of a full recycle of effluent solution to solvent extraction. Due to the high purity requirement of the water for solvent extraction, the effluent water would have to undergo full treatment and demineralisation prior to re-use. The purpose of this scenario is therefore to decrease the amount of fresh water required for demineralisation.

It can be seen from Figure 22 that a full recycle has almost no effect on the zinc production rate. The water lost via the filter cake increases by 17% to compensate for the lack of an effluent stream, but this effect is negated by the 14% reduction in fresh water required for solvent extraction. This scenario therefore results in a large amount of water saved, with no detrimental effect on the production rate. However, there is a trade-off between the cost of treatment and the environmental benefit. Skorpion is currently treating the effluent water through reverse osmosis for re-use.

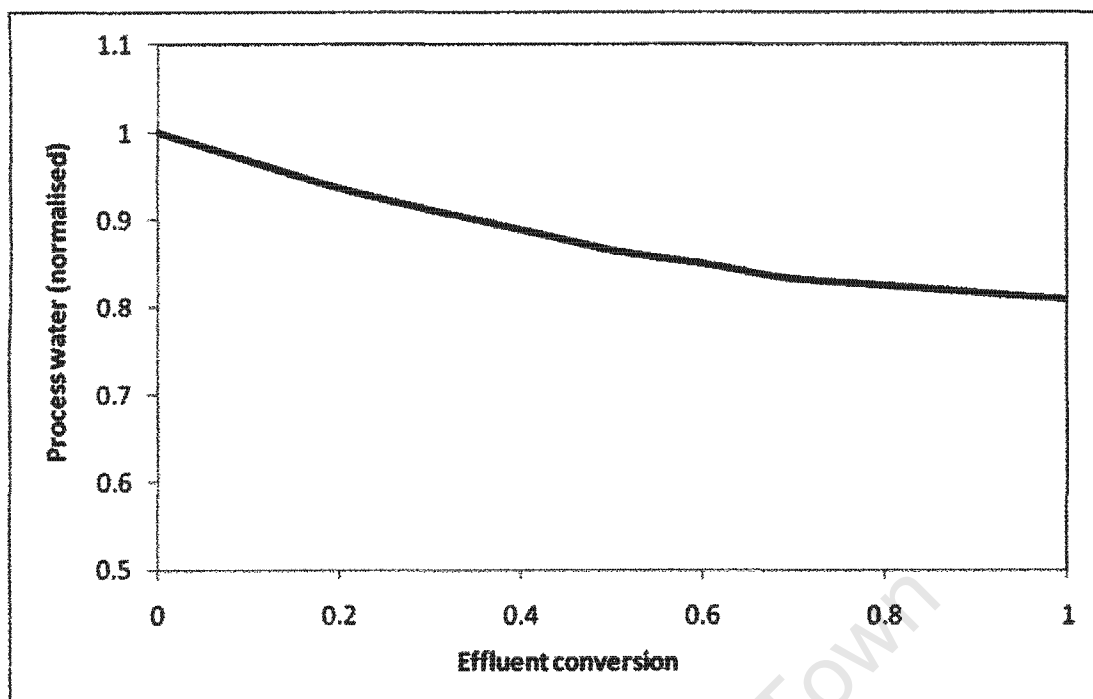


Figure 24: Effect of Full Effluent Recycle to Gland Seal

Figure 24 shows the effect of extent of effluent treatment on process water, for a full recycle of effluent water to gland seal. In this scenario, all effluent water was used to supplement gland seal water into the process. It should be noted that this graph is shown at the threshold concentrations; therefore it represents the minimum amount of process water required. This graph shows that for a full recycle of untreated water, the amount of fresh water required is unchanged. This scenario is in fact detrimental to the process, since impurities are added back into the process. However, for a full treatment of effluent water, a 19% reduction in fresh water required can be achieved before the threshold concentrations are reached.

Chapter 8 – Conclusions

This study investigated the effect of varying process operating conditions and adopting new circuit configurations on the water balance of the Skorpion Zinc operation in Namibia. A process simulation using Aspen Plus was used to carry out the investigation. In developing the simulation, a deeper understanding of the movement of various species such as water, co-extracted metals and impurities through the process was obtained. The main area of interest for this project was the water balance, due to the ecologically sensitive location of the operation.

The simulation developed was validated against plant data and showed good agreement. It was therefore judged to accurately represent the process for the purposes of the project and could be used to investigate the various operating scenarios. The benefit of the simulation was that it allowed for the tracking of key concentrations in the process

The Skorpion Zinc process was used as a case study for the water minimisation scenarios and as such, the scenarios do not completely reflect plant operating philosophy, which is to control zinc concentrations.

