AN ION EXCHANGE LOADING CORRELATION
FOR THE SIMULATION OF BASE METAL RESIN-IN-PULP CIRCUITS

by

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ABSTRACT

This thesis investigates the loading rate of nickel onto an iminodiacetic ion exchange resin, with the goal of gaining insight into operation of a base metals resin-in-pulp (RIP) circuit. A modified pH-stat method was used to generate loading data under infinite solution volume conditions. A comparison of several commercially available iminodiacetic resins was performed, using this method.

The standard linear approach to equilibrium was found to fit well to the portion of loading under film diffusion control, but none of the standard engineering approximations could adequately describe the data from the intraparticle diffusion / exchange rate limited regime. A hybrid correlation was developed and was found to adequately describe single element loading of nickel, copper, and cobalt from synthetic solution. In order to know which of the two models to use at a given point in time, a modified Helfferich number was derived. This dimensionless number can be used to track when the resin bead switches from film diffusion control to intraparticle diffusion control.

The experimental fit parameters of the film diffusion model and the hybrid correlation were used to successfully predict the results of batch experiments with varying solution concentration. The effectiveness of these equations were also assessed and verified through the operation of a five stage RIP miniplant, using synthetic solutions.

Using these circuit models, various RIP circuit operating configurations were simulated. Results from these simulations suggest that all operating configurations and strategies have both advantages and disadvantages. A table summarizing the process sensitivity of a cascade circuit to various operating conditions has been generated.
Much of the work presented in this thesis has previously been presented at conferences, or is under review for journal publication. The overall supervision of this research program was provided by Dr. Dreisinger.

Modifications to the pH-stat procedure, as described in Chapter 3, were developed by the candidate. The batch tests reported in Chapter 4 and in Figure 8.3 were performed by Ms. Abbasi; the remainder of the batch tests were performed by the candidate.

The candidate worked with the Materials Engineering Shop to design and set up the RIP miniplant. For operation of the RIP miniplant, the candidate developed the test procedures, provided training to the dayshift operators, and operated the RIP miniplant on nightshift.

The data analysis of all test results, the development of the hybrid correlation, the derivation of the modified Helfferich number, the construction of the circuit models, and the circuit sensitivity analysis of Chapter 12 was done by the candidate.

The following is a list of publications and articles submitted to a journal for consideration, that have had material reprinted as part of this thesis. The following manuscripts were prepared by the candidate and edited by Dr. Dreisinger, prior to submission for publication.

2) McKevitt, B., Abbasi, P. & Dreisinger, D. (2011) A Comparison of Large Bead Ion Exchange Resins for the Recovery of Base Metals in a Resin-in-Pulp (RIP) Circuit. Proceedings of the 6th Southern African Base Metals Conference. SAIMM: pp. 337-352. This paper was based on laboratory tests conducted by Ms. Abbasi, using the experimental procedure developed as part of this thesis. Ms. Abbasi prepared the resin samples, conducted the experiments in the laboratory, and performed the AA assays of the samples taken. Portions of this paper appear in Chapter 4.

3) McKevitt, B. & Dreisinger, D. (under consideration). Development of an engineering model for nickel loading onto an iminodiacetic resin for resin-in-pulp applications: Part I – Method development and discussion of rate limiting factors. Parts of this manuscript appear in Section 2.2.1, Chapter 3, Section 4.1, Chapter 5, Chapter 6, Section 8.1.4 and Section 8.1.5.


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<td>Atomic Absorption</td>
</tr>
<tr>
<td>AAC</td>
<td>Anglo American Corporation</td>
</tr>
<tr>
<td>ACS</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>BV</td>
<td>Bed Volumes</td>
</tr>
<tr>
<td>CCD</td>
<td>Counter-Current Decantation</td>
</tr>
<tr>
<td>CIL</td>
<td>Carbon In Leach</td>
</tr>
<tr>
<td>CIP</td>
<td>Carbon In Pulp</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>EQ</td>
<td>Equivalents</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>ISV</td>
<td>Infinite Solution Volume</td>
</tr>
<tr>
<td>IX</td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>PPM</td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>RIL</td>
<td>Resin In Leach</td>
</tr>
<tr>
<td>RIP</td>
<td>Resin In Pulp</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>SX</td>
<td>Solvent Extraction</td>
</tr>
<tr>
<td>USBM</td>
<td>United States Bureau of Mines</td>
</tr>
<tr>
<td>USSR</td>
<td>Union of Soviet Socialist Republics</td>
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### List of Symbols

- $a_1$: empirical fit parameter for a linear isotherm [-]
- $a_2$: empirical fit parameter for a Freundlich isotherm [-]
- $[A]$ concentration of ion A in bulk solution [mol A / L]
- $[A_s]$ concentration of ion A in solution at interface with resin surface [mol A / L]
- $[\bar{A}]$: concentration of ion A loaded on ion exchange resin [mol A / L resin]
- $[B]$ concentration of ion B in solution [mol B / L]
- $[B_s]$ concentration of ion B in solution at interface with resin surface [mol B / L]
- $[\bar{B}]$: concentration of ion B loaded on ion exchange resin [mol B / L resin]
- $d_c$: diameter of unreacted core [m]
- $d_p$: resin bead diameter [m]
- $D_{\text{app}}$: apparent diffusion coefficient through resin bead in hybrid correlation [m$^2$/s]
- $D_A$: isotopic intraparticle diffusion coefficient of A through resin gel [m$^2$/s]
- $D_B$: isotopic intraparticle diffusion coefficient of B through resin gel [m$^2$/s]
- $D_s$: diffusion coefficient through reacted layer in shrinking core model [m$^2$/s]
- $D_f$: diffusion coefficient through film [m$^2$/s]
- $D_p$: diffusion coefficient through resin bead [m$^2$/s]
- $E$: residence time distribution function [-]
- $f$: empirically fit Freundlich isotherm exponent [-]
- $F$: fractional attainment of equilibrium [-]
- $\langle F \rangle$: mean fractional attainment of equilibrium for resin in a tank [-]
j 

summation counter [-]

$k_c$ constant, shrinking core diffusion control [1/s]

$k_f$ constant, film diffusion control [1/s]

$k_{fwd}$ kinetic rate constant, forward reaction in pseudo-second order model [1/mol s]

$k_g$ constant, Gluckauf’s linear intraparticle diffusion control [1/s]

$k_h$ constant, diffusion control using hybrid correlation [1/s]

$k_l$ constant, linear approach to equilibrium [1/s]

$k_{rev}$ kinetic rate constant, forward reaction in pseudo-second order model [1/mol s]

$k_v$ constant, Vermeulen’s approximation to intraparticle diffusion control [1/s]

$K$ selectivity coefficient [-]

$L$ empirical fit parameter to Langmuir isotherm [-]

$[M]$ concentration of divalent ion M in solution [mol M / L]

$[M]_{eqb}$ concentration of divalent ion M in solution in equilibrium with the resin [mol M / L]

$[M]_{feed}$ concentration of M in the feed solution to an RIP contactor [mol M / L Resin]

$[\bar{M}]$ concentration of divalent ion M, loaded onto ion exchanger [mol M / L Resin]

$[\bar{M}]_{eqb}$ equilibrium concentration of M loaded onto ion exchanger [mol M / L Resin]

$[\bar{M}]_{max}$ capacity of ion exchanger for divalent ion M [mol M / L Resin]

$Q$ flowrate through an RIP circuit [L/s]

$S^A_B$ separation factor for ion exchange resin for ion A over ion B [-]

$t$ time [s]

$t_r$ time required under current conditions for resin to achieve the initial loading value [s]

$t_{1/2}$ time to reach 50% loading of an ion exchange bead [s]
\( \Delta t \) finite differences model time step [s]

\( V_R \) volume of resin in an RIP contactor [L]

\( V_S \) volume of solution in an RIP contactor [L]

\( z_A \) charge of ion A [electron charge units]

\( z_B \) charge of ion B [electron charge units]

Greek Letters:

\( \alpha \) exponent for hybrid correlation [-]

\( \delta \) film thickness [m]

\( \eta \) Gluckauf’s shape factor [-]

\( \tau_r \) average resin residence time in tank [s]
ACKNOWLEDGEMENTS

There are many people whose contributions to this research need to be acknowledged. First of all, I would like to thank my supervisor, Dr. Dreisinger, for his guidance, support and encouragement. I would also like to thank Dr. Wassink for his guidance in the lab.

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The staff of the Materials Engineering Shop did an excellent job with the construction of the RIP miniplant. Thanks to Ross McLeod for helping with the design and for overseeing the project; thanks to Carl Ng for the many hours spent constructing the miniplant; thanks to Wonsang Kim for wiring all the pH controllers; and thanks to Dave Torok for manufacturing the impeller blades.

Finally, I would like to thank the resin manufacturers: Lanxess, Purolite, and Dow for supplying the resin samples for this research. Additionally, the assistance of Dr. Fries and Dr. Halle of Lanxess for providing the detailed size analysis of their resin beads in the hydrogen form is gratefully acknowledged.
1.0 INTRODUCTION

Ion exchange (IX) is a solution processing technique where small spherical resin beads are used to extract ions from solution, while replacing them with another ion in solution. In the mining industry, ion exchange is used for recovery of pay metals, removal of impurities from process streams, and for treatment of waste streams prior to disposal. Typically, ion exchange systems consist of a series of packed beds and filtration of the feed solution is required. In order to be able to clean-up residual dissolved metals in mine waste streams containing large amounts of solids, or to be able to economically recover dissolved metals in cases where the processed ore is difficult to filter, a resin-in-pulp (RIP) process can be used. A resin-in-pulp process contacts the resin beads directly with the solution and solids, typically in a series of stirred tanks. The solids and resin beads then need to be separated, typically by screening the larger resin beads (~0.5 – 1.2 mm in diameter) from the slurry.

Commercial resin-in-pulp processes have been implemented successfully for gold and uranium, but no successful full-scale base metals resin-in-pulp plants have yet been built. The purpose of this research is to study the loading rate of base metals onto a chelating resin, under conditions that would be representative of a resin-in-pulp circuit. This work focuses primarily on the loading rate of nickel from synthetic solutions, although a few tests were also conducted for copper and cobalt removal from synthetic solutions.

A mathematical model of the system was developed to provide a means of predicting how quickly the resin will extract metals under various conditions. Once verified, the loading rate model was incorporated into a circuit model to simulate the performance of different circuit designs and operating configurations to better understand the potential behaviour of a full-scale base metal RIP circuit.
2.0 LITERATURE REVIEW

This chapter presents a review of the key literature that is relevant to the current research project. This discussion assumes a basic familiarity with ion exchangers; a detailed introduction to the subject is available in the literature (1). The review initially focuses on key concepts from ion exchange that pertain to this thesis, and then focuses specifically on the development of the RIP process.

2.1 KEY CONCEPTS FROM ION EXCHANGE FUNDAMENTALS

For base metals RIP, the most common ion exchange reaction is the loading of a divalent cation, $M^{2+}$, onto an iminodiacetic chelating resin in the hydrogen form (to be described in Section 2.1.3). This can be described by Equation 2.1, where $R$ represents the resin phase:

$$2R-H + M^{2+} \rightarrow R_2-M + 2H^+$$  

[2.1]

In this work, concentrations of ions in the solution are depicted in square brackets, e.g. $[M]$, while concentrations of ions in the resin phase use square brackets and an overbar, e.g. $\bar{[M]}$.

Most engineering models describe loading rates in terms of fractional approach to equilibrium. Therefore, knowledge of both the total amount of metal that the resin can load under the current operating conditions and the rate at which this loading occurs is required.

