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**Removal of Zinc from a Base-Metal Solution Using Ion Exchange at Rustenburg  
Base Metal Refiners**

by

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## ABSTRACT

Anglo American Platinum's expansion project, which aimed at increasing platinum production to 3.5 million oz per annum, necessitated an expansion in the Rustenburg Base Metal Refinery (RBMR) to accommodate the associated increase in the production of base metals (Cu, Ni, and Co). RBMR's name plate capacity increased from 21 000 to 33 000 tonnes of nickel per annum. The expansion project involved various brownfield and greenfield installations and was completed in 2011.

The new circuit and various process additions posed a significant risk to the nickel cathode quality with regard to zinc contamination. Mass balancing of the pre-expansion circuit showed that as much as 50% of the zinc entering the plant would exit through the nickel cathode, thus making it the major bleed for zinc from the circuit. The expansion circuit mass balance showed that although a portion of the zinc would exit through the pressure iron removal residue, this small bleed stream would not be sufficient to ensure that the nickel cathode does not exceed 50 ppm (LME specification). Another factor contributing to the zinc problem was the fact that more Platreef ore, with higher zinc levels, was being mined. These factors indicated that a dedicated zinc removal section was required to ensure a sustainable nickel cathode production containing less than 50 ppm zinc.

The objective of this research project was to find an ion-exchange resin that effectively removed zinc from a base metal solution without any significant loss of the other base metals. The ideal stream to be treated was identified within the circuit and a series of batch and continuous experiments were carried out on the selected stream. The identified stream, containing 68 g/L nickel, 0.14 g/L cobalt and 0.01 g/L zinc, was adjusted to higher concentrations of 0.05 - 0.2 g/L zinc under various experimental conditions. From these experiments, a resin (Lewatit VP OC 1026) and operating conditions were identified. The calculated experimental resin capacity of 5 g zinc per litre resin and operating pH of between 2.5 and 3.0 was used as a design basis for an ion-exchange plant at RBMR. This plant, treating 15 m<sup>3</sup>/h, was built and commissioned in early 2011. Analysis of the first six months of operating data showed that zinc in the nickel cathode was reduced by 40% since the commissioning of this ion-exchange plant and indicated that the plant has the capacity to remove around 80% of the total zinc fed to the refinery

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## GLOSSARY OF TERMS

| Symbol              | Description   | Unit                |
|---------------------|---|---------------------|
| A                   | Cross-sectional area  | m <sup>2</sup>      |
| ACP                 | Anglo Platinum converting process   |                     |
| BV                  | Bed volumes   |                     |
| $C_e$               | Equilibrium metal concentration in solution phase   | mol/m <sup>3</sup>  |
| CIX                 | Continuous ion exchange   |                     |
| $C_o$               | Initial metal concentration in solution phase   | mol/m <sup>3</sup>  |
| CRR                 | Copper removal residue  |                     |
| CRS                 | Copper removal solution   |                     |
| CTF                 | Cobalt treatment filtrate   |                     |
| CuF                 | Copper feed electrolyte   |                     |
| CuR                 | Copper removal  |                     |
| CuS                 | Copper spent electrolyte  |                     |
| CUSUM               | Cumulative sum  |                     |
| $D$                 | Distribution ratio  |                     |
| d                   | Resin bed depth   |                     |
| $D_c$               | Column diameter   | m                   |
| D <sub>2</sub> EHPA | Di(2-ethylhexyl) phosphoric acid or (C <sub>4</sub> H <sub>9</sub> CH(C <sub>2</sub> H <sub>5</sub> ))CH <sub>2</sub> ) <sub>2</sub> POOH |                     |
| df                  | Freeboard height  | m                   |
| di                  | Inert resin depth   | m                   |
| dP                  | Pressure drop   | kPa                 |
| DRC                 | Democratic Republic of Congo  |                     |
| EBCT                | Empty bed contact time  | min                 |
| FBIX                | Fixed-bed ion exchange  |                     |
| H                   | Column side wall height   | m                   |
| IX                  | Ion exchange  |                     |
| $K$                 | Separation factor   |                     |
| $K_L$               | Langmuir constant   | m <sup>3</sup> /mol |
| $I_i$               | Bed volumes to breakthrough   |                     |
| $L_i$               | Bed volumes to saturation   |                     |
| LME                 | London metal exchange   |                     |
| MTZ                 | Mass transfer zone  |                     |
| MTZL                | Mass transfer zone length   |                     |
| NAL                 | Nickel atmospheric leach  |                     |
| NALS                | Nickel atmospheric leach solution   |                     |

|                |   |                   |
|----------------|---|-------------------|
| NCM            | Nickel copper matte                                     |                   |
| NDS            | Nickel dissolution solution                             |                   |
| NiF            | Nickel feed electrolyte                                 |                   |
| NiS            | Nickel spent electrolyte                                |                   |
| NOX            | Nickel non-oxidising leach                              |                   |
| NOXS           | Nickel non-oxidising leach solution                     |                   |
| PGM            | Platinum group metals                                   |                   |
| PIR            | Pressure iron removal                                   |                   |
| PIRS           | Pressure iron removal solution                          |                   |
| PLR            | Primary leach solution                                  |                   |
| PLS            | Primary leach solution                                  |                   |
| ppm            | Parts per million                                       |                   |
| PVL            | Pressure vessel liquor                                  |                   |
| q              | Resin loading capacity (amount of metal on resin phase) | g/L               |
| Q              | Flow rate   | m <sup>3</sup> /h |
| $q_e$          | Metal exchange at equilibrium on resin phase            | mol/kg            |
| $q_{sat}$      | saturated amount of metal loaded on resin phase         | mol/kg            |
| RBMR           | Rustenburg Base Metal Refiners                          |                   |
| SFR            | Service flow rate                                       | BV/h              |
| SLR            | Secondary leach residue                                 |                   |
| SLS            | Secondary leach solution                                |                   |
| tf             | Time to saturation                                      | h                 |
| u              | Superficial velocity                                    | m/h               |
| V              | Volume of solution                                      | m <sup>3</sup>    |
| V <sub>c</sub> | Column volume   | m <sup>3</sup>    |
| V <sub>r</sub> | Resin volume  | m <sup>3</sup>    |
| W              | Weight of dry resin                                     | kg                |
| WCM            | Waterval converter matte                                |                   |
| YTD            | Year to date  |                   |

# 1. INTRODUCTION

Anglo American Platinum's expansion project, which was aimed at increasing platinum production from 2 million to 3.5 million oz of platinum per annum, necessitated an expansion in the Rustenburg Base Metal Refinery (RBMR) to accommodate the associated increase in the production of base metals (Cu, Ni, and Co). RBMR in its previous configuration had a name plate capacity of 21 000 tonnes of nickel per annum, and now has a 33 000 tonnes of nickel per annum capacity. The expansion project involved a brownfield retrofit of some areas, and a greenfield installation of a nickel atmospheric leach step, a pressure iron removal step and selenium/tellurium removal step. The old nickel electrowinning cells were converted to copper electrowinning cells, and a completely new nickel electrowinning cell house was installed. Figure 1-1 indicates the expanded circuit and shows the modifications and new additions that were made to the old circuit.

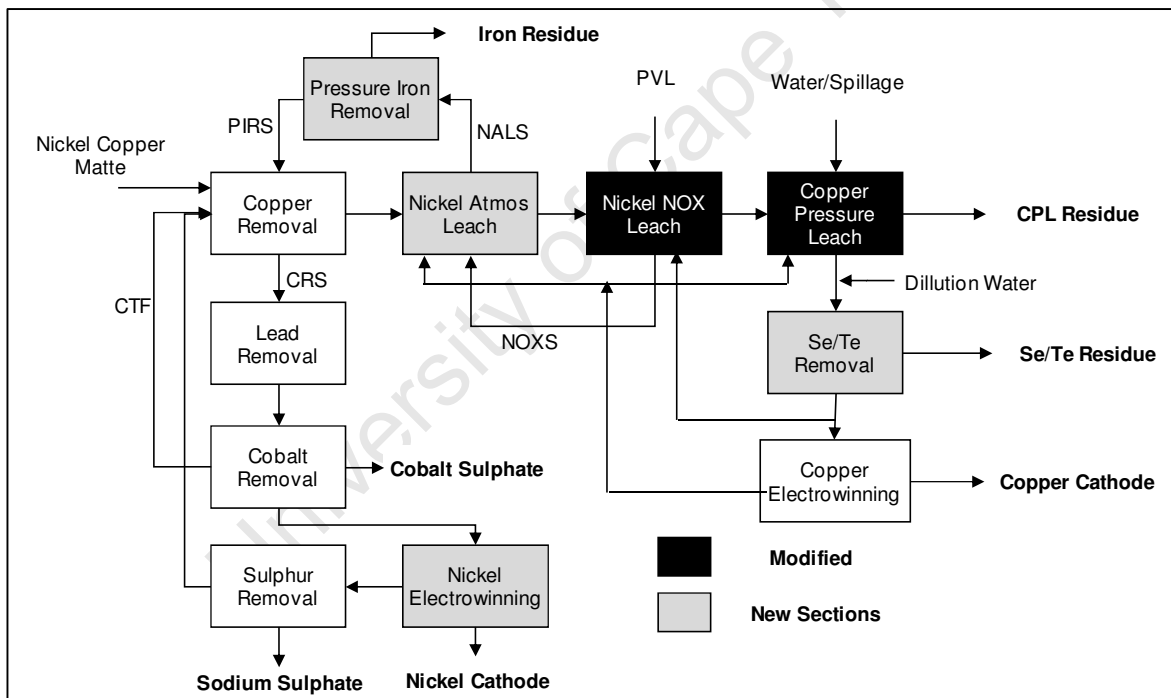


Figure 1-1: RBMR expansion block flow diagram

The circuit consists of three major processes, namely leaching, purification and electrowinning. The feed material, nickel copper matte (NCM), is contacted with primary nickel leach liquor under atmospheric oxidative conditions. The step is called copper removal (CuR). The leach liquor from copper removal reports to the purification step where lead, cobalt, and now zinc are removed before the electrolyte reports to nickel electrowinning section. The copper removal residue (CRR) reports to the nickel leach circuit where it is leached under atmospheric oxidative

(NAL) and pressure non-oxidative conditions (NOX). The acid for leaching is maintained at appropriate levels using spent copper electrolyte. The leach liquor from the nickel leach section reports to copper removal via the new pressure iron removal (PIR) section. Iron is precipitated as jarosite in a pressurised autoclave. The iron-free liquor reports to copper removal and the residue is recycled to the Anglo American Platinum smelter complex. Prior to the introduction of this step the iron was precipitated in the copper leach section. The leach residue from the nickel leach section reports to the copper pressure leach (CPL) section. Here the copper is leached under pressure oxidative conditions in three horizontal Sherritt Gordon type autoclaves. Acid is provided by spent copper electrolyte. The leach residue is sent for toll refining and the copper leach liquor reports to the selenium/tellurium removal section. After removing the selenium and tellurium the liquor is sent to copper electrowinning. Sulphur also needs to be removed from the circuit and this is done by contacting the spent nickel electrolyte with caustic soda in order to form sodium sulphate. The sodium sulphate is crystallised, dried and sold to the market as by-product. The cobalt removed during the nickel purification step is also crystallised and dried. This is then sold as cobalt sulphate crystals.

In order to increase the plant throughput capacity by 53%, the existing equipment needed to be either increased in capacity or optimised such as to achieve the new desired throughput. As indicated by Figure 1-1, some sections were modified and other sections, such as the pressure iron removal (PIR), nickel atmospheric leach (NAL), nickel electrowinning and selenium/tellurium sections were complete new additions. The nickel leach previously consisted of two horizontal Sherritt Gordon autoclaves that were operated under oxidative (compartments 1 & 2) and non-oxidative conditions (compartments 3 & 4). To increase the capacity of this section, the new NAL section was added and the autoclaves were modified to operate entirely under non-oxidative conditions now referred to as the nickel non-oxidative leach (NOX). This essentially split the dual duty of the primary autoclaves and increased the throughput capacity. The copper leach section capacity was increased by introducing 98% oxygen (instead of 32% oxygen enriched air), a flash recycle for heat removal and new agitators for better liquid/gas mass transfer. Under previous copper leach conditions, iron was precipitated as either a hematite or jarosite. The different chemistry and operation of the copper pressure leach (CPL) would not facilitate enough iron removal and thus the pressure iron removal section was added. Iron is precipitated as a jarosite under 6 bar pressure and temperature of 150°C in a SAF2205 horizontal autoclave. The selenium/tellurium capacity was increased to accommodate enough residence time for the removal of these elements. The more aggressive (higher acid and oxygen concentration) copper leach conditions create higher concentrations of selenium/tellurium in solution compared to the old circuit.

The new circuit and process additions posed a substantial risk to the nickel cathode quality with regard to zinc contamination. Mass balancing of the old circuit showed that 50% of the zinc in NCM would exit through the nickel cathode, thus making it the major exit for zinc from the circuit. The rest of the zinc bleeds out through the lead removal press cake, copper cathode and copper leach residue. During normal operation the zinc concentration builds up in the copper removal residue over a period of time. When there are pH excursions on the copper removal reactors, zinc is released into the nickel circuit and eventually ends up in the nickel feed solution to the cell house. The test work for the expansion circuit done by Dynatec (2006) showed that a portion of the zinc will exit through the residue of the new pressure iron removal. This would, however, not be enough to reduce the circulating load. The circulating load is between 80% and 90% of the total zinc fed to the plant, resulting in periodic zinc breakthroughs to the nickel cathode.

Zinc contamination of the nickel cathode has been a recurring problem since the commissioning of the refinery in 1981. As a result of mining more Platreef ore, the zinc concentration fed to the refinery has increased over the years. It is well known that the Platreef ore contains more base metals, and thus significantly more zinc, than the Merensky and UG2 ore that are the primary resource. A step change in the zinc concentration of NCM was observed when the Anglo Platinum converting process (ACP) was commissioned in 2003. This was due to the design of an improved furnace with better off-gas capturing capabilities, which resulted in higher recovery of minor elements, such as zinc, from the off-gas. Work on using ion exchange to remove zinc at RBMR has been tested by various people over the years. The results were promising, but no decision was ever taken to install an ion-exchange plant. The decision was most likely due to economic reasons as well as the increase of the internal nickel cathode zinc limit from 30 ppm to 50 ppm, which is the London Metal Exchange (LME) specification.

During 2009 and 2010, the zinc in the nickel cathodes rose to levels greater than 50 ppm over a period of months. The cathode should typically be sold at a discounted rate if the zinc exceeds 50 ppm but, due to the high demand for nickel at the time it was possible to sell these nickel cathodes at the normal market price. However, if this had not been the case, the company could have lost more than ZAR 40M in revenue during 2009 and 2010 due to the high zinc content. The potential revenue loss was calculated using the LME standard grade price, the price of melting grade nickel (Zn > 50 ppm) and the mass of melting grade nickel produced in that year. This led to an investigation to model the zinc deportment in the RBMR circuit as well as looking at ways to remove the zinc from the circuit.

## 1.1 Research Objective and Approach

The scope and objective of this research project was to propose a cost-effective, efficient and environmentally safe ion-exchange process to bleed zinc from the circuit. The main objective of this research project was to find an ion-exchange resin that will effectively remove zinc from a base-metal solution containing a high concentration of nickel in solution. This first involved selecting the best stream to treat and then performing a series of batch and continuous column experiments on the selected stream. This would then lead into the design of a full-scale ion-exchange plant.

Chapter 2 of this report will discuss the historic zinc deportment and mass balance within the plant. This is followed by Chapter 3, a literature review on ion exchange and its application in hydrometallurgy. Chapter 4 describes the stream and resin selection as well as the experimental methodology. Chapter 5 is a discussion of the test work results and Chapter 6 discusses the design, commissioning and initial operation of the installed ion-exchange plant.

## 2. ZINC DEPARTMENT AND MASS BALANCE

This chapter discusses the zinc deportment within RBMR and sheds some light on the origin of the zinc problem. Using historical plant data, a zinc deportment mass balance was compiled for major streams across the plant and a mass balance model developed to predict new steady-state concentrations should a removal stage be implemented.

Since 2002 the zinc concentration in the Waterval converter matte (WCM) increased by 60% and in the nickel copper matte (NCM) by 50%. The WCM is the product from ACP and contains the platinum group metals (PGM) and base metals. The WCM is treated through a comminution and magnetic separation process to separate the PGMs from the base metals. The non-magnetic portion, NCM, contains the base metals and forms the feed to the base metal refinery. As RBMR had no dedicated zinc-removal stage, the increasing zinc trend had resulted in more frequent and severe zinc breakthroughs to the cathode. The current zinc limit in the cathode is 50 ppm (LME specification), but prior to 1995 the nickel cathode limit for zinc was 30 ppm (plant specification). The internal plant specification was adjusted to the LME specification because the 30 ppm could not be sustained as a result of the zinc increase in WCM.

## 2.1 Historical Data Analysis

Figure 2-1 indicates zinc assay data for WCM from 1994 to 2009. The figure shows individual zinc assay data points as well as a 30-day moving average trend line and linear trend line. The values at the top of the graph represent the yearly average zinc concentrations.

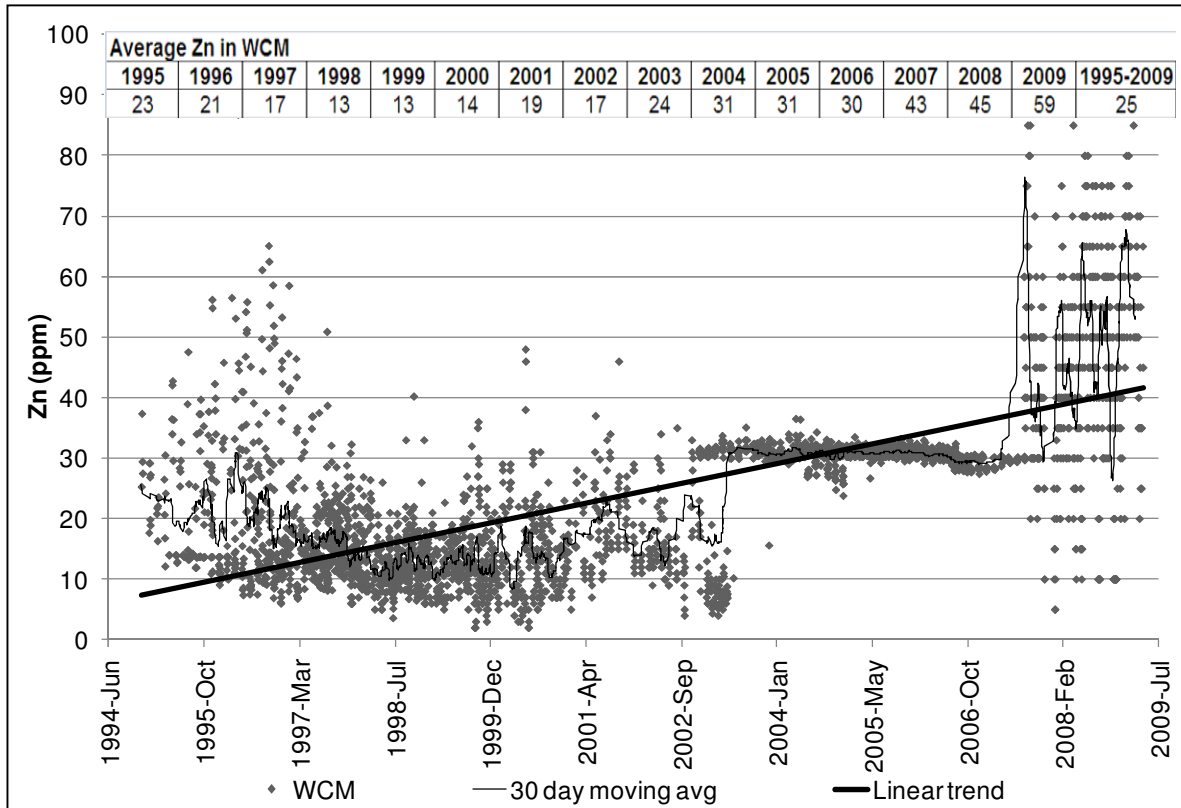
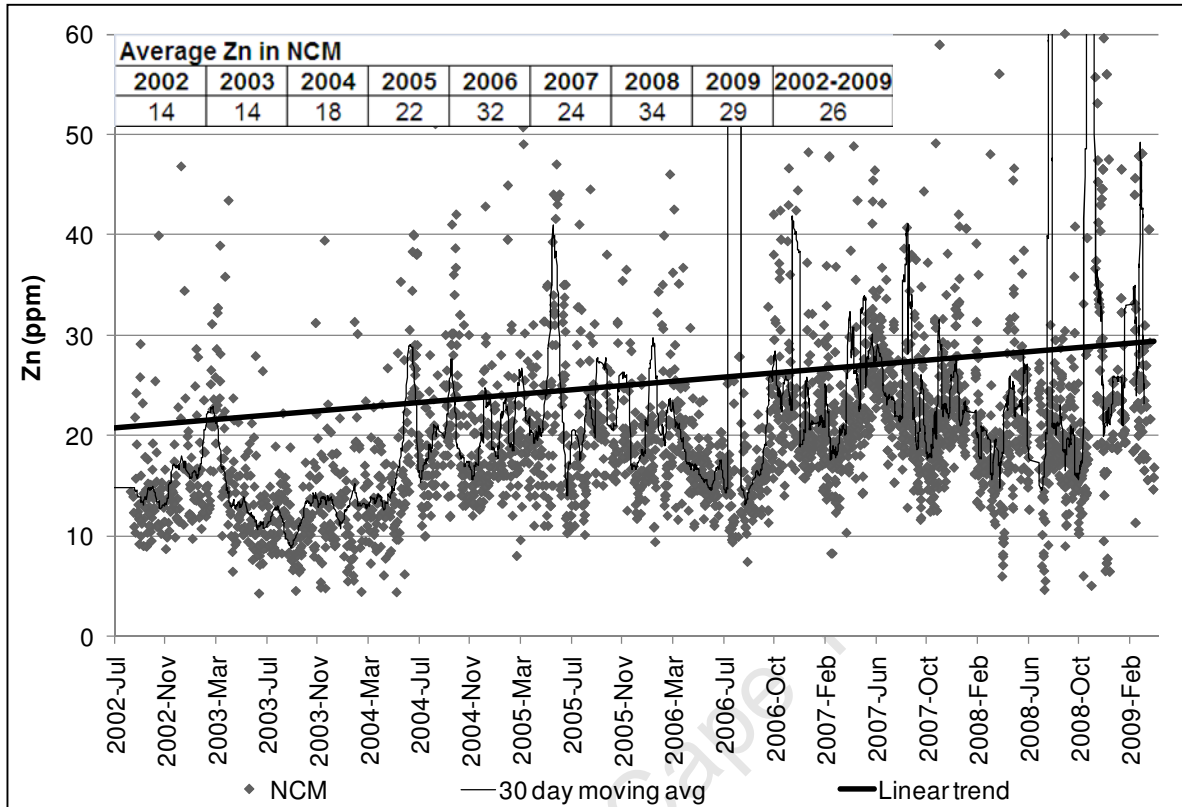


Figure 2-1: Zinc assay in WCM – 1994 to 2009.

It is clear from the data that a step change occurred in mid-2003. This is most likely as a consequence of the Anglo Platinum converting process (ACP) coming online. It is also very suspicious to see that the variability of the data decreased dramatically during the period between 2003 and 2008. It was established during this investigation that the quality control of the zinc analysis on WCM was neglected, and could explain the reduced variability. Looking at the yearly averages as depicted at the top of the graph it is clear that the zinc in WCM more than tripled, from 17 ppm in 2002 to 59 ppm in the first part of 2009.

Figure 2-2 indicates the zinc trend in NCM from 2002 to 2009. It is clear from the graph that there is a large amount of variation in this sample as well. It also looks like a step change occurred around the first quarter of 2004. The yearly averages also indicate the doubling of the zinc concentration from 14 ppm in 2002 to 29 ppm in the first quarter of 2009.



**Figure 2-2: Zinc assay in NCM – 2002 to 2009.**

There should be a direct correlation between the zinc concentration in WCM and NCM. The graphs of WCM and NCM do not correlate as well as expected, but both graphs indicate a significant increase in zinc concentration.

The NCM and nickel cathode zinc concentrations (Figure 2-3) show a distinct correlation. Figure 2-3 shows the individual zinc assays for the nickel cathode from 2002 to 2009. There was a significant increase in zinc in the nickel cathode and similarly to the NCM, it more than doubled since 2002.

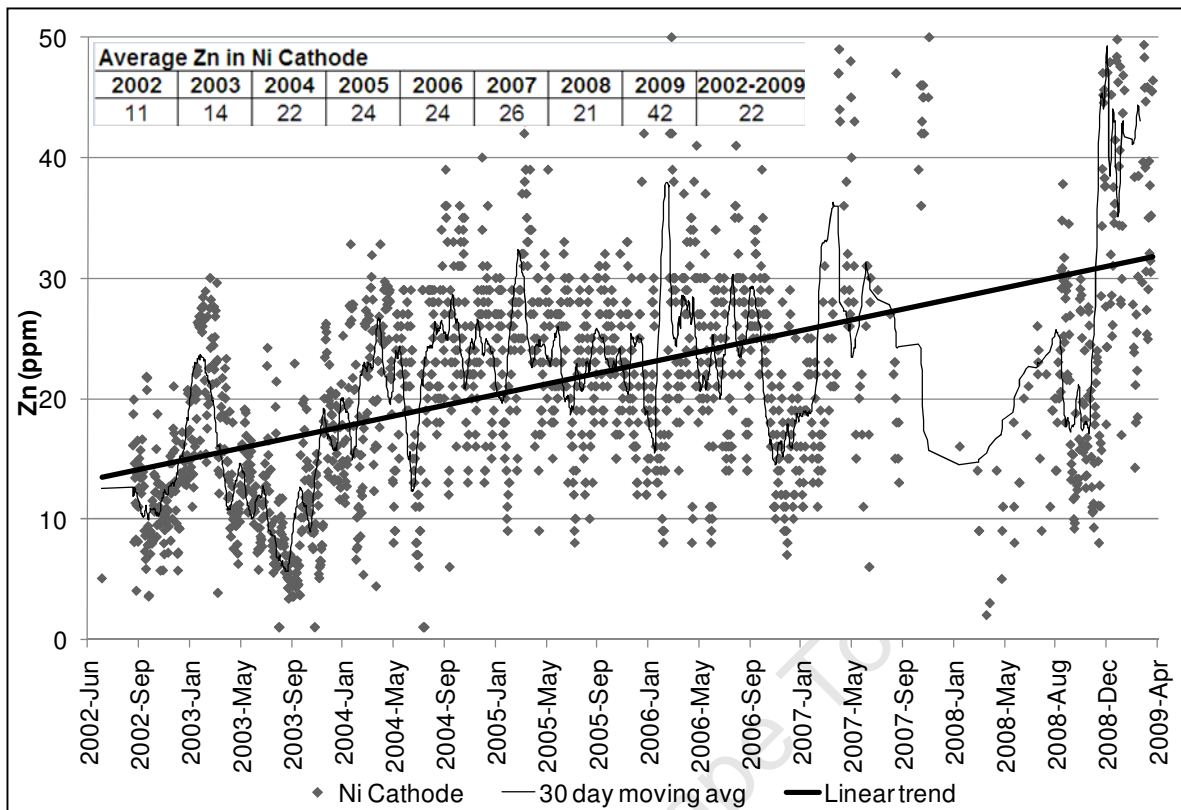


Figure 2-3: Zinc assay in Nickel Cathode – 2002 to 2009.

## 2.2 CUSUM Charts and Analysis

In statistical quality control, the CUSUM (or cumulative sum control chart) is a sequential analysis technique developed by E.S. Page of the University of Cambridge. It is typically used for monitoring change detection (Grigg *et al.*, 2003). This statistical method was used to analyse the historical plant data, in order to establish how a change in one stream will affect the downstream concentrations.

CUSUM charts are constructed by calculating and plotting a cumulative sum based on the data and is explained in Appendix E. The CUSUM chart is interpreted as follows: a segment of the CUSUM chart with an upward slope indicates a period where the values tend to be above average. Likewise, a segment with a downward slope indicates a period of time where the values tend to be below the average. Thus the CUSUM plot will indicate periods of change. It will show whether the data for certain periods were above or below the total data average.

The CUSUM plots following in this section were constructed using all the data available for a specific sample. The chart will indicate the deviation from the long-term average. To ensure

better interpretation of the data, the CUSUM plots for various streams were plotted on the same time line.

Figure 2-4 is a CUSUM plot of the WCM zinc assay data. This plot shows a distinct step change in the WCM zinc concentration around mid-2003 when ACP was commissioned. The positive slope indicates that the values were consistently above the average of 25 ppm.

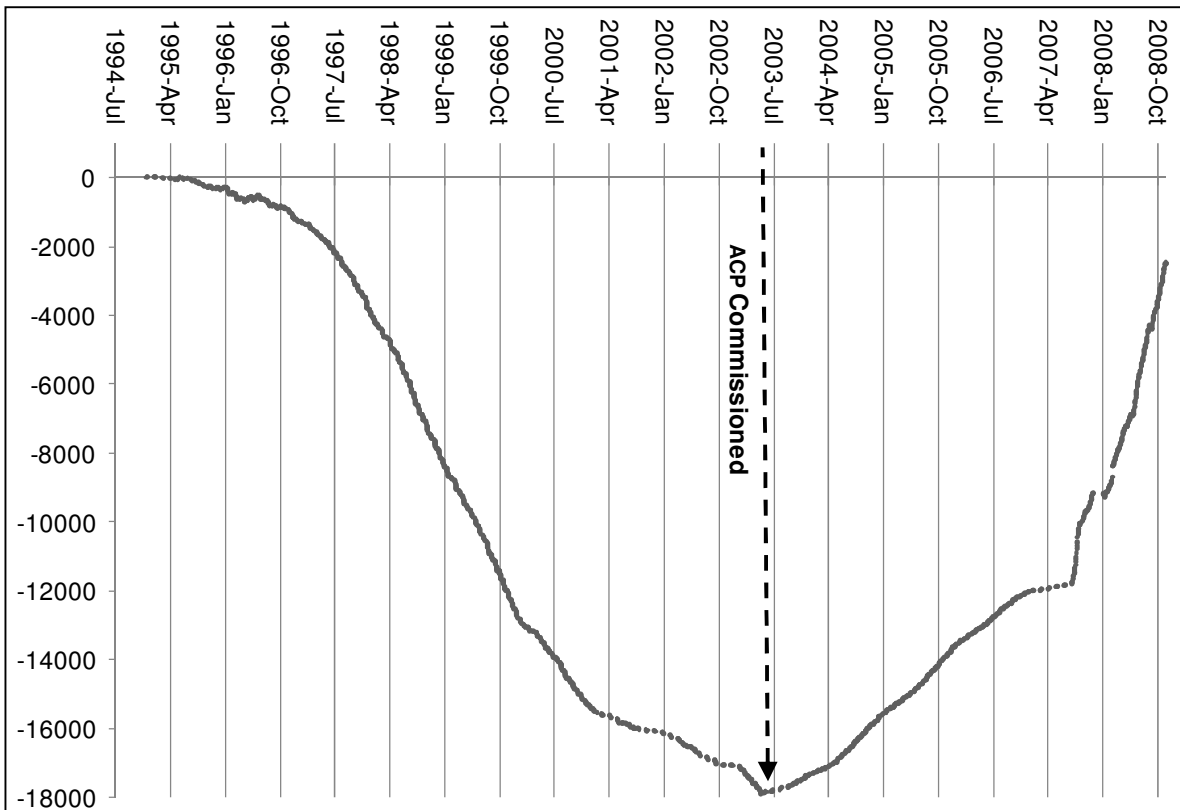
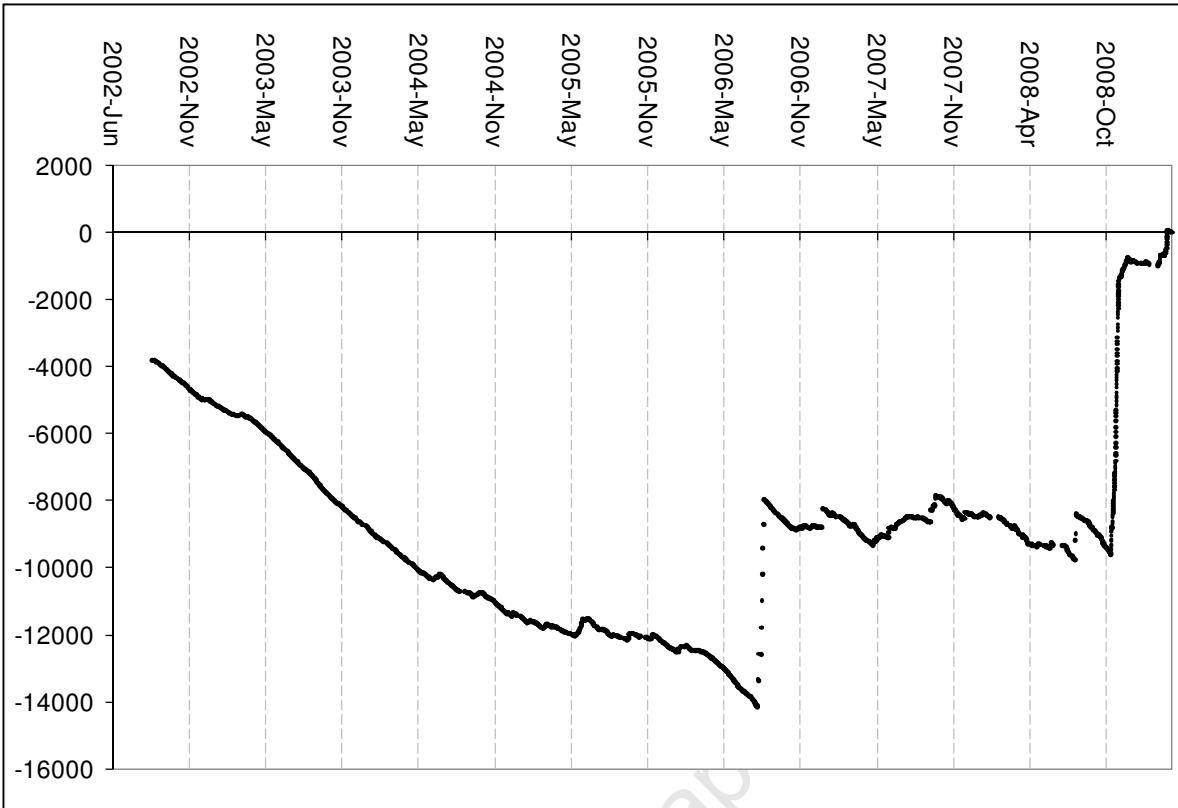


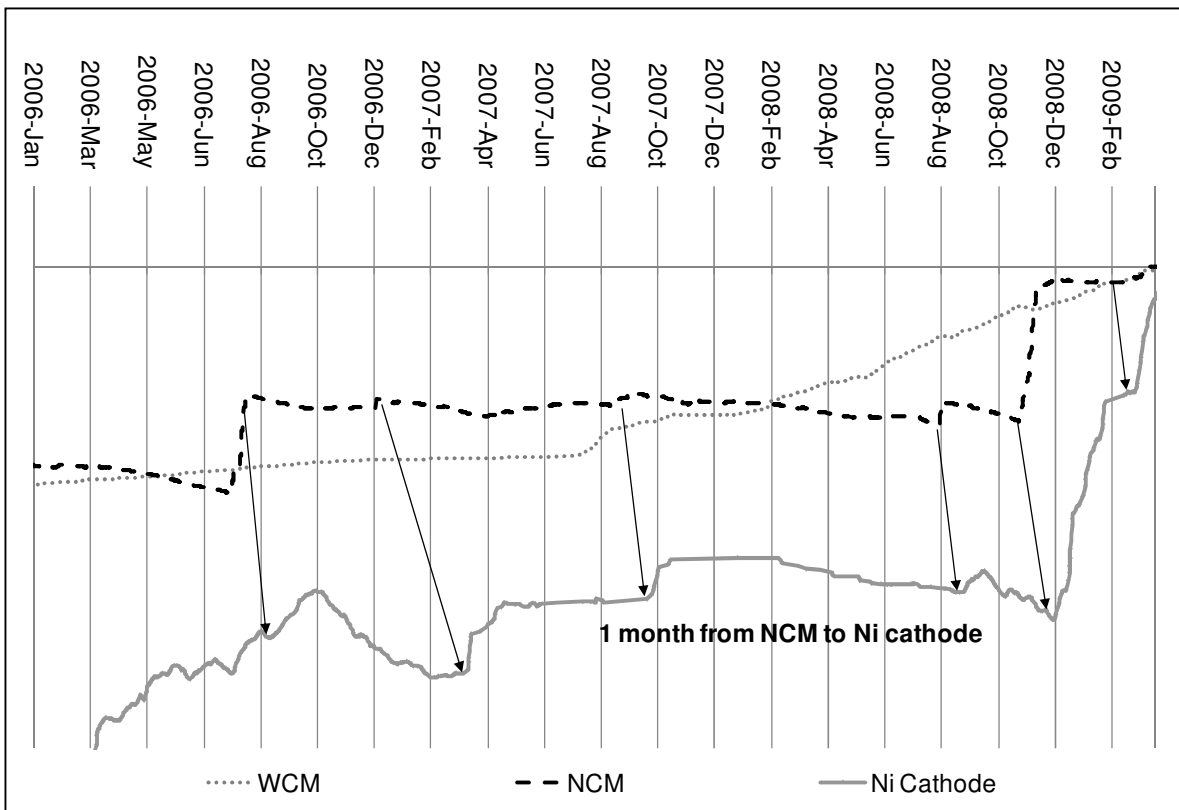
Figure 2-4: CUSUM plot for zinc in WCM – 1994 to 2009.

A similar CUSUM plot of the NCM zinc assays (Figure 2-5) shows distinct step changes towards the end of 2006 and towards the end of 2008. Similar changes were not observed in the WCM CUSUM plot. A negative slope indicates a period where the values were below the average and a positive slope indicates periods where the assays were above the average.