From this study the following conclusions may be drawn on varying process operating conditions:

- The reduction of process water into the refinery is not sufficient to optimise the water balance, since a steady build-up of salts in the process will be detrimental to the product purity. A compromise therefore has to be reached between product purity, zinc production and process water reduction. A reduction in water of 5% results in a 10% increase in concentrations, passing the maximum allowable concentration limits. This shows that for a small reduction in water, a large increase in contaminants is observed, meaning that the process is already highly optimised.

- Applying new technologies or combining unit operations can improve the efficiencies in solid-liquid separation steps. This has a negligible effect on the production rate and water flows however; and merely results in a shift in the water balance between the output streams. Improving the thickener operation has a negligible effect on the process due to the numerous recycle streams in the process compensating for any changes made. In addition, due to the nature of the solids in the process, there is little room for improvement in the filter, which has a maximum cake solids content of 70%. Trace concentrations increase in this scenario; however this is within the allowable limits.

The following conclusions related to circuit configuration changes may be drawn:

- Supplementation of demineralised fresh water with demineralised effluent water results in a 14% reduction in fresh water required, with no detrimental effect on the production rate. Since solvent extraction requires high purity water, the effluent water would have to undergo full treatment prior to reuse. A trade-off therefore has to be reached between treatment costs and benefit to the environment. Skorpion has recently implemented the treatment of effluent water through reverse osmosis for reuse.
- Supplementation of gland seal water with fully treated effluent product water results in a 19% reduction in fresh water required at the threshold point for trace concentrations. If a full treatment of the effluent water is not achieved, this scenario will be detrimental to the process since impurities that would normally be removed will be added back into the process. The percentage reduction in fresh water required is thus dependent on the efficacy of the effluent water treatment.

The findings suggest that improving efficiencies in the solid-liquid unit operations results in a shift in the water balance. The best optimisation would consist of supplementing the fresh water input with recovered and treated waste water; however the environmental benefit needs to be weighed against cost of treatment.

The main limiting factor in the water minimisation scenarios is the effect of a build-up of impurities, which affects product purity and can negatively impact the operation of the plant. This would need to be investigated in more detail. The results therefore suggest that the Skorpion process therefore already features a highly optimised water balance and thus the only effective water balance optimisation would be through the re-use of waste water in order to supplement the fresh water input.

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Chapter 9 – References

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Chapter 10 – Appendix 1: Aspen Flow Sheet