2.1.1 EQUILIBRIUM CAPACITY

The total capacity of a resin for ion $M$ is expressed in this work as $[\bar{M}]_{\text{max}}$, and uses the units mol $M$ / L resin. Under most operating conditions, the resin reaches an equilibrium loading value, $[\bar{M}]_{\text{eq}}$, which is lower than the total capacity. The equilibrium curve is typically described using an adsorption isotherm. While ion exchange is a separate phenomenon to adsorption, many engineering textbooks treat it as a special case of adsorption since many of the design techniques are similar. Isotherms are typically plotted with the solution
concentration on the horizontal axis and the resin concentration on the vertical axis. Thus, an isotherm that is concave downwards is a favourable isotherm, while an isotherm that is concave upwards is unfavourable. This is depicted in Figure 2.1.

![Figure 2.1: Favourable vs Unfavourable Equilibrium Isotherms](image)

The simplest isotherm is the linear isotherm. Strictly speaking, if a linear isotherm were used to describe the full range of exchange of two equal valence ions (ion A and ion B) in a binary mixture (i.e. from the point at which there is no ion A on the exchanger to the point at which there is no ion B on the exchanger), a linear isotherm would describe a process with no selectivity for one ion over the other. An example of an ion exchange process with no selectivity is isotopic exchange (e.g. exchange of $^{58}\text{Ni}^{2+}$ for $^{63}\text{Ni}^{2+}$). However, in systems where the resin is selective for one ion over another, the first portion of the loading curve can often be approximated by a linear isotherm. When using such an equation, it is important to be aware that it can be prone to large errors if extrapolated beyond the region for which it was developed. The equation for a linear isotherm is described in Equation 2.2.

\[
\text{Linear: } [\bar{M}]_{\text{eqb}} = a_1 [M]_{\text{eqb}} \tag{2.2}
\]

The Freundlich isotherm is an empirical equation that has been observed to fit adsorption and ion exchange data fairly well. The Freundlich isotherm is able to model both favourable and unfavourable isotherms; however it has been criticized for poor predictions at both extremes of the isotherm. It overpredicts extraction at high solution concentrations, since it does not place a limit on adsorption capacity (2), and it also tends to overpredict extraction at low solution
concentrations yielding insufficient adsorbent/resin requirements for the final stages of a plant (3). It is described by Equation 2.3, where $a_2$ and $f$ are both empirically fitted constants:

$$[\bar{M}]_{eqb} = a_2[M]_{eqb}^f \tag{2.3}$$

The Langmuir adsorption isotherm was first presented in a lengthy article on crystal structures and their impact on heterogeneous reactions, where adsorption rate was postulated as the rate of condensation of gas on a crystal surface minus the rate of evaporation of gas from the same surface (4). Inherent in the derivation of the Langmuir isotherm is that only a single layer of molecules adsorb onto an active site. The Langmuir isotherm also implies the exchange of two ions of equal valency, and becomes essentially an empirical relationship when applied to a more complex system. The Langmuir isotherm can be described by Equation 2.4, where $L$ is a constant fitted to the dataset:

$$[\bar{M}]_{eqb} = \frac{[M]_{eqb}[\bar{M}]_{max}}{1+L[M]_{eqb}} \tag{2.4}$$

When solutions contain relatively few species, ion exchange is often expressed using the Mass Action Law. This approach involves describing ion exchange as a reversible reaction, and determining the equilibrium constant for it. One problem with this method lies in the difficulty of obtaining the activity coefficients for the various species loaded on the resin. As pointed out by Reynolds, “The best solid-phase activity model is still being debated, and may not be the same for all systems.” In this same paper, it is pointed out that the activity coefficient parameters for various models are determined empirically in binary systems and that these parameters may not necessarily be extendable to systems with multiple components (5). To avoid this difficulty, the convention is to use concentrations, rather than activities in the Mass Action Law equations. This results in the development of a constant, $K$, known as the selectivity coefficient, which will vary based on the composition of the feed solution. Thus, $K$ can not be calculated from fundamental parameters, and is determined by fitting to experimental data. Therefore, there is currently minimal value gained to a design engineer in employing the Mass Action Law in lieu of one of the above mentioned isotherms as it is subject
The Mass Action Law for the binary system described in Equation 2.1, is described by Equation 2.5:

\[
\text{Mass Action Law} \quad K = \frac{[H]^2 [\bar{M}]}{[M][H]^2}
\]  

[2.5]

2.1.2 RATE OF ION EXCHANGE

In theory, there could be five possible rate limiting steps for ion exchange: diffusion of the ion to be loaded through a stagnant film around the bead, diffusion of the ion to be loaded through the ion exchange particle, the ion exchange reaction, the diffusion of the displaced ion through the ion exchange particle, and diffusion of the displaced ion through the stagnant film to the bulk solution. However, in order to maintain charge neutrality, the flux of the charge carried into the exchanger by the ions to be loaded onto the resin is equal to the flux of the charge carried by the displaced ions out of the exchanger. Therefore, there are only three possible rate limiting steps: film diffusion, intraparticle diffusion, or the ion exchange process itself.

Modeling of ion exchange loading rates is a complex process and it is important to note the difference between an engineering model and a fundamental model. The goal of a fundamental model is to describe the ion exchange loading as scientifically accurately as possible. The problem with such models is that they typically result in complex sets of differential equations with no analytical solution, and consequently are quite cumbersome when incorporated into system design equations. Typically, engineering models are much simpler, are often empirical or semi-empirical, and their goal is to adequately describe system performance. Both types of models shall be discussed in turn.

2.1.2.1 Fundamental Models for Ion Exchange Loading Rate

In terms of fundamental models, there is much debate in the literature as to the best approach to the problem. For example, even selecting the governing equations for the diffusion process
continues to be under debate. A recent paper on competitive loading used Fick’s laws and modeled the diffusion process based on diffusion gradients alone (6). However, most researchers prefer the Nernst-Planck equations, which also take into account the electric potentials. More complex than the Nernst-Planck equations are the Stefan-Maxwell equations which are based on the kinetic theory of diffusion in ideal gases. In fact, the Nernst-Planck equation can be taken as a limiting case of the Stefan-Maxwell equations (7), if one ignores frictional interactions between diffusing ions (8). Note that in a thorough fundamental study, each ion’s intraparticle diffusion coefficient should be determined experimentally, and this is typically achieved by measuring isotopic exchange with radioactive tracers (9). Using the Nernst-Planck equation to describe the exchange of ions A and B, the intraparticle diffusion coefficient through the gel phase of an exchanger can be described by Equation 2.6, where z represents the valence of the ions (10):

\[
D_p = \frac{D_A D_B (z_A^2 [\bar{A}] + z_B^2 [\bar{B}])}{z_A^2 [\bar{A}] D_A + z_B^2 [\bar{B}] D_B} \tag{2.6}
\]

For the case of chelating macroporous resins, such as those being studied in this work, a parallel diffusion mechanism based on the Nernst-Planck equations has been proposed (11). In this model, both the rate of diffusion in the macropores and in the microgel contribute significantly to the overall rate of loading. The model is demonstrated for predicting the loading rate of copper onto an iminodiacetic resin (9). It is also used by another set of researchers in a fundamental study of the sodium/nickel system for a macroporous aminophosphonic resin, where all the individual model parameters were determined experimentally (12). However, it should be noted that in the aminophosphonic resin study, the parallel diffusion equations were so complex that the authors used an alternative, approximate method that is based on the exchange of equal valence ions (13). This approximation significantly overpredicted experimental loading values (e.g. 85% final loading at 1000s vs 75% final loading observed), but was much closer than the predictions of the classic shrinking core model (to be discussed in section 2.1.2.2.3), which predicted only 10% final loading at 1000s.

One drawback with the fundamental models discussed above is that they all require numerical solutions to differential equations. While fundamental models often perform better than empirical models when extrapolated to conditions beyond those tested, their use in ion
exchange system design tends to be limited due to their complexity. Helfferich and Hwang acknowledge this limitation by stating, “In the design of ion exchange equipment –e.g. columns- there are usually so many other factors introducing uncertainties or calling for approximations that the simplest rate law seems the best choice” (14). Michael Streat also acknowledges this limitation by stating, “exact solutions of the diffusion equations exist in the literature but they are complex and ill-suited to process design calculations” (15). Since the objective of this work is to understand RIP system performance, the use of complex fundamental models would be questionable. Therefore, the decision was made to focus on the engineering models available in the literature to describe system performance.

2.1.2.2 Engineering Models for Ion Exchange Loading Rate

Studies to develop an engineering model to predict loading rates onto resin have been published for gold recovery from cyanide solutions (16) and for recovery of uranium (17). No extensive study to try to capture the loading rates over a wide range of test conditions has yet been published for the loading of nickel onto an iminodiacetic ion exchange resin. Such a model could prove useful in determining the bounds for which the linear approach to equilibrium assumption is valid and may help extend the modeling of RIP circuits in situations where this assumption does not hold.

Four engineering models that are commonly applied to ion exchange systems are: the linear approach to equilibrium, the quadratic approach to equilibrium, the shrinking core model, and the pseudo-second order reaction. These models will each be reviewed in turn.

2.1.2.2.1 Linear Approach to Equilibrium

The linear approach to equilibrium is the simplest model, and it is frequently selected over more accurate models due to ease of application. Some authors have presented their results for nickel loading onto an iminodiacetic acid resin assuming a linear approach to equilibrium based on a co-current loading test (18,19), or by assuming that the fraction of metal recovered to the resin in each tank is constant (20), which implies a linear approach to equilibrium.
Film diffusion is typically described using the linear approach to equilibrium, and Gluckauf also proposed approximating intraparticle diffusion by a linear approach to equilibrium (21). With this approach, the situation where both film diffusion and intraparticle diffusion are significant can also easily be accounted for since both film diffusion and intraparticle diffusion are described by the same equation set.