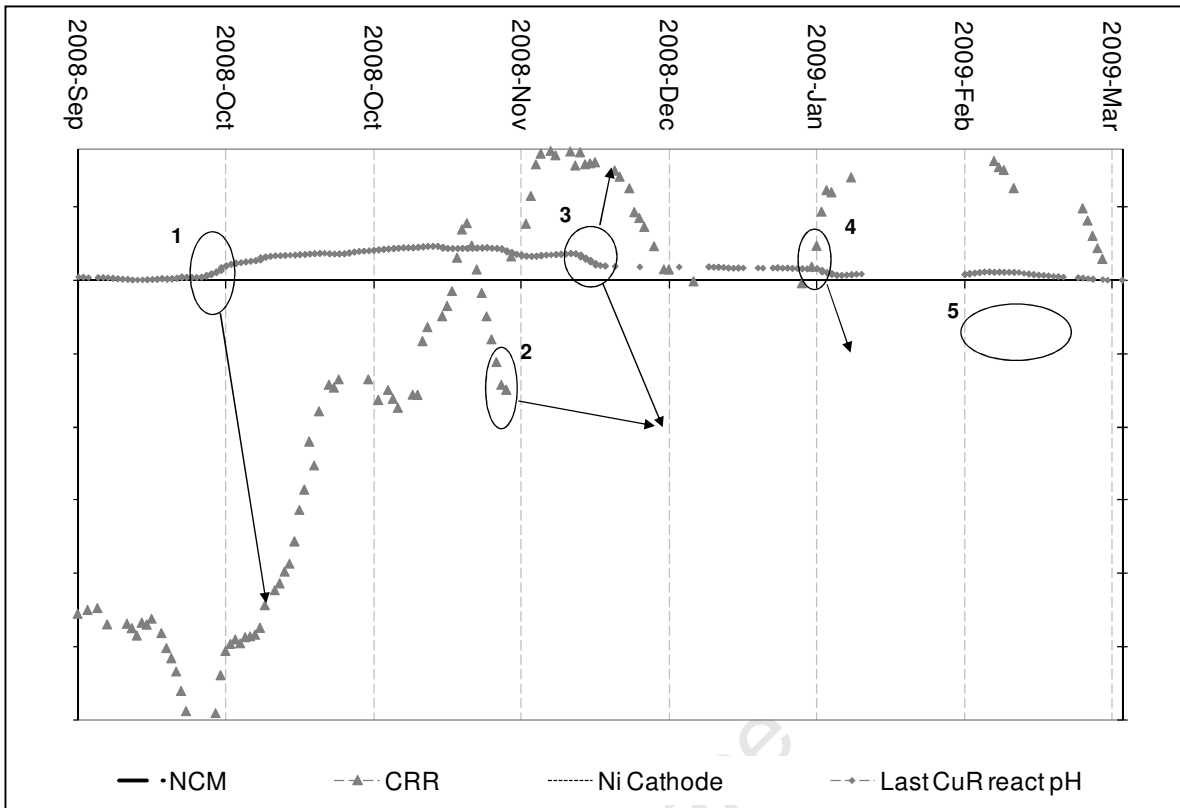
**Figure 2-5: CUSUM plot for zinc in NCM – 2002 to 2009.**

Figure 2-6 is a CUSUM plot for zinc in WCM, NCM and the nickel cathode. This plot helps to establish the time it takes to observe a change in the nickel cathode as a result of a change in NCM. It is clear that when there is an increase of zinc in NCM, about one month later there is a step change of zinc in the nickel cathode. The arrows indicated on Figure 2-6 illustrate this observation. This is also an indication that there is more confidence in the NCM zinc assay compared to that of the WCM zinc assay.



**Figure 2-6: CUSUM plot for zinc in WCM, NCM and Ni Cathode – 2006 to 2009.**

Similarly to Figure 2-6, a number of CUSUM plots for relevant streams were plotted on the same timeline. This is illustrated in Figure 2-7 and highlights five specific events. The streams indicated in Figure 2-7 are: NCM, Copper Removal Residue (CRR), nickel cathode and solution pH in the last copper-removal reactor. Event 1 shows that a slight increase in the pH of the last copper-removal reactor resulted in an increase of zinc in the copper removal residue (CRR). Events 2 and 3 indicates the combination of an increase in zinc in NCM and the pH drop in the last copper-removal reactor, releasing the zinc in CRR, resulting in an increase of zinc in the nickel cathode. Event 4 shows a drop in pH of the last copper-removal reactor resulting in a small zinc increase in the nickel cathode. Event 5 again shows an increase of zinc in NCM that resulted in an increase in the nickel cathode. The CUSUM plots illustrate the build-up of zinc in the copper-removal residue with periodic releases as the pH in the last reactor varies.



**Figure 2-7: CUSUM plot for zinc in various streams to illustrate multiple changes.**

The CUSUM analysis provided a good basis to understand the zinc problem, but further investigation in the form of a zinc department mass balance was required. Section 2.3 discusses the zinc department mass balance and model developed from the mass balance.

### 2.3 Zinc Department Mass Balance and Model

A zinc mass balance was set up for the period March to April 2009. The methodology followed was to collect flow rates and assay data for the major streams. The balance was set up in *Excel* and values with least confidence were adjusted to balance the individual nodes across the circuit as well as the overall circuit. Figure 2-8 illustrates the block flow diagram of the RBMR circuit with the zinc mass-balanced values.

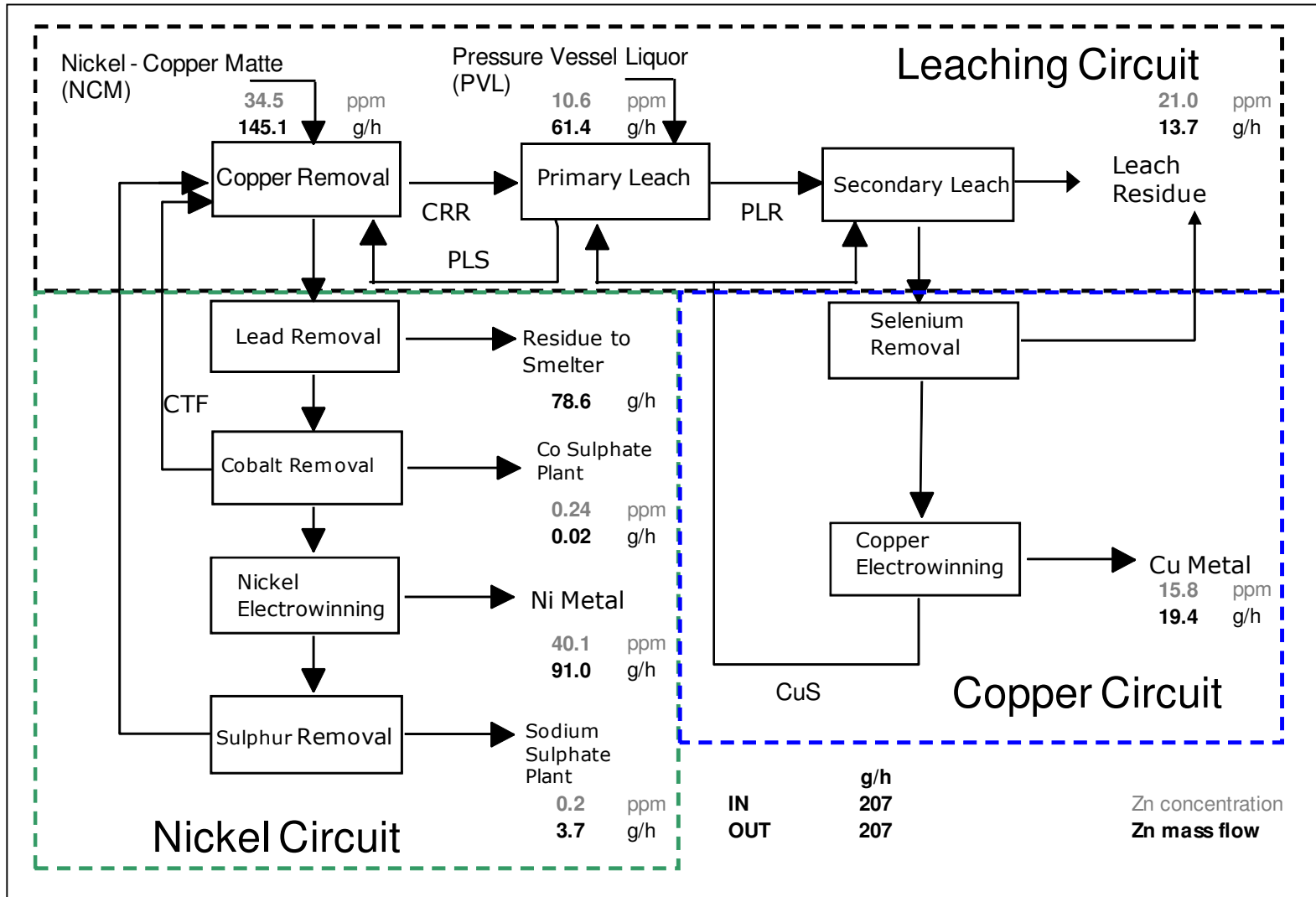


Figure 2-8: Excel model results of zinc mass balance.

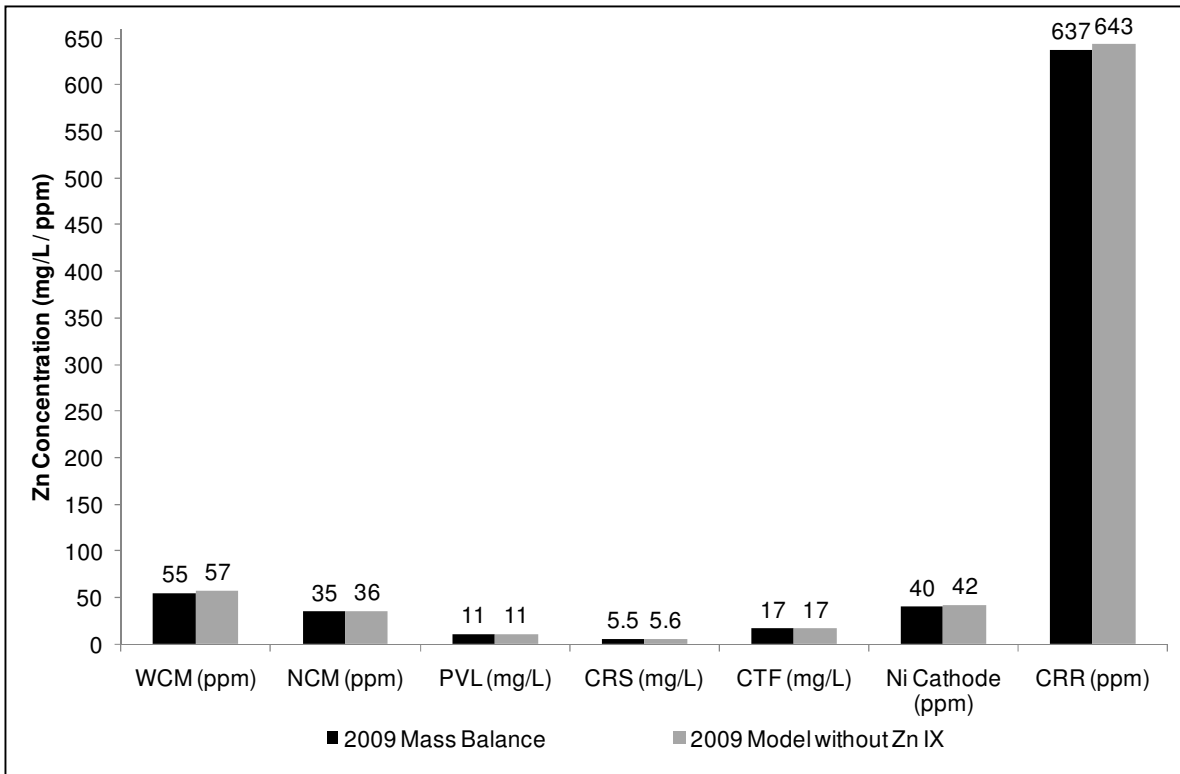
The model was then developed using the distribution ratios from the steady-state mass-balanced data and the distribution model across the smelter to ensure that any zinc recycled to the smelter was accounted for. From Table 2-1 it is clear that the model gave accurate predictions of the zinc department. The only sample that is questionable is CRR, but monitoring of the CRR zinc concentration on a daily basis, showed that it ranges from 200 – 800 ppm. The mass balance and model did not converge at CRR zinc levels of lower than 600 ppm. This and the CUSUM analysis led to the conclusion that the zinc accumulates in the CRR and that it is released periodically as a result of pH fluctuations in the copper removal reactors.

**Table 2-1: Measured, mass balance and modelled zinc assay values.**

| <b>Stream (unit)</b>         | <b>Balance</b> | <b>Model</b> | <b>Measured</b> |
|------------------------------|----------------|--------------|-----------------|
| <b>WCM (ppm)</b>             |                | 58           | 55              |
| <b>NCM (ppm)</b>             | 35             | 36           | 35              |
| <b>PVL (mg/L)</b>            | 11             | 11           | 11              |
| <b>CRR (ppm)</b>             | 660            | 643          | 205-800         |
| <b>CRS (mg/L)</b>            | 6              | 6            | 6               |
| <b>PLS (mg/L)</b>            | 63             | 63           | 63              |
| <b>PLR (ppm)</b>             | 53             | 53           | 55              |
| <b>Pb Removal Sol (mg/L)</b> | 5              | 5            |                 |
| <b>CTF (mg/L)</b>            | 17             | 17           | 25              |
| <b>NiF (mg/L)</b>            | 3              | 3            | 3               |
| <b>Ni Cathode (ppm)</b>      | 40             | 42           | 40              |
| <b>NiS (mg/L)</b>            | 2              | 2            |                 |
| <b>NDS (mg/L)</b>            | 2              | 2            | 4               |
| <b>SLS (mg/L)</b>            | 16             | 16           |                 |
| <b>SLR (ppm)</b>             | 21             | 19           |                 |
| <b>CuS (mg/L)</b>            | 26             | 26           | 26              |
| <b>Cu Cathode (ppm)</b>      | 16             | 16           |                 |

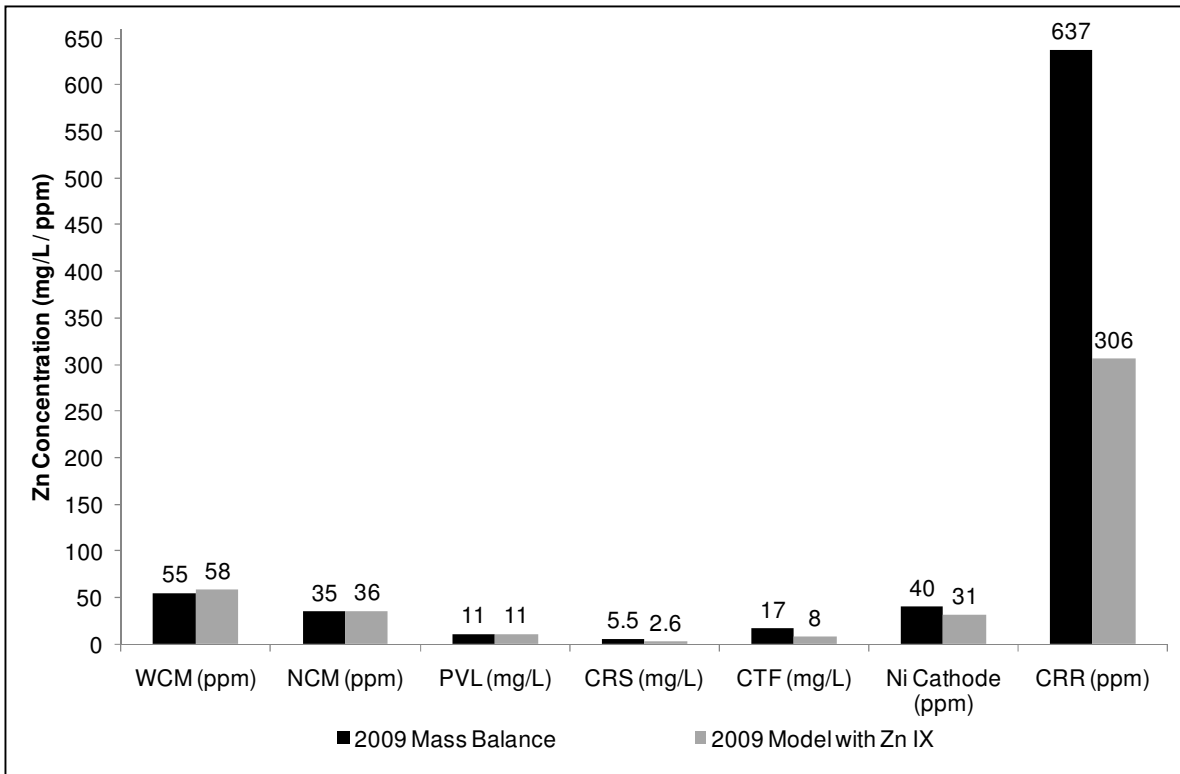
This mass balance and model assisted in obtaining a fundamental understanding of the zinc department across the circuit. Using the model it was determined how much zinc needed to be bled from the circuit to ensure that the nickel cathode always remained within specification (less than 50 ppm).

Figure 2-9 is another illustration of the comparison of the mass balanced values with the modelled values for the major streams. This shows that the model can be used to predict the zinc department across the circuit.



**Figure 2-9: Zinc department mass balance and modelled data.**

Figure 2-10 shows the model prediction, should a zinc-removal stage, on the cobalt treatment filtrate (CTF) stream, be included. The model also accounted for the recirculation of zinc from the smelter. This graph illustrates that the average zinc in the nickel cathode is expected to be reduced by 25%. The model was set up with the assumption that 90% of the zinc can be removed from the CTF stream. This zinc stream would be routed to the effluent treatment plant where zinc would be precipitated as a hydroxide and sent to the smelter complex to recover any entrained nickel or copper. The recovery of zinc to WCM, across the smelter, was assumed to be 1%, based on previous work done on the minor element department by Hundermark (2007). The mass balance thus included the subsequent zinc recycled (1% of the 90% removed) from the smelter. This results in a nett removal of zinc from the RBMR circuit.



**Figure 2-10: Zinc deportment mass balance illustrating proposed zinc removal.**

The model thus showed that a partial bleed of zinc, via the CTF stream, from the circuit would make it feasible to achieve a consistent nickel cathode specification of below 50 ppm.

Based on this work and the potential revenue loss, as calculated in Chapter 1, it was decided to approve the zinc ion exchange research project in 2009. Although the CTF stream seemed to be the ideal position for the bleed stream some other streams were also considered, and this is discussed in Section 4.2.

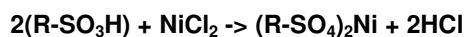
### 3. LITERATURE REVIEW AND BACKGROUND THEORY

This chapter discusses the chemistry and various research studies done on ion exchange, specifically on zinc ion exchange.

Ion exchange can be defined as a reversible exchange of ions between a solid (the resin) and a liquid (the metal-containing solution), during which there is no substantial change in the structure of the solid. The resin is generally a hydrocarbon polymer, such as polystyrene, which has been functionalised by the attachment of an ionisable group. There are five main classes of resin (Nicol, 2003):

- Strong- and weak-acid exchangers (which complex with cationic species);
- Strong- and weak-base exchange resins (which complex with anionic species);
- Chelating resins.

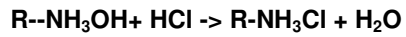
**Strong-acid cation resins** are so named because their chemical behaviour is similar to that of a strong acid. The resins are highly ionized in both the acid (R-SO<sub>3</sub>H) and salt (R-SO<sub>3</sub>Na) form. They can convert a metal salt to the corresponding acid by the following reaction:



The hydrogen and sodium forms of strong-acid resins are highly dissociated and the exchangeable Na<sup>+</sup> and H<sup>+</sup> are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. These resins would be used in the hydrogen form for complete deionisation; they are used in the sodium form for water softening (calcium and magnesium removal). After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be converted to the sodium form with a sodium chloride solution (Ion Exchange, 2008).

In a **weak-acid cation resin** the ionisable group is generally a carboxylic acid (COOH) as opposed to the sulphonic acid group (SO<sub>3</sub>H) used in strong-acid resins. These resins behave similarly to weak organic acids that are weakly dissociated. Weak-acid resins exhibit a much higher affinity for hydrogen ions than do strong-acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong-acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid. The degree of dissociation of a weak-acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH (Ion Exchange, 2008).

**Strong-base anion resins** are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH<sup>-</sup>) form for water deionization. They will react with anions in solution and can convert an acid solution to pure water (Ion Exchange, 2008).

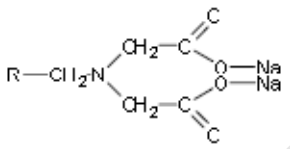
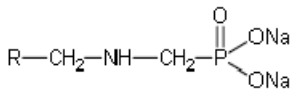
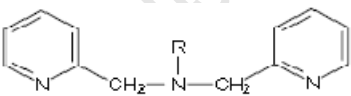
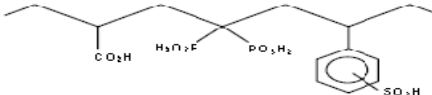


Weak-base anion resins are like weak-acid resins, in that the degree of ionisation is strongly influenced by pH. Consequently, weak-base resins exhibit minimum exchange capacity above a pH of 7.0 (Ion Exchange, 2008).

**Chelating resins** have greater specificity for various ions because their loading properties are based on the nature of complexation between the resin functional group and the ion. Some examples of resin functionalities and their applications are given in Table 3-1.

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**Table 3-1: Functionalities of ion-exchange and chelating resins (adapted from Nicol, 2003)**

| Type                              | Functional Group  | Applications   |
|-----------------------------------|---|--|
| <b>Gel and macroporous resins</b> |   |  |
| Strong acid (sulphonic)           | -SO <sub>3</sub> H  | Selectivity based on many factors, including charge and size of cation: M(III) > M(II) > M(I). Fast kinetics of loading, but low selectivity. Used for water treatment and scavenging. |
| Weak acid (carboxylic)            | -COOH   | Loading and elution dependent on pH and pK <sub>a</sub> of functional group.   |
| Strong base                       | -NR <sub>3</sub> X  | As for strong acid, but with anions  |
| Weak base                         | NR <sub>2</sub>   | Loading and elution dependent on pH. Needs to be protonated before use.  |
| <b>Chelating resins</b>           |   |  |
| Iminodiacetic acid                |    | Removal of heavy metals from high ionic strength solutions. Selectivity depends on pH. M(III) can be stripped with strong acid.  |
| Aminophosphonic acid              |  | Used for removal of Cu and Zn from Co electrolytes. Strongly adsorbs M(III) ions that cannot be stripped with strong acid alone.   |
| Picolylamine                      |  | Removal of Ni from Co electrolytes. Slow loading kinetics, but elution is rapid. Expensive.  |
| Diphonix                          |  | Removal of Fe(III) from Cu electrolytes in strong acid.  |

### 3.1 Cation Exchange

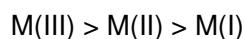
Most base metals exist as cations in sulphate media – the most common matrix in which hydrometallurgical processes are carried out. In this case, strong- and weak-acid resins are generally used for ion exchange.

In contrast to the use of liquid ion exchange (or liquid-liquid extraction), the adsorption of base-metal ions from high ionic strength sulphate media by ion-exchange resins has not been intensively studied. Many applications relating to the clean-up of waste streams and water

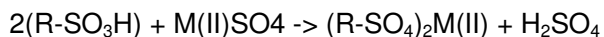
treatment are documented, but the removal of trace elements from concentrated electrolytes in hydrometallurgical applications has started to receive attention only relatively recently. There are also very few commercial applications of ion exchange in hydrometallurgy, although this is now starting to change rapidly as this technology becomes more well known and understood. Some functional groups that have been used in base metal applications are presented in the following sections (Sole & Creese, 2002).

### 3.1.1 Sulphonic-Acid Functionality

The order of selectivity of strong-acid cation exchangers containing the sulphonic-acid group (see Table 3-1) is related to the charge on the cation:



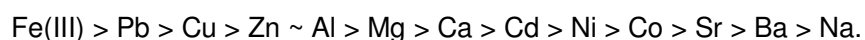
The generalised reaction is as follows:



All transition metal ions are adsorbed with fast kinetics. These resins are, however, fairly non-selective, and so may be useful as scavenging resins for clean-up of dilute solutions but are not expected to be used for other separations.

### 3.1.2 Aminophosphonic-Acid Functionality

Aminomethylphosphonate-containing resins have both acidic and chelating properties, but react as medium-acid strength cation exchangers. Aminophosphonic acid resins (such as Rohm & Haas's Duolite C747 and C467, Purolite's S950 and S940, or Dow's Dowex APA-1) have the following selectivity sequence for divalent metal cations:



These resins are suited to the removal of small quantities of copper and zinc from nickel or cobalt electrolytes. One problem, however, is that this resin functionality suffers from the irreversible loading of Fe(III) and aluminium that cannot be removed by conventional eluant compositions ( $\sim 150 \text{ g/L H}_2\text{SO}_4$ ), and so poisoning of the resin by these species occurs with time. A similar, but less severe problem occurs with loading of Co(III). No suitable elution procedure has yet been devised to overcome this limitation of the resin in hydrometallurgical applications. It

is therefore important to quantitatively remove trace amounts of these species from the feed solution to such an ion-exchange circuit. The kinetics of loading is not as fast as those of sulphonic acid resins, but is typical of medium- and weak-acid resins. Table 3-2 indicates the minimum pH for the extraction of various cations by Purolite S950.

**Table 3-2: Minimum pH required for the extraction of cations by Purolite S950 (Sole & Creese, 2002).**

| Cations    | pH    |
|------------|-------|
| Cu, Pb     | > 2.0 |
| Zn         | > 2.5 |
| Cd, Ca     | > 3.0 |
| Mg, Ni, Co | > 4.5 |

Purolite S950 was successfully used in the piloting of the flow sheet for the Kakanda project in DRC (Democratic Republic of Congo) for the removal of trace amounts of copper (~ 70 mg/L) and zinc (~ 2 mg/L) from a cobalt advance electrolyte (50 g/L Co) prior to electrowinning using a lead-lag fixed bed ion exchange configuration (Dry *et al.*, 1998; Wyethe & Kotze, 2000).

### 3.1.3 Iminodiacetic Acid Functionality

These resins include Rohm & Haas's Amberlite IRC 748, Lanxess's TP207 and TP208, and Purolite's S930. They are recommended for the removal of heavy metals from high ionic strength electrolyte solutions. The selectivity of the resin for a particular metal ion depends on its concentration, the presence of other species, and the acidity. Illustrative selectivity measured under acidic conditions is shown below:

pH 2: Fe(III) > Cu(II) > Ni(II) > Cd(II) > Fe(II) > Mn(II) > Zn(II) > Al(III) > Mg(II) > Ca(II)

pH 4: Cu(II) > Pb(II) > Ni(II) > Zn(II) > Cd(II) > Co(II) > Fe(II) > Mn(II) > Ca(II)

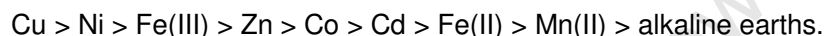
The extraction of trivalent ions by these resins is strong, and these elements require strong acids and elevated temperatures (> 50°C) for their elution. Special care is required to avoid any Co(III) in solution as it will be strongly adsorbed and will tend to damage the functionality of the resin during desorption with dilute acid.

The Goro (now Vale New Caledonia) process employs an Iminodiacetic-acid resin for the removal of trace amounts of copper from the nickel sulphate electrolyte ahead of the CYANEX 301 liquid-liquid extraction circuit (Mihaylov *et al.*, 1995; 2000).

An important advantage of this resin type in comparison with those of diamminophosphonic acid functionality is that no irreversible fouling by iron occurs. Any iron present in solution is loaded onto the resin, but is readily eluted by sulphuric acid (Sole & Creese, 2002).

### 3.1.4 Picolyamine Functionality

The selectivity order for this resin for selected metal cations is:



The kinetics of cobalt and nickel loading are very slow, requiring half-times of 30 to 80 minutes, depending on the pH. Elution is rapid. This resin can be used for the removal of copper from nickel solution; however copper is only poorly eluted with acid, and requires the use of ammonia for effective stripping of the resin. The resin has been more typically employed for the removal of nickel from cobalt electrolytes at pH 2.3. It is eluted with H<sub>2</sub>SO<sub>4</sub> and then neutralised with ammonium or sodium hydroxide (Rao *et al.*, 1993).

### 3.1.5 Diphonix Functionality

The Diphonix resin, manufactured by Eichrom Technologies Inc., is a gel-type resin with selectivity for metal ions over cations such as calcium, magnesium, and sodium. The main exchange site is a substituted diphosphonic acid, while the secondary sites are sulphonic-acid groups. A particular advantage of this resin is that complexation takes place under conditions of high acid strength (Sole, 2000). It has been commercially implemented for the removal of Fe(III) from copper electrolytes, and tested for Fe(III) removal from zinc electrolytes (Xue *et al.*, 2001).

### 3.1.6 Organic Extractant Impregnated Resins

Current ion exchange resins have the major drawback of low selectivity in the extraction of transition metals versus alkali metal ions. Furthermore, the development of highly selective chelating ion-exchange resins entails a very tedious and time-consuming search for highly selective functional groups (Cortina *et al.*, 1994). In order to overcome these difficulties, the idea

of impregnating selective extractants into low cross linked polystyrene beads and using such resins for selective separation of ions has been proposed as an alternative approach. Two approaches were developed in the preparation of impregnated resins. The first approach direct adsorption of the extractant into macroporous polymeric supports, proposed by Warshawsky (1975), to produce solvent impregnated resins; and the second approach involved polymerization of styrene and divinylcopolymers in the presence of the extractant, developed by Kroebe and Meyer (1975) at Bayer. Although numerous extractants can be used in solvent-impregnated resins, the extractants available in the impregnated resins type are at present limited to phosphoryl compounds namely: tributylphosphate, di(2-ethylhexyl)phosphoric acid and di(2,4,4-trimethylpentyl) phosphinic acid (Cortina et al, 1994).

Solvent impregnated resins bridge the gap between solvent extraction and ion exchange. They combine the advantages of ion exchange for processing very dilute solutions with the specific extraction properties of extractants. They also combine the fast mass transfer rates, high distribution and selectivity factors characteristic of the extractants dissolved in a liquid organic phase, with the simplicity of equipment and operation distinctive to ion exchange technology (Cortina et al, 1994). Consequently, these resins are very suitable for metal separation and recovery (Warshawsky, 1981; Tavlarides et al 1987)

### **3.2 Zinc Ion-Exchange Resins and Applications**

Ion exchange is commonly used in a number of industries, including water purification, food, catalysis, chemicals processing, and production of pharmaceuticals. It also plays an increasingly important role in the hydrometallurgical industry for the purification, separation, recovery and scavenging of metals. In some applications, ion exchange provides a unique solution, while in other applications it competes with other processing options, primarily liquid-liquid extraction and precipitation. Hence, ion exchange has to provide a more cost-effective solution in order to be considered on a commercial scale. The primary limitations around the use of ion exchange for hydrometallurgical applications include relatively low capacity, mechanical stability, fouling, selectivity, and wash water requirements when used for high grade applications. When ion exchange is being considered for the removal of a specific impurity, its position in the overall flow-sheet is a critical consideration (Kotze, 2012). Ion exchange is the preferred separation method to use when the concentration of the metal to be removed is between 1 mg/L and 500 mg/L (Sole, 2008). Unlike most liquid-liquid extraction processes, ion exchange does not require pH adjustment during the process and complete automation of the process is possible. The footprint for ion exchange is also significantly less than liquid-liquid extraction and precipitation circuits. The fire risk of combustible liquid-liquids, used in liquid-liquid extraction, is also avoided

when using ion exchange processes. The following section discusses research studies and industrial applications for the removal of zinc using various ion-exchange resins.

Simpson and Laurie (1998) investigated various ion-exchange resins to remove zinc from zinc-rich waste liquors. Selectivity ratios for various metals were developed for each of the 12 resins. Table 3-3 indicates the resins used during the investigation.

**Table 3-3: Summary of the resins used in Simpson and Laurie (1998).**

| Resin               | Supplier | Type                | Functional Group                 |
|---------------------|----------|---------------------|----------------------------------|
| Chelex 100          | Sigma    | chelating           | iminodiacetic                    |
| Duolite C467        | Supelco  | chelating           | aminophosphonic                  |
| Duolite GT73        | Supelco  | chelating           | thiol                            |
| Diaion CR-20        | Supelco  | chelating           | polyamine                        |
| Lewatit VP OC 1026  | Lanxess  | organic-impregnated | *D <sub>2</sub> EHPA-impregnated |
| Lewatit TP207       | Lanxess  | chelating           | iminodiacetic                    |
| Metalfix Chelamine  | Fluka    | chelating           | polyamine                        |
| Metalfix Chelosolve | Fluka    | chelating           | polyamine-acetic                 |
| Purolite C100H      | Purolite | strong acid         | sulphonate                       |
| Purolite C105       | Purolite | weak acid           | carboxylic                       |
| Purolite C160       | Purolite | strong acid         | sulphonate                       |
| Purolite S930       | Purolite | chelating           | iminodiacetic                    |

\*Di(2-ethylhexyl)phosphoric acid)

The feed solution for the experiments was an industrial chloride waste liquor solution with concentrations as noted in Table 3-4.

**Table 3-4: Composition of zinc-rich waste liquor (Simpson & Laurie,1998)**

| Metal | Concentration (mg/L) |
|-------|----------------------|
| Zn    | 480 000              |
| Pb    | 563                  |
| Cu    | 3                    |
| Ni    | 58                   |
| Co    | 1                    |
| Cd    | 9                    |
| Fe    | 9                    |

From the various experiments, it was found that Lewatit VP OC 1026 and Purolite S930 were the most selective for zinc under various impurity regimes. Table 3-5 indicates the molar ratios of the eluate stream for the two resins.

**Table 3-5: Mole ratios of metal in the eluate for the most selective resin (Simpson & Laurie, 1998)**

| Resin   | Zn/Pb | Zn/Cu | Zn/Co  | Zn/Ni | Zn/Cd   |
|---|-------|-------|--------|-------|---------|
| Lewatit VP OC 1026 <sup>a</sup>   | 3 716 | 1 857 | 10 555 | ∞     | 235 197 |
| Purolite S930 <sup>b</sup>  | 691   | 48    | ∞      | ∞     | 22 282  |
| Initial ratios Zn/Pb = 2 716, Zn/Cu = 1 555, Zn/Co = 4 326, Zn/Ni = 7 181, Zn/Cd = 82 538 |       |       |        |       |         |
| <sup>a</sup> Ni below detection limit   |       |       |        |       |         |
| <sup>b</sup> Ni & Co below detection limit  |       |       |        |       |         |

Of all the resins studied by Simpson and Laurie (1998), Lewatit VP OC 1026 showed the greatest selectivity for zinc. Fortunately, the waste liquor had low levels of iron which would otherwise be extracted in preference (Juang & Chen, 1997). The selectivity for zinc mirrors work carried out by others using resins containing D<sub>2</sub>EHPA (Cortina *et al.*, 1994; 1995).

Ion exchange using an aminophosphonic acid resin has been considered for the simultaneous removal of copper and zinc for numerous cobalt refineries in the DRC and Zambia. This included the Kakanda tailings project in the DRC, which tested Purolite S950 (Dry *et al.*, 1998; Wythe & Kotze, 2000). Bulong Nickel (now closed) implemented this technology successfully on their cobalt refinery in Kalgoorlie, Western Australia (Mayze, 1999). Swartz *et al.* (2009) also recommended the simultaneous removal of copper and zinc, using an aminophosphonic acid resin, as the basis for a zinc removal step in the purification of cobalt electrolytes. This is typically done in a fixed-bed column with a lead-lag configuration.

Numerous studies on zinc ion exchange have also been conducted at RBMR. The main streams focused on were the primary leach solution, cobalt treatment filtrate and the nickel electrowinning feed solution. The internal RBMR reports by Perry & Macintosh (1980), Kirgin (1984), Clayton (1989), Groenewegen (1990), Przywitowski (1992) and Evert (1995) showed promising results and the resin that was largely used was Lewatit VP OC 1026. Perry and Macintosh (1980) from Johannesburg Consolidated Investment Company (JCI) conducted test work on primary leach solution from RBMR. They tested Organic-impregnated and Duolite resins and concluded that the organic-impregnated resin, Lewatit VP OC 1026, was more efficient in removing zinc from a nickel sulphate solution.

From the above-mentioned work, Kirgin (1984) investigated ion exchange to remove zinc from the primary leach solution (PLS) and cobalt treatment filtrate (CTF). The organic-impregnated resin, Lewatit VP OC 1026, was used because of its high selectivity for zinc and its commercial use for zinc removal from cobalt solutions at the INCO refinery (Swami, 1993). Kirgin concluded that Lewatit VP OC 1026 was able to reduce the PLS and CTF zinc concentration from 10-40 mg/L to less than 1 mg/L. The effect of ferric ions on the resin's loading capacity was also investigated and it was found that it drastically reduced the loading capacity by as much as 100 times (depending on the ferric concentration). It was also found that copper (10 g/L) and ferrous ions (2 g/L) reduce the loading capacity by between 30%–40%.

Five years later, Clayton (1989) investigated the removal of zinc using ion exchange. Clayton's test work looked at treating the nickel electrowinning feed or primary leach solution. The effects of Fe(II), Fe(III) and Cu(II) were investigated. Clayton tested three resins, Lewatit VP OC 1026, Purolite S940 and Duolite C467. The Lewatit resin displayed the best loading capacity for zinc (3.72 g Zn/L resin) and was thus used in further experiments. The results in Table 3-6 indicate the effect of copper and iron for the Lewatit resin. The conclusion was that the removal of zinc from the circuit using ion exchange is feasible and that Lewatit VP OC 1026 extraction trends corresponded to published data. It was also noted that Fe(III) is a critical impurity that could limit the extraction capacity of the resin.

**Table 3-6: Effect of impurities on Lewatit VP OC 1026 loading capacity (Clayton, 1989).**

| Impurity | Concentration (mg/L) | Reduction of capacity (%) |
|----------|----------------------|---------------------------|
| Fe(III)  | 12                   | 12                        |
|          | 250                  | 88                        |
| Cu(II)   | 1000                 | none                      |
|          | 10000                | 40                        |
| Fe(II)   | 500                  | none                      |
|          | 5000                 | 73                        |

Groenewegen (1990) continued with the work done by Clayton and carried out test work to define the optimum parameters. The primary leach solution was chosen for safety, should a breakthrough occur in the electrowinning feed. The redox potential of the test solution was adjusted with SO<sub>2</sub> and peroxide (H<sub>2</sub>O<sub>2</sub>) to reduce any ferric ions in solution. He concluded that very little adsorption takes place at a pH below 2.5.

During 1992 Przywitowski (1992) continued with test work on the primary leach solution using Lewatit VP OC 1026. Przywitowski concluded that PLS must be filtered so that the solution contains less than 10 mg/L solids to ensure that the resin is not blocked. The ferric ions must be

controlled to levels below 50 mg/L (redox 200 -250 mV, Ag/AgCl electrode) and the pH must be maintained between 2.5 - 2.9.

A report by Evert (1995) included a preliminary design for an ion-exchange plant to treat the cobalt treatment filtrate. The proposed design was to treat the 10 m<sup>3</sup>/h CTF stream, using Lewatit VP OC 1026 resin in a 2 m<sup>3</sup> ion-exchange column with a flow rate of 5 bed volumes (BV)/h. The column would be eluted with 10% sulphuric acid and the eluate sent to the effluent plant for treatment. The raffinate would be sent to the PLS pH adjustment tank. The design was not implemented, probably due to unfavourable economics at the time.