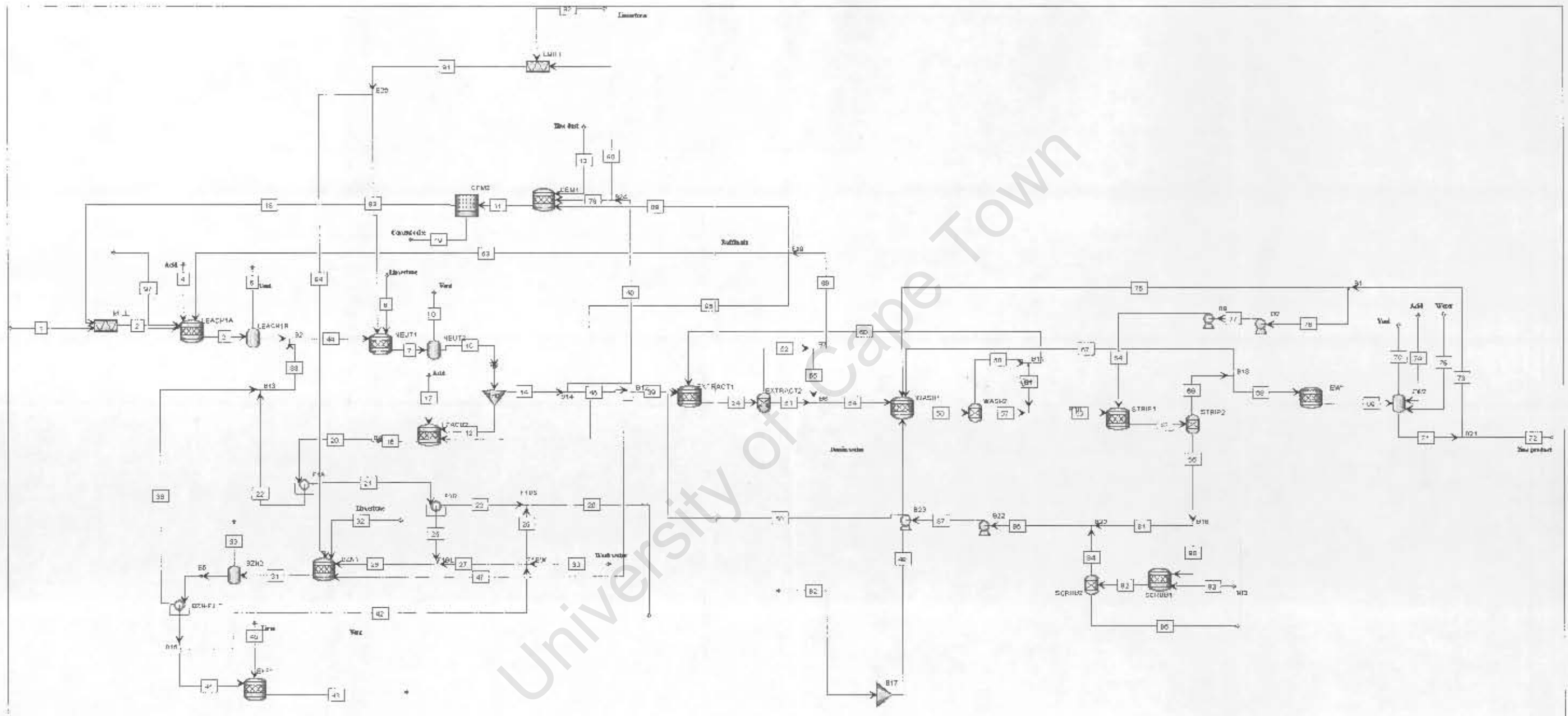


Figure 25: Aspen Flow Sheet

Chapter 11 – Appendix 2: Detailed Calculations

10.1 Wash ratio calculation

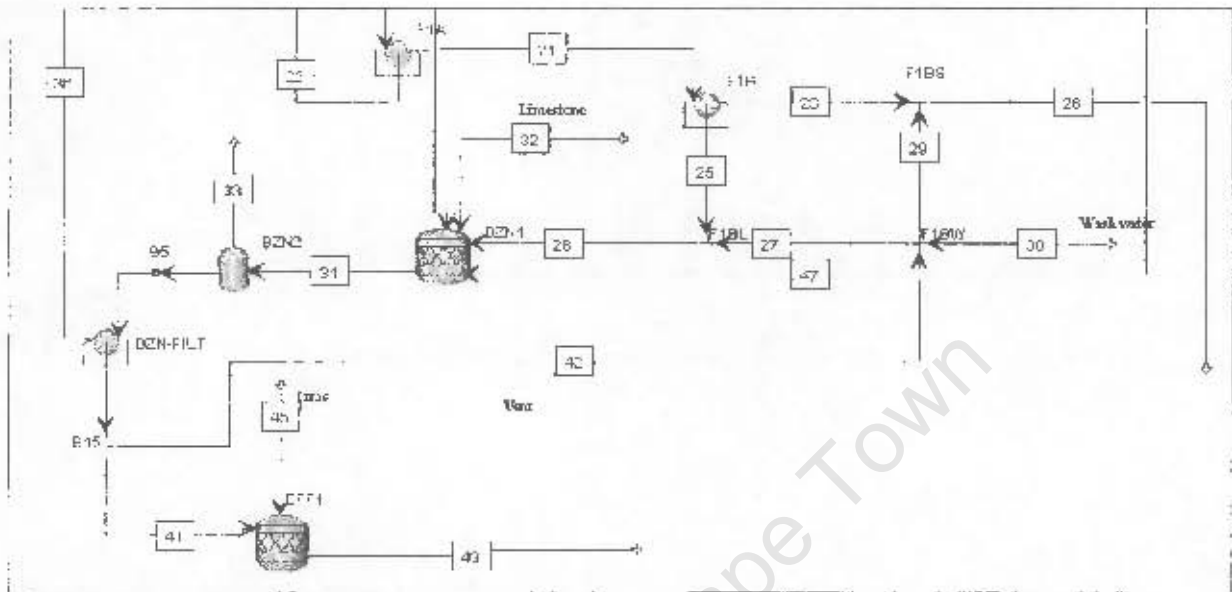


Figure 26: Washing and Filtration Section

Figure 26 is a closer view of the washing step in Figure 25.

Let F = mass flow solution in stream 21 (i.e. entering filtration)

S = mass flow solids in stream 21

$W1$ = mass flow wash water in stream 30 (set to 0 since no fresh wash water)

X = fractional split of filter F1B to stream 23 (overflow)

Y = fractional split of mixer/splitter F1BW to stream 29

$W2$ = mass flow stream 42 (wash stream)

$B15$ = fractional split of stream splitter B15 to stream 42

$T7$ = mass flow stream 37 (entering B15)

$$A = S / (F + S) \quad (\text{solids content stream 21})$$

$$R = 1 \quad (\text{wash ratio})$$

$$E = 0.8 \quad (\text{filter efficiency})$$

$$X = (S/A) * (1.0 - A) * (1.0 - E)^{(R/F)} \quad (\text{fractional split to stream 23})$$

$$B15 = ((S/A) * (1.0 - A) * R) / T7 - W1 \quad (\text{fractional split to stream 42})$$

$$Y = ((S/A) * (1.0 - A) - (X * F)) / (W1 + W2) \quad (\text{fractional split to stream 29})$$