The linear approach to equilibrium is described by Equation 2.7, with the solution in terms of fractional approach to equilibrium, F, given in Equation 2.8. The general model constant, \( k \), is described by \( k_f \) in the case of film diffusion, and by \( k_g \) in Gluckauf’s model, both described in Equation 2.9. Note that the shape factor, \( \eta \), in Gluckauf’s model is < 0.5 and that \( k_f \) is a function of solution concentration, while \( k_g \) is not.

\[
\frac{d}{dt}[\bar{M}]=k_f([\bar{M}]_{eqb}-[\bar{M}]) \quad [2.7]
\]

\[
F=\frac{[\bar{M}]}{[\bar{M}]_{eqb}}=1-\exp(-k_f t) \quad [2.8]
\]

\[
k_f=\frac{6D_f[M]}{d_p \delta [M]_{max}}; \quad k_g=\frac{D_p}{\eta d_p^2} \quad [2.9]
\]

2.1.2.2.2 Vermeulen’s Quadratic Approach to Equilibrium

Particularly in the case of gel-type exchangers, it is possible that the rate of diffusion within the actual resin bead is the rate-limiting step. This intraparticle diffusion limitation was modeled by Boyd, Adamson, and Myers and the exact solution to the differential equations for the case of isotopic exchange under infinite solution volume and constant diffusivities is the infinite series of Equation 2.10 (22):

\[
F=1-\frac{6}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp \left\{ -\frac{4D_p \pi^2 j^2 t}{d_p^2} \right\} \quad [2.10]
\]

In order to simplify the application of this result, Vermeulen developed an approximate fit to Equation 2.10, commonly referred to as Vermeulen’s quadratic approach to equilibrium. Assuming no initial loading, it is written in differential form as per Equation 2.11, with the
solution as given in Equations 2.12-2.14 (23). Note that $k_v$ is independent of solution concentration.

$$\frac{d}{dt}[\bar{M}] = \frac{2k_v([M]_{aqb}^2-[M]^2)}{[M]} \quad [2.11]$$

$$t=\frac{-1}{4k_v} \ln \left(\frac{[M]^2_{eqb}-[\bar{M}]^2}{[M]_{eqb}^2}\right) \quad [2.12]$$

$$F=\sqrt{1-\exp\{-4k_vt\}} \quad [2.13]$$

$$k_v=\frac{\pi^2 D_p}{d_p^2} \quad [2.14]$$

### 2.1.2.2.3 Shrinking Core Model

The concept of an outer layer of loaded resin surrounding an unreacted core was first proposed for ion exchange systems accompanied by reactions by Helfferich, based on theoretical considerations. The equation for this model, and its’ solution, assuming infinite solution volume and constant diffusivities are described in Equations 2.15-2.18 (24). Note that $k_c$ is a function of solution concentration.

$$\frac{dF}{dt} = \frac{k_c d_c}{2(d_p - d_c)} \quad [2.15]$$

$$t = \frac{1+2(1-F)-3(1-F)^{2/3}}{k_c} \quad [2.16]$$

$$F=1-\left\{\frac{1}{2} + \sin \left(\frac{\arcsin[1-2k_c t]}{3}\right)\right\}^3 \quad [2.17]$$

$$k_c=\frac{24D_s[M]}{d_c^2[M]_{max}} \quad [2.18]$$

Experimental observations confirming the presence of a sharp boundary between the reacted and unreacted zones have been reported for the case of acid elution of a cupric amine complex from a strong acid resin (25), acid elution of a weak acid resin (26), and for the simultaneous
advancement of a copper chelate front and a cobalt chelate front into an iminodiacetic resin in the sodium form (6).

2.1.2.2.4 Second Order Rate Model

Early attempts to model ion exchange loading often involved representing the system as a chemical reaction. A list of several of these early models is available in the literature (10). Perhaps the most famous of these was the Thomas model, in which the system is modeled as a second-order reversible reaction (27). In an early paper on the subject, it is pointed out that this model is not meant to be reflective of the mechanism, but is simply a design tool suggesting that perhaps the diffusional equations may be a similar type of differential equation as these kinetic equations (28).

While the second order reaction rate model has minimal theoretical basis, it is still employed on occasion today. In fact, The Handbook of Separation Processes states, “Rate laws that describe bimolecular second-order chemical reactions can be treated as an analogue to the ion exchange process” (29). Perry’s Chemical Engineers Handbook echoes this by stating, “When diffusion steps control the process, it is still possible to describe the system by its apparent second order kinetic behavior, since it usually provides a good approximation…” (30).

For the case of a divalent metal loading onto an iminodiacetic resin, as described in Equation 2.1, the corresponding second order differential equation is described by Equation 2.19, which can be further simplified to Equation 2.20 in a binary system. As can be seen from the form of Equation 2.19, the Thomas model is analogous to a second order reaction and not an elementary reaction. Also note that the forward ($k_{fwd}$) and reverse ($k_{rev}$) rate constants are determined empirically, and are not necessarily connected via the selectivity coefficient, K (10).

\[
2R-H + M^{2+} \rightarrow R_2-M + 2H^+ \quad [2.1]
\]

\[
\frac{d}{dt} \overline{[M]} = k_{fwd}[M][\overline{H}] - k_{rev}[H][\overline{M}] \quad [2.19]
\]

\[
\frac{d}{dt} \overline{[M]} = \{k_{fwd}[M] + 2k_{rev}[H]\} \overline{[M]} - k_{fwd}[M][\overline{M}]_{\text{max}} \quad [2.20]
\]
2.1.3 **THE IMINODIACETIC CHELATING RESIN**

As previously mentioned, the iminodiacetic chelating resin is the most commonly recommended resin for potential base metals RIP applications. The iminodiacetic group loses protons as the pH increases, as illustrated in Table 2.1 (1). The loss of a proton from the iminodiacetic acid resin at pH 4 has been confirmed by titration (31).

**TABLE 2.1: IMINODIACETIC FUNCTIONAL GROUP AT DIFFERENT pH VALUES –FROM (1)**

<table>
<thead>
<tr>
<th>pH 1.2</th>
<th>pH 4.0</th>
<th>pH 7.4</th>
<th>pH 12.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂COOH \ /</td>
<td>CH₂COO⁻ \ /</td>
<td>CH₂COO⁻ \ /</td>
<td>CH₂COO⁻ \ /</td>
</tr>
<tr>
<td>R-N⁺H \ /</td>
<td>R-N⁺H \ /</td>
<td>R-N⁺H \ /</td>
<td>R-N⁺ \ /</td>
</tr>
<tr>
<td>CH₂COOH</td>
<td>CH₂COOH</td>
<td>CH₂COO⁻</td>
<td>CH₂COO⁻</td>
</tr>
</tbody>
</table>

The selectivity of chelating resins can be difficult to define, as the apparent selectivity can vary with solution pH, temperature, solution concentration, and complexing agents. One option for quantifying the stability of the metal-iminodiacetate complexes is the pH at which desorption of metal from the resin begins. This “decomplexing pH” can provide insight into the selectivity of the resin for a given ion over the selectivity of the resin for hydrogen ions. Therefore, an ion with a low decomplexing pH will remain bound to the resin under more acidic conditions than an ion with a high decomplexing pH. One of the resin manufacturers has published decomplexing pH data for divalent ions (32). This information is displayed graphically in Figure 2.2.
2.2 DEVELOPMENT OF THE COMMERCIAL RIP PROCESS: THE URANIUM INDUSTRY

The RIP process was first developed in the early 1950s to allow for the processing of uranium without having to first clarify leach solutions. Several processes were piloted and several full-scale RIP plants were constructed. One of the major objectives of the RIP process was to generate significant capital cost savings in the construction of a uranium plant through the elimination of the filtration step. In the Union of Soviet Socialist Republics (USSR), RIP had become the industry standard by 1983 and was credited with “reduced energy costs, enhanced productivity, and saved millions of square meters of filtering fabrics and hundreds of tons of acids, alkali, and other chemicals, while the production capacity increased severalfold” (33). In the Western World, solvent extraction replaced RIP as the process of choice for uranium processing. Critics claim that one of the reasons for the demise of the RIP process in the Western World was that the high cost of specialized contactors and high operating costs for the
first generation of RIP plants generally negated the cost savings from the elimination of the thickening / filtration step (34).

2.2.1 Definition of Terms Relevant to RIP

Like many terms, the definition of RIP has evolved and changed since it was first coined. In the early days, RIP simply referred to any process that would allow for ion exchange resin to be used on a stream that had not been completely clarified. Today, it is more common to categorize ion exchange systems into four categories: fixed bed, moving packed bed, fluidized bed, and resin-in-pulp. This can lead to confusion when reading historical documentation on RIP processes. For example, the ion exchange installation at St. Pierre du Cantal in France was documented as a successful implementation of “RIP” technology (35); however, this installation used fluidized bed columns based on the United States Bureau of Mines (USBM) design, which had to be retrofitted to operate using air pulsation in 1981 due to operational problems caused by the build-up of solids on the interstage platforms (36).

For the purposes of this review, processes that involve moving packed beds (resin that moves continuously through the system in a plug-flow manner) and processes involving fluidized beds (resin that has been fluidized due to the upflow of the feed stream) will not be considered as RIP technologies. For a review of the development, commercial implementation, and current status of moving packed bed and fluidized bed technology, the reader is referred to publications available in the literature (37,38,39).

Generally speaking, an RIP system would be expected to be able to handle feed slurry with a higher solids content than a fluidized bed process. Note that care must be taken when comparing solids loadings from technologies of different eras, since advances in areas such as resin size and interstage screening can also contribute significantly to the maximum solid handling capabilities of a system.

RIP systems usually operate in counter-current fashion and are generally designed based on one of two operating strategies. The first operating strategy is the continuous or “cascade” operating strategy. In this type of system, the order in which the feed passes through the tanks remains fixed, and resin is transferred from tank to tank. Resin exiting the lead tank is directed
to a regeneration step, while the regenerated resin is returned to the final lag tank. Resin transfer between tanks can be periodic (e.g. once every 4 hours) or continuous. Depending on the method chosen for resin transfer, the degree of back-mixing of pulp can vary significantly. A three stage cascade circuit is depicted in Figure 2.3.

The second operating strategy is the semi-continuous or “carousel” operating strategy. This type of system has a continuous flow of slurry and batch processing of resin. In these systems, the order in which the slurry passes through the tanks rotates, in the same way as the order in which the feed to a multi-column fixed bed ion exchange rotates. For example, with 3 tanks in the loading circuit, if the tanks start out in the sequence 1-2-3, under normal operation the sequence of tanks would rotate through the 2-3-1, and the 3-1-2, sequences before returning to the 1-2-3 sequence. Each time the sequence changes, the resin from the lead tank would be transferred to elution and refilled with eluted resin prior to coming back into the final lag position. Alternatively, elution can be done in the same vessel, and all tanks would then cycle through the various positions in the loading and elution circuits. An example of such a circuit is depicted in Figure 2.4.
2.2.2 United States of America Basket RIP Process

The first RIP process developed in the United States of America was a semi-continuous loading operation referred to as the “Basket RIP” process. In this process, the pulp was passed through a series of tanks in which square baskets containing specially manufactured large resin beads (0.81-1.65 mm diameter) were reciprocated up and down in a “tea-bag-like movement”. Elution was done batch-wise in the same tanks used for loading (40).
A pilot plant for this process was built at Grand Junction, Colorado, in 1953 and operated on fine pulp (-325 mesh) containing approximately 8% solids. Results indicated that optimum performance would be achieved with a pulp to resin ratio of 6:1, using 6-9 banks for loading, and 6 banks for elution. Resin loadings of 3 lbs $\text{U}_3\text{O}_8$ per cubic foot of resin (~48 g $\text{U}_3\text{O}_8$ / L resin) and a concentration factor of 225 g/L $\text{U}_3\text{O}_8$ on resin / g/L $\text{U}_3\text{O}_8$ in solution were reported (40).

Six mills were constructed in the United States using this technology, and were located at: Monticello, Utah; Moab, Utah; Grants, New Mexico; Tuba City, Arizona; Jeffery City, Wyoming; and Edgemont, South Dakota (41).

The full-scale plant at the Uranium Reduction Company’s mill in Moab, Utah, consisted of two RIP circuits that operated in parallel. Each circuit contained 14 stages: 9-10 stages were used for loading, and only 4 stages for elution. Each stage contained four baskets. The resin was reported to have loaded 3.5 lbs $\text{U}_3\text{O}_8$ per cubic foot of resin (~56 g $\text{U}_3\text{O}_8$ / L resin), and an eluate grade of 9 g/L of $\text{U}_3\text{O}_8$ present as $\text{UO}_2(\text{SO}_4)_3^-$ was produced (42). By 1967, this mill had been taken over by Atlas Minerals and the RIP circuit was being used on alkaline leached ores in lieu of acid leached ores. Throughput through the alkaline leach circuit was ~850-950 tons per day, and resin losses were reported at 0.0014 cubic feet per ton ore processed. Given the resin inventory was reported at 152 cubic feet per bank (43), this calculates to approximately 10% resin inventory replacement per annum. The two RIP lines were replaced by a solvent extraction circuit in 1976 (44).