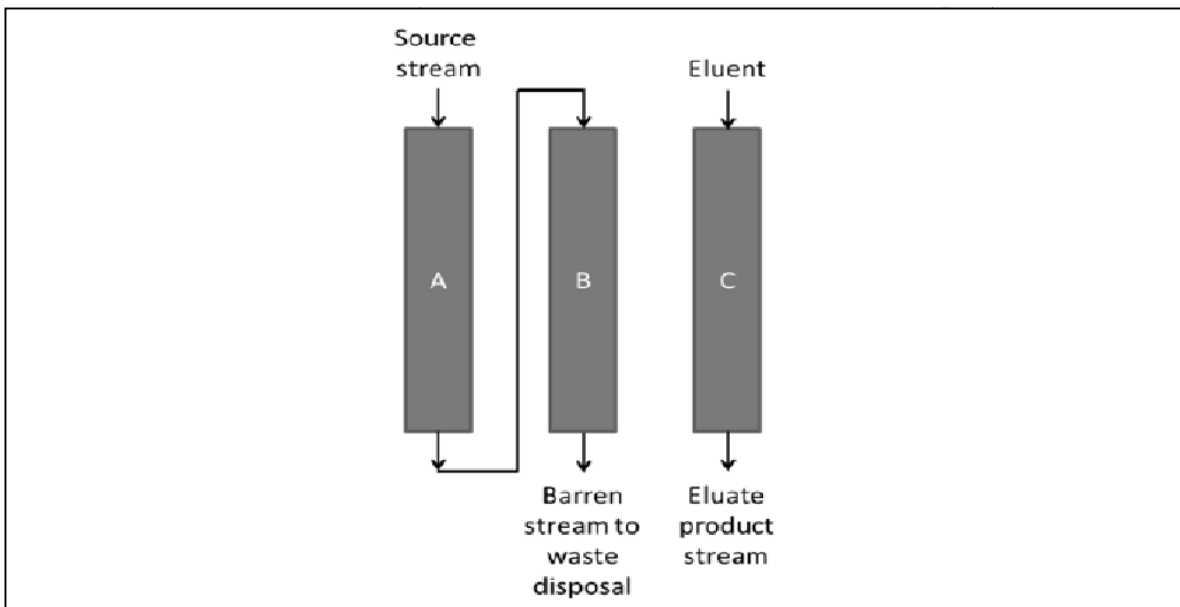
D<sub>2</sub>EHPA is a very effective organic extraction reagent for zinc removal from cobalt and nickel sulphate liquors (Sole, 2008; Kotze, 2012). Lewatit VP OC 1026 is used in several nickel plating baths for the removal of ferric iron and zinc. The flow-rates are generally in the order of 5-10 BV/h. Lewatit VP OC 1026 was also installed by INCO's Port Colbourne (Canada) refinery for the removal of zinc prior to nickel electrowinning. Although extractant loss has always been considered as a risk, this risk will be minimal if the pH of the aqueous streams (adsorption, elution and wash liquors) is lower than 4. A major advantage of this system is the relatively low co-loading of cobalt at the pH of effective zinc removal (Kotze, 2012).

From the literature review it is fair to conclude that the D<sub>2</sub>EHPA-impregnated resin, Lewatit VP OC 1026, and the aminophosphonic acid resin, Purolite S950, indicate very good results for the removal of zinc from a base-metal solution. Based on these studies, it was decided to test these two resins as part of this research project.

### 3.3 Industrial Ion Exchange Processes

There are generally two ion exchange technologies considered when treating solution streams. These are: fixed-bed ion exchange (FBIX) or continuous ion exchange (CIX). Fixed bed ion exchange is widely used in the water industry and has found application in the metallurgical industry for impurity removal from electrolytes, e.g., copper from cobalt electrolyte at Bulong Nickel in Western Australia (Mayze, 1999) and nickel from cobalt electrolyte at Chambishi Metals in Zambia (Rao *et al.*, 1993). The main advantage of fixed-bed ion exchange is that the resin inventory is confined to a single column and hence only subjected to osmotic and/or thermal shock through the introduction of different solutions. The main disadvantage is the degree of clarification required on the ion exchange feed and the control during elution to prevent precipitation of metal species which could result in blockages of the resin bed (Wyethe *et al.*, 2005).

Fixed-bed ion exchange is generally achieved by the use of a lead-lag two-column or lead-lead-lag three-column configuration. Figure 3-1 is an illustration of the lead-lag configuration. Feed solution is fed to column A (the lead column) and the outlet is fed to column B (the lag column). Lead column A will reach capacity and the resin will become completely loaded with the metal being loaded, while lag column B scavenges any residual metal that exits from column A. Column A will then be taken off-line for elution and regeneration. The feed is then fed to column B, which now becomes the lead column, and the newly regenerated column C becomes the lag column. The columns continue to rotate in this manner. There are always two columns on loading and one on elution/regeneration.



**Figure 3-1: Fixed-bed ion exchange lead-lag configuration.**

An extension of the lead-lag concept is the operation of a CIX circuit in a carousel setup. A large number of smaller columns can be employed, and the circuit operates in semi-continuous countercurrent mode, e.g., the ISEP technology (Bailey *et al.*, 2001). The resin inventory is considerably reduced in this configuration. Figure 3-2 is an illustration of the ISEP carousel system. The columns are fixed to a rotating base. As the columns being fed becomes saturated, the carousel base rotates allowing freshly regenerated columns to come online. The saturated columns then move into the elution and washing stages as the carousel rotates. The major advantages are reduced resin inventory and reduced consumption of eluate and regeneration chemicals. The main disadvantages are the maintenance around the moving carousel parts and increased capital cost compared to FBIX (Crittenden *et al.*, 2005).

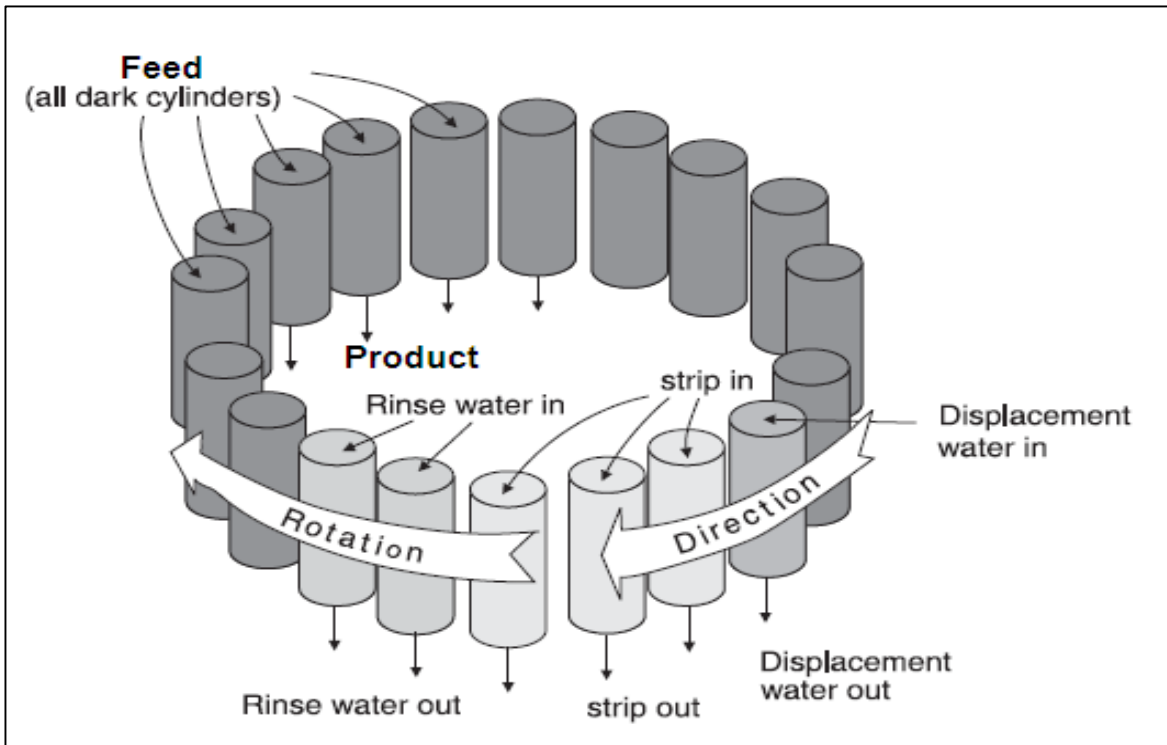


Figure 3-2: Continuous ion exchange configuration (Crittenden *et al.*, 2005).

Ion exchange can effectively be used for a number of duties in hydrometallurgical flow-sheets, especially where stringent metal specifications are to be produced, valuable metal recoveries have to be optimised, and environmental impact has to be limited. Although ion exchange is often regarded as a costly unit operation, it can provide major operating and economic benefits over conventional technologies, such as precipitation, liquid-liquid extraction, solid/liquid separation, and clarification. Resin producers are generally willing to improve commercially available products when it is clear that there would be an adequate market to justify development costs (Kotze, 2012). Primary limitations of ion exchange for hydrometallurgical applications include its relatively low capacity for adsorption, low selectivity of metal ions, poor mechanical stability of the resins, fouling, and the wash-water requirements when used for high-grade applications. Unlike most liquid-liquid-extraction processes, however, ion exchange does not require pH adjustment during the process and complete automation of the process is possible. It also uses benign reagents and does not contribute to carbon emissions or environmental damage (Sole, 2008; Kotze, 2012).

### 3.4 Distribution Ratio and Separation Factor

The distribution ratios and separation factors can be calculated from the batch equilibrium tests data. This will enable the determination of the selectivity of a target ion in a multi-component

solution being adsorbed onto the resin. The distribution ratio and separation factor for each element considered can be calculated by the following equations (Chaitanya *et al.*, 2011):

$$D = \frac{q_{e(solid)}}{C_{e(aqueous)}} \quad (3-1)$$

Where,  $D$  equals the distribution ratio,  $q_e$  is the amount of metal on the resin exchanged at equilibrium and  $C_e$  is the equilibrium solution concentration. The separation factor  $K$  is then calculated by:

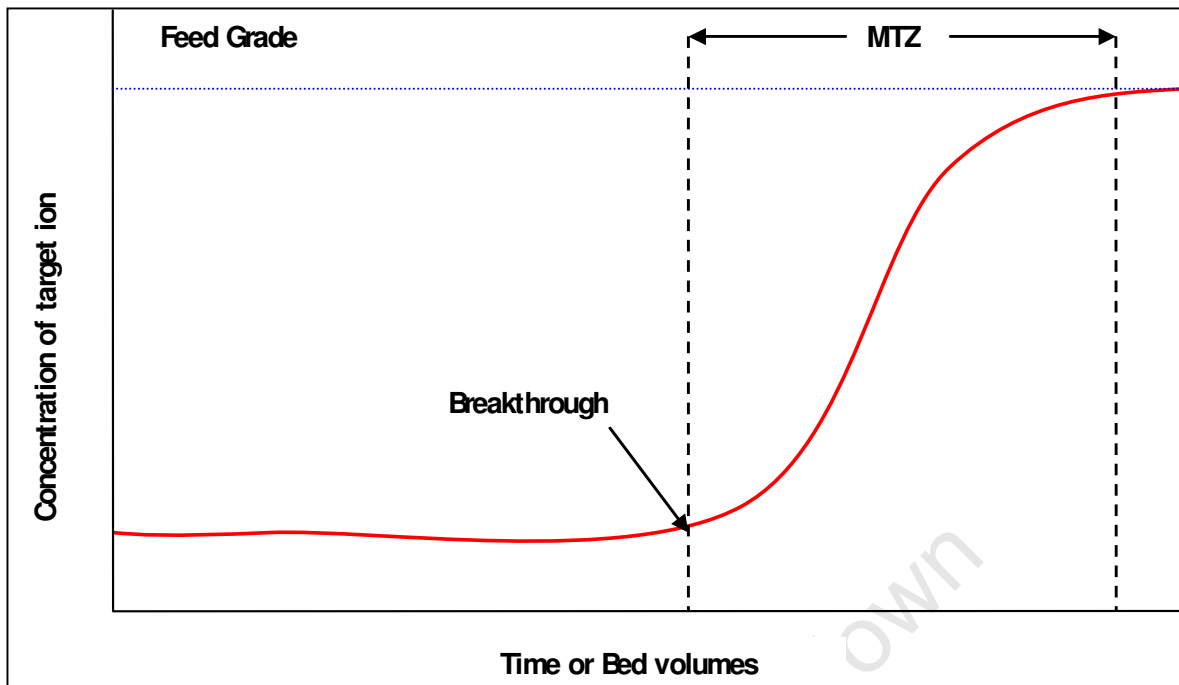
$$K_{\frac{Mt}{Mi}} = \frac{D_{Mt}}{D_{Mi}} \quad (3-2)$$

Where, the subscript  $Mt$  denotes the target metal to be extracted and  $Mi$  the other metal in the solution that is co-loaded onto the resin.

### 3.5 Column Breakthrough Theory

Ion-exchange experiments may be carried out by either batch or continuous techniques. The next sections, 3.5 and 3.6, describe the theory behind the experimental testing of ion-exchange resins on a batch and continuous scale.

In column operation the ion-exchange resin is placed in a vertical column to form a bed. The solution to be treated flows through this column until a target endpoint is reached (selected exiting concentration of the element being adsorbed). The resin is then regenerated, typically with an acidic solution, also known as elution. To be able to size a column for a particular application, it is necessary to determine how many bed volumes (BV) of solution can be treated before exceeding the target concentration leaving the column. Breakthrough curves are generated using a fixed bed of resin, passing the feed solution through the bed at constant velocity, and monitoring the output concentrations of the species of interest. The breakthrough curve, as in Figure 3-3, can be plotted and changes in the shape and duration of the curve can be manipulated by changing factors such as: feed flow rate, resin bed depth, operating temperature and pH. The object of the column test is to manipulate the column operating parameters in such a way as to give the shortest possible mass transfer zone (MTZ).



**Figure 3-3: Breakthrough curve for a continuous ion-exchange experiment.**

The overall performance of a fixed bed ion-exchange column is strongly related to the length and shape of the ion-exchange zone that develops during the solid-liquid contact. This zone develops between the section of the column that gradually becomes saturated with the loaded metal and the fresh resin section. At the very beginning of a sorption process the upper resin layer in the column is “hit” with a high metal concentration. Theoretically, this is where there is the highest mass transfer.

When the mass transfer zone eventually fully develops inside the bed, it can be followed as it advances along the length of the column. At the end of the bed, the breakthrough curve reflects the shape of the MTZ. The MTZ may be considered as a region inside the column in which the metal concentration changes from 90% to 10% of its inlet value. This is the region where most of the mass transfer takes place. The saturation of the bed within the transfer zone varies from zero (front) to the full saturation (rear). This zone of partial saturation moves through the column in the direction of the flow at a certain velocity which is predominantly determined by the metal loading, resin capacity, and the column feed rate. The column is operational until the MTZ reaches the end of the column. Until that time the effluent leaving the column is virtually metal free. When the transfer zone reaches the column end, the metal concentration in the solution starts to gradually increase. At the breakthrough point, the end-portion of the column contains the transfer zone with only partially saturated resin in it. The fact that real mass transfer zones appear S-shaped (Figure 3-3) in the plot is due to the sorption mechanism and mass transport

conditions. These parameters are generally taken into consideration in deriving the column mass balance.

Figure 3-4 illustrates the movement of this MTZ through the fixed bed ion-exchange column. The MTZ moves in the direction of the feed as the resin starts reaching its maximum loading capacity of the metal to be extracted. Ion-exchange equilibrium data are typically plotted in the form of an *adsorption isotherm* with the amount of metal on the resin on the *y*-axis and its remaining concentration in the fluid on the *x*-axis. The shape of the curve is significant and factors heavily into design. “Favourable” isotherms signify higher solid loadings at lower solution concentrations. These types of isotherms tend to start out steep and level off at higher equilibrium concentrations. Isotherms which start out flat are “unfavourable”, since such sorption systems only work well at high concentrations of the metal to be extracted (Naja & Volesky, 2006).

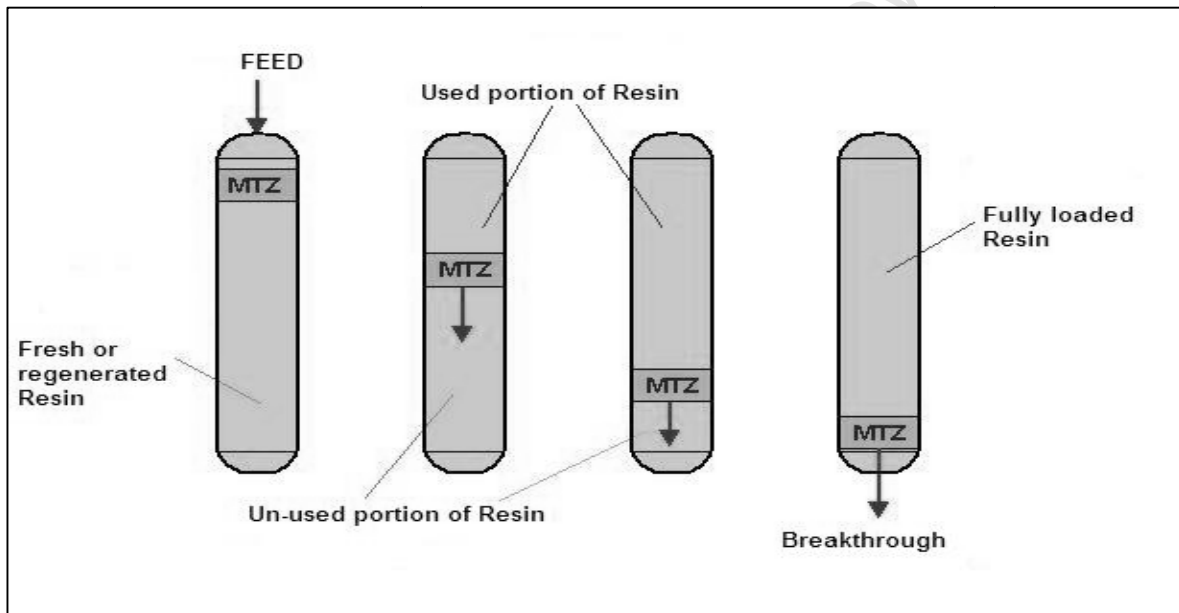


Figure 3-4: Graphical movement of MTZ through ion-exchange column (Malhotra et al., 2009).

The mass transfer zone length (MTZL) is a critical sizing parameter in ion-exchange systems since this impacts the resin vessel size. It is always good, therefore, to run these tests at a minimum of two different velocities to determine the relationship between fluid velocity and mass transfer zone length. Typically in adsorption it has a non-linear relationship as follows:

$$MTZL \propto (\text{velocity})^n \quad (3-3)$$

Where,  $n = 0.6 - 1$ .

$$\left(\frac{MTZL_1}{MTZL_2}\right) = \left(\frac{v_1}{v_2}\right)^{0.6-1.0} \quad (3-4)$$

For instance, if the MTZL at an adsorption velocity of 10 m/h (superficial linear velocity through the bed) is 1 m and taking  $n = 0.6$ , then the MTZL for the same operating conditions except for a velocity change to 20 m/h will be

$$MTZL_{20m/h} = 1 \times (20/10)^{0.6} = 1.51 \text{ m} \quad (3-5)$$

Effectively this means that by increasing the velocity the MTZL is increased by 50% while doubling the flow. This can have a significant impact when using expensive resins and reduces the ion-exchange vessel size (which is a function of resin charge) and consequently lowers the capital cost. Further, increasing the rate of mass transfer means the resin spends less time in contact with the feed solution. Resin life and fouling are often a strong function of this soaking time (Malhotra *et al.*, 2009). Thus, having a shorter MTZL could result in reduced adsorption of elements that foul the resin.

Referring to Figure 3-3, the ratio of the bed volumes to breakthrough (where curve begins to rise) and the bed volumes to saturation (where curve reaches feed level) is used to calculate the MTZL.

$$MTZL = I_i / L_i * \text{Column resin bed depth} \quad (3-6)$$

Where,  $I_i$  = bed volumes to breakthrough and  $L_i$  = bed volumes to saturation

The mass transfer length calculation can be used to establish the optimum superficial velocity and ultimate size of the ion-exchange column required.

### 3.6 Langmuir Isotherm

When a resin is identified for a potential application, the resin needs to be tested to establish the maximum loading capacity for the metal to be adsorbed. This is done by generating isotherms under specific pH and ionic concentrations as guided by the resin properties (Slater, 1982; Helfferich, 1962). Isotherms are generated by contact of the aqueous solution with a known mass of resin. The equilibrium metal concentrations of the solution are determined, and those of the resin calculated by difference. Adsorption can usually be modelled according to either the Freundlich or Langmuir equations. The Langmuir isotherm applies to adsorption on completely homogenous surface with negligible interaction between adsorbed molecules. However, the Freundlich isotherm describes equilibrium on heterogeneous surfaces and hence does not assume monolayer capacity (Misak, 1995).

The amount of metal exchanged at equilibrium,  $q_e$  (mol/kg), can be calculated by

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (3-7)$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of metal ions in the aqueous phase, respectively (mol/m<sup>3</sup>),  $W$  is the weight of dry resin (kg) and  $V$  is the volume (m<sup>3</sup>) of solution.

To obtain the equilibrium isotherm, the relationship between  $q_e$  and  $C_e$  must be plotted and the Langmuir equation fitted to the data points (see Figure 5-1). If the ion-exchange resin is thought of as a charged adsorbent, the adsorption isotherm equations are applicable. Of these equations, the Langmuir equation is widely adopted because the exchange reaction is essentially a kind of chemical reaction. The Langmuir equation applies to the ion-exchange process with specific assumptions (Misak, 1995):

- (i) Maximum adsorption depends on the saturation level of a monolayer of solute molecules on the adsorbent surface.
- (ii) The solid surface is provided with distribution uniform on the site adsorption.
- (iii) Each adsorbed matter on the site adsorption has the same affinity.
- (iv) For homovalent and heterovalent exchange, the concentration of one of the ions or of the total solution is constant.

The common two-parameter Langmuir equation is given by:

$$q_e = \frac{q_{sat} K_L C_e}{1 + K_L C_e} \quad (3-8)$$

Where  $q_{sat}$  is the saturated amount of metal exchanged at a given solution condition (mol/kg) and  $K_L$  the Langmuir constant (m<sup>3</sup>/mol). The Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \left( \frac{1}{q_{sat} K_L} \right) + \left( \frac{1}{q_{sat}} \right) C_e \quad (3-9)$$

This enables the graphical determination of the maximum loading capacity and Langmuir constant. By plotting  $C_e/q_e$  against  $C_e$  the parameters  $q_{sat}$  and  $K_L$  can be obtained from the

gradient and intercept, respectively. These values can then be compared for the relevant pH values and the best operating pH and resin can be selected.

## 4. EXPERIMENTAL PROCEDURE

The main objective of this research project was to find an ion-exchange resin that would effectively remove zinc from a base-metal solution containing a high concentration of nickel. This involved first selecting the best stream to treat and then performing a series of batch experiments on the selected stream to identify the most appropriate resin. Continuous experiments were then carried out on a selected resin to generate data required for full-scale design.

### 4.1 Stream Selection

In order to select the ideal stream on which to install a zinc-removal system, certain factors, such as the stream flow rate, pH, zinc concentration and co-extracting elements, were considered. Table 4-1 indicates the various streams considered for the removal of zinc using ion exchange. These streams were the nickel atmospheric leach solution (NALS), nickel non-oxidising leach solution (NOXS), copper removal solution (CRS), pressure iron removal solution (PIRS) and cobalt treatment filtrate (CTF). Figure 1-1 shows the location of these streams within the circuit.

**Table 4-1: Stream data for expansion circuit from the Dynatec report (Dynatec, 2006).**

| Stream                               | NALS    | NOXS   | CRS    | PIRS    | CTF       |
|--------------------------------------|---------|--------|--------|---------|-----------|
| Flow rate (m <sup>3</sup> /h)        | 50      | 35     | 160    | 45      | 15        |
| pH                                   | 1       | 0.9    | 6.8    | 3.6     | 2.5 - 3.5 |
| H <sub>2</sub> SO <sub>4</sub> (g/L) | 18      | 25     | -      | 0.1     | 15        |
| Major Elements (mg/L)                |         |        |        |         |           |
| Ni                                   | 115 000 | 90 000 | 80 000 | 120 000 | 70 000    |
| Cu                                   | 15 000  | 30 000 | 130    | 13 000  | 100       |
| Co                                   | 300     | 300    | 180    | 590     | 190       |
| Fe                                   | 5 000   | 5 000  | 14     | <1 000  | <10       |
| Minor Elements (mg/L)                |         |        |        |         |           |
| Zn                                   | 120*    | 80*    | 5      | 10*     | 20        |
| As                                   | 30      | 16     | 0.1    | 0.13    | -         |
| Pb                                   | 20      | 1      | 29     | 13      | 2.5       |
| Se                                   | 5       | 6      | 2.4    | 2.4     | 2.5       |
| Te                                   | 7       | 1.5    | 0.1    | 0.1     | -         |
| <b>*Estimates</b>                    |         |        |        |         |           |

Literature provided information on the main factors affecting the adsorption of zinc: Fe(III), Fe(II) and Cu(III) (Clayton, 1989, Simpson & Laurie, 1998; Cortina *et al.*, 1994 and Kotze, 2012). The

ideal pH for extracting zinc using the D<sub>2</sub>EHPA-impregnated resin, Lewatit VP OC 1026, was identified to be between 2.5 and 3.0 (Przywitowski, 1992; Swami, 1993). It is evident from Table 4-1, that the cobalt-treatment filtrate is the ideal stream as it is already at the correct pH and contains very little of the metals such as copper and iron that affect the loading capacity. The copper-removal solution stream would also be a good consideration but the large volumetric flow rate and high pH made this an unattractive option. All the other streams contain significant amounts of iron which will affect the loading capacity of the resin. Clayton (1989) showed that the zinc loading capacity of the Lewatit VP OC 1026 resin is significantly reduced when concentrations of Fe(II) exceed 500 mg/L (Table 3-6). These considerations along with the mass balance findings led to choosing the cobalt-treatment filtrate as the stream on which to evaluate zinc removal by ion exchange.

## 4.2 Resin Selection

There are four resins, identified in the literature review, that are prominent for the removal of zinc. These are:

- Lewatit VP OC 1026;
- Purolite S950 or S940;
- Duolite C467;
- Dowex APA-1;

Lewatit VP OC 1026 is a D<sub>2</sub>EHPA liquid-liquid-impregnated resin whereas the other three resins have an aminophosphonic acid functional group. The aim of this research project was to test these two resins in the batch experiments, since they were the most prominent resins, in literature, used for zinc removal from base metal solutions. The aminophosphonic acid resin, Purolite S950, was chosen for the batch tests as it was successfully tested for a hydrometallurgical application (Dry *et al.*, 1998; Wythe & Kotze, 2000). The best performing resin in the batch tests was then used in the column experiments.

Table 4-2 shows the physical and chemical characteristics of the two resins chosen.

**Table 4-2: Physical and chemical characteristics of Lewatit VP OC 1026 and Purolite S950 (Adapted from Appendix C).**

| Characteristics                  | Value                    |  |
|----------------------------------|--------------------------|--|
|                                  | Lewatit VP OC 1026       | Purolite S950  |
| <i>Physical characteristics</i>  |                          |  |
| Appearance                       | white opaque beads       | white opaque beads   |
| Ionic forms as shipped           | -                        | Na <sup>+</sup>  |
| Mean particle size (mm) (>90%)   | 0.31 -1.6                | 0.3 -1.2   |
| Temperature limitations (°C)     | 80                       | 90   |
| <i>Chemical characteristics</i>  |                          |  |
| Structure                        | macroporous              | macroporous  |
| Matrix                           | cross-linked polystyrene | styrene-divinylbenzene                                       |
| Functional group                 | D <sub>2</sub> EHPA      | Aminophosphonic acid   |
| pH range                         | 1 - 4                    | 2 - 6 (H <sup>+</sup> form)<br>6 - 11 (Na <sup>+</sup> form) |
| Minimum exchange capacity (eq/L) | 0.4                      | 1.3  |
| Minimum exchange capacity (g/L)  | 13 (Zn)                  | 40 (Cu)  |
| Density (g/ml)                   | 0.97                     | 1.13   |
| Water retention (%)              | -                        | 60% - 65%  |
| Bulk density (g/L)               | 600                      | 710  |
| Storability (max. year)          | 2                        |  |

It is interesting to note that the Purolite S950 resin has more than three times the metal loading capacity than the Lewatit VP OC 1026 resin.

### 4.3 Feed Solution Preparation

A 100-litre sample of cobalt treatment filtrate (CTF) obtained directly from the plant was used as basis of the test solution. Table 4-3 represents the typical composition of the CTF as well as the range of variability of the CTF. For the various batch and column experiments the CTF was spiked with chemical-grade ZnSO<sub>4</sub>·7H<sub>2</sub>O to ensure a consistent zinc concentration as well as to test the resin at various zinc concentrations in this solution matrix. The pH for individual batch experiments was adjusted with 0.1 mol/L NaOH until the desired pH was reached.

**Table 4-3: Typical CTF solution.**

|                               | Ni<br>(g/L) | Cu<br>(mg/L) | Co<br>(mg/L) | Fe<br>(mg/L) | Pb<br>(mg/L) | Zn (mg/L)     | pH      |
|-------------------------------|-------------|--------------|--------------|--------------|--------------|---------------|---------|
| <b>Typical plant solution</b> | 68          | 66           | 143          | 3            | 1            | 12            | 2.8     |
| <b>Range</b>                  | 55-70       | 50-100       | 100-300      | 2-15         | 1-10         | 10-50         | 2.0-3.5 |
| <b>Batch test solution</b>    | 56          | 98           | 246          | 11           | 7            | 180 –<br>200* | 2.0-3.5 |

\* varied by spiking with ZnSO<sub>4</sub>.7H<sub>2</sub>O (un-spiked solution = 12 mg/L Zn)

## 4.4 Batch Test Methodology

### 4.4.1 Batch Loading

The batch shake-out test was used to determine the exchange equilibrium, at various pH and initial metal concentrations, which is represented by adsorption isotherms. The equilibrium isotherm describes how the metal ion interacts with the resin and is used to optimize the use of the resin. These batch tests were used to compare the exchange equilibrium of the two resins Lewatit VP OC 1026 and Purolite S950 (Na<sup>+</sup> form) (Appendix C). Both resins were used in the form they were shipped in i.e. no pre-treatment was done to convert the resin to a different ionic form. The resin mass and volume were measured in the dry-tapped form.

A known mass of resin was placed in a 250 ml glass flask to which the aqueous metal-containing solution (CTF) was added (Figure 4-1). The flask was then shaken for a 24-hour period, in a thermally controlled bath (Figure 4-2), to ensure equilibrium was reached. Each batch experiment consisted of five flasks containing 150 ml of CTF spiked with a known amount of zinc and adjusted to the desired pH. A specific mass of resin ranging from 0.3 g to 9.0 g was added to each flask.



**Figure 4-1: Flasks used for batch experiments.**



**Figure 4-2: Thermal shaker bath used for batch experiments.**

At the end of each experiment each sample was filtered, using a Buchner-type filter with a perforated glass disc, to separate the resin from the solution. The pH of the resin-free solution was then measured. A sample of 50 ml from each flask was then submitted for nickel, copper, cobalt, iron, lead and zinc analysis. The analyses were done on an inductively coupled plasma mass spectrometer (ICP-MS) at the Anglo American Research Laboratory's Germiston campus. A series of six batch experiments was done for both the Lewatit VP OC 1026 and Purolite S950 resins. Table 4-4 indicates the parameters for each batch experiment and Table 4-5 indicates the mass of resin used per flask for each experiment.

**Table 4-4: Batch experiment setup parameters.**

| Experiment No | Initial pH | Initial [Zn] (mg/L) | Test Temperature (°C) | Test Duration (h) | Resin    |
|---------------|------------|---------------------|-----------------------|-------------------|----------|
| 1             | 1.8        | 10                  | 25                    | 24                | Lewatit  |
| 2             | 2.0        | 195                 | 25                    | 24                | Lewatit  |
| 3             | 2.5        | 216                 | 25                    | 24                | Lewatit  |
| 4             | 3.0        | 196                 | 25                    | 24                | Lewatit  |
| 5             | 2.5        | 200                 | 25                    | 2                 | Lewatit  |
| 6             | 3.5        | 198                 | 25                    | 24                | Purolite |
| 7             | 4.0        | 198                 | 25                    | 24                | Purolite |
| 8             | 4.5        | 206                 | 25                    | 24                | Purolite |
| 9             | 2.5        | 199                 | 25                    | 24                | Purolite |
| 10            | 3.0        | 191                 | 25                    | 3                 | Lewatit  |
| 11            | 4.0        | 193                 | 25                    | 3                 | Purolite |
| 12            | 4.0        | 198                 | 50                    | 12                | Purolite |
| 13            | 3.5        | 194                 | 50                    | 12                | Lewatit  |

Experiment 1 was regarded as a scouting test. To ensure more accurate and measurable results, the initial zinc concentration and resin mass per flask were increased for the rest of the experiments. Experiments 10 and 11 were done to see whether equilibrium is reached in less than 24 hours. Experiments 12 and 13 were done at 50°C to accelerate the kinetics and to ensure equilibrium was reached in less than 12 hours. The resin mass for experiments 10 to 13 was increased to ensure a better graphical representation of the extraction profile.

**Table 4-5: Batch experiment resin mass per flask.**

| Experiment No   | Resin Mass (g) |         |         |         |         |
|-----------------|----------------|---------|---------|---------|---------|
|                 | Flask 1        | Flask 2 | Flask 3 | Flask 4 | Flask 5 |
| 1               | 0.97           | 2.40    | 4.80    | 9.70    | 24.30   |
| 2,3,4,5,6,7,8,9 | 0.30           | 0.60    | 1.20    | 2.10    | 3.20    |
| 10              | 0.90           | 1.50    | 2.00    | 3.00    | 5.00    |
| 11              | 1.00           | 2.00    | 5.00    | 7.00    | 9.00    |
| 12              | 1.00           | 2.00    | 5.00    | 7.00    | 9.00    |
| 13              | 0.90           | 1.50    | 2.00    | 3.00    | 5.00    |

#### 4.4.2 Batch Elution

Two sets of batch elution tests were conducted to establish the extent of zinc and iron removal from the resin. Two synthetic solutions using analytical-grade zinc sulphate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and ferric sulphate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ ) were made up to the required compositions.

The first solution was made up to contain 227 mg/L of zinc and 60 mg/L of iron as ferrous iron. The resin (5.1 g) was contacted with 150 ml of this solution for 12 hours in a thermally controlled shaker bath. The second solution was made up to contain 197 mg/L zinc and 50 mg/L iron as ferric iron. Similarly to the first solution, 5.1g of resin was contacted with 150 ml of solution 2 for 12 hours in a thermally controlled shaker bath.

Both solution tests were done in triplicate to ensure reproducibility. The resin and solution were separated after 12 hours. The solution was analysed for zinc and iron using atomic absorption spectroscopy (AAS) at the RBMR laboratory. Each resin was then placed into a new flask containing 150 ml of 10% sulphuric acid and shaken for another 12 hours in a thermally controlled bath. After 12 hours the resin and acid solution were separated and the solution again analysed for zinc and iron using AAS. The data were then used to calculate the extraction of zinc and iron from the feed solution and finally the recovery of zinc and iron from the eluted resin.

## 4.5 Column Test Methodology

A series of eight loading experiments was performed using the Lewatit VP OC 1026 resin. The experiments were conducted using a 258 mm glass column with an inner diameter of 22.2 mm. Figure 4-3 is an illustration of the experimental setup. A perforated glass disc at the bottom of the column allowed containment of the resin. A mass of 97 g of resin in the dry-tapped form (1 BV = 100 ml) was placed in the column for each experiment. A small peristaltic pump with a variable speed control drive was used to feed the solution, in a downward flow, through the column. The flow rate was controlled using the pump speed control and checking the flow at regular intervals using a measuring cylinder and stopwatch. All experiments were conducted at ambient temperature of 25°C.

The feed solution to the column was prepared CTF solution sampled from the plant. The zinc concentration was adjusted using analytical-grade zinc sulphate. The pH for the CTF solution was not adjusted and was used as sampled on the plant. Thus all the experiments were conducted at a feed pH of between 2.6 and 2.8. Samples were taken at certain intervals, as can be seen in Table 4-6. A sample of 50 ml was taken each time, the pH was measured, and it was submitted for analysis.

Table 4-6 indicates the amount of solution used, zinc concentration, feed pH, feed flow rate and sample frequency for each experiment.

**Table 4-6: Column test feed properties for all experiments.**

| <b>Experiment No</b> | <b>Feed solution volume (L)</b> | <b>Feed concentration (mg/L) Zn</b> | <b>Feed pH</b> | <b>Feed flow rate (BV/h)</b> | <b>Sample Frequency (BV)</b> |
|----------------------|---------------------------------|-------------------------------------|----------------|------------------------------|------------------------------|
| <b>Exp1</b>          | 5                               | 183                                 | 2.8            | 5                            | 3                            |
| <b>Exp2</b>          | 5                               | 179                                 | 2.8            | 7                            | 3                            |
| <b>Exp3</b>          | 5                               | 200                                 | 2.7            | 10                           | 3                            |
| <b>Exp4</b>          | 5                               | 183                                 | 2.7            | 15                           | 3                            |
| <b>ExpS1</b>         | 16                              | 97                                  | 2.7            | 20                           | 10                           |
| <b>ExpS2</b>         | 16                              | 93                                  | 2.7            | 10                           | 10                           |
| <b>ExpS3</b>         | 22                              | 48                                  | 2.7            | 19                           | 10                           |
| <b>ExpS4</b>         | 22                              | 45                                  | 2.7            | 10                           | 10                           |



**Figure 4-3: Laboratory column experimental setup.**

The samples produced during the column test campaign were all analysed using the ICP MS at Anglo American Research Laboratory's Germiston campus. The samples were first appropriately diluted before analysed for Cu, Co, Fe, Ni, Pb and Zn with matrix-matched standards and simultaneous background correction. The analytical results were used to plot the breakthrough curves in order to calculate the MTZL and resin capacity for each experiment.

## 5. RESULTS AND DISCUSSION

In this chapter the results of the laboratory experiments are discussed. The experiments are divided into three sub-sections namely: batch test results, column test results and the batch elution results.

### 5.1 Batch Test Results

The batch tests were used to compare the exchange equilibrium of the two resins Lewatit VP OC 1026 and Purolite S950. The objective was to compare the two resins and choose the best performing resin to conduct the column tests. To evaluate the performance the following were considered:

1. Equilibrium isotherm – determining the saturated (maximum) loading capacity;
2. Zinc loading as a function of pH;
3. Resin selectivity.