Anaconda’s Bluewater Mill near Grants, New Mexico, started up their basket RIP circuit in 1955 (45), and it appears to have been operating on acid leached slurries with minimal design changes as late as 1974 (46). The mill had a capacity of 3000-3300 tons per day, although in 1967 was operating at a “reduced capacity” (actual rate not specified). Bluewater operated two RIP circuits in parallel, each circuit containing 14 sections and a resin inventory of 140 cubic feet per section. Resin losses were reported at 100 cubic feet per month (43), which calculates to 30% resin replacement per annum. While this value appears higher than what was reported at the plant in Moab, this plant was likely operating at a higher throughput value. If the plant had been operating at capacity, the resin losses would calculate to approximately 0.0010 cubic feet per ton of ore processed, which is less than the value reported at Moab; so it is likely that
the resin losses were comparable. A photograph of the RIP section of this mill is available in the literature (46).

A number of challenges have been reported with the Basket process. The Mill at Tuba City (Rare Metals Corporation / El Paso Natural Gas) processed ore with a high bentonite clay content and reported problems with resin beads cementing together. Root cause of this problem was not determined; however, it appears to have cleared up around the time pH adjustment was switched from ammonia to lime (43).

The Mill at Moab reported severe corrosion of the baskets when the process was converted from an acid leach process to an alkaline leach process; however, the problem appears to have been addressed by utilizing polyethylene screens in lieu of the stainless steel screens. The polyethylene screens were also found to have the following additional benefits over the original stainless steel screens: lower cost, easier to repair small tears, and improved drainage of pulp from the baskets (47).

Himsley criticized the Basket design by stating, “high maintenance costs of the mechanical equipment along with excessive resin losses in the region of 30% (due mainly to mechanical failures) and the high initial costs resulted in that method becoming obsolete” (48).

### 2.2.3 South Africa: Floating Resin Processes

In order to avoid using screens to separate the resin from the pulp, research was performed in South Africa to develop a process to take advantage of the difference in density between resin and the pulp. It had been observed that when agitation was stopped, resin tended to float on top of the pulp surface, and several attempts were made to develop a process to move the resin between stages by taking advantage of this phenomenon.

Results of the first two attempts were published in 1959 and 1960. The first attempt involved a circuit consisting of air agitated Pachuca tanks, each coupled with a settler, in which the separation of resin from pulp would occur (49). The second attempt involved the design and construction of a pilot plant that utilized one long rectangular tank, subdivided into fourteen small agitated stages, much like a bank of flotation cells. In these tests, resin was transferred counter-current to the movement of pulp by a set of mechanical scoops attached to an
oscillating line shaft. Within each stage, the pulp density was maintained at an SG of 1.4-1.5 so that the resin would float on top of the cell. Difficulty in maintaining resin inventories in the various stages was reported (50).

The third attempt was known as the Relix process. This was developed and piloted in the early 1970s. The principle of the Relix process was to create an “inverted fluidized bed” by having the resin float on a pulp containing 61% solids and using a Pachuca tank to circulate the pulp to a level above the resin. The inverted fluidized bed would then be created as the pulp percolated down through the resin layer. The resin-slurry separation between stages could not be achieved at the West Driefontein Pilot Plant, which ran from 1971-1973. During piloting, airlifts were used to move resin and significant back-mixing of pulp occurred. After the installation of interstage screening, better metallurgical performance was obtained; however, computer simulation of results after the piloting was complete demonstrated significant breakthrough of resin due to screen apertures being too large on the pulp discharge of the tanks and significant recirculating loops of resin within the tanks (51).

No full scale plants based on a floating resin technique were built. A major design flaw with transferring floating resin is that there is a significant difference in density in resin beads when they are loaded with uranium compared to when they have been regenerated. In the pulsed bed at Saint-Pierre du Cantal in France, eluted resin was reported as having an SG of 1.12 and resin loaded with 60 g/L uranium as having an SG of 1.34 (36). Consequently, the resin that is most buoyant, and hence most likely to float and be moved to the previous stage, is small beads with minimal loadings, while the resin most likely to remain in the current tank is large beads with significant resin loadings.

2.2.4 United States of America: Continuous RIP

The continuous counter-current RIP process was developed and implemented by the same organization as the Basket RIP process. A pilot plant was run from August 12-23, 1957. The RIP adsorption train consisted of 3 conical bottomed tanks, each with a residence time of 3 hours. Both the pulp and the resin, in a ratio of 50:1, flowed by gravity from each contactor to a 50 mesh Sweco screen. The resin (screen overflow) then advanced to the previous tank by
gravity, while the pulp (screen underflow) was pumped to the next tank. Resin losses were of the order of 300 mL per ton of ore processed (52).

Test results indicated that uranium could be adsorbed in significantly fewer contactors than were required for the basket RIP process (3-4 stages vs. 8-10 stages for basket). Elution was developed utilizing continuous countercurrent elution in columns or tanks. Due to the success of these tests, the first continuous countercurrent RIP circuit was built at Maybell Mill in Colorado (41). The Maybell Mill operated from 1957-1964 and utilized 6 stages for adsorption and 10 stages for elution and was able to treat slurry containing 20-30% solids (43). This plant used Infilco CST Exchangers to try and perform a separation of resin and slurry based on the difference in specific gravity. In direct contrast to the South African floating resin techniques, the Infilco CST Exchanger was designed based on the pulp floating and the resin sinking to the bottom of the settling chamber. In these exchangers, a slurry of incoming liquid and resin was fed down through a feed pipe to a distributor near the base of the reactor. Air was sparged through porous fabric covering a perforated plate on the bottom of the reactor. The slurry and resin mixture would rise up through a contacting compartment, and then overflow over internal baffling to a settling compartment of the reactor. Piloting trials using this system on ore from Charles A. Steen’s Mi Vida Mine near Moab, Utah, showed promising results and a commercial installation was built and scheduled to come on-line in October 1957 (53). Unfortunately, settling of the resin in the full scale units could not provide a satisfactory separation of resin from the slurry in the adsorption circuit and vibrating screens needed to be added to perform resin and slurry separation (43).

Three commercial installations were operating in 1967 using continuous counter-current RIP in the Gas Hills area of Wyoming. The Federal-American Partners Mill processed acid leached material through seven mechanically agitated loading tanks, and the regenerated resin passed through a 13 stage elution circuit (final stage of elution circuit a water wash). The Union Carbide Mill (Umetco) used air agitation in their tanks, allowing for the operation of up to 30% solids in the feed (the mechanical agitation used at the other two plants limited operation to a maximum of 11-12% solids). Umetco used six stages for loading and 10 stages in the elution circuit: the first seven elution tanks were for stripping the resin and the final three elution tanks were used to convert the resin from nitric acid form to sulphuric acid form. Western Nuclear’s Split Rock Mill (Jeffery City) was upgraded from a Basket RIP circuit to continuous counter-
current RIP in October 1966. Their RIP circuit consisted of eight mechanically agitated tanks for loading and fourteen for elution (43).

These plants all used interstage transfer of resin and pulp by airlifting to screens. After separation on the screen deck, the pulp would proceed to the downstream tank, while the resin would be directed to the upstream tank. This resulted in resin content of less than 5 vol% in the adsorption tanks. At the Union Carbide plant, it was desired to increase the resin content in the tanks to 5-10 vol%, so a portion of the resin was recycled to the tank it came from (54). The Federal American Partners Mill reported that screen decks required replacement every 50-60 days and resin inventory losses of 0.076% per day (43), which would equate to approximately 25-28% per year. It should be noted when comparing this number to the losses incurred in Basket RIP that the overall resin inventory in a continuous plant is typically less than in a Basket plant.

The continuous countercurrent RIP system has been criticized for unpredictable metallurgical performance due to difficulty in maintaining the appropriate resin inventories in the various tanks (48).

### 2.2.5 Davy-McKee Contactor

The Davy-McKee Contactor was designed to try and develop a more compact RIP circuit. It consisted of a long rectangular cell, subdivided into a series of agitated compartments, much like a bank of flotation cells. Between each compartment was a common wall containing an air-swept screen that would retain resin in the compartment, but allow pulp to pass through. The pilot RIP cell was tested on an unspecified leached uranium ore for 48 hours. The slurry tested was 40% solids and contained 25 vol% resin. The pilot plant was also run for a CIP application (55).

Two demonstration plants were operated at Rand Mines’ ERPM Boksburg gold plant. The first demonstration plant was run with both resin and carbon to test screen throughput at a flowrate of 60 m³/h. The second demonstration plant was to evaluate the rate of carbon adsorption. Based on the success of the demonstration runs, Davy McKee was contracted to fabricate and
supply two 3000 tpd CIP contactors to the Ashanti gold plant in Ghana for commissioning in 1987 (56). No follow up information on these full scale units could be found in the literature.

2.2.6 UNION OF THE SOVIET SOCIALIST REPUBLICS TECHNOLOGIES

In the USSR, a “nonfiltrational sorptive-extractive method … of dense and viscous pulp” was developed in 1953, and had become their industry standard by 1983. In a discussion about various forms of industrial ion exchange equipment, “standard reactors with mechanical mixing mounted as cascades of 3-6 plants” and “units with pneumatic mixing of a volume from 0.3 to 500m$^3$ for processing of dense pulp up to solid-to-liquid ratio 1:1” were listed in addition to various forms of ion exchange columns (33). Both pneumatic mixing and mechanical mixing systems were built on an industrial scale. Pneumatic mixing was used for ores containing at least 95% size fraction less than 150 microns, in a slurry with a specific gravity of no more than 1.5. Resin was continuously transferred countercurrent to the pulp, by use of special airlifts in these systems. Mechanical mixing systems consisted of contact tanks with impeller mixers, which were described as follows: “Contact tanks at each sorption stage are combined into cascades of 3-6 apparatuses with a total of 3-5 stages” (57). Details of the resin transfer mechanism for the mechanical mixing systems were not reported.

RIP was also used extensively for gold recovery in the USSR and is believed to have been a carry-over of the uranium technology. The first resin in pulp process for gold in the USSR was built in the early 1970s. This plant was located in Western Uzbekistan, and processed ore from the Muruntau deposit. The RIP circuit utilized Pachuca tanks and gold was loaded onto the resin in a countercurrent fashion to the pulp flow. This technology was considered a success and rapidly spread through the Soviet Union. For example, the Ararat Mill for the Zod deposit was originally planned to use conventional processing, but the design switched to resin in pulp due to the success of the process at Muruntau (58).

The separation of resin and pulp has been reported as “using flat external screens”, which were “manually cleaned once per day with the help of compressed air”. Each tank was equipped with 8-12 screens with an area of one square meter and with apertures of 0.5 mm. One screen would collect resin for interstage transfer, while all other screens would direct the resin back to the tank it came from. At the time of the review, 50% of the gold produced in the former
Soviet Union was reported as coming from RIP processes. Mills were typically grinding to a d95 of 74 microns and the resin was added to the last RIP tank at a concentration of 2.5-3 vol%. One of the most significant drawbacks to the traditional Soviet RIP process for gold was the elution method used resulted in large resin inventories and gold lockup (59).

It is clear, and well known, that several resin-in-pulp processes were used extensively in the USSR for uranium and gold extraction; however, it is difficult to find published primary data on these plants, or to find a published comparison of the performance of the various methods employed.

2.3 Modern RIP Installations (Commercial Scale)

There are a few commercial scale RIP and resin-in-leach (RIL) plants that have been built and operated in more recent years. These will be reviewed by industry.

2.3.1 Gold RIP

In the western world, RIP/RIL for gold has been used for highly preg-robbing ores (i.e. ores containing carbonaceous material that adsorbs the gold cyanide complex). There have been three commercial scale RIP/RIL plants that have been operated: Golden Jubilee, Penjom Gold Mine, and Barbrook.

The Golden Jubilee Mine converted its’ process from carbon-in-leach (CIL) to RIP in February 1988. It operated as a semi-continuous operation with pulp transfer between tanks occurring by air-lifting the resin-pulp mixture to a screen. Pulp would advance to the next tank in series, while the resin would return to the tank it originated from. Once per day, a portion of resin would be collected and manually transferred to the previous tank (60,61,62). Golden Jubilee was closed due to depleted gold reserves; however, it is important to note that the RIP circuit operated successfully for six years (63).

The Penjom Gold Mine converted its’ process from a CIL process to a batch RIL process in 1998, and then upgraded to a continuous RIL process in 2000, once an appropriate gold-selective resin was available. Dramatic increases in gold recoveries were obtained (64) as
Table 2.2: Gold Recoveries at the Penjom Gold Mine 1998-2002

<table>
<thead>
<tr>
<th>Year Ending</th>
<th>Process Recovery (67,68,69,70)</th>
<th>Process Recovery Including Tailings Retreatment (71)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prior to April 1997</td>
<td>&gt; 90%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>March 31, 1998</td>
<td>86%</td>
<td></td>
<td>Started processing carbonaceous ore</td>
</tr>
<tr>
<td>March 31, 1999</td>
<td>62%</td>
<td>63%</td>
<td>Hit low of &lt; 50% recovery at some point</td>
</tr>
<tr>
<td>March 31, 2000</td>
<td>70% (66% Apr-Sep; 74% Oct-Mar)</td>
<td>71%</td>
<td>Continuous gold RIL circuit implemented</td>
</tr>
<tr>
<td>March 31, 2001</td>
<td>78%</td>
<td>84%</td>
<td>First Full year with RIL circuit</td>
</tr>
<tr>
<td>March 31, 2002</td>
<td></td>
<td>87%</td>
<td></td>
</tr>
</tbody>
</table>

The RIL circuit at the Barbrook Mill was commissioned in mid-December of 2002. The RIL circuit was a semi-continuous circuit, consisting of six Anglo-American Corporation (AAC) Pump cells, provided by Kemix (72). This site was placed on care and maintenance due to industrial action caused by labour unrest in the fourth quarter of 2006 (73).

2.3.2 Uranium RIP

The RIP process has once again become quite topical in the uranium industry as it is perceived to hold promise for the economic extraction of high throughputs of low grade ores (74,75). Many uranium projects are evaluating RIP as a potential processing option. For example, pilot plant results for RIP feasibility studies at SGS Lakefield have recently been published (76,77); an RIP circuit has been selected in the development plan by Khan Resources for their Dornod
Project in Mongolia (78); Mantra Resources has reported that RIP would be preferable to CCD/SX for their Mkuju River Project in Southern Tanzania (79), AREVA has conducted testwork for applying RIP to Cominak’s mill site in Niger, as well as for the Kiggavik project in Nunavut (80); and a demonstration plant (scale 1:150) has been operated for uranium recovery at Harmony gold mine (81,82). Perhaps most significant of all is that a full scale RIP circuit for uranium recovery has been built by Paladin Resources for their Kayelekera Project in Northern Malawi (83).

The Kayelekera Mine utilizes a sulphuric acid leach process. Since there is some tetravalent uranium in the ore, it is first oxidized to hexavalent uranium using ferric as an oxidant. Ferrous is then oxidized back to ferric using hydrogen peroxide (84). The RIP loading circuit consists of ten Kemix Pumpcells, which will be discussed in detail in Section 2.3.4.1. The operational design was to have eight pumpcells on-line at any given time, with the other two pumpcells offline and isolated from the circuit. One of the offline contactors would be transferring resin to the elution circuit, while the other offline contactor would be in the process of being refilled with stripped resin. Reduced foot-print, elimination of the SX fire hazard, elimination of the requirement for solution clarity, increased recoveries and reduction in concerns for health, safety, and the environment were listed in the reasons for the choice of RIP over a conventional CCD/SX process (85).

2.3.3 BASE METALS RIP

To date, the only full scale RIP circuit that has been constructed for base metals RIP was at Compass Resources’ Browns Oxide Plant in Australia. At the Brown’s Oxide operation, leached slurry was directed to a counter current decantation (CCD) circuit. The CCD overflow reported to copper solvent extraction and electrowinning, while the CCD underflow was to report first to an RIP circuit for copper recovery and then to a second RIP circuit for nickel and cobalt recovery (86). The first copper cathode from this plant was stripped in September, 2008. At this time, the RIP circuit was reported as having been constructed, and commissioning was scheduled for October 2008 (87). Mining stopped December 15th, 2008 (88), and Compass Resources went into administration in January 2009, citing the fall in metals prices and the
delays encountered to full metals production at the Browns Oxide Plant as the cause (89). It has since been reported that no nickel or cobalt was produced at this site (90).

**2.3.4 MODERN RIP SYSTEMS MARKETED IN THE LITERATURE**

There are a number of companies that have published papers in recent years on RIP system design, and three such systems are reviewed here.

**2.3.4.1 Anglo American Corporation (AAC) / Kemix Pump Cells**

The AAC pumpcell was developed as an alternative configuration for carbon-in-pulp circuits. The AAC pumpcell process uses a cascade operating philosophy to allow for the elimination of interstage transfer of carbon, thus reducing the problems of maintaining adsorbent inventory in the various loading stages and eliminating the inefficiencies associated with pulp back-mixing.

The AAC pumpcell was developed and tested from 1987-1990, was used commercially for scavenger duties starting in 1991, and has been used for gold recovery from cyanide leach liquors since 1998. Residence times for pulp in the AAC pumpcell are typically < 10 minutes per stage and the gold loading on the carbon is typically double that of conventional CIP circuits (91).

At the heart of the pumpcell process is Kemix’s Mineral Processing Separating Pumping (MPS(P)) Interstage Screen. In addition to the agitator blades, the central shaft in a pumpcell also provides the rotation for screen cleaning and turns the pumping impeller to discharge the screened slurry from the cell (92). The interested reader is directed to the referenced paper for a sketch of this mechanism.

There have been two commercial RIP/RIL installations of the AAC / Kemix Pump cell to date. The first is at the Barbrook Gold Mine for a resin in leach gold recovery circuit. The second installation is the uranium RIP circuit at Paladin Resources’ Kayelekera uranium project in Northern Malawi.
2.3.4.2 Mintek / Bateman MetRIX

A continuous RIP configuration, marketed under the name of MetRIX, was developed by Mintek and Bateman. Pulp flows continuously through submerged interstage screens to the next contactor, while resin is transferred hydraulically to the previous contactor and the interested reader is directed to the reference paper for a sketch of this process (93). Since the mechanisms of resin and pulp transfer are completely independent of each other, this allows for easily operating the circuit with significantly different residence times for the resin compared to the pulp. In order to address the question of the most durable resin for uranium RIP applications, Mintek has published a paper detailing their development of accelerated resin degradation test procedures for uranium ion exchange resins; however, results do not include the names of the resins tested (94).

A cost comparison performed by Mintek and Bateman suggested that a MetRIX circuit combined with solvent extraction of the eluate would be advantageous over a conventional CCD circuit followed by solvent extraction for uranium feed grades of $< 900 \text{ ppm } U_3O_8$, where Bateman Pulsed Columns were used for the cost evaluation of the solvent extraction circuits (95,96). No mention of an industrial MetRIX plant could be found in the literature.

2.3.4.3 Clean-TeQ Clean iX

Clean-TeQ also markets an RIP system for slurries consisting of 10-60% solids: “Clean-iX cRIP”. This system is a continuous counter-current system in a series of either air-agitated (“Clean-iX Air”) or mechanically agitated (“Clean-iX Mech”) tanks. Resin and pulp are “continuously separated and transported counter-currently” by airlifting to flexible woven wire static screens located above the contactors (97).

The Clean-TeQ technology is likely based on the RIP technology developed in the Soviet Union. As per their 2009 annual report: “Clean-TeQ has been granted the exclusive rights, outside the former USSR, to the Base Technology developed by the All Russian Research Institute of Chemical Technology in Moscow”. Clean-TeQ has granted exclusive rights to their cRIP system to BHP Billiton and Vale for nickel and cobalt extraction, while still retaining the
rights for all other metals (98). No reference to a full-scale Clean-iX plant could be found in the literature.

2.4 RESEARCH STUDIES FOR BASE METALS RIP

While there has not yet been a successful implementation of base metals RIP, a significant amount of research has been published by several authors on this subject.

2.4.1 MINTEK STUDIES

Mintek began work on developing a base metals RIP process in the late 1990s. Early work identified that an iminodiacetic chelating resin was preferable over a weak acid selective resin, and that further work with the iminodiacetic resin was warranted (99). An early study was sponsored by Billiton to investigate the potential of recovering copper from CCD underflows. Preliminary batch tests suggested that the circuit pH would need to be greater than 2.5 to load the resin to near capacity; however, ferric precipitation tests at this low pH suggested that some iron (6 g Fe / L Resin) would co-load with the copper (47 g Cu / L Resin). A carousel miniplant was run and preliminary plant economics provided for copper feed concentrations of 4, 1, and 0.5 g/L (100).

Anglovaal Mining hired Mintek to evaluate RIP for recovery of copper, nickel, and cobalt from a thickener underflow stream. Three processing options were considered, all of which contained a ferric precipitation step upstream of the RIP circuit to avoid loading ferric onto the unnamed resin. The various options were evaluated through miniplant campaigns using a carousel arrangement for the RIP step. Based on results and preliminary costing, the authors concluded that a copper RIP plant would not be economical for this particular stream, but that a combined copper-nickel-cobalt RIP plant could be (101).

Mintek also worked with Zincor to evaluate RIP as an option for recovering soluble zinc from their lead-silver leach residue and their iron precipitation residue. In this study, the TP207 resin was used in an on-site four stage pilot carousel circuit (150L / stage), held at pH 4.5 with the addition of lime slurry. For the lead-silver residue, soluble zinc was reduced from
concentration of 2000-6800 ppm in the feed to a barren concentration of 12-80 ppm. For the iron residue, the soluble zinc was reduced from a feed concentration of 800 – 4400 ppm to a barren concentration of 15 – 105 ppm. Of note is that zinc adsorbed on the iron residue was observed to have loaded onto the resin, which had not been taken into account in the sizing of the pilot circuit (102).

A recent study on loading of copper and cobalt from a tailings dump material suggested that optimum total recovery could be achieved if the pH set point was increased across the RIP circuit. The rationale is to have a lower pH in the first tank where copper precipitation is likely, and then to increase the pH in later tanks to maximize the recovery of cobalt. The objective is to use sufficient resin to minimize copper displacing cobalt from the resin. Scale-up from preliminary laboratory tests to a four stage carousel miniplant was done using a McCabe-Thiele diagram, and assuming stage efficiencies of 60%, 70%, 85%, 100%. These stage efficiencies were estimated from the fractional attainment of equilibrium observed in batch loading tests (103).