#### 5.1.1 Batch Test Results: Maximum Loading Curves (Equilibrium Isotherm)

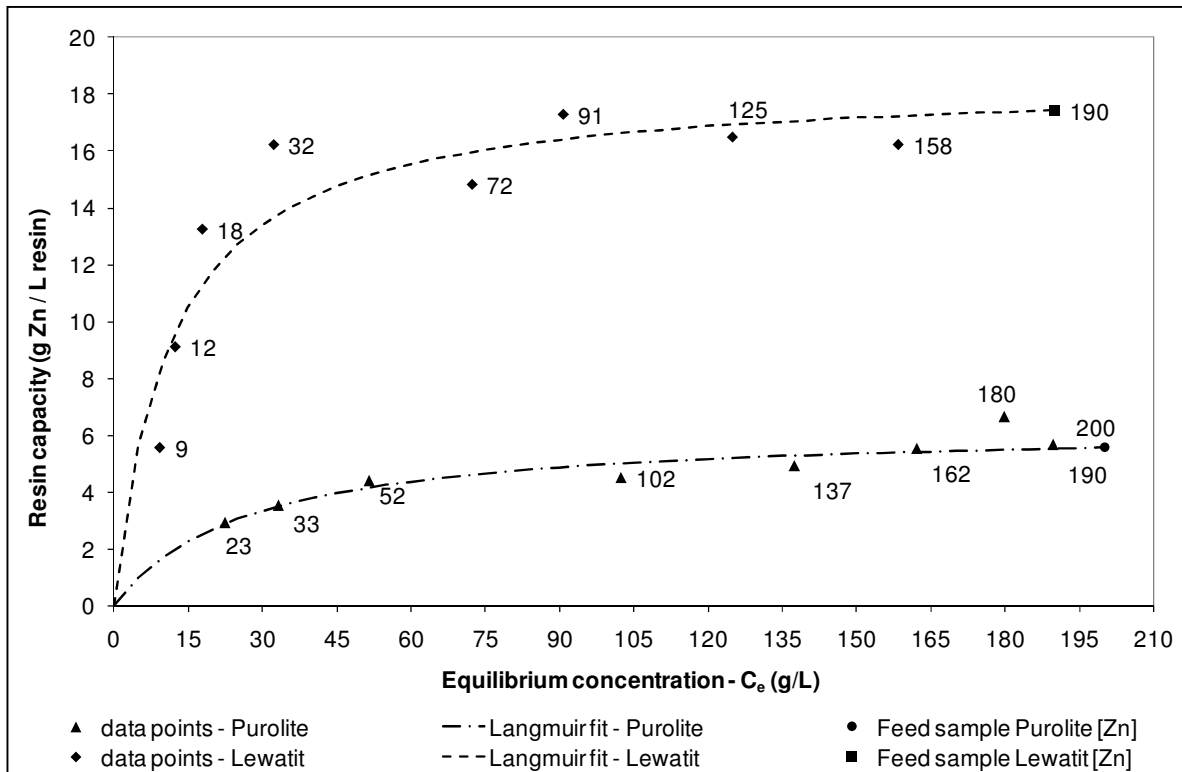
Figure 5-1 indicates the loading capacity graphs for the Lewatit and Purolite resins. The dashed line on the graph represents the Langmuir isotherm plot. Figure 5-2 indicates the plots of  $C_e/q_e$  against  $C_e$  to determine the Langmuir parameters as discussed in Section 3.3. The parameter  $q_{sat}$  can be obtained from the gradient (slope =  $1/q_{sat}$ ) and represents the saturated amount of metal exchanged for a given solution. These plots represent data from Lewatit resin experiments with an equilibrium pH of between 2.7 and 3.1 and the Purolite resin experiments with an equilibrium pH of between 3.7 and 4.2. The loading capacity was at maximum for these equilibrium pH values. The following  $q_{sat}$  values were calculated:

Lewatit (pH = 2.7 – 3.1):  $q_{sat} = 0.017$  g zinc per g resin (16.8 g Zn/L resin)

Purolite (pH = 3.7 – 4.2):  $q_{sat} = 0.005$  g zinc per g resin (5.7 g Zn/L resin)

The value for Lewatit VP OC 1026 is slightly higher than the minimum loading capacity for zinc (13 g/L) specified by the resin information sheet (Appendix C). The Purolite S950 information sheet (Appendix C) shows the minimum loading capacity of copper as 1.3 eq/L which corresponds to 40 g/L. This value should be similar for zinc, as zinc and copper have a similar molecular mass. The co-loading metals such as copper and iron are reducing the zinc loading capacity for the Purolite S950 resin.

These tests indicate that the Lewatit resin can load more than double the amount of zinc per unit volume of resin than the Purolite resin at these given solution concentrations. Figure 5-1 also shows that the Langmuir isotherm fit the raw data very well. The coefficient of determination, indicated by  $R^2$  in Figure 5-2, for both the Lewatit and the Purolite plot is greater than 0.98. This indicates that the linear regression line is a good fit, proving that the Langmuir isotherm correlates well. The validity of the Langmuir isotherm assumes the fact that the retention of zinc cations can be described as a monolayer sorption. According to this model, surface of the sorbent under study can be considered homogeneous equivalent from energetically point of view and with the same accessibility.



**Figure 5-1: Lewatit VP OC 1026 and Purolite S950 - loading capacity graphs.**

Figure 5-1 also shows that the Lewatit resin is able to load more metal at lower solution metal concentrations than the Purolite resin. The graph also indicates that the Lewatit resin can load three times more zinc per unit volume of resin than the Purolite resin for the given experimental conditions. According to Naja & Volesky (2006), “favourable” isotherms signify higher solid loadings at lower solution concentrations, represented by a steep initial slope and levelling off at higher equilibrium concentrations. Isotherms which start out flat are “unfavourable”, since such sorption systems only work well at high concentrations of the metal to be extracted. Figure 5-1 would suggest that the Purolite resin isotherm is unfavourable by this definition compared to that of the Lewatit resin isotherm.

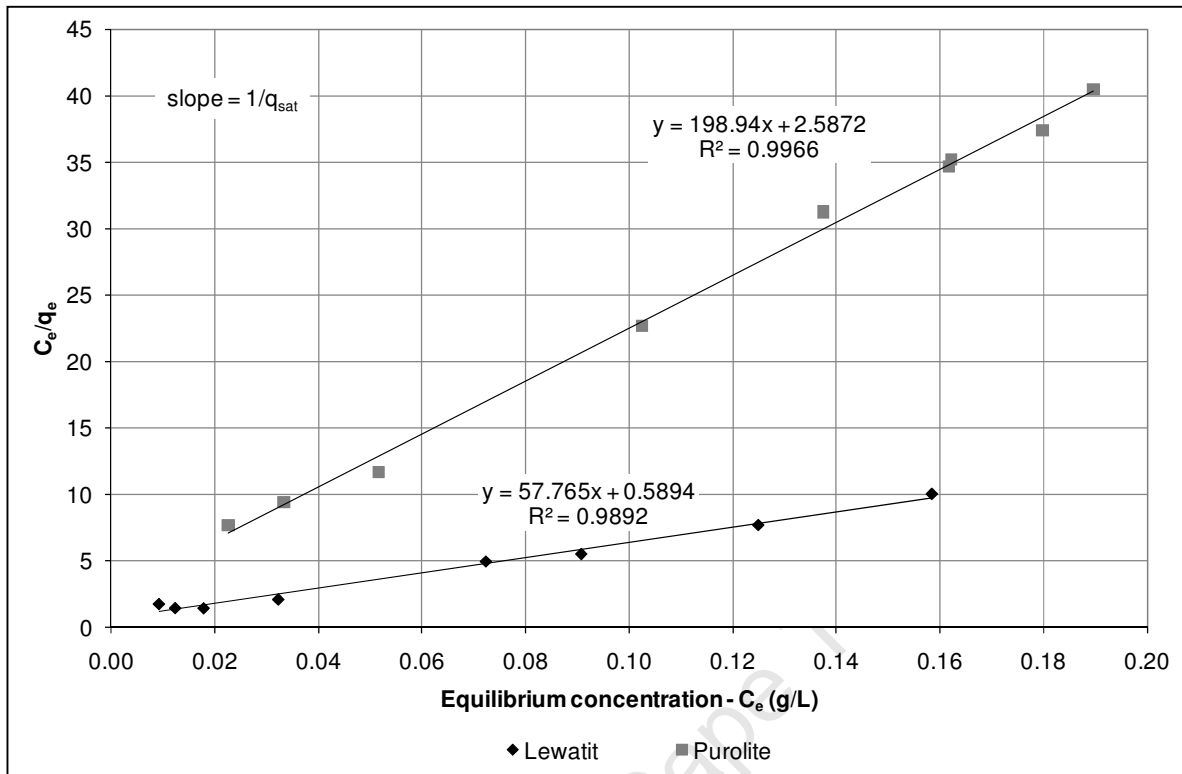


Figure 5-2: Lewatit vs. Purolite – Langmuir slope calculations.

### 5.1.2 Batch Test Results: Zinc Loading as a Function pH

Figure 5-3 shows the batch curves for the various Lewatit experiments. The y-axis represents the equilibrium concentration for a specific amount of resin (x-axis) obtained during the shake tests. The first data point for each curve, at a resin mass equal to zero, represents the feed concentration. It is evident from the graph that more zinc per mass of resin is loaded at pH values greater than 2.5. This corresponds well with the reported values of between 2.5 and 3.5 by Calyton (1989) and Swami (1993).

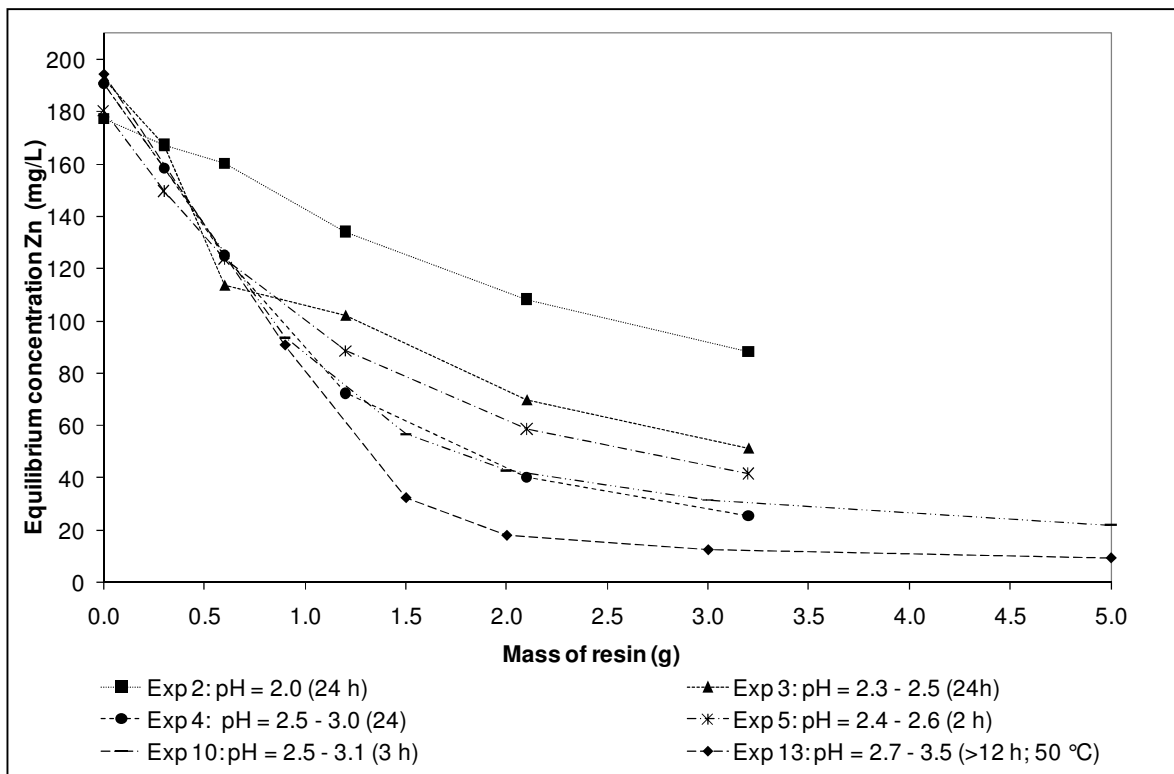


Figure 5-3: Lewatit VP OC 1026: batch loading curves.

Experiment 13, done at 50°C, showed the most favourable zinc loading results. This can be attributed to better loading kinetics and the fact that the initial pH of 3.5 was slightly higher than the other experiments.

Figure 5-4 represents the Purolite batch data curves. Similarly to the above plots, the data indicate more zinc loading per mass of resin at a pH greater than 3.5. The Purolite S950 information sheet (Appendix C) indicates that a minimum pH of 2.5 is needed for zinc extraction. This would explain the poor results obtained for experiment 9, as the initial solution pH was 2.5. Experiment 11 showed the least favourable extraction, which is most likely due to the experiment not reaching equilibrium within three hours. Experiments 6 and 12 were done at the same pH values and illustrated the most favourable zinc extraction. Experiment 12 was done at

50°C and contacted with the resin for just over 12 hours. The increased temperature must have improved the loading kinetics and overall extraction as this experiment showed the most favourable results.

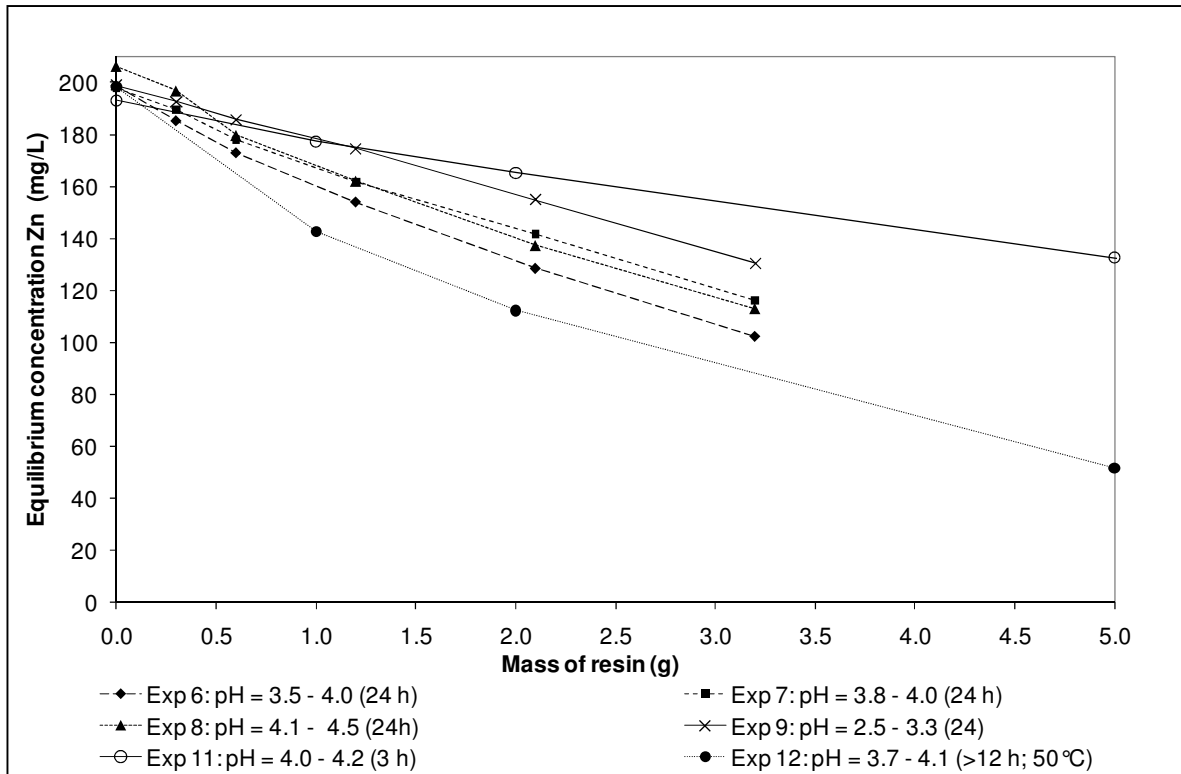


Figure 5-4: Purolite S950: batch loading curves.

For both the Lewatit and Purolite experiments done at 50°C there was a significant improvement of zinc extraction. This was expected and can be attributed to improved kinetics at elevated temperatures. However, these resins are only stable up to a maximum of 80°C for the Lewatit VP OC 1026 resin and 90°C for the Purolite S950 resin (Appendix C). At higher temperatures the resin bead structures will not be stable and loss of the active functional groups will occur. The plant CTF stream temperature is between 70 °C and 72 °C, thus below the maximum operating temperature of the resins.

### 5.1.3 Batch Test Results: Resin Selectivity

Another factor to consider is the selectivity of the resin in terms of what other elements are co-loaded with the zinc and ultimately take up the capacity of the resin. Valuable metals, such as cobalt and nickel, could also be lost through this process or require a complicated elution process to recover if they are co-loaded with zinc. Figure 5-5 illustrates typical selectivity curves obtained during the batch shake tests for the Lewatit resin. In order to evaluate the selectivity of

the resin the distribution ratios and separation factors were calculated for each element. Table 5-1 represents the distribution ratio for each element for a specific mass of resin.

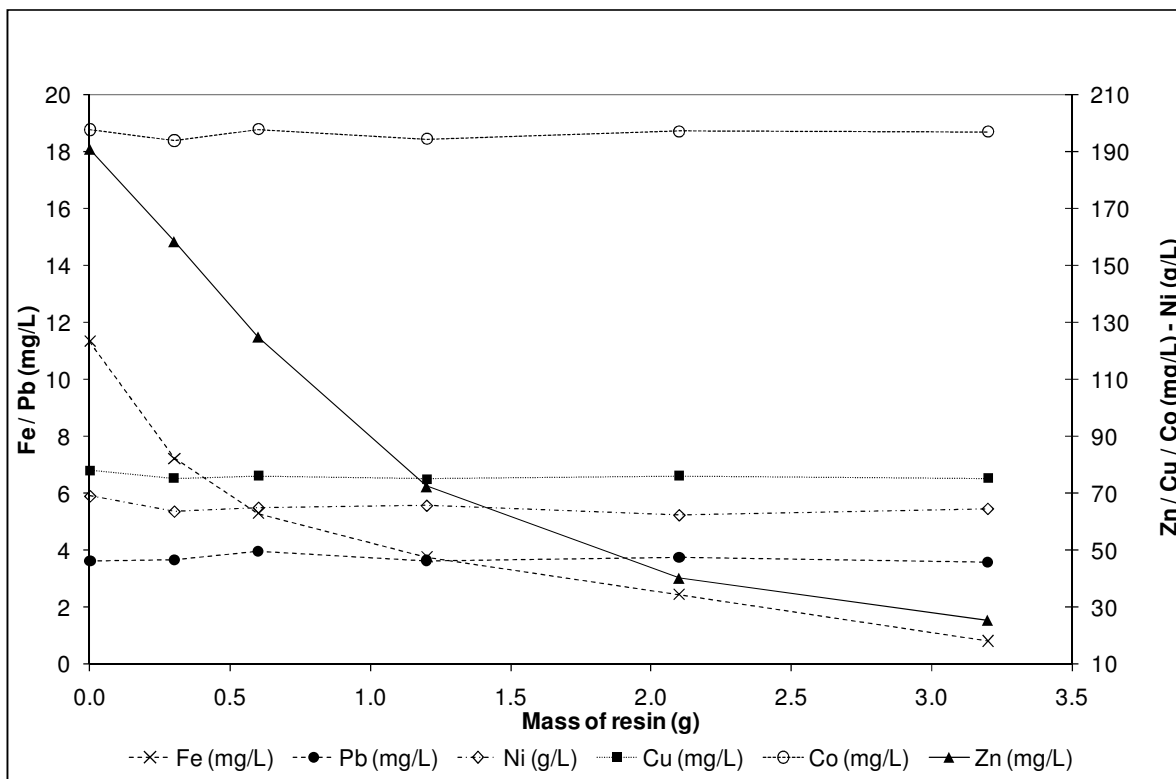


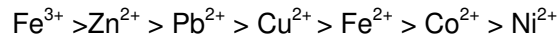
Figure 5-5: Lewatit VP OC 1026: batch selectivity curves.

Table 5-1: Distribution ratios for Lewatit VP OC 1026 batch experimnet.

| Resin Mass (g) | Distribution ratio |       |        |       |        |       |
|----------------|--------------------|-------|--------|-------|--------|-------|
|                | Ni                 | Cu    | Co     | Fe    | Pb     | Zn    |
| 0.3            | 0.042              | 0.019 | 0.010  | 0.284 | 0.002  | 0.102 |
| 0.6            | 0.015              | 0.006 | 0.002  | 0.285 | 0.001  | 0.132 |
| 1.2            | 0.006              | 0.005 | 0.002  | 0.252 | 0.001  | 0.205 |
| 2.1            | 0.008              | 0.002 | <0.001 | 0.261 | <0.001 | 0.268 |
| 3.2            | 0.003              | 0.002 | <0.001 | 0.613 | <0.001 | 0.305 |

The smaller the distribution ratio, the less of the element is adsorbed. As the mass of resin increases, the distribution ratios for Ni, Cu, Co and Pb decrease and increase for Fe and Zn. This could be due to the fact that the loading capacities of Zn and Fe increase as those of the other elements decrease. The distribution ratios for Fe and Zn are similar, indicating similar adsorption characteristics.

Table 5-2 shows the separation factors increasing, for Ni, Cu, Co and Pb, with increasing resin mass. The separation factor for Fe is between 0 and 1 indicating no selectivity between Fe and Zn. The selectivity order given by the Lewatit VP OC 1026 information sheet (Appendix C) is as follows:

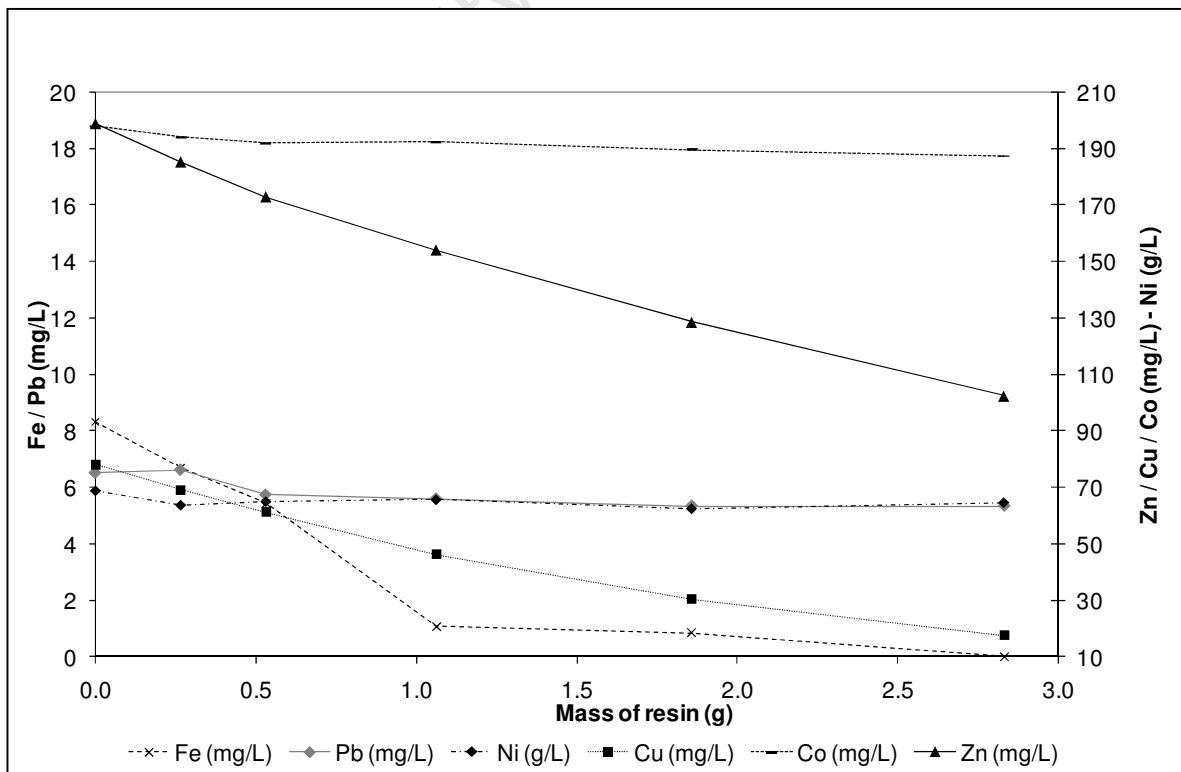


**Table 5-2: Separation factors for Lewatit VP OC 1026 batch experiment.**

| Resin Mass (g) | Separation Factor  |                    |                    |                    |                    |
|----------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                | K <sub>Zn/Ni</sub> | K <sub>Zn/Cu</sub> | K <sub>Zn/Co</sub> | K <sub>Zn/Fe</sub> | K <sub>Zn/Pb</sub> |
| 0.3            | 2                  | 6                  | 10                 | 0                  | 45                 |
| 0.6            | 9                  | 23                 | 80                 | 0                  | 160                |
| 1.2            | 33                 | 43                 | 97                 | 1                  | 270                |
| 2.1            | 35                 | 151                | 1246               | 1                  | 779                |
| 3.2            | 95                 | 185                | 1760               | 0                  | 1188               |

This order of selectivity supports the findings of the batch tests and confirms that the iron in solution is present as the ferric ion.

Similar selectivity curves for the Purolite resin indicated in Figure 5-6, show that there was significant co-loading of some of the other metals analysed. The major metals that co-loaded with the zinc were copper and iron.



**Figure 5-6: Purolite S950: batch selectivity curves.**

The distribution ratios indicated in Table 5-3 show high ratios for Fe and Cu. Similarly to the Lewatit experiments, the distribution ratios increase with increase in resin mass. The Zn distribution ratio for the Purolite resin is an order of magnitude smaller than the Zn distribution ratio for the Lewatit resin.

**Table 5-3: Distribution ratios for Purolite S950 batch experiments.**

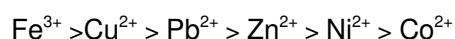
| Resin Mass (g) | Distribution ratio |       |       |        |       |       |
|----------------|--------------------|-------|-------|--------|-------|-------|
|                | Ni                 | Cu    | Co    | Fe     | Pb    | Zn    |
| 0.30           | 0.042              | 0.066 | 0.010 | 0.121  | 0.026 | 0.036 |
| 0.6            | 0.015              | 0.069 | 0.008 | 0.132  | 0.034 | 0.037 |
| 1.2            | 0.006              | 0.086 | 0.004 | 0.837  | 0.021 | 0.036 |
| 2.1            | 0.008              | 0.112 | 0.003 | 0.623  | 0.016 | 0.039 |
| 3.2            | 0.003              | 0.161 | 0.003 | 30.488 | 0.010 | 0.044 |

The separation factors in Table 5-4 indicate no selectivity in separation between Zn and Cu and Zn and Fe. The separation factors for Ni, Co and Pb are also orders of magnitude smaller than that of the Lewatit resin.

**Table 5-4: Separation factors for Purolite S950 batch experiments.**

| Resin Mass (g) | Separation Factor |             |             |             |             |
|----------------|-------------------|-------------|-------------|-------------|-------------|
|                | $K_{Zn/Ni}$       | $K_{Zn/Cu}$ | $K_{Zn/Co}$ | $K_{Zn/Fe}$ | $K_{Zn/Pb}$ |
| 0.30           | 1                 | 1           | 4           | 0           | 1           |
| 0.6            | 2                 | 1           | 5           | 0           | 1           |
| 1.2            | 6                 | 0           | 10          | 0           | 2           |
| 2.1            | 5                 | 0           | 13          | 0           | 2           |
| 3.2            | 14                | 0           | 17          | 0           | 4           |

The selectivity order given by the Purolite S950 information sheet (Appendix C) is as follows:



These selectivity orders again confirm what was observed in the batch test work. The distribution ratios and separation factors show why the loading capacity for the Purolite resin is lower than that of the Lewatit resin: the co-loading of copper (~ 80 mg/L) and Fe (~ 8 mg/L) significantly reduces the loading capacity of the Purolite resin. The selectivity orders also prove that the iron must be present as ferric, because of the resin's high adsorption of iron.

For the given batch experimental solution pH conditions, it is fair to say that the Lewatit VP OC 1026 loads more zinc per unit volume of resin and is more selective in loading zinc based on the calculated distribution ratios and separation factors. The research objective was to take the best performing resin forward for column testing. The Lewatit VP OC 1026 was considered to have performed the best and was thus used for the column tests.

## 5.2 Column Test Results

The batch tests showed that the Lewatit VP OC 1026 performed better than the Purolite S950 under the tested conditions and thus only the Lewatit VP OC 1026 resin was evaluated in the continuous column tests. Three different feed concentrations and two flow rates were evaluated. These test results enabled the calculation of the mass transfer zone length (MTZL) and the average loading capacity which provides the critical parameters that are used during the design process of the industrial ion-exchange column.

### 5.2.1 Column Test Results: Breakthrough Curves

Figure 5-7 represents the breakthrough curves for the six experiments considered for the calculation of the MTZL. Refer to Table 4-6 in Section 4.5 for the experimental conditions.

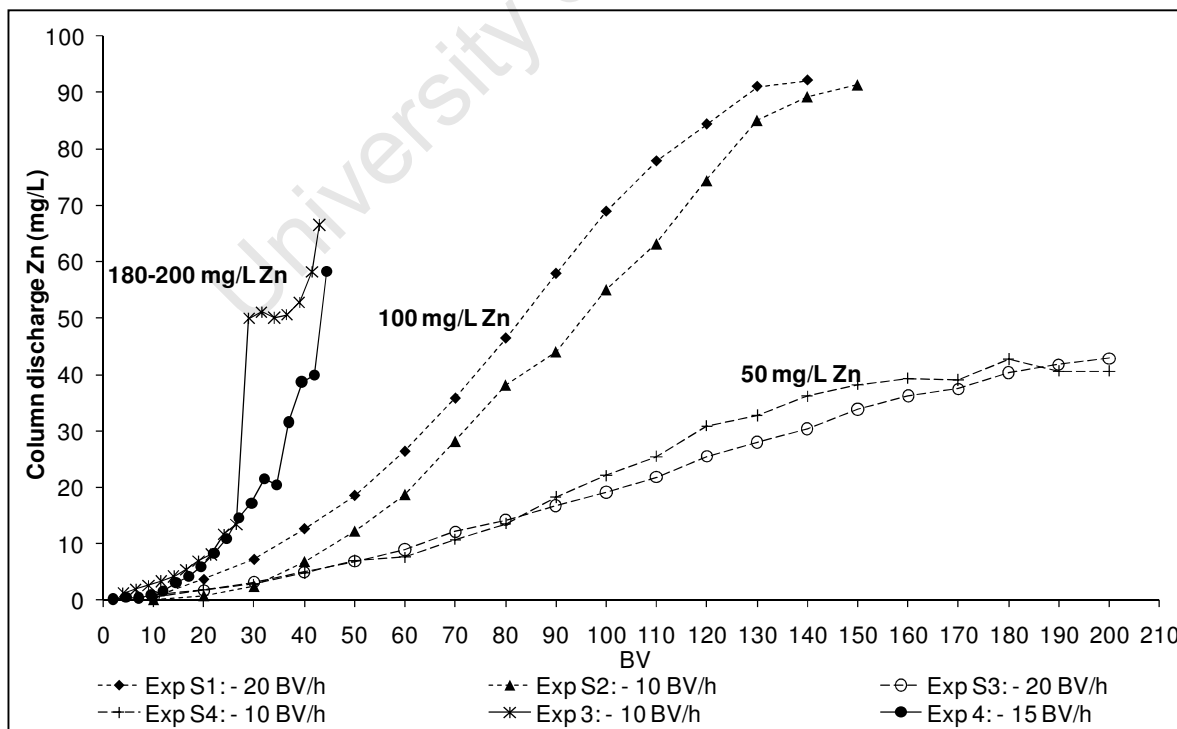


Figure 5-7: Breakthrough curves measured at feed flowrates of 10, 15 and 20 BV/h.

To calculate the MTZL, the bed volumes at breakthrough (exit concentration equal to 10% of feed concentration) and saturation (90% of feed concentration) are needed, along with the resin bed length. The MTZL values in Table 5-5 were calculated using the following equation:

$$MTZL = l_i / L_i * \text{Column resin bed depth} \quad (5-1)$$

**Table 5-5: Mass Transfer Zone Length calculations.**

| Experiment No | Feed concentration (mg/L) Zn | Feed flow rate (BV/h) | Resin bed length (mm) | Bed Volumes to Breakthrough - $l_i$ (BV) | Bed Volumes to Saturation - $L_i$ (BV) | MTZL (mm) | MTZL as percent of bed length (%) |
|---------------|------------------------------|-----------------------|-----------------------|--|--|-----------|-----------------------------------|
| Exp3          | 200                          | 10                    | 258                   | 28                                       | -                                      | -         | -                                 |
| Exp4          | 183                          | 15                    | 258                   | 30                                       | -                                      | -         | -                                 |
| ExpS1         | 97                           | 20                    | 258                   | 35                                       | 125                                    | 72        | 28                                |
| ExpS2         | 93                           | 10                    | 258                   | 45                                       | 128                                    | 91        | 35                                |
| ExpS3         | 48                           | 19                    | 258                   | 40                                       | 200                                    | 52        | 20                                |
| ExpS4         | 45                           | 10                    | 258                   | 35                                       | 170                                    | 53        | 21                                |

The MTZL for Exp3 and Exp4 could not be calculated as the experiments were not run to resin saturation. The shorter the MTZL, the less resin volume is required to achieve the same results for a specific condition. The results for ExpS1 and ExpS2 indicate that it would be better to operate at a flow rate of 20 BV/h for a feed concentration of 100 mg/L zinc. The MTZL for ExpS1 is shorter, therefore requiring a smaller amount of resin to achieve the same results. This is an indication that the resin kinetics is fairly fast and suggests that by increasing the flow rate, the mass transfer rate is increased. This however, is not true for all solution concentrations, as can be seen for ExpS3 and ExpS4 in Table 5-5. The MTZL for these experiments are similar, indicating no benefit in running at a higher flow rate.

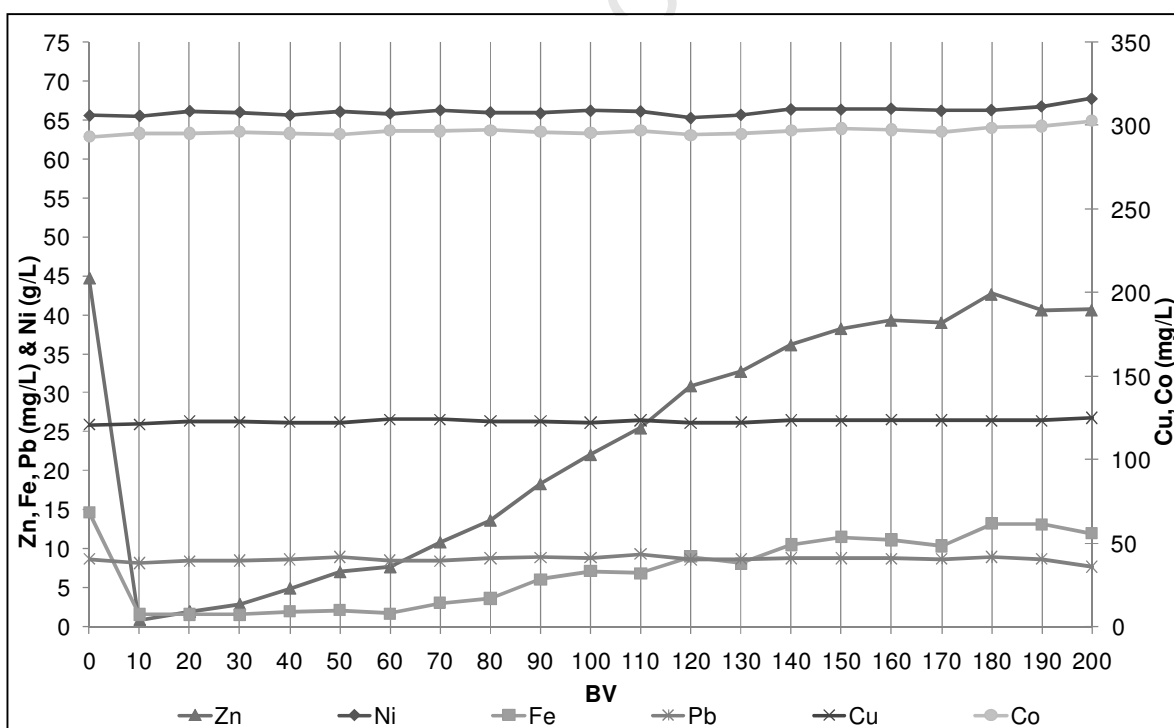
Table 5-6 indicates the zinc loading capacity at saturation. The lower loading capacities observed for ExpS3 and ExpS4 were not expected. The only explanation would be the reduced concentration gradient and constant iron loading that could have reduced the loading capacity.

**Table 5-6: Resin loading capacity for zinc at resin saturation.**

| Experiment No | Feed concentration (mg/L) Zn | Feed flow rate (BV/h) | Bed Volumes to Saturation | Loading Capacity (g Zn / L resin) |
|---------------|------------------------------|-----------------------|---------------------------|-----------------------------------|
| Exp3          | 200                          | 10                    | -                         | >7.5                              |
| Exp4          | 183                          | 15                    | -                         | >7.5                              |
| ExpS1         | 97                           | 20                    | 125                       | 7.2                               |
| ExpS2         | 93                           | 10                    | 128                       | 7.7                               |
| ExpS3         | 48                           | 19                    | 200                       | 5.3                               |
| ExpS4         | 45                           | 10                    | 170                       | 4.3                               |

### 5.2.2 Column Test Results: Resin Selectivity

The selectivity of the resin with regard to other metal cations was also evaluated. All solution samples were assayed for nickel, copper, cobalt, iron and lead, in conjunction with zinc. Figure 5-8 represents the metal loading curves for experiment ExpS4. The data for Ni, Cu, Co and Pb for the other column tests showed very similar results (Appendix B). The zero point on the x-axis represents the feed concentration of each metal ion displayed on the y-axis. The y-axis represents the discharge metal concentrations from the column.



**Figure 5-8: Resin loading curves for Ni, Cu, Co, Fe, Pb and Zn – ExpS4, 10 BV/h, 45 mg/L Zn, 15 mg/L Fe.**

Figure 5.8 shows that iron is the only other metal that co-loads with zinc, confirming the results of the batch tests (section 5.1.3). The zinc and iron curve have similar shapes and can be expected as the batch experiments showed similar distribution ratios. Figure 5-9 also indicate co loading of iron, but the curve is not as steep as in Figure 5-8. The major difference in these two experiments is the ratio of Zn:Fe. The iron loading for both these experiments were 1.6 g iron/L resin. The iron loading for Exp S1 and S3 were 1.4 and 1.8 g iron/L resin respectively. This suggests that the iron loading is constant and is not affected by the Zn:Fe ratio and feed rate.

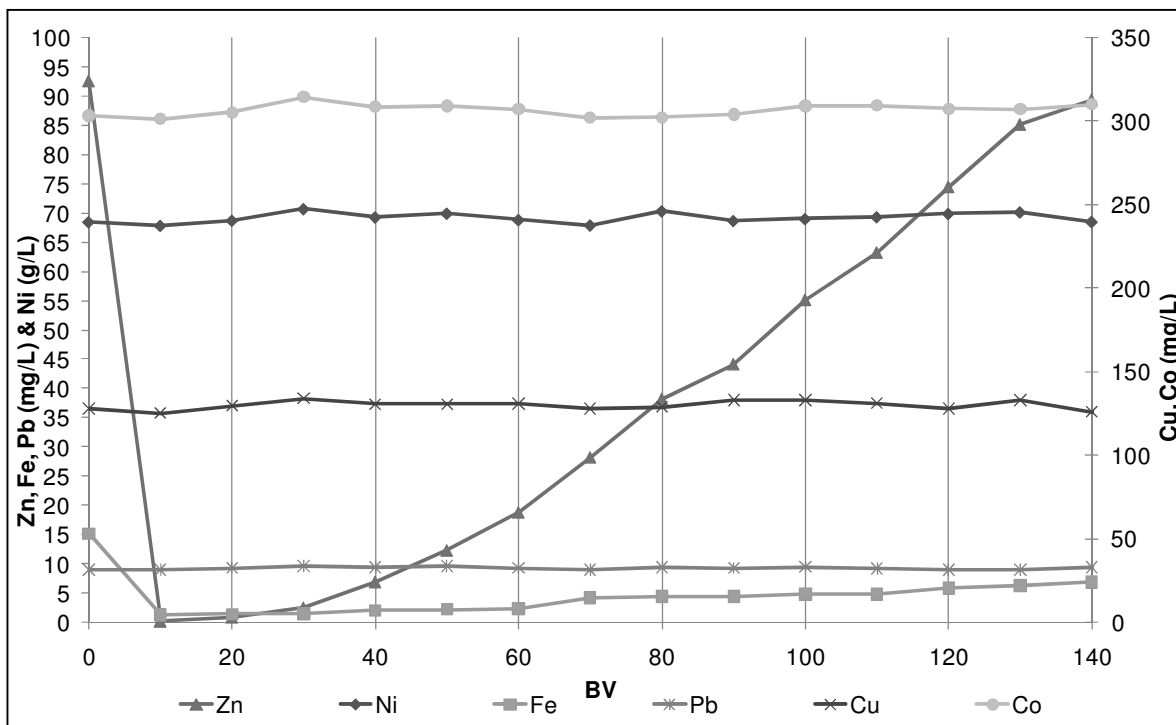


Figure 5-9: Resin loading curves for Ni, Cu, Co, Fe, Pb and Zn – ExpS2, 10 BV/h, 93 mg/L Zn, 15 mg/L Fe.