2.4.2 **Clean-TeQ Study**

Clean-TeQ has published preliminary laboratory data and circuit sizing information to evaluate the use of an RIP circuit to replace a CCD circuit as well as to evaluate the benefits of an RIP circuit installed after a CCD circuit. In both cases, iron was precipitated at pH 4 ahead of the RIP process. This resulted in nickel units lost to the solid phase due to precipitation, but these nickel units were subsequently recovered during the RIP process due to a “sorption leach” phenomenon. The approach taken by Clean-TeQ in the lab was to use repeat contact tests. In these tests a single pulp sample was contacted with samples of fresh resin until all the nickel had been recovered. Based on the lab results, a ten stage full scale plant was proposed as an alternative to a CCD circuit (104).

2.4.3 **Tshwane University Study**

A master’s thesis was conducted at the Tshwane University of Technology to evaluate the effect of different operating strategies on the metallurgical performance of different resin
transfer strategies for a zinc RIP circuit. Miniplant tests were conducted under carousel operation, discreet movement of resin built up on transfer screens every 30 minutes, and continuous counter-current operation. Results indicated that resin loadings under all three resin transfer strategies were similar for all three cases. Furthermore, it was reported that increasing the average resin residence time through the circuit resulted in higher resin loadings, while changes to pulp residence time had minimal effect on resin loadings (105).

2.4.4 Vale Study

A study on nickel RIP from a laterite process was published by the Companhia Vale do Rio Doce (now Vale), using the iminodiacetic resin Amberlite 748. In this work, an RIP process was simulated in two sets of experiments, both conducted at pH 4. In the first set of experiments, a single 500 mL pulp sample was contacted five times with 30g fresh resin in the sodium form. In the second set of experiments, a single 100g resin sample was contacted 8 times with fresh 500 mL pulp samples. In both cases, evidence of nickel extracted from the solid phase was observed (106).

2.4.5 UBC Study

An RIP study on the tailings from the Moa Bay laterite operation was carried out at the University of British Columbia, using Lewatit TP207 and Lewatit Monoplus TP207 iminodiacetic resins. In this work, soluble iron was oxidized and precipitated upstream of the RIP circuit. Much of the copper present in the slurry was found to precipitate at the optimum circuit pH of 4, but a substantial amount was found to redissolve into solution during the RIP trial. Of note, is that no recovery of nickel and cobalt from the solid phase was reported in this work (107).

2.4.6 Murdoch Study

An extensive study on recovery of nickel from laterite tails was carried out at Murdoch University. Laboratory tests, miniplant tests consisting of five 2L contactors, and pilot testing
using five 40L contactors were all performed. Testing was done using the iminodiacetic resin Amberlite IRC 748 and slurry supplied by Anaconda Nickel, and partial recovery of nickel from the solids phase of the tails was observed (18).

Laboratory tests were first performed with synthetic solutions (no solids) to determine the equilibrium loading isotherms for four species: nickel, cobalt, manganese, and magnesium. Each species was studied in isolation at pH 3, 4, and 5. Automatic addition of NaOH was done to neutralize the hydrogen ions released from the resin as the metals loaded. Results showed that the selectivity of the resin could be described as Ni > Co >> Mn, Mg. Both the Freundlich isotherm and the Langmuir isotherm were fit to these curves; the better fit typically being the Langmuir isotherm. Loading rate could not be determined from the rate of addition of NaOH since a significant amount of sodium co-loaded onto the resin during these tests (108).

Laboratory tests were also performed to compare the loading rates of several different iminodiacetic resins during a four hour co-current loading test. Results indicated the following order of resin loading rates: Lewatit TP207MP > Amberlite IRC 748 > Purolite S930 > Lewatit TP207 > Lewatit TP208. Once again loading rate was modeled using a linear approach to equilibrium (19).

Amberlite IRC 748 was selected as the optimum resin, and it was used for testing in the miniplant and pilot scale evaluations (note: TP207MP was not available in the early stages of Zainol’s testwork). The loading kinetics from a co-current laboratory test “… fitted well to a simple rate equation based on a first-order approach to equilibrium as a result of rate-determining mass transport in the pulp phase” (18). Process simulation was performed using these laboratory results and software developed for the carbon in pulp process. A graph showing good correlation between simulator predictions and a miniplant run was included in this work. The loading rate model described in the thesis appears to be based on the CIP model published for a linear approach to a linear isotherm (109,110).

2.5 CHALLENGES FOR BASE METAL RIP CIRCUITS

Although RIP has been implemented successfully in the gold and uranium industries, many still consider it an unproven technology for base metals. Base metal circuits differ from gold RIP
circuits since the upgrading ratio (concentration of metal on resin / concentration of metal in feed) is orders of magnitude smaller in a base metals application (101), resulting in shorter resin loading cycles and a requirement for higher resin inventories (93). These differences suggest that the optimum design configuration / design methodology for a base metals circuit could well differ from the optimum design configuration / methodology for a gold RIP circuit. A few of the challenges facing base metals RIP circuits will be reviewed.

2.5.1 RESIN LOSSES

One very important factor for RIP technology is the question of resin life. This question is particularly pertinent for the case of base metals RIP since resin inventories are much higher than in gold RIP circuits.

Resin losses are due to several factors including: osmotic shock as the resin expands and contracts due to changes in solution chemistry, mechanical attrition from contact with pulp, agitators, pumps, and screens, as well as from resin spillage when the resin is moved between equipment, and resin lost through tears in retention screens. Predicting actual expected resin losses in a full scale plant from laboratory tests is extremely difficult.

Mintek is working on developing a set of standard procedures to compare the relative expected life of different resins in RIP applications. In their paper, various lab resin durability tests are conducted for various uranium RIP resins, and compared to the results obtained by cycling the resin through their demonstration-scale MetRIX plant. No single test procedure was shown to be conclusive for predicting the resin losses observed in the demonstration plant (94).

Quantifying resin losses in small scale miniplants is also very difficult. When working with a relatively small resin volume (a few litres) for short periods of time (a few days), any small spill during the manual transfer of resin would result in large, erroneous resin loss predictions. Thus, extended pilot scale / demonstration scale testing would be required to even attempt predicting resin losses.

In terms of actual resin losses observed in operating RIP plants, there is some data published in the literature. For gold RIP/RIL plants, a resin consumption rate of 10 g / t ore processed has
been reported for the strong base resin used at Golden Jubilee and a resin consumption rate of < 5 g / t ore processed has been reported for the Minix resin at the Penjom Gold Mine (111).

For the uranium plants operating in the former Soviet Union, a resin consumption rate of 360-560 mL / t ore processed has been reported (112).

For the historical uranium plants that operated in the United States, resin losses can be estimated from numbers published in Merritt’s 1967 survey of uranium mills (113,114). The Moab Mill basket plant reported 0.0014 ft³/ton ore processed (44 mL / tonne), and the Federal American Partners mechanically agitated continuous RIP plant reported a throughput of 950 ton per day, 0.076% resin consumption per day, and a resin inventory of 825 cubic feet (converts to 21 mL / tonne). While these numbers are significantly lower than those reported for plants operating in the former Soviet Union, it is important to remember that the percent solids of the slurries being handled has changed significantly. Typical percent solids in a basket plant were reported as 7-10%, 11-12% for a mechanically agitated continuous RIP circuit (43), while the plants operating in the Soviet Union reported significantly higher percent solids of 40-50% (33,115).

2.5.2 RESIN DISTRIBUTION ACROSS RIP CIRCUIT

Another question raised for RIP is how robust the process will be for fluctuations in resin inventories. As mentioned in section 2.2.4, this was one of the criticisms of the first generation of continuous uranium RIP plants, and is one of the reasons carousel plants are selected over continuous cascade plants.

The question of carousel vs cascade operation for base metal RIP circuits was investigated experimentally in the Tshwane University study (105); however, this study did not address the question of how a continuous cascade circuit would respond to operational fluctuations in resin inventory control across the circuit. The results of an error in resin inventory control in one of the tests reported by Nicol and Zainol suggest that a base metals RIP process should have some process forgiveness (18); however, no model to quantify the effect of varying resin inventory has yet been published.
The question of whether transferring slurry to upstream contactors with the resin would have a deleterious effect on circuit performance was investigated experimentally in the Tshwane University master’s thesis (105). Results indicated that the circuit could operate adequately without removing the slurry from the resin transfer streams, but no attempt to quantify the effect was made. Furthermore, it is reasonable to expect that the effect of such back-mixing may be dependent on circuit operating conditions or on the base metal being loaded. The ability to quantify such effects with a model could be beneficial for circuit design.

2.6 Objectives for Current Work

Based on the findings from the literature review, the following three objectives for the current research program were set:

- Based on batch laboratory data obtained under infinite solution volume conditions, use an engineering model to adequately describe the loading rate for the range of 50 – 5000 ppm nickel in solution.

- Verify the applicability of the engineering model to non infinite solution volume conditions through batch experiments with variable solution concentrations and through the operation of an RIP miniplant.

- Once a useful RIP circuit model is available, use this model to quantify the effect of various different operating configurations. In particular, compare cascade operation to carousel operation, quantify the effect of solution back-mixing during resin transfer, and quantify the process sensitivity of a cascade circuit to fluctuations in resin inventory.
3.0 Method Development for Batch Tests

For the initial tests, the hydrogen form of Lanxess Lewatit Monoplus TP207 (TP207MP) was used to evaluate the loading of nickel. The capacity for this resin is rated at 2.0 eq/L. Prior to use, the resin was wet-screened to remove the small amount of fines (<500 micron) and oversize (>600 micron). Note that all resin volumes reported in this thesis correspond to the bulk volume of the resin in the hydrogen form. Bulk volumes were obtained by wet-settling the resin in a graduated cylinder and tapping the cylinder until the settled resin volume remained unchanged.

To try and best simulate an RIP environment, batch tests for nickel recovery were carried out in beakers. Overhead mixers were operated at 300 RPM to ensure good suspension of the resin in the test beaker. The pH-stat method developed by Babjak in his studies of nickel and cobalt loading onto a bispicolyamine resin (116) was initially considered for this work.

In the pH-stat method, a pH electrode and controller are used to maintain a constant pH in the test solution. By tracking the rate at which base needs to be added to the solution to maintain constant pH, one can estimate the rate at which a resin in the hydrogen form is loading cations. One significant advantage of the pH-stat method over other infinite solution volume methods is that it produces a nearly continuous data-set, as opposed to a series of discreet data points corresponding to samples taken during the test.

Preliminary runs with the pH-stat method for loading an iminodiacetic acid resin from synthetic solutions of nickel sulphate, maintained at a pH of four by the addition of sodium hydroxide were performed. Unfortunately, even though the resin was equilibrated to pH 4 ahead of time, significant mass balance errors were observed between the estimated nickel level based on the sodium hydroxide added and the nickel stripped from the resin beads. This suggests that the resin must have been co-loading another cation. The only other cation present in the solution was the sodium from the sodium hydroxide added to maintain constant pH. The loading of some sodium is not surprising since the iminodiacetic group loses protons as the pH increases, as was discussed in Section 2.1.3.

In order to maintain the ability to obtain a near-continuous set of data, work was done to modify the pH-stat method and develop a test procedure to minimize the amount of co-loading.
This chapter discusses the modifications made to the procedure, and then provides a detailed description of the experimental method.

3.1 Method Development

The first modification made to the pH-stat method was to hold the nickel concentration, in addition to the pH, constant for the duration of the test. This was achieved by adding a second pump head to the motor being used to drive the pump that was adding the sodium hydroxide. The second pump was used to add a stock solution of nickel, made up by calculating the amount of nickel sulphate needed to maintain constant nickel concentration in the test beaker. A photograph of the equipment used for the loading tests can be found in Figure 3.1. Note that this photograph depicts two sets of equipment that are being operated in parallel.

![Figure 3.1: Batch Loading Equipment](image)

To confirm constant nickel concentration in the beaker, samples were typically taken at the beginning, after 1 hour, after 4 hours, and at the end of the test (approximately 20 hours) and assayed by atomic absorption. Results for tests run at 50, 500, and 5000 ppm nickel are displayed in Figure 3.2 and illustrate that nearly constant nickel concentrations were maintained for the duration of the tests.
The second parameter investigated to minimize co-loading onto the resin, was the effect of different alkali hydroxides. It has been reported that alkali loading onto iminodiacetic acid polyurethane foams at pH 4 showed a preference for Na > Li > K at pH 4, based on batch tests with 2 ppm alkali in the feed (117). Consequently a series of blank tests were run to determine the effect of changing the alkali hydroxide used. Additionally, a baseline was run in which the resin was placed into a beaker of deionized (DI) water and the effect of using ammonia as a neutralizing agent was also investigated.

For a blank test, 10 mL of resin was placed in a small beaker containing 15 mL of deionized water, and drops of the appropriate base were added until the water and resin were equilibrated at a pH of 4. The conditioned resin was then placed into a beaker containing 500 mL of a 0.0325 M alkali sulphate solution, and stirred with an overhead mixer. A pH controller was used to add the appropriate amount of a 0.5 M alkali hydroxide solution to maintain a pH of 4.0
+/− 0.1 in the test beaker. These tests were then repeated using 5 mL of resin, 0.0187 M alkali sulphate, and 0.25 M alkali hydroxide solution. Note that 0.0187 M alkali corresponds to the expected final value after fully loading 5 mL of a 2.2 eq/L resin and adding 88 mL of stock solution to the test beaker, and thus over-represents the worst-case scenario. The 0.0325 M alkali sulphate solution does not represent this same worst-case scenario, but was based on observations of the amount of sodium hydroxide added during an early, preliminary run in a nickel sulphate solution. Equilibrium was observed to be attained within 30 minutes, and early runs showed minimal change between 1 and 8 hours; therefore, most tests were shut-off after one hour. The loaded resins were stripped using 5 bed volumes (BV) of 100 g/L sulphuric acid and select samples were submitted to a commercial laboratory for ICP assays. Results from the blank tests are summarized in Table 3.1.

### Table 3.1: Results of Blanks with Different Neutralizing Agents

<table>
<thead>
<tr>
<th>Cation</th>
<th>mL Resin</th>
<th>eq/L loaded</th>
<th>Fraction capacity of a 2.0 eq/L resin</th>
<th>Estimated ppm in Strip Solution</th>
<th>ICP Assay of Strip Solution [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI H₂O</td>
<td>10</td>
<td>0.002</td>
<td>0.1 %</td>
<td>*After 2 hours, using NaOH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.004</td>
<td>0.2 %</td>
<td>*After 8 hours, using NaOH</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>10</td>
<td>0.144</td>
<td>7.2 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.139</td>
<td>7.0 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium</td>
<td>10</td>
<td>0.104</td>
<td>5.2 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.118</td>
<td>5.9 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.058</td>
<td>2.9 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>10</td>
<td>0.114</td>
<td>5.7 %</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.100</td>
<td>5.0 %</td>
<td>92</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.070</td>
<td>3.5 %</td>
<td>32</td>
<td>34</td>
</tr>
<tr>
<td>Potassium</td>
<td>10</td>
<td>0.118</td>
<td>5.9%</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.124</td>
<td>6.2%</td>
<td>194</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.079</td>
<td>4.0%</td>
<td>62</td>
<td>65</td>
</tr>
</tbody>
</table>
These results show that reducing the concentration of resin in the test beaker (and therefore the final total concentration of alkali in the test solution) has a much greater impact than changing the alkali used. Although it appears that the amount of alkali loading appears to follow the order $K > Na > Li$, the repeat tests for lithium and sodium at 10 mL resin suggest that the differences between these two elements are within experimental error. Consequently, it was decided that sodium hydroxide would be used for the experiments and that 5 mL of resin would be used in future tests.

Repeatability of the method was examined by running three tests at 250 ppm nickel concentration. Results are shown in Figure 3.3, and indicate good repeatability with an experimental error of approximately $\pm 2 \text{ g Ni / L Resin}$. 

![Figure 3.3: Repeatability at 250 ppm Nickel TP207MP Resin, pH 4, 30°C](image)
To determine the amount of sodium that co-loaded when the concentration of nickel was kept constant, a sample of the strip solution from one of the tests run at 250 ppm nickel was submitted for ICP analysis. Results showed that, under these conditions, only 0.004 eq/L of sodium was stripped from the resin. Therefore, it is believed that the procedures developed allow for near-continuous measurement of the rate of nickel loading, with minimal interference from the sodium introduced to maintain constant pH.

In order to ensure that the agitation speed was sufficient to not limit the loading rate, a test was performed at 250 ppm nickel and the agitation rate increased from 300 RPM to 450 RPM. Results from the increased RPM test are displayed in Figure 3.4, together with the three baseline tests. Results clearly indicate that at 300 RPM, agitation speed is not limiting the loading rate at 250 ppm nickel.

Figure 3.4: Effect of Increasing Agitation Speed at 250 ppm Nickel

*TP207MP Resin, pH 4, 30°C*
3.2 Detailed Description of Experimental Procedure

A detailed description of the finalized experimental procedure is described in this section. Check sheets were used to ensure that all tests were carried out using the same procedure. A copy of a blank test sheet can be found in Appendix A.

Batch tests were conducted using synthetic solutions, made up from American Chemical Society (ACS) grade reagents. The test beaker was initially filled with 500 mL of test solution containing the desired concentration of nickel. This beaker was then placed in a hot water bath at 30°C, and overhead stirring applied using a propeller-type impeller rotated at 300 RPM. A pH probe with temperature compensation was calibrated using pH buffers 7 and 4. The pH probe was then used to equilibrate 5 mL of the resin being tested with 15 mL deionized water at pH 4. As the pH of the deionized water dropped, sodium hydroxide was added until the resin and water were in equilibrium at a pH of 3.9 - 4.1. The pH probe was then rinsed and placed into the beaker of nickel test solution, which was adjusted to pH 3.9 - 4.1, through the addition of a few drops of dilute sulphuric acid. Baffling in the test beaker was provided by the pH probe itself, and by placing an additional length of ½” (~13mm) polyethelene rod into the beaker.

A stock solution of 0.25 M sodium hydroxide and a stock solution of > 0.125 M nickel sulphate were made up and their specific gravities were measured by weighing 10 mL of each solution. The actual concentration of the nickel stock solution was slightly higher than 0.125 M and was calculated such that the solution concentration in the test beaker would remain constant for the duration of the test. The target stock nickel concentration, therefore, varied from test to test, depending on the solution concentration in the test beaker and on the slight differences in pumping rates, depending on which pump heads and motor was being used at the time of the test.

The two flasks containing the stock solutions were weighed individually and then placed on a Sartorius TE4101 scale, which was connected to a computer through an RS-232 serial port. Windmill software was used to communicate with the balance and collect the weight on the scale every 15 seconds.

To start the test, the 5 mL of equilibrated resin was transferred to the test beaker using graduated 10 mL pipettes in an “upside-down” fashion (i.e. pipette bulb placed over the tip).
The resin in the pipettes was left to settle before being added to the test beaker to minimize the amount of water that was added to the test beaker with the resin. Time of transfer of the resin was typically less than 30 seconds.

A Jenco 3676 controller was used to maintain the pH and nickel concentration in the test beaker. When the pH dropped below 3.9, the controller would turn on a single motor drive with two Masterflex L/S 13 pumpheads mounted on it. One pumphead would deliver the stock solution of sodium hydroxide, while the other pumphead would deliver the stock solution of nickel sulphate. Once the pH reached 4.1, the motor would turn off. Due to the on/off nature of the controller, the speed of the motor was manually adjusted during the first hour or two of the test to minimize overshooting and undershooting, and the actual pH in the beaker was maintained at 4.0 +/- 0.2. To ensure constant nickel concentration over the course of the test, samples were taken after approximately 1, 4, and 20 hours. The test was ended after approximately 20 hours, and the final weight of the two stock solution beakers was obtained.

The resin was then stripped downflow at 10 BV/h in a 25 mL burette. Resin stripping consisted of 5 BV deionized water wash, 5 BV strip with 100 g/L sulphuric acid, a 20 hour acid hold, followed by a 10 BV strip wash with deionized water. The strip and strip wash solutions were collected in a 100 mL volumetric flask. Typically, three different dilutions of the final strip sample were run by AA in order to check instrument reliability, and the average value taken for mass balance calculations.
4.0 COMPARISON OF LARGE BEAD IMINODIACETIC RESINS

As mentioned in Chapter 2, the study at Murdoch University included a comparison of various commercially available resins, and these results have recently been published (3,19). However, since this work was done, several resin manufacturers have developed large bead products, specifically for use in base metals RIP applications. The focus of this chapter is to evaluate these new large bead resins (Ambersep XE818, Lewatit MonoPlus TP207XL, Purolite S930+/4888) and compare their performance to several of the traditional resins evaluated in the study of Zainol and Nicol (Amberlite 748, Lewatit TP207, Lewatit MonoPlus TP207, Purolite S930). Additionally, the traditional size of the new Purolite S930+ product was included in this comparison. Resins were compared based on size distribution, loading rate, loading capacity, and stripping rate. Appendix B contains a summary of resin properties reported by the various manufacturers in their resin data sheets.

4.1 SIZE DISTRIBUTIONS OF RESINS

Resin bead size is an important factor for RIP circuits. It is well known that loading rates decrease as the resin bead sizes increases (as illustrated in Equations 2.9, 2.10, 2.14, 2.18). However, for RIP, the resin beads need to be separated from the solids present in the slurry, and the larger the beads, the easier the separation of the two phases. Consequently, in RIP applications, large bead products are generally preferred.

The resins were converted to the hydrogen form in a column, by passing 5 BV of 100 g/L sulphuric acid, and 10 BV deionized water wash over the resin. The converted resin was wet-screened to determine the cumulative fraction passing curves. The bulk volume change for each resin as it was converted from sodium form to hydrogen form was recorded and these values are plotted in Figure 4.1. Note that three samples of the TP207 resin and two samples of the TP207MP resin were converted from sodium form to hydrogen form to get a sense of the error in these measurements.
Results from Figure 4.1 indicate that, with the exception of the Purolite S930, there is typically a bulk volume change of 15-30% associated with the conversion from sodium form to hydrogen form. For the three new large bead products, the resin with the least volume change is the Amberlite XE818, followed by the Purolite S930+/4888, and then the Lewatit TP207XL.

The results from wet-screening the resin beads are plotted in Figure 4.2. Recall that all volumes in this work correspond to the bulk volume of resin in the hydrogen form, the resin beads are spherical, and all resin bead diameters reported correspond to the diameter of the resin beads in the hydrogen form.
Of interest from Figure 4.2 is that the resin with the largest beads is the Ambersep XE818, followed by the Purolite S930+/4888. The size distribution of the new Purolite S930+ is very similar to the Lewatit TP207. Also note how the Lewatit MonoPlus TP207 was mostly retained on a single screen size, and that this was also observed, to a slightly lesser degree for the Lewatit MonoPlus TP207XL. The manufacturer (Lanxess) was contacted regarding how best to estimate the typical bead diameter when their resin is used in the hydrogen form. In response, the manufacturer provided typical size distributions for the TP207, TP207MP, and the TP207XL in the hydrogen form. The cumulative fraction passing curves from the data provided by Lanxess are displayed in Figure 4.3, along with the wet-sieved data.
Reasonably good agreement between the data provided and the measured wet-sieved data was observed. From the detailed supplier size data, an “effective resin bead diameter” for each screen size was calculated for modeling purposes. The effective diameter was based on the size and number of particles present within each size fraction. These values are displayed in Table 4.1.