### 5.3 Batch Elution Results

The following sets of experiments were conducted to evaluate the elution of the Lewatit resin with regard to zinc and iron. These were done to evaluate how easily zinc and iron can be stripped from the resin. The iron was of special interest as it is normally not easily stripped from D<sub>2</sub>EHPA with sulphuric acid. The common practice in liquid-liquid extraction applications, where D<sub>2</sub>EHPA is the organic extractant, is to remove iron by stripping the organic phase with an HCl solution (Akhlaghi *et al.*, 2010). The use of HCl in industrial metallurgical plants is not favoured as the materials of construction for mechanical equipment become very expensive.

Two synthetic solutions, one containing iron as ferrous and one as ferric, were made up. Table 5-7 indicates that 90% of the zinc in solution and all the iron, introduced as ferrous, in solution were loaded onto the resin. The resin was then eluted with 10% sulphuric acid. Table 5-7 indicates a 100% recovery of the loaded zinc, but only 10% to 15% of the iron. This would indicate that 90% of the iron loaded remained on the resin.

**Table 5-7: Elution batch test results for Fe(II).**

| Sample   | Zn (mg/L)    | Fe(II) (mg/L) |                    |                    |
|--|--------------|---------------|--------------------|--------------------|
| <b>Feed</b>  | <b>227.7</b> | <b>60.7</b>   | <b>Zn</b>          | <b>Fe(II)</b>      |
| <b>Raffinate</b>                                   |              |               | <b>% Loaded</b>    | <b>% Loaded</b>    |
| Ferrous 1  | 17.0         | 0.9           | 92.5               | 98.6               |
| Ferrous 2  | 22.5         | 0.2           | 90.1               | 99.6               |
| Ferrous 3  | 23.7         | 0.2           | 89.6               | 99.6               |
| <b>Eluted with 10% H<sub>2</sub>SO<sub>4</sub></b> |              |               | <b>% Recovered</b> | <b>% Recovered</b> |
| Eluate 01  | 222.9        | 5.9           | 105.8              | 9.9                |
| Eluate 02  | 209.6        | 8.8           | 102.2              | 14.6               |
| Eluate 03  | 196.4        | 9.2           | 96.3               | 15.1               |

Similarly the experiments were repeated for iron in the ferric state. Table 5-8 indicates that 90% of the zinc was extracted and almost 100% of the iron. After elution 100% of the zinc was recovered and only 11% to 14% of the iron.

**Table 5-8: Elution batch test results for Fe(III).**

| Sample   | Zn (mg/L)    | Fe(III) (mg/L) |                    |                    |
|--|--------------|----------------|--------------------|--------------------|
| <b>Feed</b>  | <b>196.9</b> | <b>50.3</b>    | <b>Zn</b>          | <b>Fe(III)</b>     |
| <b>Raffinate</b>                                   |              |                | <b>% Loaded</b>    | <b>% Loaded</b>    |
| Ferric 01  | 14.3         | 2.2            | 92.7               | 95.6               |
| Ferric 02  | 14.2         | 2.5            | 92.8               | 95.0               |
| Ferric 03  | 13.4         | 1.6            | 93.2               | 96.9               |
| <b>Eluted with 10% H<sub>2</sub>SO<sub>4</sub></b> |              |                | <b>% Recovered</b> | <b>% Recovered</b> |
| Eluate 1   | 185.0        | 5.8            | 101.4              | 12.0               |
| Eluate 2   | 182.2        | 6.8            | 99.7               | 14.2               |
| Eluate 3   | 175.8        | 5.5            | 95.8               | 11.2               |

The selectivity order for Lewatit VP OC 1026 shows that Fe(III) > Zn > Fe(II). This would suggest that the iron in solution converted to Fe(III) on exposure to air and explains why the results in Table 5-8 and Table 5-9 are very similar. These two tests would also suggest that a 10% sulphuric acid solution is not adequate to remove all the iron from the resin. The resin will foul with iron and needs to be eluted with a stronger acid or different acid, such as HCl.

Column elution test were not conducted for the Lewatit VP OC 1026, however, section 6.5 describes the plant elution results. The batch elution test proved to be adequate to show that zinc elutes easily and completely. The resin would therefore foul with iron in the long run. At the

time this was not considered to be a major issue as the iron in CTF was expected to reduce when the RBMR expansion project's new PIR section came online.

Another consideration was to remove the resin periodically and to elute it with HCl to remove the iron. This would have had to be done off-site as the availability and use of HCl at RBMR was not an option. The risk of revenue loss, due to zinc contamination of the nickel cathode, outweighed the risk of fouling the resin with iron.

Both the Lewatit VP OC 1026 and Purolite S950 correlated well with the Langmuir isotherm fit. According to the Purolite S950 data sheet, it has a minimum loading capacity of 40 g/L of copper and should be similar for zinc. The co-loading of iron, copper and lead thus reduced the loading capacity for zinc to around 5.7 g/L. The calculated loading capacity for the Lewatit VP OC 1026 of 15.8 g/L was considered to be acceptable, as the data sheet reports a minimum loading capacity for zinc as 13 g/L. The selectivity orders for both resins correlated well with what is reported in the resin data sheet and in literature. The distribution ratios for zinc and iron on the Lewatit resin were very similar and the separation factor was between 0 and 1, indicating no separation selectivity. The Purolite S950 showed the highest separation factors for nickel and cobalt to zinc. These were however, orders of magnitude smaller than the Lewatit VP OC 1026 separation factors. The Lewatit VP OC 1026 was considered the most appropriate resin to use for the column test because of the following findings:

- Higher loading capacity for zinc;
- Higher separation factors with regard to Ni, Cu, Co and Pb;
- No pH adjustment of the CTF feed solution required.

The column tests for Lewatit VP OC 1026 indicated significantly lower loading capacities compared to the maximum loading capacity obtained in the batch experiments. The column tests showed a constant iron loading of between 1.4 and 1.8 g Fe/L resin. The experiment with feed solution at 48 mg/L Zn indicated a resin loading capacity of 5.3 g/L. This 48 mg/L Zn solution compares well with the real CTF plant solution of between 10 and 50 mg/L Zn. The selectivity of the Lewatit resin under column operation displayed similar results as in the batch experiments with only iron co-loading. The batch elution tests showed that the zinc is easily and completely eluted with a 10% sulphuric acid solution. The iron loaded on the resin did not elute completely and only 15% to 20% was recovered from the resin. This would suggest that a stronger acid, such as HCl would be required to strip the iron, as the ferric ion, off the resin (Akhlaghi *et al.*, 2010).

The experimental results provided enough information with regard to feed flow rate, pH and zinc loading capacity to be able to design a full-scale ion-exchange plant. Chapter 6 explains the design considerations, commissioning of the installed plant and the results for the first six months of operation.

## 6. PLANT DESIGN, COMMISSIONING AND OPERATION

This chapter contains the design parameter calculations, commissioning results and the first six months of plant operating data for the ion-exchange plant installed at Rustenburg Base Metal Refiners. The experimental data as described in this thesis were used to design this plant and provide appropriate operating conditions to achieve the zinc removal required from the circuit.

### 6.1 Plant Design

This section explains the ion-exchange design considerations and the procedure to specify the design criteria for equipment manufacturing.

#### 6.1.1 Design Procedure

A single fixed bed ion-exchange column was considered for this plant. A lead-lag system could also work for this application, but would require more equipment, resulting in a higher capital cost. The main reason a single column was chosen above the lead-lag system was that this plant was designed to bleed zinc from the circuit and not ensure a constant zinc-free product. This means that no zinc removal would take place during elution, but that the plant is adequately sized to remove enough zinc during the loading cycle.

The plant was mechanically designed and built by Roymec Technologies, Woodmead. Table 6.1 and 6.2 indicates the design feed specification that was supplied to Roymec Technologies.

**Table 6-1: Zn ion exchange feed specification.**

| Cobalt Treatment Filtrate      | Unit              | Value | Comment       |
|--------------------------------|-------------------|-------|---------------|
| Flow rate                      | m <sup>3</sup> /h | 15.0  | maximum       |
| Temperature                    | °C                | 72    | maximum       |
| Co                             | mg/L              | 143   |               |
| Cu                             | mg/L              | 66    |               |
| Fe                             | mg/L              | 3     |               |
| Zn                             | mg/L              | 30    | range 10 - 50 |
| Ni                             | g/L               | 68    |               |
| H <sub>2</sub> SO <sub>4</sub> | g/L               | 1     |               |
| pH                             | -                 | 2.8   |               |

The increased temperature of this stream compared to the experimental conditions will improve the loading kinetics and a higher loading capacity can be expected.

The design procedure detailed below was adapted from Crittenden *et al.* (2005). These steps assisted in developing the design criteria for a full-scale design. The following aspects were considered:

- Scale-up considerations;
- Column design details, including volume of resin, surface area of columns, number of columns, sidewall height, pressure drop, and inlet and outlet arrangements;
- Overall cycle time.

Table 6-2 represents the selected data from the experimental results that were considered to calculate the full-scale design parameters.

**Table 6-2: Experimental data required for full-scale design.**

| Experimental parameter                           | Symbol/formula | Value | Unit           |
|--|----------------|-------|----------------|
| Resin: Lewatit VP OC 1026                        | -              | -     | -              |
| Resin loading capacity                           | q              | 5*    | g Zn / L resin |
| Service flow rate                                | SFR            | 10    | BV/h           |
| Superficial velocity                             | u              | 2.5   | m/h            |
| Bed depth  | d              | 258   | mm             |
| Bed volume                                       | BV             | 100   | ml             |
| Empty bed contact time                           | EBCT           | 6.2   | min            |
| *Loading capacity obtained in column experiments |                |       |                |

The first step was to calculate the volume of resin required for a specific service flow rate (SFR). This flow rate is expressed in bed volumes per hour (BV/h). The required design flow rate of the plant (Q) divided by the SFR will yield the amount of resin required for the full-scale plant.

The next step is to calculate the cross-sectional area of the resin bed required, based on the volume of resin and the selected resin bed depth. The typical resin bed depth for industrial applications ranges between 0.75 m and 3 m. The resin bed depth selected for this application was 1.0 m. Table 6-3 indicates the calculation of the resin bed cross-sectional area as in m<sup>2</sup>. The column diameter required was then calculated using the calculated cross-sectional area.

The empty bed contact time (EBCT) for the full-scale design should correspond with the experimental EBCT in order to expect similar results. The EBCT for the full-scale plant design using Table 6-3 is slightly longer than that of the experimental data (Table 6-2), and is acceptable.

To calculate the side wall height, the total resin bed depth and column freeboard is required. The supplier data sheet for Lewatit VP OC 1026 resin (Appendix C) specifies a 10% freeboard if adequate pre-filtration is done as well as the use of an inert resin (Lewatit IN42) to ensure that the fine resin particles do not block the head distributor. The suspended solids concentration in the CTF is between 50 and 100 mg/L, thus a pre-filtration step is required to reduce this to less than 10 mg/L. A freeboard of 20% was chosen to allow for future addition of more resin, should it be required.

**Table 6-3: Design criteria calculation procedure for the full-scale plant.**

| Description                           | Symbol/formula              | Unit                 | Comment                          |
|---------------------------------------|-----------------------------|----------------------|----------------------------------|
| <b>Plant solution data</b>            |                             |                      |                                  |
| Plant design flow rate                | Q                           | m <sup>3</sup> /h    | Specify maximum flow             |
| Zn concentration                      | Co                          | g/L                  | Use average concentration        |
| <b>IX Column Design</b>               |                             |                      |                                  |
| Service flow rate for plant           | SFR                         | BV/h                 | Experimental condition           |
| <b>Volume of resin</b>                | $V_r = Q/SFR$               | m <sup>3</sup>       | Calculated resin bed volume      |
| Choose bed depth                      | d                           | m                    | industry range = 0.75 to 3 m     |
| <b>Resin bed cross-sectional area</b> | $A = V/d$                   | m <sup>2</sup>       |                                  |
| Superficial velocity                  | $u = Q/A$                   | m/h                  | industry range = 10 - 36 m/h     |
| Empty Bed Contact Time                | $EBCT = d/u$                | min                  | Should be similar to experiments |
| Column diameter                       | $D_c = (4/\pi * A)^{0.5}$   | m                    |                                  |
| <b>Side wall height</b>               | $H = d + d_i + d_f$         | m                    |                                  |
| Inert resin (Lewatit IN42)            |                             | m <sup>3</sup>       | to avoid plugging of distributor |
| Inert resin depth                     | $d_i$                       | m                    |                                  |
| Required freeboard                    |                             | %                    | Specified by resin manufacturer  |
| Freeboard                             | $d_f$                       | m                    |                                  |
| Total column volume                   | $V_c = A * H$               | m <sup>3</sup>       |                                  |
| <b>Pressure Drop</b>                  | $dP = dP_s * Q / (d + d_i)$ | kPA                  | Specified by resin manufacturer  |
| Specific pressure drop                | $dP_s$                      | kPa.h/m <sup>2</sup> | for water                        |
| Zn mass flow to column                | $Q * Co$                    | kg/h                 |                                  |
| Total resin capacity                  | $V * q$                     | kg                   |                                  |
| Time for full loading                 | $t_f = V * q / Q * Co$      | h                    | resin saturation                 |
| Elute every                           | $t_f * SFR$                 | BV                   |                                  |

The column pressure drop needed to be checked to ensure that the maximum pressure drop for the ion-exchange resin bed did not exceed 172 kPa (Crittenden *et al.*, 2005). Manufacturers provide specific pressure drop curves for commercially available resins. The superficial velocity for this system is 7.5 m/h; the initial pressure drop through the resin is 1.1 kPa.h/m<sup>2</sup>, as provided by the Lewatit VP OC 1026 data sheet (Appendix C). For a resin depth of 1.0 m, the clean-water pressure drop is 1.1 kPa.h/m<sup>2</sup> or 13.2 kPa (see Table 6-3 for pressure drop calculation). The clean-water pressure drop column design is well below the maximum allowable pressure drop. The CTF solution density is about 1200 kg/m<sup>3</sup> therefore the pressure drop could thus be slightly higher compared to the clean-water pressure drop.

Table 6.4 indicates the design and operating parameters for the full-scale design.

**Table 6-4: Zinc ion-exchange design and operating parameters.**

| Process                 |                                | Unit             | Value                 | Comment                         |
|-------------------------|--------------------------------|------------------|-----------------------|---------------------------------|
| IX type                 |                                | -                | Fixed Bed             |                                 |
| Resin type              |                                | -                | Lewatit OC-1026       | D <sub>2</sub> EHPA impregnated |
| Bulk density            |                                | t/m <sup>3</sup> | 0.6                   |                                 |
| Size                    |                                | P90 - μm         | 310                   |                                 |
| Volume                  |                                | m <sup>3</sup>   | 2.0                   | 1 BV = 2 m <sup>3</sup>         |
| Metal loading           |                                |                  |                       |                                 |
| Zn                      |                                | g/L              | 5.0                   | minimum                         |
| Feed rate               |                                | BV/h             | 7.5                   | maximum                         |
| <b>Cycle times</b>      |                                |                  |                       |                                 |
|                         | Loading                        | h                | 22                    |                                 |
|                         | Elution                        | h                | 1                     | standard practice               |
|                         | Wash                           | h                | 1                     | standard practice               |
| <b>Volumes</b>          |                                |                  |                       |                                 |
|                         | Wash                           | BV               | 2.5                   |                                 |
|                         | Elution                        | BV               | 2.5                   |                                 |
| <b>Volumetric flows</b> |                                |                  |                       |                                 |
|                         | Wash                           | BV/h             | 2.5                   |                                 |
|                         | Elution                        | BV/h             | 2.5                   |                                 |
| <b>Compositions</b>     |                                |                  |                       |                                 |
| Wash                    |                                |                  |                       |                                 |
|                         | Type                           | -                | Acidified demin water |                                 |
|                         | pH                             | -                | <4                    | supplier data sheet             |
| Eluant                  |                                |                  |                       |                                 |
|                         | Type                           | -                | 10% Sulphuric acid    |                                 |
|                         | H <sub>2</sub> SO <sub>4</sub> | g/L              | 100.0                 |                                 |

The final design, done by Roymec Technologies, corresponded well with the design values that can be calculated using the method described in Table 6-3.

The sizes of the complete installed mechanical equipment represented in Figure 6.1 are shown in Table 6-5. The equipment was specified and sized as per Roymec Technologies' calculations and best practice.

**Table 6-5: Zinc ion exchange mechanical equipment sizes.**

| Process Units    | Size                 | No | Comments   |
|------------------|----------------------|----|--|
| Zn IX column     | 3 m <sup>3</sup>     | 1  | 2 m <sup>3</sup> Lewatit resin; 0.5 m <sup>3</sup> Inert resin |
| Feed tank        | 10 m <sup>3</sup>    | 1  |  |
| Eluate tank      | 5 m <sup>3</sup>     | 1  |  |
| Raffinate tank   | 10 m <sup>3</sup>    | 1  |  |
| Media filter     | 15 m <sup>3</sup> /h | 1  | 800 L of media - garnet, anthracite and silica                 |
| Cartridge filter | 15 m <sup>3</sup> /h | 2  | 5 µm - 5 x polypropylene cartridges per filter                 |

All the equipment, except for the tanks, was designed to fit on a skid. The plant was thus manufactured and assembled off-site. The skid-mounted plant was then delivered to site for final installation. The piping, electrical and instrumentation connections were then done. The material of construction for all vessels is 316L stainless steel. The ion-exchange column and media filter were designed to the American Society of Mechanical Engineers (ASME) code which classes these items as pressure vessels.



**Figure 6-1: Zinc ion-exchange plant at RBMR.**

### 6.1.2 Process Description

Figure 6-2 shows the process flow diagram of the zinc ion-exchange plant. The entire plant is automated and requires minimal interaction from the operators. CTF is received directly from the cobalt filter presses; at the filter press feed pump pressure. An actuated isolation valve is installed upstream of the feed tank TK-020 to prevent overflowing of the tank, should the plant be off-line or on reduced flow. A flow meter is used to measure the flow rate of the incoming CTF. The feed to the ion-exchange plant must be controlled at a pH of 2.7-3.0, and spent nickel electrolyte is fed into an inline mixer together with the CTF to control this. The flow of CTF from tank TK-020 to the media filter is based on the level of the tank. The flow is set to a linear algorithm that controls the tank level between 50% and 80%, with a maximum flow of 15 m<sup>3</sup>/h. The flow set-point will increase incrementally on an increase in level, and decrease on a decrease in level. As the flow into the tank is highly fluctuating, an incremental change is preferred in order to keep the flow to the ion exchange as stable as possible.

The CTF from the feed tank is passed through a multimedia filter (FIL-008) in order to remove as much of the entrained suspended solids as possible. The CTF suspended solids concentration is generally between 50 and 100 mg/L. The flow through the filter continues until a pre-set pressure drop over the filter, measured by comparing the inlet and outlet pressures, is reached. This increase in pressure drop initiates the backwash sequence. The backwash sequence is also programmed to run every 12 hours making sure that the bed does not become saturated with solids. A turbidity meter is installed on the feed line to TK-020 to monitor the turbidity (suspended solids) and to by-pass the ion exchange in case of high turbidity (> 100 mg/L).

A duplex polishing filter set is installed to remove any remaining suspended solids from the CTF to less than 10 mg/L. The filters have cartridges that need to be replaced once loaded with solids. When a pre-set pressure drop is measured over the cartridge filters, an alarm displays to notify the operator to manually change the cartridges. This is the only manual operation required for the entire ion-exchange plant.

The feed, elution and wash solution all enter the column from the bottom. This up-flow operation is done to ensure that the liquid distributors inside the column does not block with resin. The resin has a lower specific gravity than water and therefore floats and would cause a blockage in a down-flow operation. The resin manufacturer also recommends up-flow operation.

The ion-exchange column (TK-023) is loaded with Lewatit VP OC 1026 ion-exchange resin that selectively removes zinc from the CTF stream. The zinc-free solution discharging the column, called raffinate, flows into the raffinate storage tank (TK-021). This solution is then pumped back into the process. Zinc is loaded progressively over time onto the resin, until it is fully loaded (or

saturated) with zinc. This is determined by monitoring the feed and raffinate zinc concentrations and calculating the number of bed volumes when the raffinate zinc concentration reaches a value 80% of the feed value. At this point, the ion-exchange column must be eluted. The control system is set up to input a bed volume set point when the column must be eluted.

The zinc is eluted by passing a 10% sulphuric acid solution through the ion-exchange resin bed. The elution sequence is initiated after the pre-set number of bed volumes. The acid solution is passed through the column at 5 BV/h for a pre-set time and the eluate transferred to the eluate storage tank (TK-022). When elution is complete, a wash step is initiated. Demineralised water is passed through the column to wash the resin after elution and is directed to the eluate storage tank (TK-022). The pH of the demineralised water must not exceed pH 5. A pH greater than 5 will cause the D<sub>2</sub>EHPA extractant impregnated in the resin to be displaced. The pH is maintained between 3 and 5 by contacting the demineralised water with 10% sulphuric acid before it enters the column.

The acidic zinc solution in the eluate tank (TK-022) is then pumped to the effluent treatment plant. This effluent plant treats all the effluent from the RBMR and this is done by adjusting the pH of the effluent solution to pH 10, in order to precipitate the contained zinc and base metals as hydroxide species. This solution is then filtered to remove the zinc and base metal hydroxides. The filter cake is then transported to the smelter complex to ensure that any co-precipitated base metals are recovered. The zinc is rejected to the slag in the smelting process.

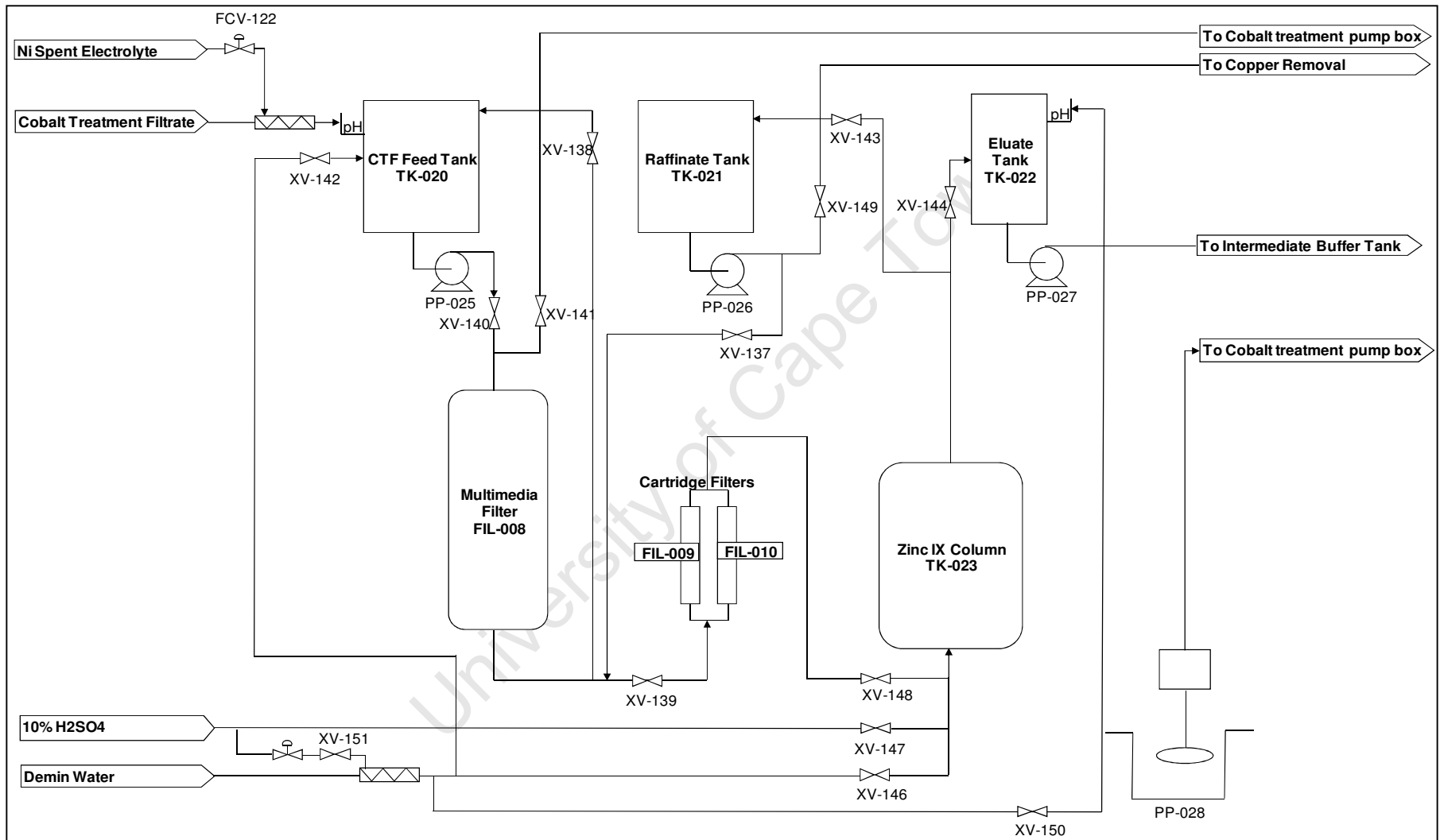


Figure 6-2: Zinc ion-exchange plant process flow diagram.

## 6.2 Plant Commissioning

The ion-exchange plant was successfully commissioned over a period of three months during 2011. Table 6-6 indicates the various commissioning stages undertaken during the execution of the project. My responsibility involved complete management of the commissioning process, with regard to safety, operation, training and final hand over to the plant.

**Table 6-6: Commissioning stages.**

| Stage | Description                             |
|-------|---|
| C0    | Commissioning Preparation               |
| C1    | Construction/Installation               |
| C2    | Electrical/Instrumentation Loop Testing |
| C3    | Wet Commissioning                       |
| C4    | First Fill                              |
| C5    | Hot Commissioning and Stabilization     |
| C6    | Ramp up & Optimization                  |

C0 – Commissioning preparation included the following tasks:

- Setup commissioning team with all relevant disciplines.
- Prepare commissioning method statement.
- Conduct a risk assessment on the fabricated equipment.
- Conduct a commissioning risk assessment.
- Review the training documents and operating instructions.
- Review the critical spares required.
- Review the planned maintenance scheduled.
- Factory acceptance testing of the process control software and sequences.

The C1 stage involved the installing the last pieces of equipment and compiling a punch list. The punch list highlighted areas where the equipment deviates from the design or need to be modified due to safety and operational requirements. Once the items on the punch list were completed, the construction completion certificates were signed off.

C2 commissioning involved the testing of electrical motors and instrumentation control loops. Once again a punch list was compiled to identify problematic areas that needed to be corrected before wet commissioning could commence.

The C3 wet commissioning involved filling all process equipment with water and pressure testing the ion-exchange column and media filter. This was done to identify any leaks and that the valves sealed correctly, before process solution was introduced. The plant was then started up with water, making sure that all equipment was functional and that all instrumentation operated correctly.

During C4 commissioning the ion-exchange column was filled with resin and the media filter with the required filter media. The feed tank was then filled with CTF solution and all the pH probes calibrated.

C5 hot commissioning involved the start-up of the ion-exchange plant with process solution. During this period a slight modification had to be made to the feed tank pH pot. A longer breather pipe was installed on the pH pot to ensure that solution was not discharged through the breather pipe. The level-indicating probes did not operate correctly as the build-up of condensate caused the sensors to give incorrect readings. This was corrected by using longer bolts and spacers so that the vapour could escape between the tank flange and the instrument flange. The plant was then operated as per the design specifications and continuously monitored.

During the C6 commissioning stage, the various operating parameters were reviewed. The number of bed volumes before elution was calculated based on the loading of the resin during continuous operation. During this stage, the elution profile was checked and adjusted to ensure minimum loss of nickel to the eluate and minimum contamination of zinc in the raffinate.

The commissioning of the ion-exchange plant was regarded as a success, with no injuries or incidents reported during the execution. The ion-exchange plant operated to the design specifications and achieved the required zinc removal, as indicated in the following section.

### **6.3 Plant Operation and Verification of Plant Performance**

The zinc ion-exchange plant was started on 24 March 2011. The plant was operated to elute every 250 bed volumes, which is every ~33 hours. Figure 6-3 indicates the zinc ion-exchange feed and raffinate concentrations. Samples were taken every 8 hours and the graph below indicates the daily averages. The average feed concentration for this period was 18 mg/L zinc and average raffinate concentration for this period was 9 mg/L.

Figure 6-4 indicates the nickel cathode product zinc concentration for a period before and after the zinc ion-exchange plant start-up. It is evident from the graph that a step change in the nickel cathode zinc concentration occurred when the ion-exchange plant was started. The average zinc concentration in the nickel cathode for the period before the ion-exchange start-up was 32 ppm and this dropped to 18 ppm for the period after the ion exchange was started.

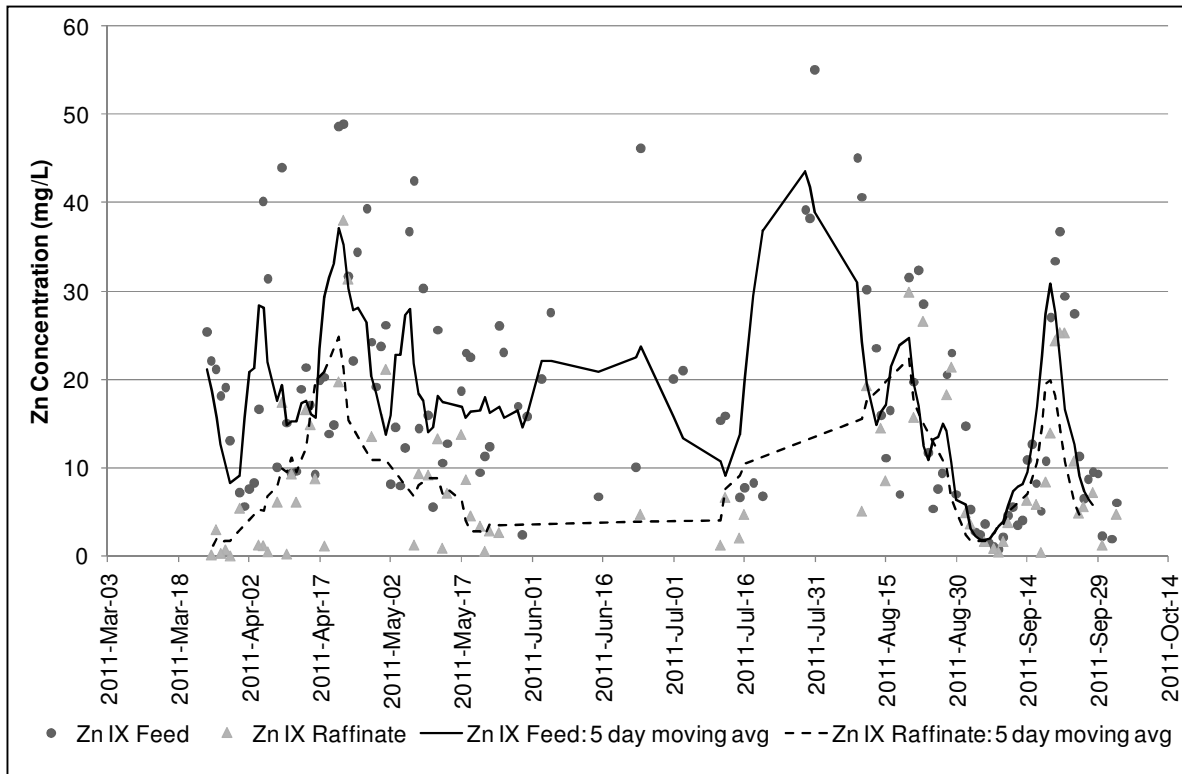
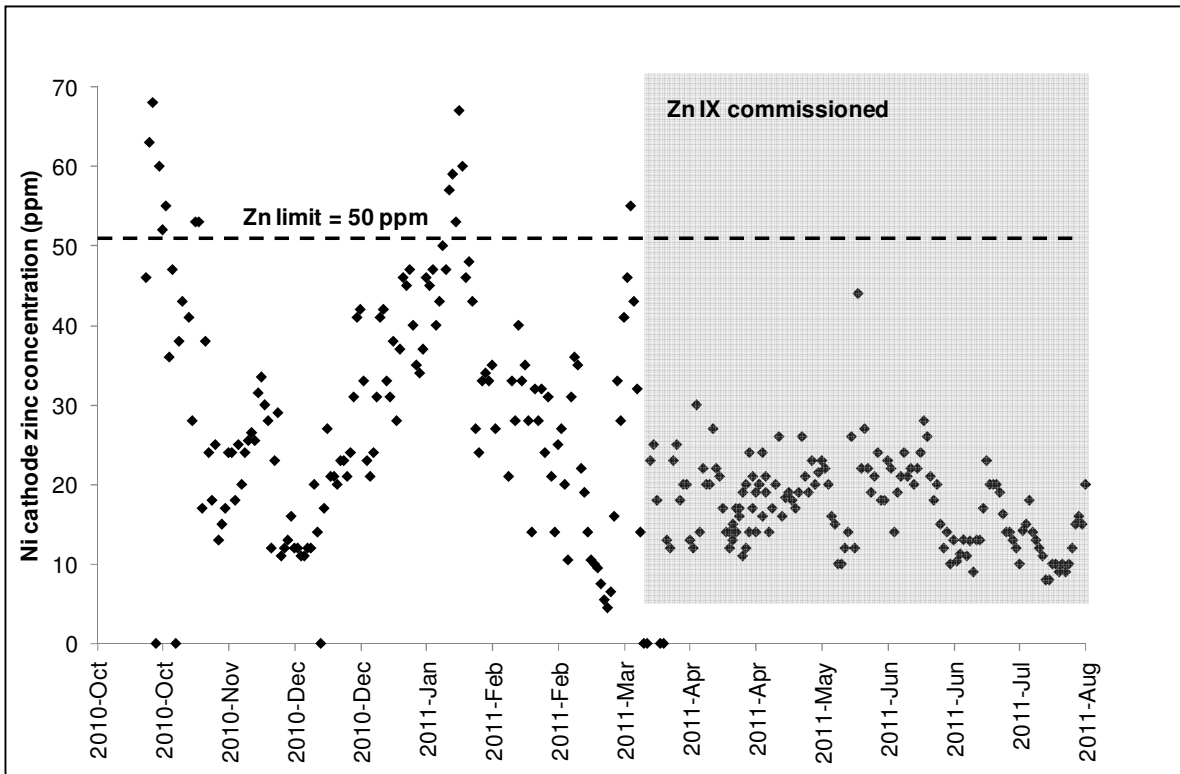


Figure 6-3: Zinc ion-exchange plant feed and raffinate concentrations.



**Figure 6-4: Zinc department to the nickel cathode before and after commissioning of zinc ion-exchange plant.**

To evaluate whether this was a real step change as a result of the zinc ion-exchange plant, the zinc in the feed to the refinery had to be compared for the two periods. Figure 6-5 indicates similar zinc concentrations for WCM, NCM and PVL, the feed samples to the refinery, for both periods. The mass flows to the refinery for these periods were also similar. It is therefore correct to state that the step change in zinc concentration could be attributed to the start of the ion-exchange plant. The zinc inventory reduced significantly and can be deduced from the drop in the copper removal residue (CRR) zinc concentration. It was shown in the mass balancing exercise that the main build-up of zinc occurs in the copper removal residue.

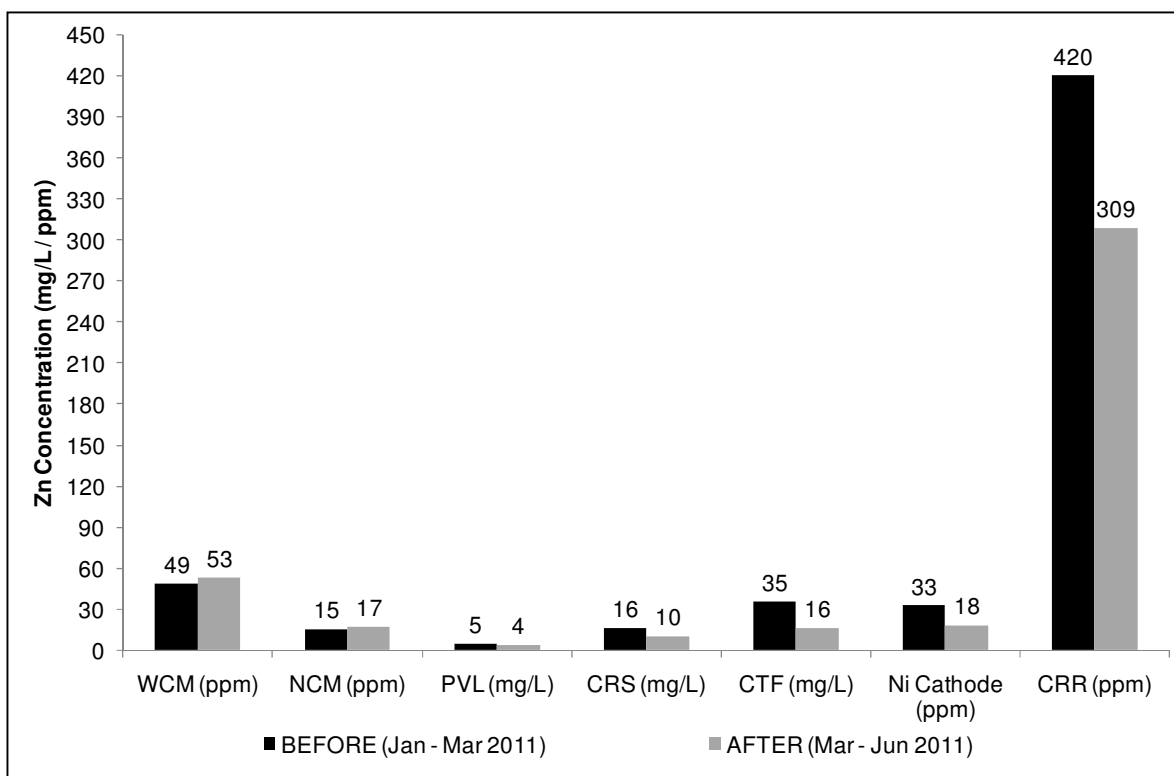
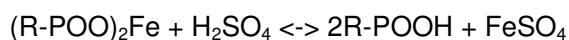
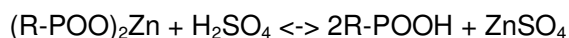


Figure 6-5: Zinc department before and after the zinc ion-exchange plant commissioning.

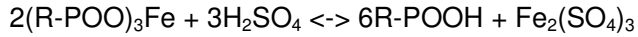
Based on the above data, it was calculated that the zinc ion-exchange plant can remove 40% of the total zinc that enters RBMR. This is more than adequate to ensure a nickel cathode product containing less than 50 ppm zinc. The remaining zinc still leaves the circuit through the nickel cathode, copper cathode, iron residue and lead removal residue.

#### 6.4 Plant Elution Data

This section discusses the elution data obtained during two elution cycles of the ion-exchange plant. This was done to check whether the initial design elution time was correct and to confirm the stripping behaviour of iron from the resin using 10% sulphuric acid. When the 10% sulphuric acid contacts the resin, there is a large shift of equilibrium in  $H^+$  ions in solution to the resin and can be represented by the following reactions:



Where, R-POOH represents the  $D_2EHPA$  on the resin. This happens rapidly and does not require a long contact time. The elution of ferric is represented by the following reaction:



This reaction is not favourable and requires a strong acid such as HCl for complete removal (Akhlaghi, 2010).



The first elution was initiated after 250 bed volumes of plant operation. Figure 6-6 indicates the elution profile for zinc and iron. The zinc spiked to a maximum of 6800 mg/L and the iron to a maximum of 8.5 mg/L. The elution cycle started with a 40 minute acid contact and 40 min acidified demineralised water wash at a flow rate of 5 BV/h.

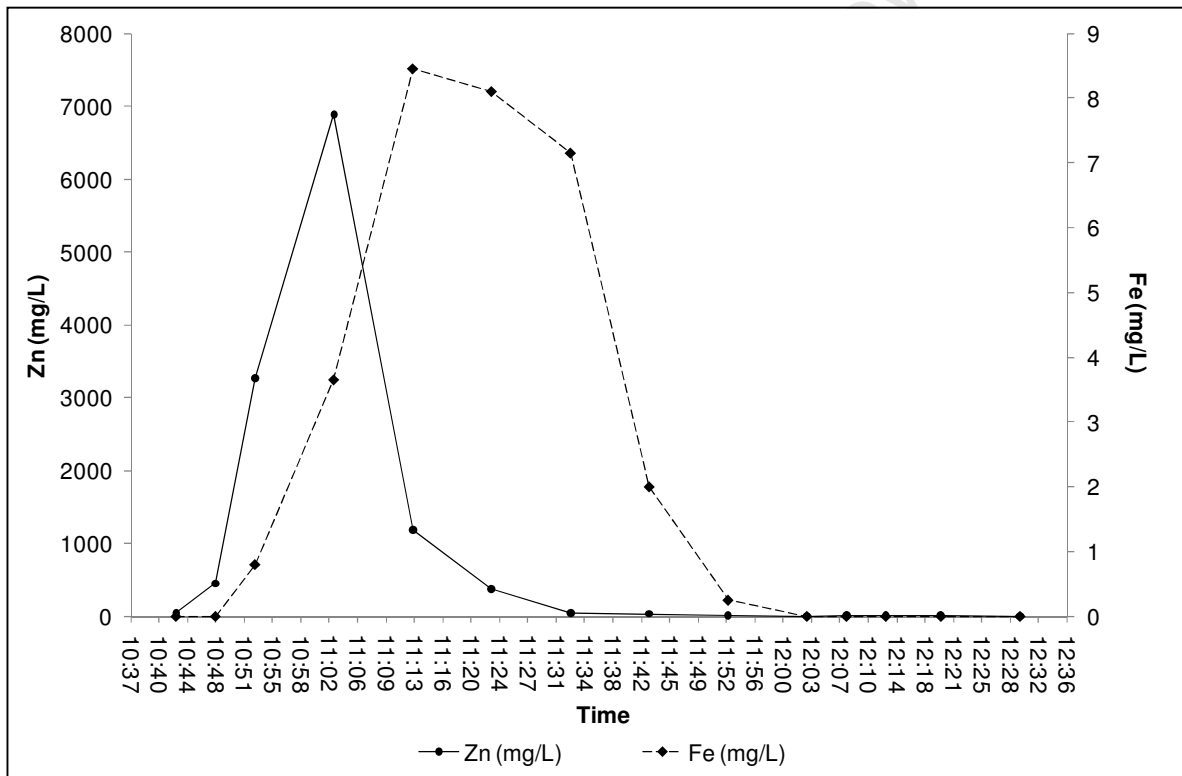


Figure 6-6: Zinc ion-exchange plant elution profile – 250 BV.

A mass balance was done for the elution profile and the values are shown in Table 6-7. The table indicates that 93.4% of the total zinc fed to the column was extracted and only 11.6% of the iron. The metal eluted was calculated as a percentage of the metal loaded. This shows that 93.7% of the zinc on the resin was eluted and only 20.9% of the iron. The 20.9% elution of iron corresponds with the batch elution test results. This translates to only 2% of the iron present in the feed solution reporting to the eluate.

**Table 6-7: Mass balance data and calculation of eluted metal after 250 BV.**

| Volume treated                   |      |                | Mass of metal fed    |        | Base           |
|----------------------------------|------|----------------|----------------------|--------|----------------|
| BV before elution                | 250  | BV             | Zn                   | 9950 g | 100 %          |
| Volume                           | 500  | m <sup>3</sup> | Fe                   | 1050 g | 100 %          |
| Average feed concentrations      |      |                | Mass of metal loaded |        | % Metal loaded |
| Zn                               | 19.9 | mg/L           | Zn                   | 9290 g | 93.4 %         |
| Fe                               | 2.1  | mg/L           | Fe                   | 122 g  | 11.6 %         |
| Average raffinate concentrations |      |                | Mass of metal eluted |        | % Metal eluted |
| Zn                               | 1.3  | mg/L           | Zn                   | 8703 g | 93.7 %         |
| Fe                               | 1.9  | mg/L           | Fe                   | 25 g   | 20.9 %         |

Table 6-8 represents the same calculations as in Table 6-7 after 200 bed volumes of plant operation. It must be noted that the average zinc concentration was five times lower for these calculations.

**Table 6-8 Mass balance data and calculation of eluted metal after 200 BV.**

| Volume treated                   |      |                | Mass of metal fed    |        | Base           |
|----------------------------------|------|----------------|----------------------|--------|----------------|
| BV before elution                | 200  | BV             | Zn                   | 1680 g | 100 %          |
| Volume                           | 400  | m <sup>3</sup> | Fe                   | 584 g  | 100 %          |
| Average feed concentrations      |      |                | Mass of metal loaded |        | % Metal loaded |
| Zn                               | 4.2  | mg/L           | Zn                   | 1200 g | 71.4 %         |
| Fe                               | 1.46 | mg/L           | Fe                   | 8 g    | 1.4 %          |
| Average raffinate concentrations |      |                | Mass of metal eluted |        | % Metal eluted |
| Zn                               | 1.2  | mg/L           | Zn                   | 1078 g | 89.9 %         |
| Fe                               | 1.44 | mg/L           | Fe                   | 2 g    | 22.5 %         |

Table 6-8 shows that only 71.4% of the total zinc fed to the column was loaded and 89.9% of the loaded zinc stripped during elution. Only 1.4% of the total iron loaded and again only 22.5% was stripped from the resin. In both cases the iron elution corresponded with the percentage eluted in the batch elution experiment (Section 5.3). Figure 6-7 shows the elution profile after 200 bed volumes with zinc reaching a maximum of 1162 mg/L and iron at a maximum of only 4 mg/L. The lower values are attributed to the total metal loaded as the average feed concentration to the column was significantly lower during this particular test.

In both elution graphs the discharge concentrations of the eluted resin approach zero. This would suggest that all the zinc is being stripped off the resin, but the calculations indicate that this value is between 90% and 93%. This could suggest that 40 minutes of acid contact is slightly short and should probably be extended by another 10 minutes.

The iron remains a problem as it does not elute completely, but the overall extraction of iron is lower than expected. This would suggest that the majority of the iron must be present as ferrous

and that only the ferric is co-loaded. The order of selectivity for Lewatit VP OC 1026 with regard to iron is Fe(III) > Zn > Fe(II). The ferric will foul the resin over time and thus the resin should be eluted with HCl at least on a yearly basis.

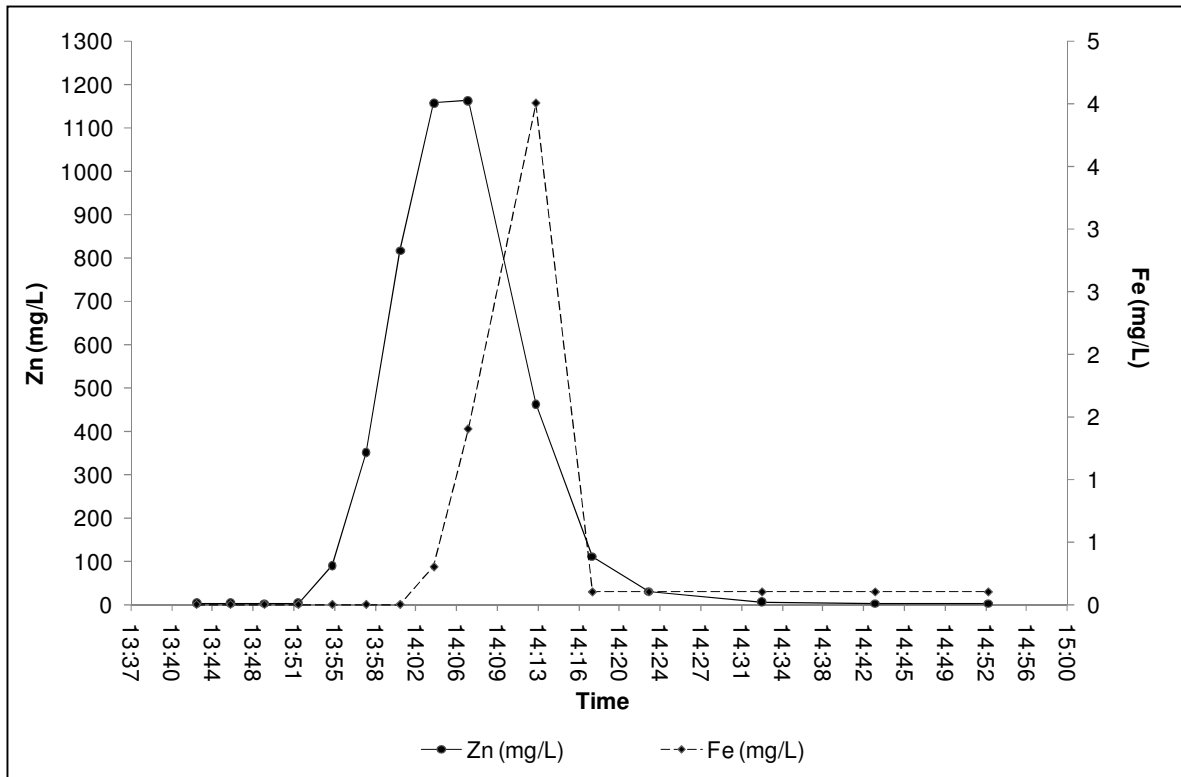


Figure 6-7: Zinc ion-exchange plant elution profile – 200 BV.

The operating data in this section prove that the ion-exchange process works and that it can remove up to 40% of the total zinc that enters RBMR. The plant design is robust and fully automated, ensuring maximum operating time. The low iron loading during the plant operation also provides evidence that most of the iron is present as ferrous. The higher iron loading observed during the experimental test work could be attributed to ferric loading, as the ferrous could have easily oxidised to ferric during the sampling and feed solution preparation. This is less likely to occur in the plant operation as there is reduced air access to the system.

## 7. CONCLUSIONS AND RECOMMENDATIONS

The objective of this research project was to find an ion-exchange resin that effectively removes zinc from a base metal solution, to reduce the zinc inventory in the RBMR circuit, and which would lead to the reduction of zinc in the nickel cathode. The ideal stream, CTF, was identified within the circuit and a series of batch experiments were conducted with Purolite S950 and Lewatit VP OC 1026 resins. The best performing resin from the batch experiments, Lewatit VP OC 1026, was used to conduct column experiments to identify operating conditions. The identified operating conditions were used as a design basis for an ion-exchange plant at RBMR. This plant was built and commissioned in early 2011. The following conclusions and recommendations are based on the results from the laboratory experiments as well as the operating data from the ion-exchange plant installed at RBMR. The conclusions are:

- 1) The CTF stream was selected for the experiments as it was already at the correct pH, the iron and copper concentrations were relatively low compared to the other streams considered and the zinc concentration was in the range that is acceptable for ion exchange. The total volumetric flow for CTF was also much lower than other streams considered.
- 2) The calculated maximum zinc loading capacity for the Lewatit VP OC 1026 resin was more than double that of the Purolite S950 resin. It was found that the co-loading of iron, copper and lead reduced the loading capacity of Purolite S950.
- 3) Both resins displayed the same order of selectivity and minimum pH for zinc extraction as described in the resin data sheets in Appendix C. The Lewatit VP OC 1026 resin had significantly higher separation factors between zinc and the other metals present. This indicated that Lewatit VP OC 1026 was orders of magnitude more selective for zinc compared to Purolite S950.
- 4) The separation factors of zinc and iron for both resins were between 0 and 1 demonstrating that iron is very strongly co-loaded with zinc.
- 5) Batch results at 50°C showed improved loading capacities for both resins. This showed that a better loading capacity can be expected for the CTF (70°C) due to increased mass transfer kinetics. The recommended operating temperatures from the resin supplier should, however, not be exceeded as this will damage the resin structure.
- 6) The column tests showed that, for a feed flow rate of a 100 mg/L zinc solution, running at 20 BV/h gives a better loading capacity than running at 10 BV/h. The shorter MTZL implies that less resin would be required for the same amount of zinc being removed.
- 7) The loading of iron remained constant for different Zn:Fe ratios and column feed rates.
- 8) The batch elution tests showed only 20% recovery of the loaded ferric species. Although a ferrous solution was also tested, the oxidation of ferrous to ferric happens rapidly in air. The

similar results for both tests suggest the iron was in the ferric form under these laboratory conditions.

- 9) Plant elution data showed that only between 1% and 12% of the total iron fed to the column was loaded onto the resin and that only 20% of the loaded iron was eluted from the resin. This suggests that the majority of the iron in the plant CTF solution is in the ferrous state and does not load, whereas the small amount of ferric does load. This is supported by the batch elution results only achieving 20% elution of the iron.
- 10) The loaded ferric will foul the resin, reducing the zinc loading capacity, in the long term and needs to be eluted with HCl to remove the iron completely.
- 11) The plant elution profile also indicated that the zinc elution with 10% sulphuric acid is rapid and that almost all the zinc is removed during the 80 minute elution cycle.
- 12) The plant design calculations corresponded well with the Roymec Technologies final design and show that the scale-up of ion-exchange columns can directly be linked to the laboratory-scale experiment.
- 13) The plant data for the first six months of operation indicated that the ion-exchange plant reduced the zinc inventory in the circuit which, in turn, reduced the average nickel cathode zinc concentration from an average of 33 ppm to 18 ppm.

The following recommendations are based on the plant elution data:

- 1) The 40 minute acid contact during the elution cycle could be extended by 10 minutes to ensure complete elution of zinc.
- 2) Periodic elution with HCl should be considered to possibly remove the loaded ferric ions. Additional test work could also be considered to possibly remove the ferric by first contacting the resin with a reducing agent, to reduce the ferric ions to ferrous ions, before eluting with sulphuric acid.
- 3) Alternatively, an investigation could be done to find the impact of pre-treating the CTF with a reducing agent, to ensure reduction of ferric ions to ferrous ions, before it reports to the ion-exchange plant.

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## APPENDIX A: BATCH TEST DATA

### Lewatit VP OC 1026 Batch Test Data

Table A 1: Experiment 1 conditions.

|                     |                     |                                      |   |           |
|---------------------|---------------------|--------------------------------------|---|-----------|
| <b>Experiment 1</b> | 24hr                |                                      |   |           |
| <b>Temperature</b>  | 25                  |                                      |   |           |
| <b>pH</b>           | 1.78                |                                      |   |           |
| <b>Solution (L)</b> | <b>0.25</b>         |                                      |   |           |
| <b>Resin</b>        | Lewatit             |                                      |   |           |
| <b>Vol (ml)</b>     | <b>X = Mass (g)</b> | <b>C<sub>f</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 1.0                 | 0.97                | 9.4                                  | 0.4   | 1.77      |
| 2.5                 | 2.4                 | 8.8                                  | 0.2   | 1.74      |
| 5.0                 | 4.9                 | 8.8                                  | 0.1   | 1.74      |
| 10.0                | 9.7                 | 6.1                                  | 0.1   | 1.74      |
| 25.0                | 24.3                | 5.5                                  | 0.1   | 1.72      |
|                     |                     | <b>C<sub>0</sub></b>                 |   |           |
| <b>Feed</b>         |                     | 10.7                                 |   |           |

Table A 2: Experiment 1 assay results.

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-1    |                | 68.9     | 127.5     | 315.9     | 14.8      | 9.7       | 10.7      |
| 1-1       | 0.97           | 63.5     | 116.9     | 287.4     | 7.7       | 8.7       | 9.4       |
| 1-2       | 2.4            | 64.9     | 118.2     | 293.0     | 6.5       | 8.8       | 8.8       |
| 1-3       | 4.9            | 65.6     | 123.7     | 306.1     | 7.6       | 9.0       | 8.8       |
| 1-4       | 9.7            | 62.3     | 115.6     | 286.2     | 1.2       | 8.6       | 6.1       |
| 1-5       | 24.3           | 64.5     | 119.9     | 300.7     | 1.5       | 8.6       | 5.5       |

Table A 3: Experiment 1 distribution ratios and separation factors.

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | CU      | Co      | Fe      | Pb      | Zn    |
| 1-1       | 0.013              | 0.014   | 0.015   | 0.140   | 0.018   | 0.023 |
| 1-2       | 0.004              | 0.005   | 0.005   | 0.079   | 0.006   | 0.013 |
| 1-3       | 0.002              | 0.001   | 0.001   | 0.029   | 0.002   | 0.007 |
| 1-4       | 0.002              | 0.002   | 0.002   | 0.171   | 0.002   | 0.012 |
| 1-5       | 0.000              | <0.001  | <0.001  | 0.055   | 0.001   | 0.006 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 1-1       | 2                  | 2       | 1       | 0       | 1       |       |
| 1-2       | 4                  | 3       | 3       | 0       | 2       |       |
| 1-3       | 4                  | 7       | 7       | 0       | 3       |       |
| 1-4       | 7                  | 7       | 7       | 0       | 6       |       |
| 1-5       | 14                 | 15      | 19      | 0       | 7       |       |

**Table A 4: Experiment 2 conditions.**

|                     |                     |                                      |   |           |
|---------------------|---------------------|--------------------------------------|---|-----------|
| <b>Experiment 2</b> |                     | 24hr                                 |   |           |
| Temperature         |                     | 25                                   |   |           |
| pH                  |                     | 2                                    |   |           |
| Solution (L)        |                     | <b>0.15</b>                          |   |           |
| Resin               |                     | Lewatit                              |   |           |
| <b>Vol (ml)</b>     | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>i</sub>)V/X</b> | <b>pH</b> |
| 0.3                 | 0.30                | 167.4                                | 5.0   | 2.09      |
| 0.6                 | 0.60                | 160.4                                | 4.3   | 2.08      |
| 1.2                 | 1.20                | 134.2                                | 5.4   | 2.08      |
| 2.2                 | 2.10                | 108.3                                | 4.9   | 2.06      |
| 3.3                 | 3.20                | 88.2                                 | 4.2   | 2.1       |
| <b>Feed</b>         |                     | <b>C<sub>0</sub></b><br>177.5        | 2   |           |

**Table A 5: Experiment 2 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-2    |                | 55.0     | 98.8      | 244.5     | 11.6      | 7.6       | 177.5     |
| 2-1       | 0.30           | 53.9     | 97.7      | 241.5     | 1.6       | 7.5       | 167.4     |
| 2-2       | 0.60           | 54.1     | 98.5      | 243.3     | 0.6       | 7.2       | 160.4     |
| 2-3       | 1.20           | 53.2     | 97.2      | 241.1     | 0.3       | 7.6       | 134.2     |
| 2-4       | 2.10           | 52.8     | 96.3      | 239.3     | 0.2       | 7.2       | 108.3     |
| 2-5       | 3.20           | 52.9     | 98.0      | 245.1     | 0.6       | 7.8       | 88.2      |

**Table A 6: Experiment 2 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | CU      | Co      | Fe      | Pb      | Zn    |
| 2-1       | 0.010              | 0.006   | 0.006   | 3.066   | 0.010   | 0.030 |
| 2-2       | 0.004              | 0.001   | 0.001   | 4.879   | 0.016   | 0.027 |
| 2-3       | 0.004              | 0.002   | 0.002   | 4.864   | <0.001  | 0.040 |
| 2-4       | 0.003              | 0.002   | 0.002   | 4.107   | 0.004   | 0.046 |
| 2-5       | 0.002              | <0.001  | <0.001  | 0.923   | -0.001  | 0.047 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 2-1       | 3                  | 5       | 5       | 0       | 3       |       |
| 2-2       | 6                  | 31      | 21      | 0       | 2       |       |
| 2-3       | 9                  | 19      | 23      | 0       | 255     |       |
| 2-4       | 15                 | 24      | 29      | 0       | 12      |       |
| 2-5       | 25                 | 121     | -415    | 0       | -45     |       |

**Table A 7: Experiment 3 conditions.**

|                     |                     |                                      |   |           |
|---------------------|---------------------|--------------------------------------|---|-----------|
| <b>Experiment 3</b> |                     | 24hr                                 |   |           |
| Temperature         |                     | 25                                   |   |           |
| pH                  |                     | 2.5                                  |   |           |
| Solution (L)        |                     | <b>0.15</b>                          |   |           |
| Resin               |                     | Lewatit                              |   |           |
| <b>Vol (ml)</b>     | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 0.3                 | 0.30                | 167.2                                | 12.8  | 2.5       |
| 0.6                 | 0.60                | 113.7                                | 19.8  | 2.46      |
| 1.2                 | 1.20                | 102.1                                | 11.3  | 2.41      |
| 2.2                 | 2.10                | 69.7                                 | 8.8   | 2.37      |
| 3.3                 | 3.20                | 51.2                                 | 6.6   | 2.33      |
|                     |                     | <b>C<sub>0</sub></b>                 |   |           |
| <b>Feed</b>         |                     | 192.8                                | 2.58  |           |

**Table A 8: Experiment 3 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-3    |                | 43.3     | 83.8      | 207.7     | 9.8       | 6.4       | 192.8     |
| 3-1       | 0.3            | 42.0     | 83.5      | 205.5     | 1.1       | 6.6       | 167.2     |
| 3-2       | 0.6            | 42.6     | 67.4      | 172.3     | 0.3       | 5.5       | 113.7     |
| 3-3       | 1.2            | 42.0     | 82.3      | 208.3     | 0.2       | 6.3       | 102.1     |
| 3-4       | 2.1            | 42.4     | 82.3      | 210.8     | 0.2       | 6.7       | 69.7      |
| 3-5       | 3.2            | 44.2     | 88.3      | 221.7     | 0.2       | 6.7       | 51.2      |

**Table A 9: Experiment 3 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | CU      | Co      | Fe      | Pb      | Zn    |
| 3-1       | 0.015              | 0.002   | 0.005   | 3.787   | -0.015  | 0.077 |
| 3-2       | 0.004              | 0.061   | 0.051   | 8.063   | 0.039   | 0.174 |
| 3-3       | 0.004              | 0.002   | <0.001  | 4.863   | 0.003   | 0.111 |
| 3-4       | 0.002              | 0.001   | -0.001  | 2.763   | -0.003  | 0.126 |
| 3-5       | -0.001             | -0.002  | -0.003  | 2.638   | -0.002  | 0.130 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 3-1       | 5                  | 42      | 14      | 0       | -5      |       |
| 3-2       | 40                 | 3       | 3       | 0       | 4       |       |
| 3-3       | 29                 | 48      | -343    | 0       | 36      |       |
| 3-4       | 83                 | 99      | -121    | 0       | -47     |       |
| 3-5       | -130               | -54     | -44     | 0       | -68     |       |

**Table A 10: Experiment 4 conditions.**

| <b>Experiment 4</b> |              | 24hr                             |   |      |
|---------------------|--------------|----------------------------------|---|------|
| Temperature         |              | 25                               |   |      |
| pH                  |              | 3                                |   |      |
| Solution (L)        |              | <b>0.15</b>                      |   |      |
| Resin               |              | Lewatit                          |   |      |
| Vol (ml)            | X = Mass (g) | C <sub>r</sub> - Zn assay (mg/L) | C <sub>a</sub> /X = (C <sub>0</sub> - C <sub>f</sub> )V/X | pH   |
| 0.3                 | 0.30         | 158.4                            | 16.2  | 2.95 |
| 0.6                 | 0.60         | 124.9                            | 16.5  | 2.82 |
| 1.2                 | 1.20         | 72.4                             | 14.8  | 2.71 |
| 2.2                 | 2.10         | 40.2                             | 10.8  | 2.63 |
| 3.3                 | 3.20         | 25.5                             | 7.8   | 2.58 |
| <b>Feed</b>         |              | <b>C<sub>0</sub></b><br>190.9    |   | 3.06 |

**Table A 11: Experiment 4 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-4    |                | 68.9     | 77.9      | 197.6     | 10.1      | 3.6       | 190.9     |
| 4-1       | 0.3            | 63.5     | 75.1      | 193.7     | 0.0       | 3.6       | 158.4     |
| 4-2       | 0.6            | 64.9     | 76.1      | 196.3     | 0.0       | 3.6       | 124.9     |
| 4-3       | 1.2            | 65.6     | 75.0      | 194.3     | 0.0       | 3.6       | 72.4      |
| 4-4       | 2.1            | 62.3     | 76.0      | 197.0     | 0.0       | 3.6       | 40.2      |
| 4-5       | 3.2            | 64.5     | 75.2      | 196.8     | 0.0       | 3.6       | 25.5      |

**Table A 12: Experiment 4 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | CU      | Co      | Fe      | Pb      | Zn    |
| 4-1       | 0.042              | 0.019   | 0.010   | 0.284   | 0.002   | 0.102 |
| 4-2       | 0.015              | 0.006   | 0.002   | 0.285   | 0.001   | 0.132 |
| 4-3       | 0.006              | 0.005   | 0.002   | 0.252   | 0.001   | 0.205 |
| 4-4       | 0.008              | 0.002   | <0.001  | 0.261   | <0.001  | 0.268 |
| 4-5       | 0.003              | 0.002   | <0.001  | 0.613   | <0.001  | 0.305 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 4-1       | 2                  | 6       | 10      | 0       | 45      |       |
| 4-2       | 9                  | 23      | 80      | 0       | 160     |       |
| 4-3       | 33                 | 43      | 97      | 1       | 270     |       |
| 4-4       | 35                 | 151     | 1246    | 1       | 779     |       |
| 4-5       | 95                 | 185     | 1760    | 0       | 1188    |       |

**Table A 13: Experiment 5 conditions.**

|                     |                     |                                       |   |           |
|---------------------|---------------------|---------------------------------------|---|-----------|
| <b>Experiment 5</b> |                     | 2hr                                   |   |           |
| Temperature         |                     | 25                                    |   |           |
| pH                  |                     | 2.5                                   |   |           |
| Solution (L)        |                     | <b>0.15</b>                           |   |           |
| Resin               |                     | Lewatit                               |   |           |
| <b>Vol (ml)</b>     | <b>X = Mass (g)</b> | <b>C<sub>r</sub>- Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 0.3                 | 0.30                | 149.7                                 | 15.4  | 2.57      |
| 0.6                 | 0.60                | 123.8                                 | 14.2  | 2.53      |
| 1.2                 | 1.20                | 88.5                                  | 11.5  | 2.48      |
| 2.2                 | 2.10                | 58.7                                  | 8.7   | 2.44      |
| 3.3                 | 3.20                | 41.6                                  | 6.5   | 2.4       |
| <b>Feed</b>         |                     | <b>C<sub>0</sub></b><br>180.4         |   | 2.6       |

**Table A 14: Experiment 5 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-5    |                | 45.6     | 85.0      | 213.3     | 11.3      | 4.4       | 180.4     |
| 5-1       | 0.3            | 44.4     | 82.9      | 208.4     | 7.2       | 4.5       | 149.7     |
| 5-2       | 0.6            | 45.1     | 83.4      | 210.0     | 5.3       | 4.4       | 123.8     |
| 5-3       | 1.2            | 45.0     | 83.7      | 210.3     | 3.8       | 4.6       | 88.5      |
| 5-4       | 2.1            | 45.1     | 84.0      | 210.5     | 2.4       | 4.3       | 58.7      |
| 5-5       | 3.2            | 45.1     | 83.1      | 211.4     | 0.8       | 4.7       | 41.6      |

**Table A 15: Experiment 5 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | CU      | Co      | Fe      | Pb      | Zn    |
| 5-1       | 0.013              | 0.013   | 0.012   | 0.284   | -0.012  | 0.103 |
| 5-2       | 0.003              | 0.005   | 0.004   | 0.285   | -0.003  | 0.114 |
| 5-3       | 0.002              | 0.002   | 0.002   | 0.252   | -0.005  | 0.130 |
| 5-4       | 0.001              | 0.001   | 0.001   | 0.261   | 0.001   | 0.148 |
| 5-5       | 0.001              | 0.001   | <0.001  | 0.613   | -0.003  | 0.156 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 5-1       | 8                  | 8       | 9       | 0       | -8      |       |
| 5-2       | 39                 | 23      | 29      | 0       | -35     |       |
| 5-3       | 71                 | 66      | 73      | 1       | -25     |       |
| 5-4       | 188                | 165     | 157     | 1       | 121     |       |
| 5-5       | 280                | 144     | 364     | 0       | -57     |       |

**Table A 16: Experiment 10 conditions.**

|                      |                     |                                      |   |           |
|----------------------|---------------------|--------------------------------------|---|-----------|
| <b>Experiment 10</b> |                     | 3hr                                  |   |           |
| Temperature          |                     | 25                                   |   |           |
| pH                   |                     | 3                                    |   |           |
| Solution (L)         |                     | <b>0.15</b>                          |   |           |
| Resin                |                     | Lewatit                              |   |           |
| <b>Vol (ml)</b>      | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 0.9                  | 0.90                | 93.7                                 | 16.2  | 2.87      |
| 1.5                  | 1.50                | 56.6                                 | 13.4  | 2.72      |
| 2.1                  | 2.00                | 42.9                                 | 11.1  | 2.66      |
| 3.1                  | 3.00                | 31.4                                 | 8.0   | 2.6       |
| 5.2                  | 5.00                | 21.7                                 | 5.1   | 2.52      |
| <b>Feed</b>          |                     | <b>C<sub>0</sub></b><br>191.0        | 3.12  |           |

**Table A 17: Experiment 10 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-10   |                | 68.9     | 121.1     | 307.7     | 14.3      | 10.0      | 191.0     |
| 10-1      | 0.9            | 63.5     | 119.5     | 304.0     | 2.5       | 10.0      | 93.7      |
| 10-2      | 1.5            | 64.9     | 118.9     | 305.2     | 0.7       | 9.9       | 56.6      |
| 10-3      | 2.0            | 65.6     | 119.2     | 304.3     | 0.4       | 9.9       | 42.9      |
| 10-4      | 3.0            | 62.3     | 118.9     | 305.6     | 0.5       | 9.9       | 31.4      |
| 10-5      | 5.0            | 64.5     | 117.2     | 304.7     | 0.5       | 9.3       | 21.7      |

**Table A 18: Experiment 10 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | CU      | Co      | Fe      | Pb      | Zn    |
| 10-1      | 0.014              | 0.002   | 0.002   | 0.778   | 0.001   | 0.173 |
| 10-2      | 0.006              | 0.002   | 0.001   | 1.858   | 0.001   | 0.237 |
| 10-3      | 0.004              | 0.001   | 0.001   | 2.666   | 0.001   | 0.259 |
| 10-4      | 0.005              | 0.001   | <0.001  | 1.497   | 0.001   | 0.254 |
| 10-5      | 0.002              | 0.001   | <0.001  | 0.785   | 0.002   | 0.233 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 10-1      | 12                 | 82      | 85      | 0       | 166     |       |
| 10-2      | 38                 | 130     | 288     | 0       | 180     |       |
| 10-3      | 69                 | 221     | 306     | 0       | 280     |       |
| 10-4      | 48                 | 285     | 730     | 0       | 264     |       |
| 10-5      | 114                | 239     | 799     | 0       | 94      |       |

**Table A 19: Experiment 13 conditions.**

|                      |                     |                                      |  |           |
|----------------------|---------------------|--------------------------------------|--|-----------|
| <b>Experiment 13</b> |                     | >12hr                                |  |           |
| Temperature          |                     | 50                                   |  |           |
| pH                   |                     | 3.5                                  |  |           |
| Solution (L)         |                     | <b>0.15</b>                          |  |           |
| Resin                |                     | Lewatit                              |  |           |
| <b>Vol (ml)</b>      | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)/V/X</b> | <b>pH</b> |
| 0.9                  | 0.90                | 90.8                                 | 17.3   | 3.07      |
| 1.5                  | 1.50                | 32.3                                 | 16.2   | 2.94      |
| 2.1                  | 2.00                | 17.9                                 | 13.2   | 2.91      |
| 3.1                  | 3.00                | 12.4                                 | 9.1  | 2.87      |
| 5.2                  | 5.00                | 9.2                                  | 5.6  | 2.77      |
|                      |                     | <b>C<sub>0</sub></b>                 |  |           |
| <b>Feed</b>          |                     | 194.5                                | 3.49   |           |

**Table A 20: Experiment 13 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-13   |                | 52.9     | 121.5     | 304.5     | 9.9       | 9.9       | 194.5     |
| 13-1      | 0.9            | 52.9     | 120.2     | 302.8     | 1.9       | 9.8       | 90.8      |
| 13-2      | 1.5            | 52.9     | 120.0     | 302.2     | 1.7       | 10.0      | 32.3      |
| 13-3      | 2.0            | 52.9     | 118.6     | 300.5     | 1.5       | 9.6       | 17.9      |
| 13-4      | 3.0            | 52.9     | 116.5     | 300.6     | 1.1       | 9.6       | 12.4      |
| 13-5      | 5.0            | 52.9     | 112.6     | 298.0     | 1.1       | 9.0       | 9.2       |

**Table A 21: Experiment 13 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | CU      | Co      | Fe      | Pb      | Zn    |
| 13-1      | <0.001             | 0.002   | 0.001   | 0.706   | 0.002   | 0.190 |
| 13-2      | <0.001             | 0.001   | 0.001   | 0.477   | -0.001  | 0.502 |
| 13-3      | <0.001             | 0.002   | 0.001   | 0.406   | 0.003   | 0.742 |
| 13-4      | <0.001             | 0.002   | 0.001   | 0.386   | 0.001   | 0.736 |
| 13-5      | <0.001             | 0.002   | 0.001   | 0.235   | 0.003   | 0.602 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 13-1      | -                  | 108     | 193     | 0       | 78      |       |
| 13-2      | -                  | 397     | 644     | 1       | -866    |       |
| 13-3      | -                  | 398     | 725     | 2       | 291     |       |
| 13-4      | -                  | 345     | 1131    | 2       | 528     |       |
| 13-5      | -                  | 254     | 920     | 3       | 188     |       |

## Purolite S950 Batch Test Data

Table A 22: Experiment 6 conditions.

| <b>Experiment 6</b> |              | 24hr                             |  |      |
|---------------------|--------------|----------------------------------|--|------|
| Temperature         |              | 25                               |  |      |
| pH                  |              | 3.5                              |  |      |
| Solution (L)        |              | <b>0.15</b>                      |  |      |
| Resin               |              | Purolite                         |  |      |
| Vol (ml)            | X = Mass (g) | C <sub>r</sub> - Zn assay (mg/L) | C <sub>a</sub> /X = (C <sub>0</sub> - C <sub>f</sub> )/V/X | pH   |
| 0.3                 | 0.30         | 185.2                            | 6.7  | 3.77 |
| 0.5                 | 0.6          | 172.9                            | 6.4  | 3.82 |
| 1.1                 | 1.2          | 154.0                            | 5.6  | 3.9  |
| 1.9                 | 2.1          | 128.5                            | 5.0  | 4.00 |
| 2.8                 | 3.2          | 102.5                            | 4.5  | 4.06 |
| <b>Feed</b>         |              | C <sub>0</sub><br>198.6          | 3.56   |      |

Table A 23: Experiment 6 assay results.

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-6    |                | 68.9     | 78.1      | 197.8     | 8.3       | 6.5       | 198.6     |
| 6-1       | 0.30           | 63.5     | 69.1      | 194.1     | 6.7       | 6.6       | 185.2     |
| 6-2       | 0.6            | 64.9     | 61.3      | 191.9     | 5.4       | 5.7       | 172.9     |
| 6-3       | 1.2            | 65.6     | 46.2      | 192.4     | 1.1       | 5.6       | 154.0     |
| 6-4       | 2.1            | 62.3     | 30.5      | 189.6     | 0.9       | 5.3       | 128.5     |
| 6-5       | 3.2            | 64.5     | 17.6      | 187.3     | 0.0       | 5.3       | 102.5     |

Table A 24: Experiment 6 distribution ratios and separation factors.

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | Cu      | Co      | Fe      | Pb      | Zn    |
| 6-1       | 0.042              | 0.066   | 0.010   | 0.121   | 0.026   | 0.036 |
| 6-2       | 0.015              | 0.069   | 0.008   | 0.132   | 0.034   | 0.037 |
| 6-3       | 0.006              | 0.086   | 0.004   | 0.837   | 0.021   | 0.036 |
| 6-4       | 0.008              | 0.112   | 0.003   | 0.623   | 0.016   | 0.039 |
| 6-5       | 0.003              | 0.161   | 0.003   | 30.488  | 0.010   | 0.044 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 6-1       | 1                  | 1       | 4       | 0       | 1       |       |
| 6-2       | 2                  | 1       | 5       | 0       | 1       |       |
| 6-3       | 6                  | 0       | 10      | 0       | 2       |       |
| 6-4       | 5                  | 0       | 13      | 0       | 2       |       |
| 6-5       | 14                 | 0       | 17      | 0       | 4       |       |

**Table A 25: Experiment 7 conditions.**

|                     |                     |                                      |   |           |
|---------------------|---------------------|--------------------------------------|---|-----------|
| <b>Experiment 7</b> |                     | 24hr                                 |   |           |
| <b>Temperature</b>  |                     | 25                                   |   |           |
| <b>pH</b>           |                     | 4                                    |   |           |
| <b>Solution (L)</b> |                     | <b>0.15</b>                          |   |           |
| <b>Resin</b>        |                     | Purolite                             |   |           |
| <b>Vol (ml)</b>     | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 0.3                 | 0.30                | 189.6                                | 4.2   | 3.92      |
| 0.5                 | 0.6                 | 177.9                                | 5.0   | 3.92      |
| 1.1                 | 1.2                 | 161.7                                | 4.5   | 3.92      |
| 1.9                 | 2.1                 | 141.8                                | 4.0   | 3.95      |
| 2.8                 | 3.2                 | 116.1                                | 3.8   | 4.00      |
|                     |                     | <b>C<sub>0</sub></b>                 |   |           |
| <b>Feed</b>         |                     | 198.0                                | 3.87  |           |

**Table A 26: Experiment 7 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-7    |                | 55.0     | 121.4     | 306.1     | 12.7      | 9.9       | 198.0     |
| 7-1       | 0.30           | 53.9     | 107.8     | 302.2     | 11.6      | 9.7       | 189.6     |
| 7-2       | 0.6            | 54.1     | 98.0      | 301.0     | 11.1      | 9.6       | 177.9     |
| 7-3       | 1.2            | 53.2     | 79.2      | 298.7     | 9.6       | 9.0       | 161.7     |
| 7-4       | 2.1            | 52.8     | 59.4      | 297.2     | 8.5       | 9.1       | 141.8     |
| 7-5       | 3.2            | 52.9     | 38.3      | 293.0     | 7.1       | 8.6       | 116.1     |

**Table A 27: Experiment 7 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | Cu      | Co      | Fe      | Pb      | Zn    |
| 7-1       | 0.010              | 0.063   | 0.006   | 0.046   | 0.010   | 0.022 |
| 7-2       | 0.004              | 0.060   | 0.004   | 0.036   | 0.009   | 0.028 |
| 7-3       | 0.004              | 0.067   | 0.003   | 0.041   | 0.014   | 0.028 |
| 7-4       | 0.003              | 0.075   | 0.002   | 0.036   | 0.007   | 0.028 |
| 7-5       | 0.002              | 0.102   | 0.002   | 0.037   | 0.007   | 0.033 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 7-1       | 2                  | 0       | 3       | 0       | 2       |       |
| 7-2       | 6                  | 0       | 7       | 1       | 3       |       |
| 7-3       | 6                  | 0       | 9       | 1       | 2       |       |
| 7-4       | 9                  | 0       | 13      | 1       | 4       |       |
| 7-5       | 17                 | 0       | 16      | 1       | 5       |       |

**Table A 28: Experiment 8 conditions.**

|                     |                     |                                       |   |           |
|---------------------|---------------------|---------------------------------------|---|-----------|
| <b>Experiment 8</b> |                     | 24hr                                  |   |           |
| Temperature         |                     | 25                                    |   |           |
| pH                  |                     | 4.5                                   |   |           |
| Solution (L)        |                     | <b>0.15</b>                           |   |           |
| Resin               |                     | Purolite                              |   |           |
| <b>Vol (ml)</b>     | <b>X = Mass (g)</b> | <b>C<sub>r</sub>- Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 0.3                 | 0.30                | 196.9                                 | 4.7   | 4.3       |
| 0.5                 | 0.6                 | 179.8                                 | 6.6   | 4.17      |
| 1.1                 | 1.2                 | 162.1                                 | 5.5   | 4.11      |
| 1.9                 | 2.1                 | 137.4                                 | 4.9   | 4.09      |
| 2.8                 | 3.2                 | 113.1                                 | 4.4   | 4.09      |
| <b>Feed</b>         |                     | <b>C<sub>0</sub></b><br>206.3         | 4.57  |           |

**Table A 29: Experiment 8 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-8    |                | 68.9     | 121.3     | 305.4     | 13.2      | 9.6       | 206.3     |
| 8-1       | 0.3            | 63.5     | 108.5     | 319.4     | 13.2      | 9.3       | 196.9     |
| 8-2       | 0.6            | 64.9     | 90.5      | 300.4     | 12.1      | 8.8       | 179.8     |
| 8-3       | 1.2            | 65.6     | 71.7      | 298.6     | 10.8      | 8.3       | 162.1     |
| 8-4       | 2.1            | 62.3     | 49.6      | 296.5     | 9.5       | 7.8       | 137.4     |
| 8-5       | 3.2            | 64.5     | 32.2      | 292.1     | 7.9       | 7.7       | 113.1     |

**Table A 30: Experiment 8 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | Cu      | Co      | Fe      | Pb      | Zn    |
| 8-1       | 0.042              | 0.059   | -0.022  | 0.003   | 0.013   | 0.024 |
| 8-2       | 0.015              | 0.085   | 0.004   | 0.025   | 0.022   | 0.037 |
| 8-3       | 0.006              | 0.086   | 0.003   | 0.028   | 0.020   | 0.034 |
| 8-4       | 0.008              | 0.103   | 0.002   | 0.029   | 0.016   | 0.036 |
| 8-5       | 0.003              | 0.129   | 0.002   | 0.031   | 0.011   | 0.039 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 8-1       | 1                  | 0       | -1      | 9       | 2       |       |
| 8-2       | 2                  | 0       | 9       | 2       | 2       |       |
| 8-3       | 5                  | 0       | 12      | 1       | 2       |       |
| 8-4       | 5                  | 0       | 17      | 1       | 2       |       |
| 8-5       | 12                 | 0       | 18      | 1       | 3       |       |

**Table A 31: Experiment 9 conditions.**

|                     |                     |                                      |  |           |
|---------------------|---------------------|--------------------------------------|--|-----------|
| <b>Experiment 9</b> |                     | 24hr                                 |  |           |
| Temperature         |                     | 25                                   |  |           |
| pH                  |                     | 2.5                                  |  |           |
| Solution (L)        |                     | <b>0.15</b>                          |  |           |
| Resin               |                     | Purolite                             |  |           |
| <b>Vol (ml)</b>     | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)/V/X</b> | <b>pH</b> |
| 0.3                 | 0.30                | 192.7                                | 3.2  | 2.67      |
| 0.5                 | 0.6                 | 185.7                                | 3.3  | 2.75      |
| 1.1                 | 1.2                 | 174.6                                | 3.1  | 2.91      |
| 1.9                 | 2.1                 | 154.8                                | 3.2  | 3.12      |
| 2.8                 | 3.2                 | 130.5                                | 3.2  | 3.30      |
| <b>Feed</b>         |                     | <b>C<sub>0</sub></b><br>199.1        | 2.59   |           |

**Table A 32: Experiment 9 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-9    |                | 55.0     | 122.4     | 307.7     | 14.9      | 9.5       | 199.1     |
| 9-1       | 0.30           | 53.9     | 107.0     | 302.6     | 13.3      | 9.6       | 192.7     |
| 9-2       | 0.6            | 54.1     | 95.1      | 301.8     | 12.6      | 9.0       | 185.7     |
| 9-3       | 1.2            | 53.2     | 95.8      | 302.7     | 11.3      | 8.5       | 174.6     |
| 9-4       | 2.1            | 52.8     | 77.3      | 296.5     | 9.3       | 8.4       | 154.8     |
| 9-5       | 3.2            | 52.9     | 57.4      | 289.2     | 5.7       | 7.6       | 130.5     |

**Table A 33: Experiment 9 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | Cu      | Co      | Fe      | Pb      | Zn    |
| 9-1       | 0.010              | 0.072   | 0.008   | 0.062   | -0.008  | 0.017 |
| 9-2       | 0.004              | 0.072   | 0.005   | 0.046   | 0.014   | 0.018 |
| 9-3       | 0.004              | 0.035   | 0.002   | 0.039   | 0.013   | 0.018 |
| 9-4       | 0.003              | 0.042   | 0.003   | 0.042   | 0.009   | 0.020 |
| 9-5       | 0.002              | 0.053   | 0.003   | 0.075   | 0.011   | 0.025 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 9-1       | 2                  | 0       | 2       | 0       | -2      |       |
| 9-2       | 4                  | 0       | 4       | 0       | 1       |       |
| 9-3       | 4                  | 1       | 9       | 0       | 1       |       |
| 9-4       | 7                  | 0       | 8       | 0       | 2       |       |
| 9-5       | 13                 | 0       | 8       | 0       | 2       |       |

**Table A 34: Experiment 11 conditions.**

|                      |                     |                                      |   |           |
|----------------------|---------------------|--------------------------------------|---|-----------|
| <b>Experiment 11</b> |                     | 3 hr                                 |   |           |
| Temperature          |                     | 25                                   |   |           |
| pH                   |                     | 4                                    |   |           |
| Solution (L)         |                     | <b>0.15</b>                          |   |           |
| Resin                |                     | Purolite                             |   |           |
| <b>Vol (ml)</b>      | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 0.9                  | 1.00                | 177.3                                | 2.4   | 4.11      |
| 1.8                  | 2.0                 | 165.3                                | 2.1   | 4.08      |
| 4.4                  | 5.0                 | 132.6                                | 1.8   | 4.12      |
| 6.2                  | 7.0                 | 114.4                                | 1.7   | 4.15      |
| 8.0                  | 9.0                 | 97.3                                 | 1.6   | 4.18      |
| <b>Feed</b>          |                     | <b>C<sub>0</sub></b><br>193.0        | 3.95  |           |

**Table A 35: Experiment 11 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-11   |                | 55.0     | 120.8     | 306.6     | 10.6      | 9.7       | 193.0     |
| 11-1      | 1.00           | 53.9     | 104.3     | 299.3     | 8.4       | 8.7       | 177.3     |
| 11-2      | 2.0            | 54.1     | 90.3      | 297.2     | 10.0      | 8.9       | 165.3     |
| 11-3      | 5.0            | 53.2     | 57.7      | 287.5     | 8.9       | 8.4       | 132.6     |
| 11-4      | 7.0            | 52.8     | 43.7      | 281.7     | 6.3       | 7.7       | 114.4     |
| 11-5      | 9.0            | 52.9     | 32.1      | 273.7     | 8.2       | 7.7       | 97.3      |

**Table A 36: Experiment 11 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | Cu      | Co      | Fe      | Pb      | Zn    |
| 11-1      | 0.003              | 0.024   | 0.004   | 0.038   | 0.018   | 0.013 |
| 11-2      | 0.001              | 0.025   | 0.002   | 0.004   | 0.007   | 0.013 |
| 11-3      | 0.001              | 0.033   | 0.002   | 0.006   | 0.005   | 0.014 |
| 11-4      | 0.001              | 0.038   | 0.002   | 0.014   | 0.006   | 0.015 |
| 11-5      | 0.001              | 0.046   | 0.002   | 0.005   | 0.004   | 0.016 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 11-1      | 4                  | 1       | 4       | 0       | 1       |       |
| 11-2      | 10                 | 0       | 5       | 3       | 2       |       |
| 11-3      | 13                 | 0       | 7       | 2       | 3       |       |
| 11-4      | 16                 | 0       | 8       | 1       | 3       |       |
| 11-5      | 24                 | 0       | 8       | 3       | 4       |       |

**Table A 37: Experiment 12 conditions.**

|                      |                     |                                      |   |           |
|----------------------|---------------------|--------------------------------------|---|-----------|
| <b>Experiment 12</b> |                     | > 12 hr                              |   |           |
| Temperature          | 50                  |                                      |   |           |
| pH                   | 4                   |                                      |   |           |
| Solution (L)         | <b>0.15</b>         |                                      |   |           |
| Resin                | Purolite            |                                      |   |           |
| <b>Vol (ml)</b>      | <b>X = Mass (g)</b> | <b>C<sub>r</sub> Zn assay (mg/L)</b> | <b>C<sub>a</sub>/X = (C<sub>0</sub> - C<sub>f</sub>)V/X</b> | <b>pH</b> |
| 0.9                  | 1.0                 | 142.7                                | 8.3   | 3.76      |
| 1.8                  | 2.0                 | 112.3                                | 6.5   | 3.69      |
| 4.4                  | 5.0                 | 51.6                                 | 4.4   | 3.72      |
| 6.2                  | 7.0                 | 33.3                                 | 3.5   | 3.78      |
| 8.0                  | 9.0                 | 22.6                                 | 2.9   | 3.85      |
| <b>Feed</b>          |                     | <b>C<sub>0</sub></b><br>198.4        | 4.07  |           |

**Table A 38: Experiment 12 assay results.**

| Sample No | Resin Mass (g) | Ni (g/L) | Cu (mg/L) | Co (mg/L) | Fe (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|----------------|----------|-----------|-----------|-----------|-----------|-----------|
| Feed-12   |                | 52.9     | 122.4     | 305.9     | 9.0       | 9.4       | 198.4     |
| 12-1      | 1.0            | 52.9     | 71.2      | 299.4     | 3.8       | 8.8       | 142.7     |
| 12-2      | 2.0            | 52.9     | 47.1      | 296.0     | 3.6       | 8.5       | 112.3     |
| 12-3      | 5.0            | 52.9     | 15.1      | 286.3     | 2.5       | 7.8       | 51.6      |
| 12-4      | 7.0            | 52.9     | 8.9       | 278.7     | 2.3       | 7.5       | 33.3      |
| 12-5      | 9.0            | 52.9     | 6.1       | 272.4     | 2.2       | 7.4       | 22.6      |

**Table A 39: Experiment 12 distribution ratios and separation factors.**

| Sample No | Distribution ratio |         |         |         |         |       |
|-----------|--------------------|---------|---------|---------|---------|-------|
|           | Ni                 | Cu      | Co      | Fe      | Pb      | Zn    |
| 12-1      | <0.001             | 0.108   | 0.003   | 0.203   | 0.009   | 0.058 |
| 12-2      | <0.001             | 0.120   | 0.003   | 0.112   | 0.008   | 0.058 |
| 12-3      | <0.001             | 0.213   | 0.002   | 0.076   | 0.006   | 0.085 |
| 12-4      | <0.001             | 0.272   | 0.002   | 0.062   | 0.005   | 0.106 |
| 12-5      | <0.001             | 0.318   | 0.002   | 0.052   | 0.005   | 0.130 |
| Sample No | Separation Factor  |         |         |         |         |       |
|           | K Zn/Ni            | K Zn/Cu | K Zn/Co | K Zn/Fe | K Zn/Pb |       |
| 12-1      | -                  | 1       | 18      | 0       | 6       |       |
| 12-2      | -                  | 0       | 23      | 1       | 8       |       |
| 12-3      | -                  | 0       | 41      | 1       | 14      |       |
| 12-4      | -                  | 0       | 51      | 2       | 20      |       |
| 12-5      | -                  | 0       | 63      | 3       | 29      |       |

## APPENDIX B: COLUMN TEST DATA

### Lewatit VP OC 1026 Column Test Data

**Table B 1: Test column setup.**

| Test Column Setup       |                     |
|-------------------------|---------------------|
| Column outside diameter | 24 mm               |
| Wall thickness          | 1.8 mm              |
| Column inside diameter  | 22.2 mm             |
| Column length           | 600 mm              |
| Resin volume            | 100 ml              |
| Resin depth             | 258 mm              |
| Cross sectional area    | 3.9 cm <sup>2</sup> |

**Table B 2: Experiment 1 conditions.**

| Experiment 1 |       |      |
|--------------|-------|------|
| Feed pH      | 2.78  |      |
| Temperature  | 25    | °C   |
| Flow rate    | 4 - 6 | BV/h |
| Feed [Zn]    | 183.4 | mg/L |

**Table B 3: Experiment 1 experimental results.**

| Time  | Sample | BV | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (mg) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|----|----------|-------|------|-------------------------|----------------|-------------------------|--------------------|------------------------------|
| 07:20 | Feed   |    |          |       | 2.78 | 183.4                   |                |                         |                    |                              |
| 07:50 | 1      | 3  | 300      | 55    | 2.36 | 2.2                     | 54.4           | 54                      | 10.00              | 0.9                          |
| 08:20 | 2      | 5  | 500      | 92    | 2.45 | 8.2                     | 35.0           | 89                      | 6.67               | 0.9                          |
| 09:00 | 3      | 8  | 800      | 147   | 2.49 | 7.1                     | 52.9           | 142                     | 7.50               | 1.4                          |
| 09:40 | 4      | 11 | 1100     | 202   | 2.52 | 6.9                     | 52.9           | 195                     | 7.50               | 2.0                          |
| 10:20 | 5      | 14 | 1400     | 257   | 2.53 | 7.4                     | 52.8           | 248                     | 7.50               | 2.5                          |
| 11:00 | 6      | 17 | 1700     | 312   | 2.54 | 7.8                     | 52.7           | 301                     | 7.50               | 3.0                          |
| 11:40 | 7      | 20 | 2000     | 367   | 2.55 | 8.3                     | 52.5           | 353                     | 7.50               | 3.5                          |
| 12:20 | 8      | 23 | 2300     | 422   | 2.56 | 9.0                     | 52.3           | 406                     | 7.50               | 4.1                          |
| 13:00 | 9      | 26 | 2600     | 477   | 2.56 | 9.5                     | 52.2           | 458                     | 7.50               | 4.6                          |
| 13:40 | 10     | 29 | 2900     | 532   | 2.57 | 10.5                    | 51.9           | 510                     | 7.50               | 5.1                          |
| 14:20 | 11     | 32 | 3200     | 587   | 2.57 | 11.8                    | 51.5           | 561                     | 7.50               | 5.6                          |
| 15:00 | 12     | 35 | 3500     | 642   | 2.57 | 12.9                    | 51.2           | 612                     | 7.50               | 6.1                          |
| 15:40 | 13     | 38 | 3800     | 697   | 2.58 | 18.7                    | 49.4           | 662                     | 7.50               | 6.6                          |
| 16:20 | 14     | 41 | 4100     | 752   | 2.66 | 41.6                    | 42.5           | 704                     | 7.50               | 7.0                          |
| 17:00 | 15     | 44 | 4400     | 807   | 2.61 | 43.6                    | 41.9           | 746                     | 7.50               | 7.5                          |
| 17:30 | 16     | 47 | 4700     | 862   | 2.61 | 61.5                    | 36.6           | 783                     | 10.00              | 7.8                          |
| 17:45 | 17     | 50 | 5000     | 917   | 2.62 | 61.3                    | 36.6           | 820                     | 20.0               | 8.2                          |

**Table B 4: Experiment 1 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Feed-E1   | 283.7     | 120.4     | 14.4      | 63859.5   | 8.1       | 183.4     |
| 1-1       | 283.7     | 111.2     | 1.3       | 63736.9   | 7.8       | 2.2       |
| 1-2       | 285.6     | 117.9     | 1.1       | 64218.8   | 7.6       | 8.2       |
| 1-3       | 286.8     | 122.4     | 1.4       | 64128.8   | 8.2       | 7.1       |
| 1-4       | 287.5     | 124.0     | 1.2       | 64030.0   | 8.1       | 6.9       |
| 1-5       | 286.5     | 123.6     | 1.5       | 64102.7   | 8.4       | 7.4       |
| 1-6       | 288.6     | 124.1     | 1.2       | 64623.0   | 8.3       | 7.8       |
| 1-7       | 287.5     | 123.0     | 1.2       | 64325.7   | 8.6       | 8.3       |
| 1-8       | 288.0     | 122.7     | 1.4       | 64326.8   | 7.9       | 9.0       |
| 1-9       | 287.5     | 122.2     | 1.7       | 64245.1   | 8.2       | 9.5       |
| 1-10      | 287.8     | 122.7     | 1.3       | 64433.7   | 7.9       | 10.5      |
| 1-11      | 287.0     | 121.9     | 1.3       | 64485.6   | 8.3       | 11.8      |
| 1-12      | 288.5     | 122.3     | 1.2       | 64552.0   | 8.0       | 12.9      |
| 1-13      | 287.1     | 121.9     | 1.3       | 64211.1   | 8.1       | 18.7      |
| 1-14      | 288.2     | 122.4     | 1.7       | 64173.9   | 8.4       | 41.6      |
| 1-15      | 286.5     | 122.1     | 1.6       | 63765.8   | 8.0       | 43.6      |
| 1-16      | 286.6     | 122.1     | 4.3       | 63999.1   | 7.8       | 61.5      |
| 1-17      | 287.1     | 122.7     | 2.5       | 64255.5   | 8.4       | 61.3      |

**Table B 5: Experiment 2 conditions.**

| Experiment 2 |       |      |
|--------------|-------|------|
| Feed pH      | 2.77  |      |
| Temperature  | 25    | °C   |
| Flow rate    | 6 - 8 | BV/h |
| Feed [Zn]    | 178.6 | mg/L |

**Table B 6: Experiment 1 experimental results.**

| Time  | Sample | BV   | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (mg) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|------|----------|-------|------|-------------------------|----------------|-------------------------|--------------------|------------------------------|
| 08:29 | Feed   |      |          |       | 2.82 | 178.6                   |                |                         |                    |                              |
| 09:09 | 1      | 4.0  | 400      | 71    | 2.37 | 0.000                   | 71.4           | 71                      | 10.0               | 0.7                          |
| 09:26 | 2      | 6.5  | 650      | 116   | 2.45 | 0.000                   | 44.6           | 116                     | 14.7               | 1.2                          |
| 09:43 | 3      | 9.0  | 900      | 161   | 2.49 | 0.000                   | 44.6           | 161                     | 14.7               | 1.6                          |
| 10:08 | 4      | 11.5 | 1150     | 205   | 2.52 | 0.000                   | 44.6           | 205                     | 10.0               | 2.1                          |
| 10:28 | 5      | 14.0 | 1400     | 250   | 2.54 | 0.000                   | 44.6           | 250                     | 12.5               | 2.5                          |
| 10:48 | 6      | 16.5 | 1650     | 295   | 2.55 | 0.000                   | 44.6           | 295                     | 12.5               | 2.9                          |
| 11:08 | 7      | 19.0 | 1900     | 339   | 2.56 | 0.000                   | 44.6           | 339                     | 12.5               | 3.4                          |
| 11:32 | 8      | 21.5 | 2150     | 384   | 2.57 | 0.538                   | 44.5           | 384                     | 10.4               | 3.8                          |
| 11:56 | 9      | 24.0 | 2400     | 429   | 2.57 | 1.089                   | 44.4           | 428                     | 10.4               | 4.3                          |
| 12:21 | 10     | 26.5 | 2650     | 473   | 2.57 | 2.008                   | 44.1           | 472                     | 10.0               | 4.7                          |
| 12:44 | 11     | 29.0 | 2900     | 518   | 2.57 | 3.582                   | 43.7           | 516                     | 10.9               | 5.2                          |
| 13:07 | 12     | 31.5 | 3150     | 562   | 2.57 | 5.330                   | 43.3           | 559                     | 10.9               | 5.6                          |
| 13:30 | 13     | 34.0 | 3400     | 607   | 2.58 | 7.709                   | 42.7           | 602                     | 10.9               | 6.0                          |
| 13:53 | 14     | 36.5 | 3650     | 652   | 2.58 | 11.115                  | 41.9           | 644                     | 10.9               | 6.4                          |
| 14:15 | 15     | 39.0 | 3900     | 696   | 2.59 | 15.970                  | 40.6           | 685                     | 11.4               | 6.8                          |
| 14:38 | 16     | 41.5 | 4150     | 741   | 2.59 | 27.832                  | 37.7           | 722                     | 10.9               | 7.2                          |
| 15:00 | 17     | 44.0 | 4400     | 786   | 2.6  | 32.216                  | 36.6           | 759                     | 11.4               | 7.6                          |
| 15:18 | 18     | 46.0 | 4600     | 821   | 2.61 | 36.542                  | 28.4           | 787                     | 11.1               | 7.9                          |

**Table B 7: Experiment 2 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Feed-E2   | 278.2     | 117.4     | 13.5      | 63171.6   | 10.9      | 178.6     |
| 2-1       | 276.0     | 111.1     | 0.4       | 63081.7   | 10.3      | 0.0       |
| 2-2       | 277.8     | 116.0     | 0.6       | 63344.0   | 10.8      | 0.0       |
| 2-3       | 278.5     | 118.5     | 0.4       | 63041.4   | 10.9      | 0.0       |
| 2-4       | 278.3     | 119.7     | 0.6       | 63225.9   | 11.0      | 0.0       |
| 2-5       | 278.0     | 119.2     | 0.5       | 63245.7   | 11.2      | 0.0       |
| 2-6       | 278.1     | 119.5     | 0.5       | 63327.3   | 10.7      | 0.0       |
| 2-7       | 277.8     | 118.3     | 0.7       | 63200.8   | 10.9      | 0.0       |
| 2-8       | 277.7     | 118.4     | 0.7       | 63425.7   | 11.0      | 0.5       |
| 2-9       | 280.0     | 119.0     | 0.6       | 63223.2   | 11.5      | 1.1       |
| 2-10      | 277.6     | 118.1     | 0.7       | 63190.1   | 11.3      | 2.0       |
| 2-11      | 279.9     | 118.4     | 0.7       | 63492.4   | 10.3      | 3.6       |
| 2-12      | 278.2     | 118.3     | 0.8       | 63343.1   | 11.1      | 5.3       |
| 2-13      | 277.8     | 117.8     | 0.8       | 63207.1   | 11.0      | 7.7       |
| 2-14      | 277.1     | 117.3     | 0.9       | 62153.9   | 11.0      | 11.1      |
| 2-15      | 278.1     | 118.4     | 0.7       | 63175.5   | 11.1      | 16.0      |
| 2-16      | 277.5     | 118.0     | 1.1       | 62902.2   | 11.2      | 27.8      |
| 2-17      | 277.9     | 118.3     | 1.0       | 63024.0   | 10.7      | 32.2      |
| 2-18      | 278.0     | 118.7     | 0.6       | 63021.9   | 11.0      | 36.5      |

**Table B 8: Experiment 3 conditions.**

| Experiment 3 |        |      |
|--------------|--------|------|
| Feed pH      | 2.67   |      |
| Temperature  | 25     | °C   |
| Flow rate    | 8 - 10 | BV/h |
| Feed [Zn]    | 200.2  | mg/L |

**Table B 9: Experiment 3 experimental results.**

| Time  | Sample | BV   | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (mg) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|------|----------|-------|------|-------------------------|----------------|-------------------------|--------------------|------------------------------|
| 09:07 | Feed   | 0    |          |       | 2.67 | 200.2                   |                |                         |                    |                              |
| 09:31 | 1      | 4.0  | 400      | 80    | 2.29 | 1.3                     | 79.6           | 80                      | 16.7               | 0.8                          |
| 09:46 | 2      | 6.5  | 650      | 130   | 2.35 | 2.0                     | 49.6           | 129                     | 16.7               | 1.3                          |
| 10:01 | 3      | 9.0  | 900      | 180   | 2.39 | 2.6                     | 49.4           | 179                     | 16.7               | 1.8                          |
| 10:16 | 4      | 11.5 | 1150     | 230   | 2.41 | 3.4                     | 49.2           | 228                     | 16.7               | 2.3                          |
| 10:31 | 5      | 14.0 | 1400     | 280   | 2.43 | 4.2                     | 49.0           | 277                     | 16.7               | 2.8                          |
| 10:48 | 6      | 16.5 | 1650     | 330   | 2.44 | 5.5                     | 48.7           | 325                     | 14.7               | 3.3                          |
| 11:05 | 7      | 19.0 | 1900     | 380   | 2.45 | 7.0                     | 48.3           | 374                     | 14.7               | 3.7                          |
| 11:22 | 8      | 21.5 | 2150     | 430   | 2.45 | 8.1                     | 48.0           | 422                     | 14.7               | 4.2                          |
| 11:39 | 9      | 24.0 | 2400     | 481   | 2.45 | 11.7                    | 47.1           | 469                     | 14.7               | 4.7                          |
| 11:55 | 10     | 26.5 | 2650     | 531   | 2.45 | 13.4                    | 46.7           | 516                     | 15.6               | 5.2                          |
| 12:19 | 11     | 29.0 | 2900     | 581   | 2.57 | 49.9                    | 37.6           | 553                     | 10.4               | 5.5                          |
| 12:34 | 12     | 31.5 | 3150     | 631   | 2.50 | 51.1                    | 37.3           | 590                     | 16.7               | 5.9                          |
| 12:49 | 13     | 34.0 | 3400     | 681   | 2.50 | 50.1                    | 37.5           | 628                     | 16.7               | 6.3                          |
| 13:04 | 14     | 36.5 | 3650     | 731   | 2.50 | 50.5                    | 37.4           | 665                     | 16.7               | 6.7                          |
| 13:20 | 15     | 39.0 | 3900     | 781   | 2.50 | 52.8                    | 36.9           | 702                     | 15.6               | 7.0                          |
| 13:34 | 16     | 41.5 | 4150     | 831   | 2.50 | 58.2                    | 35.5           | 738                     | 17.9               | 7.4                          |
| 13:41 | 17     | 43.0 | 4300     | 861   | 2.50 | 66.5                    | 20.1           | 758                     | 21.4               | 7.6                          |

**Table B 10: Experiment 3 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Feed-E3   | 332.3     | 139.2     | 17.5      | 76213.0   | 9.5       | 200.2     |
| 3-1       | 332.6     | 133.8     | 1.3       | 76152.5   | 9.2       | 1.3       |
| 3-2       | 335.9     | 138.8     | 2.1       | 76082.0   | 9.7       | 2.0       |
| 3-3       | 332.9     | 140.7     | 1.2       | 76096.0   | 9.9       | 2.6       |
| 3-4       | 334.1     | 141.7     | 1.4       | 80574.1   | 10.1      | 3.4       |
| 3-5       | 335.7     | 141.3     | 1.4       | 76202.7   | 10.1      | 4.2       |
| 3-6       | 334.0     | 140.6     | 1.5       | 76243.1   | 10.3      | 5.5       |
| 3-7       | 335.4     | 141.9     | 1.6       | 76406.5   | 10.0      | 7.0       |
| 3-8       | 335.3     | 140.5     | 1.6       | 75949.0   | 9.7       | 8.1       |
| 3-9       | 334.9     | 139.8     | 3.1       | 76143.6   | 10.1      | 11.7      |
| 3-10      | 336.0     | 140.9     | 1.7       | 76120.3   | 10.2      | 13.4      |
| 3-11      | 306.3     | 126.5     | 1.9       | 68490.0   | 7.7       | 49.9      |
| 3-12      | 345.0     | 145.1     | 2.2       | 78220.5   | 10.3      | 51.1      |
| 3-13      | 341.8     | 144.5     | 3.6       | 77201.6   | 9.9       | 50.1      |
| 3-14      | 342.1     | 144.3     | 2.1       | 77203.0   | 9.7       | 50.5      |
| 3-15      | 345.8     | 146.3     | 2.3       | 78519.5   | 10.2      | 52.8      |
| 3-16      | 346.8     | 147.5     | 2.9       | 78845.0   | 9.5       | 58.2      |
| 3-17      | 347.3     | 147.1     | 2.5       | 78667.4   | 9.8       | 66.5      |

**Table B 11: Experiment 4 conditions.**

| Experiment 4 |       |      |
|--------------|-------|------|
| Feed pH      | 2.71  |      |
| Temperature  | 25    | °C   |
| Flow rate    | 15    | BV/h |
| Feed [Zn]    | 183.4 | mg/L |

**Table B 12: Experiment 4 experimental results.**

| Time  | Sample | BV   | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (mg) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|------|----------|-------|------|-------------------------|----------------|-------------------------|--------------------|------------------------------|
| 08:24 | Feed   | 0    |          |       | 2.71 | 183.4                   |                |                         |                    |                              |
| 08:32 | 1      | 2.0  | 200      | 37    | 2.32 | 0.2                     | 36.6           | 37                      | 25.0               | 0.4                          |
| 08:45 | 2      | 4.5  | 450      | 83    | 2.41 | 0.6                     | 45.7           | 82                      | 19.2               | 0.8                          |
| 08:55 | 3      | 7.0  | 700      | 128   | 2.46 | 0.4                     | 45.8           | 128                     | 25.0               | 1.3                          |
| 09:05 | 4      | 9.5  | 950      | 174   | 2.49 | 1.0                     | 45.6           | 174                     | 25.0               | 1.7                          |
| 09:15 | 5      | 12.0 | 1200     | 220   | 2.52 | 1.6                     | 45.5           | 219                     | 25.0               | 2.2                          |
| 09:25 | 6      | 14.5 | 1450     | 266   | 2.52 | 3.1                     | 45.1           | 264                     | 25.0               | 2.6                          |
| 09:35 | 7      | 17.0 | 1700     | 312   | 2.53 | 4.2                     | 44.8           | 309                     | 25.0               | 3.1                          |
| 09:45 | 8      | 19.5 | 1950     | 358   | 2.53 | 6.0                     | 44.4           | 353                     | 25.0               | 3.5                          |
| 09:55 | 9      | 22.0 | 2200     | 404   | 2.54 | 8.3                     | 43.8           | 397                     | 25.0               | 4.0                          |
| 10:05 | 10     | 24.5 | 2450     | 449   | 2.54 | 10.9                    | 43.1           | 440                     | 25.0               | 4.4                          |
| 10:15 | 11     | 27.0 | 2700     | 495   | 2.54 | 14.7                    | 42.2           | 483                     | 25.0               | 4.8                          |
| 10:25 | 12     | 29.5 | 2950     | 541   | 2.55 | 17.2                    | 41.6           | 524                     | 25.0               | 5.2                          |
| 10:35 | 13     | 32.0 | 3200     | 587   | 2.55 | 21.6                    | 40.5           | 565                     | 25.0               | 5.6                          |
| 10:46 | 14     | 34.5 | 3450     | 633   | 2.55 | 20.4                    | 40.8           | 605                     | 22.7               | 6.1                          |
| 10:56 | 15     | 37.0 | 3700     | 679   | 2.56 | 31.6                    | 38.0           | 643                     | 25.0               | 6.4                          |
| 11:06 | 16     | 39.5 | 3950     | 725   | 2.57 | 38.7                    | 36.2           | 680                     | 25.0               | 6.8                          |
| 11:16 | 17     | 42.0 | 4200     | 770   | 2.57 | 39.9                    | 35.9           | 715                     | 25.0               | 7.2                          |
| 11:26 | 18     | 44.5 | 4450     | 816   | 2.58 | 58.2                    | 31.3           | 747                     |                    | 7.5                          |

**Table B 13: Experiment 4 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Feed-E4   | 299.2     | 123.2     | 14.4      | 68907.1   | 8.6       | 183.4     |
| 4-1       | 297.3     | 114.1     | 1.5       | 67314.3   | 8.5       | 0.2       |
| 4-2       |           |           |           |           |           | 0.6       |
| 4-3       |           |           |           |           |           | 0.4       |
| 4-4       |           |           |           |           |           | 1.0       |
| 4-5       |           |           |           |           |           | 1.6       |
| 4-6       | 299.5     | 125.7     | 1.9       | 68242.9   | 9.0       | 3.1       |
| 4-7       |           |           |           |           |           | 4.2       |
| 4-8       | 299.4     | 125.2     | 2.1       | 66808.6   | 8.8       | 6.0       |
| 4-9       |           |           |           |           |           | 8.3       |
| 4-10      | 299.8     | 125.4     | 2.4       | 66931.1   | 8.8       | 10.9      |
| 4-11      |           |           |           |           |           | 14.7      |
| 4-12      | 299.7     | 125.7     | 2.5       | 66929.0   | 8.7       | 17.2      |
| 4-13      | 300.6     | 125.7     | 2.7       | 66861.0   | 8.9       | 21.6      |
| 4-14      |           |           |           |           |           | 20.4      |
| 4-15      | 301.5     | 125.3     | 2.4       | 66865.0   | 9.0       | 31.6      |
| 4-16      | 298.1     | 124.7     | 2.6       | 66872.6   | 9.2       | 38.7      |
| 4-17      |           |           |           |           |           | 39.9      |
| 4-18      | 298.5     | 124.4     | 3.0       | 66588.2   | 8.6       | 58.2      |

**Table B 14: Experiment S1 conditions.**

| Experiment S1 |      |      |
|---------------|------|------|
| Feed pH       | 2.68 |      |
| Temperature   | 25   | °C   |
| Flow rate     | 19.7 | BV/h |
| Feed [Zn]     | 96.5 | mg/L |

**Table B 15: Experiment S1 experimental results.**

| Time  | Sample | BV  | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (mg) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|-----|----------|-------|------|-------------------------|----------------|-------------------------|--------------------|------------------------------|
| 07:10 | Feed   | 0   |          |       | 2.68 | 96.5                    |                |                         |                    |                              |
| 07:39 | 1      | 10  | 1000     | 97    | 2.26 | 0.6                     | 95.9           | 96                      | 34.5               | 1.0                          |
| 08:09 | 2      | 20  | 2000     | 193   | 2.51 | 3.7                     | 92.8           | 189                     | 33.3               | 1.9                          |
| 08:39 | 3      | 30  | 3000     | 290   | 2.54 | 7.3                     | 89.3           | 278                     | 33.3               | 2.8                          |
| 09:10 | 4      | 40  | 4000     | 386   | 2.54 | 12.7                    | 83.9           | 362                     | 32.3               | 3.6                          |
| 09:41 | 5      | 50  | 5000     | 483   | 2.54 | 18.6                    | 78.0           | 440                     | 32.3               | 4.4                          |
| 10:11 | 6      | 60  | 6000     | 579   | 2.54 | 26.4                    | 70.1           | 510                     | 33.3               | 5.1                          |
| 10:42 | 7      | 70  | 7000     | 676   | 2.56 | 35.8                    | 60.7           | 571                     | 32.3               | 5.7                          |
| 11:13 | 8      | 80  | 8000     | 772   | 2.56 | 46.4                    | 50.1           | 621                     | 32.3               | 6.2                          |
| 11:44 | 9      | 90  | 9000     | 869   | 2.58 | 57.9                    | 38.7           | 660                     | 32.3               | 6.6                          |
| 12:14 | 10     | 100 | 10000    | 965   | 2.6  | 68.9                    | 27.6           | 687                     | 33.3               | 6.9                          |
| 12:46 | 11     | 110 | 11000    | 1062  | 2.62 | 77.8                    | 18.7           | 706                     | 31.3               | 7.1                          |
| 13:17 | 12     | 120 | 12000    | 1158  | 2.62 | 84.3                    | 12.2           | 718                     | 32.3               | 7.2                          |
| 13:49 | 13     | 130 | 13000    | 1255  | 2.64 | 91.0                    | 5.6            | 724                     | 31.3               | 7.2                          |
| 14:20 | 14     | 140 | 14000    | 1351  | 2.66 | 92.1                    | 4.4            | 728                     | 32.3               | 7.3                          |

**Table B 16: Experiment S1 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Feed-S1   | 303.4     | 124.6     | 14.5      | 68756.0   | 8.2       | 96.5      |
| S1-1      | 326.5     | 123.2     | 1.5       | 74001.2   | 8.4       | 0.6       |
| S1-2      | 311.4     | 129.1     | 2.0       | 70032.1   | 8.5       | 3.7       |
| S1-3      | 316.0     | 130.9     | 2.5       | 70858.5   | 9.3       | 7.3       |
| S1-4      | 329.3     | 136.5     | 3.0       | 74627.9   | 9.1       | 12.7      |
| S1-5      | 313.8     | 129.2     | 3.4       | 70695.3   | 9.2       | 18.6      |
| S1-6      | 312.5     | 129.4     | 4.0       | 71505.1   | 8.6       | 26.4      |
| S1-7      | 317.1     | 131.4     | 4.1       | 71568.2   | 8.8       | 35.8      |
| S1-8      | 317.3     | 131.4     | 4.6       | 71399.1   | 8.9       | 46.4      |
| S1-9      | 317.7     | 131.2     | 5.1       | 71284.9   | 9.2       | 57.9      |
| S1-10     | 320.1     | 132.5     | 5.3       | 71842.0   | 9.2       | 68.9      |
| S1-11     | 318.8     | 132.2     | 5.6       | 71716.3   | 9.2       | 77.8      |
| S1-12     | 314.1     | 129.6     | 6.1       | 70169.4   | 9.1       | 84.3      |
| S1-13     | 319.7     | 132.3     | 6.7       | 71730.6   | 9.3       | 91.0      |
| S1-14     | 309.8     | 127.9     | 8.6       | 69738.4   | 9.2       | 92.1      |

**Table B 17: Experiment S2 conditions.**

| Experiment S2 |      |      |
|---------------|------|------|
| Feed pH       | 2.7  |      |
| Temperature   | 25   | °C   |
| Flow rate     | 9.6  | BV/h |
| Feed [Zn]     | 92.5 | mg/L |

**Table B 18: Experiment S2 experimental results.**

| Time  | Sample | BV  | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (mg) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|-----|----------|-------|------|-------------------------|----------------|-------------------------|--------------------|------------------------------|
| 05:57 | Feed   | 0   |          |       | 2.71 | 92.5                    |                |                         |                    |                              |
| 07:09 | 1      | 10  | 1000     | 93    | 2.25 | 0.2                     | 92.3           | 92                      | 18.9               | 0.9                          |
| 08:21 | 2      | 20  | 2000     | 185   | 2.50 | 0.9                     | 91.7           | 184                     | 16.4               | 1.8                          |
| 09:33 | 3      | 30  | 3000     | 278   | 2.53 | 2.5                     | 90.0           | 274                     | 16.1               | 2.7                          |
| 10:45 | 4      | 40  | 4000     | 370   | 2.54 | 6.9                     | 85.6           | 360                     | 16.4               | 3.6                          |
| 11:57 | 5      | 50  | 5000     | 463   | 2.55 | 12.3                    | 80.2           | 440                     | 15.4               | 4.4                          |
| 13:09 | 6      | 60  | 6000     | 555   | 2.55 | 18.8                    | 73.7           | 513                     | 13.3               | 5.1                          |
| 14:21 | 7      | 70  | 7000     | 648   | 2.56 | 28.2                    | 64.3           | 578                     | 16.1               | 5.8                          |
| 15:33 | 8      | 80  | 8000     | 740   | 2.56 | 38.2                    | 54.3           | 632                     | 16.1               | 6.3                          |
| 16:45 | 9      | 90  | 9000     | 833   | 2.59 | 44.1                    | 48.4           | 680                     | 15.7               | 6.8                          |
| 17:57 | 10     | 100 | 10000    | 925   | 2.62 | 55.1                    | 37.4           | 718                     | 15.6               | 7.2                          |
| 19:09 | 11     | 110 | 11000    | 1018  | 2.64 | 63.2                    | 29.3           | 747                     | 15.5               | 7.5                          |
| 20:21 | 12     | 120 | 12000    | 1110  | 2.64 | 74.4                    | 18.1           | 765                     | 15.4               | 7.7                          |
| 21:33 | 13     | 130 | 13000    | 1203  | 2.65 | 85.1                    | 7.4            | 773                     | 15.4               | 7.7                          |
| 22:45 | 14     | 140 | 14000    | 1295  | 2.66 | 89.3                    | 3.2            | 776                     | 15.7               | 7.8                          |
| 23:57 | 15     | 150 | 15000    | 1388  | 2.68 | 91.4                    | 1.1            | 777                     | 15.6               | 7.8                          |

**Table B 19: Experiment S2 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| S2-Feed   | 303.3     | 127.9     | 15.2      | 67974.2   | 9.0       | 92.5      |
| S2-1      | 301.4     | 125.3     | 1.3       | 67352.0   | 9.0       | 0.2       |
| S2-2      | 305.1     | 129.6     | 1.4       | 68089.3   | 9.3       | 0.9       |
| S2-3      | 314.3     | 133.9     | 1.5       | 70555.1   | 9.6       | 2.5       |
| S2-4      | 308.7     | 130.7     | 2.0       | 68917.2   | 9.4       | 6.9       |
| S2-5      | 309.1     | 130.5     | 2.2       | 69386.7   | 9.6       | 12.3      |
| S2-6      | 307.2     | 130.9     | 2.3       | 68506.8   | 9.3       | 18.8      |
| S2-7      | 302.0     | 128.0     | 4.2       | 67848.0   | 9.0       | 28.2      |
| S2-8      | 302.2     | 129.0     | 4.4       | 67917.0   | 9.4       | 38.2      |
| S2-9      | 304.0     | 133.0     | 4.4       | 69953.0   | 9.3       | 44.1      |
| S2-10     | 309.0     | 133.0     | 4.8       | 69839.0   | 9.5       | 55.1      |
| S2-11     | 309.3     | 131.0     | 4.9       | 70174.0   | 9.2       | 63.2      |
| S2-12     | 307.5     | 128.0     | 5.8       | 69828.0   | 9.0       | 74.4      |
| S2-13     | 307.2     | 133.0     | 6.3       | 70456.0   | 9.0       | 85.1      |
| S2-14     | 310.1     | 126.0     | 6.9       | 68303.0   | 9.4       | 89.3      |
| S2-15     | 305.0     | 132.0     | 8.8       | 69290.0   | 9.2       | 91.4      |

**Table B 20: Experiment S3 conditions.**

| Experiment S3 |     |      |
|---------------|-----|------|
| Feed pH       | 2.7 |      |
| Temperature   | 25  | °C   |
| Flow rate     | 19  | BV/h |
| Feed [Zn]     | 48  | mg/L |

**Table B 21: Experiment S3 experimental results.**

| Time  | Sample | BV  | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (g) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|-----|----------|-------|------|-------------------------|----------------|------------------------|--------------------|------------------------------|
| 08:55 | Feed   | 0   |          |       | 2.71 | 48.0                    |                |                        |                    |                              |
| 09:26 | 1      | 10  | 1000     | 48    | 2.53 | 0.6                     | 47.3           | 47                     |                    | 0.5                          |
| 09:57 | 2      | 20  | 2000     | 96    | 2.62 | 1.7                     | 46.2           | 94                     | 32.3               | 0.9                          |
| 10:28 | 3      | 30  | 3000     | 144   | 2.64 | 3.2                     | 44.7           | 138                    | 32.3               | 1.4                          |
| 11:01 | 4      | 40  | 4000     | 192   | 2.66 | 5.0                     | 42.9           | 181                    | 32.3               | 1.8                          |
| 11:34 | 5      | 50  | 5000     | 240   | 2.66 | 6.9                     | 41.1           | 222                    | 30.3               | 2.2                          |
| 12:07 | 6      | 60  | 6000     | 288   | 2.67 | 8.9                     | 39.0           | 261                    | 31.3               | 2.6                          |
| 12:39 | 7      | 70  | 7000     | 336   | 2.67 | 12.2                    | 35.8           | 297                    | 30.3               | 3.0                          |
| 13:10 | 8      | 80  | 8000     | 384   | 2.67 | 14.2                    | 33.8           | 331                    | 31.3               | 3.3                          |
| 13:41 | 9      | 90  | 9000     | 432   | 2.67 | 16.8                    | 31.2           | 362                    | 32.3               | 3.6                          |
| 14:11 | 10     | 100 | 10000    | 480   | 2.69 | 19.1                    | 28.8           | 391                    | 32.3               | 3.9                          |
| 14:43 | 11     | 110 | 11000    | 528   | 2.69 | 21.8                    | 26.2           | 417                    | 33.3               | 4.2                          |
| 15:15 | 12     | 120 | 12000    | 576   | 2.69 | 25.5                    | 22.5           | 440                    | 31.3               | 4.4                          |
| 15:47 | 13     | 130 | 13000    | 624   | 2.69 | 28.0                    | 20.0           | 460                    | 31.3               | 4.6                          |
| 07:35 | 14     | 140 | 14000    | 672   | 2.70 | 30.4                    | 17.6           | 477                    | 31.3               | 4.8                          |
| 08:07 | 15     | 150 | 15000    | 720   | 2.70 | 33.8                    | 14.1           | 491                    | 31.3               | 4.9                          |
| 08:38 | 16     | 160 | 16000    | 767   | 2.70 | 36.2                    | 11.7           | 503                    | 32.3               | 5.0                          |
| 09:10 | 17     | 170 | 17000    | 815   | 2.70 | 37.4                    | 10.5           | 514                    | 31.3               | 5.1                          |
| 09:41 | 18     | 180 | 18000    | 863   | 2.71 | 40.3                    | 7.6            | 521                    | 32.3               | 5.2                          |
| 10:13 | 19     | 190 | 19000    | 911   | 2.71 | 41.8                    | 6.2            | 527                    | 31.3               | 5.3                          |
| 10:44 | 20     | 200 | 20000    | 959   | 2.71 | 42.8                    | 5.1            | 532                    | 32.3               | 5.3                          |

**Table B 22: Experiment S3 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Feed-S3   | 305.4     | 127.8     | 15.4      | 68685.3   | 8.8       | 48.0      |
| 3-1       | 302.6     | 124.1     | 2.8       | 67901.6   | 8.5       | 0.6       |
| 3-2       | 312.5     | 131.0     | 2.8       | 70281.9   | 9.4       | 1.7       |
| 3-3       | 306.7     | 129.5     | 2.9       | 68989.1   | 8.5       | 3.2       |
| 3-4       | 311.9     | 131.8     | 3.3       | 70236.1   | 8.8       | 5.0       |
| 3-5       | 312.3     | 131.0     | 3.4       | 70434.9   | 9.0       | 6.9       |
| 3-6       | 307.6     | 128.7     | 3.5       | 69282.7   | 9.1       | 8.9       |
| 3-7       | 310.6     | 130.6     | 5.0       | 69863.7   | 9.2       | 12.2      |
| 3-8       | 312.0     | 130.9     | 4.3       | 69820.0   | 9.1       | 14.2      |
| 3-9       | 309.7     | 129.2     | 4.8       | 69679.9   | 8.8       | 16.8      |
| 3-10      | 309.8     | 130.1     | 5.1       | 70482.0   | 8.7       | 19.1      |
| 3-11      | 308.1     | 129.8     | 5.6       | 69110.5   | 8.8       | 21.8      |
| 3-12      | 308.8     | 129.3     | 6.5       | 69325.7   | 8.7       | 25.5      |
| 3-13      | 310.6     | 129.8     | 6.7       | 69736.3   | 8.9       | 28.0      |
| 3-14      | 314.8     | 132.9     | 8.1       | 70749.7   | 8.9       | 30.4      |
| 3-15      | 313.1     | 131.4     | 9.0       | 70228.5   | 8.7       | 33.8      |
| 3-16      | 312.8     | 131.8     | 9.3       | 70282.4   | 8.8       | 36.2      |
| 3-17      | 307.2     | 129.2     | 9.3       | 68903.8   | 8.9       | 37.4      |
| 3-18      | 314.1     | 132.2     | 10.1      | 70450.5   | 8.8       | 40.3      |
| 3-19      | 313.1     | 131.5     | 10.4      | 70455.3   | 8.6       | 41.8      |
| 3-20      | 312.0     | 131.1     | 10.6      | 70146.3   | 8.6       | 42.8      |

**Table B 23: Experiment S4 conditions.**

| Experiment S4 |      |      |
|---------------|------|------|
| Feed pH       | 2.7  |      |
| Temperature   | 25   | °C   |
| Flow rate     | 10   | BV/h |
| Feed [Zn]     | 44.7 | mg/L |

**Table B 24: Experiment S4 experimental results.**

| Time  | Sample | BV  | Vol (ml) | mg Zn | pH   | Zn Concentration (mg/L) | Zn loaded (mg) | Cumulative loading (mg) | Flow rate (ml/min) | Resin Loading (g Zn/L resin) |
|-------|--------|-----|----------|-------|------|-------------------------|----------------|-------------------------|--------------------|------------------------------|
| 09:39 | Feed   | 0   |          |       | 2.7  | 44.8                    |                |                         |                    |                              |
| 10:39 | 1      | 10  | 1000     | 45    | 2.54 | 0.9                     | 43.9           | 44                      | 16.7               | 0.4                          |
| 11:40 | 2      | 20  | 2000     | 90    | 2.6  | 1.9                     | 42.8           | 87                      | 16.4               | 0.9                          |
| 12:41 | 3      | 30  | 3000     | 134   | 2.65 | 2.9                     | 41.9           | 129                     | 16.4               | 1.3                          |
| 13:55 | 4      | 40  | 4000     | 179   | 2.66 | 4.9                     | 39.9           | 169                     | 13.5               | 1.7                          |
| 15:00 | 5      | 50  | 5000     | 224   | 2.65 | 7.0                     | 37.8           | 206                     | 15.4               | 2.1                          |
| 08:17 | 6      | 60  | 6000     | 269   | 2.65 | 7.6                     | 37.1           | 243                     | 16.7               | 2.4                          |
| 09:16 | 7      | 70  | 7000     | 313   | 2.65 | 10.8                    | 33.9           | 277                     | 16.9               | 2.8                          |
| 10:16 | 8      | 80  | 8000     | 358   | 2.64 | 13.6                    | 31.1           | 308                     | 16.7               | 3.1                          |
| 11:17 | 9      | 90  | 9000     | 403   | 2.64 | 18.3                    | 26.5           | 335                     | 16.4               | 3.3                          |
| 12:16 | 10     | 100 | 10000    | 448   | 2.64 | 22.1                    | 22.7           | 358                     | 16.9               | 3.6                          |
| 13:16 | 11     | 110 | 11000    | 492   | 2.66 | 25.5                    | 19.3           | 377                     | 16.7               | 3.8                          |
| 14:16 | 12     | 120 | 12000    | 537   | 2.67 | 30.9                    | 13.9           | 391                     | 16.7               | 3.9                          |
| 15:13 | 13     | 130 | 13000    | 582   | 2.68 | 32.7                    | 12.0           | 403                     | 17.5               | 4.0                          |
| 08:10 | 14     | 140 | 14000    | 627   | 2.68 | 36.2                    | 8.6            | 411                     | 16.7               | 4.1                          |
| 09:09 | 15     | 150 | 15000    | 671   | 2.69 | 38.3                    | 6.5            | 418                     | 16.9               | 4.2                          |
| 10:10 | 16     | 160 | 16000    | 716   | 2.69 | 39.3                    | 5.4            | 423                     | 16.7               | 4.2                          |
| 11:01 | 17     | 170 | 17000    | 761   | 2.69 | 39.0                    | 5.7            | 429                     | 19.6               | 4.3                          |
| 12:14 | 18     | 180 | 18000    | 806   | 2.69 | 42.7                    | 2.1            | 431                     | 13.7               | 4.3                          |
| 13:13 | 19     | 190 | 19000    | 850   | 2.70 | 40.6                    | 4.1            | 435                     | 16.9               | 4.4                          |
| 14:08 | 20     | 200 | 20000    | 895   | 2.70 | 40.6                    | 4.1            | 439                     | 18.2               | 4.4                          |

**Table B 25: Experiment S4 assay results.**

| Sample No | Co (mg/L) | Cu (mg/L) | Fe (mg/L) | Ni (mg/L) | Pb (mg/L) | Zn (mg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Feed-S4   | 293.3     | 120.8     | 14.7      | 66178.8   | 8.7       | 44.8      |
| 4-1       | 295.1     | 121.1     | 1.6       | 66510.8   | 8.1       | 0.9       |
| 4-2       | 295.3     | 123.1     | 1.6       | 66559.5   | 8.4       | 1.9       |
| 4-3       | 296.2     | 122.6     | 1.5       | 66504.6   | 8.5       | 2.9       |
| 4-4       | 295.2     | 122.3     | 1.9       | 66690.4   | 8.6       | 4.9       |
| 4-5       | 294.8     | 122.4     | 2.1       | 66589.6   | 9.0       | 7.0       |
| 4-6       | 297.0     | 123.9     | 1.7       | 66870.3   | 8.5       | 7.6       |
| 4-7       | 296.6     | 124.0     | 3.0       | 66878.5   | 8.4       | 10.8      |
| 4-8       | 297.1     | 123.1     | 3.6       | 66639.8   | 8.8       | 13.6      |
| 4-9       | 296.1     | 123.0     | 6.1       | 66793.3   | 8.9       | 18.3      |
| 4-10      | 295.4     | 122.1     | 7.1       | 66750.2   | 8.8       | 22.1      |
| 4-11      | 297.0     | 123.4     | 6.9       | 66836.2   | 9.3       | 25.5      |
| 4-12      | 294.2     | 121.9     | 9.0       | 66129.1   | 8.6       | 30.9      |
| 4-13      | 294.9     | 122.2     | 8.1       | 66225.7   | 8.7       | 32.7      |
| 4-14      | 297.0     | 123.6     | 10.5      | 66883.0   | 8.8       | 36.2      |
| 4-15      | 298.0     | 123.3     | 11.5      | 66759.4   | 8.8       | 38.3      |
| 4-16      | 297.5     | 123.8     | 11.1      | 67094.0   | 8.7       | 39.3      |
| 4-17      | 296.2     | 123.6     | 10.4      | 67080.8   | 8.7       | 39.0      |
| 18        | 298.5     | 123.2     | 13.2      | 67256.9   | 8.9       | 42.7      |
| 4-19      | 299.6     | 123.2     | 13.1      | 67528.4   | 8.7       | 40.6      |
| 4-20      | 302.8     | 125.1     | 11.9      | 68283.7   | 7.7       | 40.6      |

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## APPENDIX C: RESIN INFORMATION SHEETS

### Lewatit VP OC 1026 Information Sheet

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PRODUCT INFORMATION  
LEWATIT® VP OC 1026

 **Lewatit®**

**Lewatit® VP OC 1026** is a crosslinked polystyrene based macroporous resin which contains Di-2-ethylhexylphosphat (D2EHPA). This active ingredient is directly incorporated during the formation of the copolymer and is fixed by adsorption. This gives a resin of very good matrix and - compared with impregnated resins a relatively high concentration of active ingredient; in addition, loss of extractant during operation is minimized (as long as the pH of the process solution as well as rinse water is kept below pH 4). Cations are adsorbed by **Lewatit® VP OC 1026** in the following order:  $Ti^{4+} > Fe^{3+} > In^{3+} > Sn^{2+/4+} > Sb^{3+} > Bi^{3+} > V^{5+} > Be^{2+} > Al^{3+} > Zn^{2+} > Pb^{2+} > Cd^{2+} > Ca^{2+} > Mn^{2+} > Cu^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > Cr^{2+} >>> Alkali$

Fields of application:

As given by the effectiveness of this extractant, **Lewatit® VP OC 1026** can be used to remove certain metal ions from acidic and neutral solutions.

Generally it can be assumed that ions which can be removed which D2EHPA will presumably also be adsorbed by **Lewatit® VP OC 1026**; primarily heavy metal ions from sulphate or chloride solutions, as a function of pH, e.g.:

- » divalent ions of zinc, uranium ( $UO_2^{2+}$ ), vanadium ( $VO^{2+}$ )
- » trivalent ions of lathanides, indium, iron, aluminium
- » tetravalent ions of actinides, titanium

Advantages of **Lewatit® VP OC 1026** compared to solvent extraction:

- » no organic solvent required
- » no phase separation problems
- » simple equipment similar to conventional bead type ion exchange resins

Important hints for application:

There is a marked distinction in its physical and chemical properties from those of the known ion exchange resins. The product data summarized in the following pages should be carefully observed. It has to be emphasized that: The active ingredient of **Lewatit® VP OC 1026** is in the form of the acid ester. This means that the form supplied can be directly used. **Exposure to sodium hydroxide or sodium carbonate should be avoided since the active ingredient will be displaced from the resin. Also the pH of process solution and rinse water should always be < pH 4.** The resin is floating to the liquid surface. Therefore the column should be equipped with an adequate distribution plate at the column's head and be operated upstream.

Due to the specific method of manufacturing the resin has a relatively high percentage of fine beads. Therefore it is recommended to use inert resin (**Lewatit® IN 42**) to protect the head distributor against plugging. To protect the bottom distributor a gravel layer can be applied.

Backwash can only be carried out in downflow mode by means of an acidic, in minimum 4 % salt containing solution. Backwash water is discharged through a special out pipe positioned below the ion exchange bed.

The resin can be used without backwashing only in the case that a thorough - pre filtration is carried out. In this case the column is designed with a packed bed, having only 10 % freeboard.

This document contains important information and must be read in its entirety.

Edition: 2011-10-13  
Previous Edition: 2011-05-12

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**LANXESS**  
Energizing Chemistry

PRODUCT INFORMATION  
LEWATIT® VP OC 1026



The special properties of this product can only be fully utilized if the technology and process used correspond to the current state-of-the-art. Further advice in this matter can be obtained from Lanxess, Business Unit Ion Exchange Resins.

This document contains important information and must be read in its entirety.

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### General Description

|                  |                         |
|------------------|-------------------------|
| Functional group | D2EHPA                  |
| Matrix           | crosslinked polystyrene |
| Structure        | macroporous             |

### Physical and Chemical Properties

|                |                   | metric units |                 |
|----------------|-------------------|--------------|-----------------|
| Zinc capacity* |                   | min. g/l     | 13              |
| Bead size*     | > 90 %            | mm           | 0.31 - 1.6<br>5 |
| Bulk density   | (+/- 5 %)         | g/l          | 600             |
| Density        |                   | approx. g/ml | 0.97            |
| Stability      | at pH-range       |              | < 4             |
| Stability      | temperature range | °C           | -20 - 40        |
| Storability    | of the product    | max. years   | 2               |
| Storability    | temperature range | °C           | -20 - 40        |

\* Specification values subjected to continuous monitoring.

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Recommended Operating Conditions\*

|                         |                               | metric units                 |       |                                |
|-------------------------|-------------------------------|------------------------------|-------|--------------------------------|
| Operating temperature   |                               | max. °C                      | 80    |                                |
| Operating pH-range      |                               |                              | 1 - 4 |                                |
| Bed depth               |                               | min. mm                      | 800   |                                |
| Specific pressure drop  | (15 °C)                       | approx. kPa*h/m <sup>2</sup> | 1.1   |                                |
| Pressure drop           |                               | max. kPa                     | 250   |                                |
| Linear velocity         | operation                     | max. m/h                     | 10    |                                |
| Freeboard               | backwash<br>(extern / intern) | vol. %                       | 10    |                                |
| Regenerant              |                               |                              | HCl   | H <sub>2</sub> SO <sub>4</sub> |
| Co current regeneration | level                         | approx. g/l                  | 100   | 200                            |
| Co current regeneration | concentration                 | approx. wt. %                | 5     | 15                             |
| Linear velocity         | regeneration                  | approx. m/h                  | 5     |                                |
| Linear velocity         | rinsing                       | approx. m/h                  | 5     |                                |
| Rinse water requirement | only acidic water             | approx. BV                   | 2 - 4 |                                |

\* The recommended operating conditions refer to the use of the product under normal operating conditions. It is based on tests in pilot plants and data obtained from industrial applications. However, additional data are needed to calculate the resin volumes required for ion exchange units. These data are to be found in our Technical Information Sheets.

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## Additional Information & Regulations

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### **Safety precautions**

Strong oxidants, e.g. nitric acid, can cause violent reactions if they come into contact with ion exchange resins.

### **Toxicity**

The safety data sheet must be observed. It contains additional data on product description, transport, storage, handling, safety and ecology.

### **Disposal**

In the European Community Ion exchange resins have to be disposed, according to the European waste nomenclature which can be accessed on the internet-site of the European Union.

### **Storage**

It is recommended to store ion exchange resins at temperatures above the freezing point of water under roof in dry conditions without exposure to direct sunlight. If resin should become frozen, it should not be mechanically handled and left to thaw out gradually at ambient temperature. It must be completely thawed before handling or use. No attempt should be made to accelerate the thawing process.

This information and our technical advice – whether verbal, in writing or by way of trials – are given in good faith but without warranty, and this also applies where proprietary rights of third parties are involved. Our advice does not release you from the obligation to check its validity and to test our products as to their suitability for the intended processes and uses. The application, use and processing of our products and the products manufactured by you on the basis of our technical advice are beyond our control and, therefore, entirely your own responsibility. Our products are sold in accordance with the current version of our General Conditions of Sale and Delivery.

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**LANXESS**  
Energizing Chemistry

## Purolite S950 Information Sheet



**S 950**

**PUROLITE S 950** is a macroporous amino-phosphonic acid chelating resin, designed for the removal of cations of toxic metals such as lead, copper and zinc from industrial effluents at low pH. At somewhat higher pH values, calcium, magnesium and barium, as well as the toxic metals cadmium, nickel, and cobalt are strongly complexed and may be separated from quite high concentrations of univalent cations.

Unlike **PUROLITE S 930**, the well known iminodiacetic acid resin, which is selective for heavy metal ions, but not for common divalent ions (calcium and magnesium), **PUROLITE S 950** is more highly selective (under the appropriate conditions) for a range of both heavy metal and common divalent ions. Hence its use may be recommended where it is necessary to remove calcium or magnesium in order to avoid possible precipitation, or where its selectivity for a particular range of metals offers advantages.

### TYPICAL PHYSICAL AND CHEMICAL CHARACTERISTICS

|   |   |
|---|---|
| Polymer structure                             | Macroporous styrene-divinylbenzene                          |
| Physical form and appearance                  | Spherical beads   |
| Functional groups                             | $RCH_2NHC_2H_4PO_3$   |
| Ionic form, as shipped                        | $Na^+$  |
| Total copper uptake capacity, $Na^+$ form     | 1.3 eq/l min  |
| Moisture retention, $Na^+$ form               | 60 - 65%  |
| Bead size range                               | 0.3 - 1.2 mm<br>with 1% max < 0.3 mm<br>and 5% max > 1.2 mm |
| Reversible swelling, $H^+ \rightarrow Na^+$   | 45% max   |
| Specific gravity                              | 1.13  |
| Shipping weight                               | 710 - 745 g/l   |
| Maximum operating temperature, $Ca^{2+}$ form | 90 °C   |
| pH limits (operating), $H^+$ form             | 2 - 6   |
| $Na^+$ form                                   | 6 - 11  |

## CHEMICAL STABILITY

**PUROLITE S 950** is insoluble in acids, alkalies and all common solvents at normally encountered temperatures (although oxidizing agents like concentrated nitric and perchloric acid at elevated temperatures will destroy its structure and solubilise the resin. Care should be taken when using strong nitric acid, as explosive hazards have been reported on polystyrene-based anion exchange resins with this reagent). However exposure, even at ambient temperatures, to certain other strong oxidizing agents such as chlorine causes irreversible damage to this resin and must be kept to the absolute minimum.

## HYDRAULIC CHARACTERISTICS

The pressure drop (or head loss) across a properly classified bed of ion exchange resin depends on the particle size distribution, bed depth, and voids volume of the exchange solution, and on the flow rate and viscosity (and hence on the temperature) of the influent solution. Anything affecting any of these parameters, for example the presence of particulate matter filtered out by the bed, abnormal compaction of the resin bed, or the incomplete classification of the resin spheres, will have an adverse effect, and result in an increased head loss.

Service flow rates from 8-16 bed volumes per hour, depending on the application, may be regarded as the normal range used on this resin. Typical pressure drop figures to be expected for ordinary aqueous solutions, are given in Fig. 1.

Fig. 1. PRESSURE DROP VS FLOW RATE

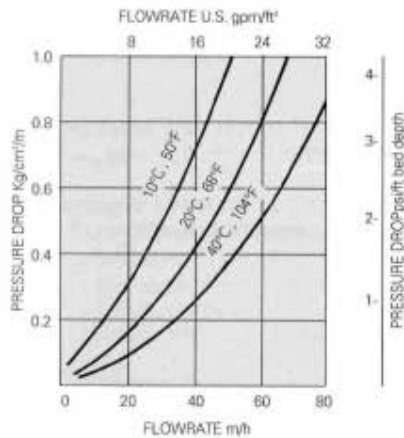
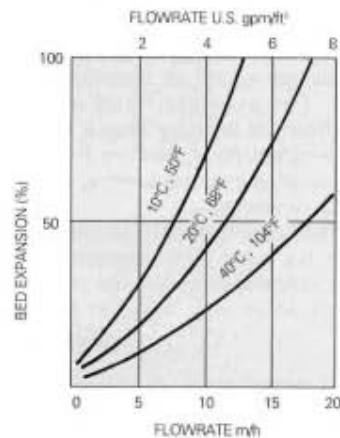


Fig. 2. BACKWASH EXPANSION (exhausted form)



The recommended operating conditions for **PUROLITE S 950** used for the removal of heavy metals from waste waters are summarised in the following table.

### RECOMMENDED OPERATING CONDITIONS

|                                    |   |
|------------------------------------|---|
| Service flow rate                  | 8 to 16 BV/h                                |
| Bed depth, recommended minimum     | 1000 - 1200 mm<br>900 mm                    |
| Backwash flow rate                 | 6 m/h at 20°C<br>to get a 50% bed expansion |
| Regeneration,                      |   |
| 1 <sup>st</sup> step : 10% HCl     | 2 BV in 30-45 minutes                       |
| slow rinse : soft water            | 2 BV in 30-45 minutes                       |
| 2 <sup>nd</sup> step : 2 - 3% NaOH | 3 BV in 45-60 minutes                       |
| slow rinse : soft water            | 2 BV in 30-45 minutes                       |
| fast rinse : soft water            | 4-6 BV in 45-60 minutes                     |

During up-flow backwash, the resin bed should be expanded in volume by between 50 and 75%, in order to free it from any particulate matter from the influent solution, to clear the bed of bubbles and voids, and to reclassify the resin particles as much as possible, ensuring minimum resistance to flow.

Bed expansion increases with flow rate and decreases with temperature, as shown in Fig. 2 for a typical exhausted form of the resin. Care should always be taken to avoid resin loss by over-expansion of the bed.

### AFFINITY ORDER FOR TYPICAL CATIONS

The **PUROLITE S 950** affinity order varies as a function of solution pH:

Acidic pH:  $H^+ > Fe^{3+} > Pb^{2+} > Zn^{2+}, Al^{3+} > Mg^{2+} > Ca^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Na^+$

Alkaline pH:  $Cd^{2+}, Mg^{2+} > Ca^{2+} > Sr^{2+}, Al^{3+} > Ba^{2+} \gg Na^+, K^+$

It should be noted that **PUROLITE S 950** is capable of operating under acidic, neutral, or alkaline conditions; its operating capacity for any of the chelated ions is a function of pH, and consequently there are minimum values of pH below which removal of a given cation from the influent solution is not feasible. Relevant figures are given below:

| CATION SPECIES              | pH  |
|-----------------------------|-----|
| $Cu^{2+}, Pb^{2+}$          | 2   |
| $Zn^{2+}$                   | 2.5 |
| $Cd^{2+}, Ca^{2+}$          | 3   |
| $Mg^{2+}, Ni^{2+}, Co^{2+}$ | 4.5 |

## APPLICATIONS

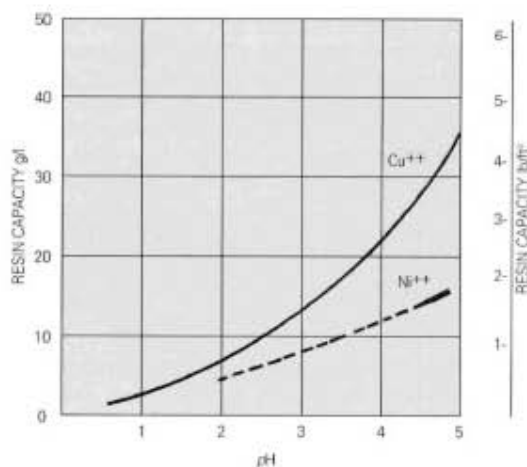
- Extracting heavy metal ions from leach liquors, tailings runoff, or from industrial effluents. For example, lead may be removed from oil refinery waste liquors, solvents and aqueous wastes from the manufacture of paints and printing inks, or battery factory wastes.
- Recovery of zinc from cooling-tower waters, etc, where it is used as a corrosion inhibitor
- Refining of metal salt solutions by selective removal of individual ions.
- "Polishing" of aqueous organic and inorganic solutions for the removal of trace metals.

## OPERATING PERFORMANCE

Before attempting to use **PUROLITE S 950** for any industrial application, it is strongly recommended that laboratory column tests are carried out on the solution which is to be treated, so as to determine the operating performance in terms of both treated solution quantity and quality once the chosen equilibrium cycle conditions have been established. This may take several cycles.

The curves for copper and nickel for **PUROLITE S 950** given in fig. 3 may serve as a guide to the maximum exchange capacity obtainable from a feed of 2g/l metal as a function of pH. In practice, lower capacities will usually be obtained, depending upon regeneration level chosen, having regard to the leakage of metal acceptable.

Fig. 3. RESIN CAPACITY



EB/eb  
09/05

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## APPENDIX D: PLANT ELUTION DATA

Table D 1: Elution mass balance after 250 bed volumes of operation:

| Volume treated                   |      |                | Mass of metal fed    |        | Base           |
|----------------------------------|------|----------------|----------------------|--------|----------------|
| BV before elution                | 250  | BV             | Zn                   | 9950 g | 100 %          |
| Volume                           | 500  | m <sup>3</sup> | Fe                   | 1050 g | 100 %          |
| Average feed concentrations      |      |                | Mass of metal loaded |        | % Metal loaded |
| Zn                               | 19.9 | mg/L           | Zn                   | 9290 g | 93.4 %         |
| Fe                               | 2.1  | mg/L           | Fe                   | 122 g  | 11.6 %         |
| Average raffinate concentrations |      |                | Mass of metal eluted |        | % Metal eluted |
| Zn                               | 1.3  | mg/L           | Zn                   | 8703 g | 93.7 %         |
| Fe                               | 1.9  | mg/L           | Fe                   | 25 g   | 20.9 %         |

Table D 2: Elution profile after 250 bed volumes of operation:

| Sample  | Date/Time        | Fe (mg/L) | Zn (mg/L) | Ni (g/L) |
|---------|------------------|-----------|-----------|----------|
| ZIXE 1  | 2011/03/28 10:43 | 0.0       | 42.8      | 57.4     |
| ZIXE 2  | 2011/03/28 10:48 | 0.0       | 449.2     | 54.1     |
| ZIXE 3  | 2011/03/28 10:53 | 0.8       | 3267.2    | 46.2     |
| ZIXE 4  | 2011/03/28 11:03 | 3.7       | 6885.7    | 25.1     |
| ZIXE 5  | 2011/03/28 11:13 | 8.5       | 1181.4    | 14.8     |
| ZIXE 6  | 2011/03/28 11:23 | 8.1       | 370.5     | 8.0      |
| ZIXE 7  | 2011/03/28 11:33 | 7.2       | 40.3      | 4.3      |
| ZIXE 8  | 2011/03/28 11:43 | 2.0       | 32.6      | 4.0      |
| ZIXE 9  | 2011/03/28 11:53 | 0.3       | 14.2      | 1.2      |
| ZIXE 10 | 2011/03/28 12:03 | 0.0       | 1.9       | 7.8      |
| ZIXE 11 | 2011/03/28 12:08 | 0.0       | 9.0       | 0.7      |
| ZIXE 12 | 2011/03/28 12:13 | 0.0       | 8.7       | 0.7      |
| ZIXE 13 | 2011/03/28 12:20 | 0.0       | 5.7       | 0.6      |
| ZIXE 14 | 2011/03/28 12:30 | 0.0       | 0.4       | 0.5      |

**Table D 3: Elution mass balance after 200 bed volumes of operation:**

| Volume treated                   |      |                | Mass of metal fed    |        | Base           |
|----------------------------------|------|----------------|----------------------|--------|----------------|
| BV before elution                | 200  | BV             | Zn                   | 1680 g | 100 %          |
| Volume                           | 400  | m <sup>3</sup> | Fe                   | 584 g  | 100 %          |
| Average feed concentrations      |      |                | Mass of metal loaded |        | % Metal loaded |
| Zn                               | 4.2  | mg/L           | Zn                   | 1200 g | 71.4 %         |
| Fe                               | 1.46 | mg/L           | Fe                   | 8 g    | 1.4 %          |
| Average raffinate concentrations |      |                | Mass of metal eluted |        | % Metal eluted |
| Zn                               | 1.2  | mg/L           | Zn                   | 1078 g | 89.9 %         |
| Fe                               | 1.44 | mg/L           | Fe                   | 2 g    | 22.5 %         |

**Table D 4: Elution profile after 200 bed volumes of operation:**

| Sample name | Date/Time        | Fe (mg/L) | Zn (mg/L) | Ni (g/L) |
|-------------|------------------|-----------|-----------|----------|
| ZIXE 1      | 2011/04/04 13:43 | 0.00      | 2.32      | 56.00    |
| ZIXE 2      | 2011/04/04 13:46 | 0.00      | 2.21      | 57.00    |
| ZIXE 3      | 2011/04/04 13:49 | 0.00      | 2.00      | 57.00    |
| ZIXE 4      | 2011/04/04 13:52 | 0.00      | 2.30      | 58.00    |
| ZIXE 5      | 2011/04/04 13:55 | 0.00      | 90.00     | 49.00    |
| ZIXE 6      | 2011/04/04 13:58 | 0.00      | 350.10    | 52.00    |
| ZIXE 7      | 2011/04/04 14:01 | 0.00      | 815.60    | 44.50    |
| ZIXE 8      | 2011/04/04 14:04 | 0.30      | 1156.00   | 38.60    |
| ZIXE 9      | 2011/04/04 14:07 | 1.40      | 1162.00   | 32.90    |
| ZIXE 10     | 2011/04/04 14:13 | 4.00      | 462.00    | 23.30    |
| ZIXE 11     | 2011/04/04 14:18 | 0.10      | 110.10    | 12.90    |
| ZIXE 12     | 2011/04/04 14:23 | 0.10      | 29.80     | 19.60    |
| ZIXE 13     | 2011/04/04 14:33 | 0.10      | 5.50      | 12.70    |
| ZIXE 14     | 2011/04/04 14:43 | 0.10      | 1.60      | 9.00     |
| ZIXE 15     | 2011/04/04 14:53 | 0.10      | 1.52      | 5.30     |

## APPENDIX E: CUSUM PLOT METHODOLOGY

The cumulative sums are calculated as follows:

1. First calculate the average:

$$\bar{X} = \frac{X_1 + X_2 + \dots + X_{24}}{24}$$

2. Start the cumulative sum at zero by setting  $S_0 = 0$ .
3. Calculate the other cumulative sums by adding the difference between current value and the average to the previous sum, i.e.: for  $i=1, 2, \dots, 24$ .

$$S_i = S_{i-1} + (X_i - \bar{X})$$

The cumulative sum is not the cumulative sum of the values. Instead, it is the cumulative sum of *differences* between the values and the average. Because the average is subtracted from each value, the cumulative sum also ends at zero ( $S_{24} = 0$ ). Let  $X_1, X_2, \dots, X_{24}$  represent 24 data points. From this, the cumulative sums  $S_0, S_1, \dots, S_{24}$  are calculated. Notice that 24 data points lead to 25 (0 through 24) sums.

The CUSUM chart is interpreted as follows: a segment of the CUSUM chart with an upward slope indicates a period where the values tend to be above average. Likewise, a segment with a downward slope indicates a period of time where the values tend to be below the average. Thus the CUSUM plot will indicate periods of change. It will show whether the data for certain periods were above or below the total data average.