**Figure 4.3: Comparison of Wet-Screened Results with Data Provided by Lanxess**
TABLE 4.1: EFFECTIVE RESIN DIAMETERS FOR MODELING PURPOSES

<table>
<thead>
<tr>
<th>Screen Size (microns)</th>
<th>TP207</th>
<th>TP207 MP</th>
<th>TP207XL</th>
</tr>
</thead>
<tbody>
<tr>
<td>+500 – 600</td>
<td>555</td>
<td>552</td>
<td></td>
</tr>
<tr>
<td>+600 – 710</td>
<td>653</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+710 – 850</td>
<td>770</td>
<td></td>
<td>736</td>
</tr>
<tr>
<td>+850 – 1000</td>
<td>901</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+1000 – 1180</td>
<td>1050</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2 LOADING RATE AND CAPACITIES

Loading rate and capacity of various size fractions of each resin were determined using synthetic solutions of nickel sulphate at pH 4, and the procedure described in Section 3.2. Capacity of the resins can be inferred from the final loading value obtained at the end of the 20 hour loading rate tests.

Each resin was evaluated at both 500 ppm nickel and 2500 ppm nickel. Loading rate curves were generated at three size fractions: 500 – 600 micron, 710 – 850 micron, and 1000 – 1180 micron. Note that due to the size distributions of the resins, many resins could only be tested at one size fraction, and no resin was tested at all size fractions.

4.2.1 LOADING RATE AT 500 PPM NICKEL

Results for the 500 – 600 micron size fraction are displayed in Figure 4.4, which contains an inset with the first four hours of loading.
The results in Figure 4.4 clearly illustrate the large variation in resin capacities (final loading values). It also shows that the new Purolite S930+ product has a much larger capacity than the old Purolite S930 and loads at a similar rate as the Lewatit TP207. Note that the error bars in the graph are based on the evaluation of experimental repeatability, reported in Figure 3.3.

Most of the resins in Figure 4.4 were previously tested by Zainol and Nicol in a four hour batch loading test with a sample of CCD tails obtained from industry. In their work, it was found that the rate of resin loading followed the following order: TP207MP >> IRC748 > S930 > TP207 (19). The results presented in Figure 4.4 confirm that the rate of loading of the TP207MP is noticeably faster than the other resins tested. This makes sense in terms of data published by this resin manufacturer, which states that the MonoPlus TP207 has a larger internal surface area and more porosity than the traditional TP207 product (118).
However, these results do not indicate that the rate of loading of TP207 is slower than the other resins. This is likely reflective of the fact that these tests were done under constant nickel composition, in the absence of impurities that would co-load onto the resin. Of note from the assays in the work of Zainol and Nicol, was that the manganese content of the TP207 was significantly higher than for the IRC748 and S930 resins. This suggests that in the presence of high levels of impurities (as one would expect to see in an actual RIP slurry), the impurities initially load onto the resin and are then displaced by nickel. It is reasonable to expect that the rates associated with this displacement process could be different from the rates of nickel loading directly onto a resin in the hydrogen form. This highlights the importance of testing ion exchange resins under conditions that are reflective of their actual anticipated operating conditions.

Results for loading onto resins in the 710 – 850 micron size fraction are displayed in Figure 4.5.
In Figure 4.5, the new TP207XL is shown to have a faster loading rate than the other resins tested. This is not surprising as this resin is considered a larger version of the TP207MP. In this test, the new S930+ performs almost identically as the TP207, and the large RIP product S930+/4888 is slightly lower than these two curves; however, the results from all three of these curves are within experimental error.

Results for loading onto resins in the 1000 – 1180 micron size fraction are displayed in Figure 4.6.

![Figure 4.6: Loading of 1000-1180 micron beads at 500 ppm nickel. Iminodiacetic chelating resins, pH 4, 30°C.](image)

In Figure 4.6, the new S930+/4888 resin is shown to load to a higher capacity than the new XE818 resin.

After loading, all resins were stripped using 100 g/L sulphuric acid and the strip solution was assayed to provide a mass balance check on the resin capacity (final loading value). Early tests
showed incomplete stripping of resins, so a 20-hour acid hold step was incorporated into the stripping procedure. Strip assays were obtained as either the average of three separate dilutions assayed by AA (analysis error of 5%), or are the average of two indirect EDTA titrations using zinc sulphate. One sample was assayed using both methods and assay results between the two methods were within 2%. The mass balance results are displayed in Table 4.2.

<table>
<thead>
<tr>
<th>Resin</th>
<th>+500 -600 μm</th>
<th>+710 -850 μm</th>
<th>+1000 -1180 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load</td>
<td>Strip</td>
<td>Load</td>
</tr>
<tr>
<td>IRC 748</td>
<td>41.2</td>
<td>40.3</td>
<td>-</td>
</tr>
<tr>
<td>XE 818</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S930</td>
<td>19.6</td>
<td>20.8</td>
<td>20.8</td>
</tr>
<tr>
<td>S930+</td>
<td>57.8</td>
<td>55.8</td>
<td>58.2</td>
</tr>
<tr>
<td>S930+4888</td>
<td>-</td>
<td>-</td>
<td>55.6</td>
</tr>
<tr>
<td>TP207</td>
<td>61.7</td>
<td>61.0</td>
<td>58.1</td>
</tr>
<tr>
<td>TP207MP</td>
<td>55.5</td>
<td>54.8</td>
<td>-</td>
</tr>
<tr>
<td>TP207XL</td>
<td>-</td>
<td>-</td>
<td>55.6</td>
</tr>
</tbody>
</table>

* indicates samples without the 20-hour acid hold step

All values are reported as g Ni / L Resin. AA Assay error +/- 5%

### 4.2.2 Loading Rate at 2500 ppm Nickel

Loading rate tests were repeated, using fresh resin samples, at a feed concentration of 2500 ppm nickel. Figure 4.7 displays the results for the 500 – 600 micron size fraction.
Results from Figure 4.7 are quite interesting in that, under these conditions, the TP207MP does not appear to be loading nickel any faster than the TP207 or the S930+. This was unexpected, and so the test for the TP207MP was repeated and gave virtually the same loading curve. This suggests that for this size of resin bead in a feed solution of 2500 ppm nickel, the resin porosity is no longer contributing significantly to the overall resin loading rate. Further work would be required to determine what factors are truly limiting the nickel loading rate under these conditions.

Results for loading onto resins in the 710 – 850 micron size fraction are displayed in Figure 4.8.
Results in Figure 4.8 are more in-line with the observations made at 500 ppm nickel. The TP207XL is once again loading at a significantly higher rate than the other resins tested. However, since loading rate is known to decrease as resin diameter increases, these results in no way invalidate the observations made with the smaller resin beads (Figure 4.7).

Results for the 1000 – 1180 micron size fraction are displayed in Figure 4.9. Note that repeat loading tests for each resin were performed, and both results are displayed in this graph to demonstrate the repeatability of the method used.
Mass balances from the resins loaded at 2500 ppm nickel are displayed in Table 4.3. Note that the strip values come from the cumulative stripping curves (to be discussed in Section 4.3).
Table 4.3: Mass Balances and Capacities at 2500 ppm Nickel

<table>
<thead>
<tr>
<th>Resin</th>
<th>+500-600 μm</th>
<th>+710-850 μm</th>
<th>+1000-1180 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load</td>
<td>Strip</td>
<td>Load</td>
</tr>
<tr>
<td>IRC 748</td>
<td>41.6</td>
<td>43.3</td>
<td>-</td>
</tr>
<tr>
<td>XE 818</td>
<td>-</td>
<td>-</td>
<td>40.7</td>
</tr>
<tr>
<td>S930</td>
<td>19.5</td>
<td>22.0</td>
<td>20.8</td>
</tr>
<tr>
<td>S930+</td>
<td>60.9</td>
<td>60.1</td>
<td>61.1</td>
</tr>
<tr>
<td>S930+4888</td>
<td>-</td>
<td>-</td>
<td>59.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP207</td>
<td>65.6</td>
<td>65.9</td>
<td>60.5</td>
</tr>
<tr>
<td>TP207MP</td>
<td>56.1</td>
<td>55.3</td>
<td>55.1</td>
</tr>
<tr>
<td>TP207XL</td>
<td>-</td>
<td>-</td>
<td>57.7</td>
</tr>
</tbody>
</table>

*All values are reported as g Ni / L Resin. AA Assay error +/- 5%*

4.3 Stripping Comparison

The stripping comparison of the resins was conducted on the resins loaded at 2500 ppm nickel. Five bed volumes (BV) of wash water were passed over the resin at 10 BV/hr, followed by 5 BV of 100 g/L sulphuric acid. Cumulative nickel stripped curves were obtained by collecting strip solutions after 1.0, 2.0, 2.6, 3.2, 3.8, 4.4, and 5.0 BV. A 20 hour acid hold was initiated and then deionized water was used for a 10 BV strip wash. In the graphs that follow, the strip wash is plotted as the 6th BV of acid to pass over the resin. All assays for this portion of the work are based on a single sample dilution analyzed by AA.
Results from the 500 – 600 micron beads are plotted in Figure 4.10:

![Figure 4.10: Cumulative Nickel Stripped from 500 – 600 Micron Beads](image)

The results in Figure 4.10 demonstrate that, under the conditions tested, the rate of nickel stripped follows the order: TP207 > S930+ ~ TP207MP ~ IRC748 >> S930. This is in direct contrast to the results reported by Zainol and Nicol: IRC748 > TP207 ~ S930 (3). Both sets of tests were loaded with synthetic solutions containing only nickel cations, and used similar strengths of sulphuric acid to strip the resins. The only known significant difference between the two sets of tests is that the work of Zainol & Nicol was done upflow at 2 BV / h, while this work was done downflow at 10 BV/hr, due to the small resin volumes used in the loading tests (5 mL).

To determine if the difference in flow rates was the source of the discrepancy, 20 mL of the IRC748 and 20 mL of the TP207 were loaded at 2500 ppm nickel. The resins were then
stripped at 2 BV/hr, downflow. Results are displayed in Figure 4.11, along with the stripping curves for these resins generated at 10 BV/h.

![Figure 4.11: Effect of Stripping Flowrate on IRC78 and TP207 (500-600 Micron)](image)

*Figure 4.11: Effect of Stripping Flowrate on IRC78 and TP207 (500-600 Micron)*

*Iminodiacetic Chelating Resins, pH 4, 30°C*

As one might expect, Figure 4.11 shows that at 2 BV/h both resins stripped with less acid than at 10 BV/h. The rate of stripping for the two resins appeared to be approximately the same at 2 BV/h. Of note, is that for the TP207, the amount of resin stripped before the acid hold step is the same at 2 BV/h and 10 BV/h. This suggests that if this resin is used in an RIP application, it will either be returned to the loading tanks after incomplete stripping or a long acid hold step to fully strip the resin will be required. The implication of this on circuit performance will be explored in Section 12.6.4.

Perhaps part of the reason Zainol & Nicol noticed fastest stripping kinetics in the IRC748 was due to the size of the resin beads. In their work, resin beads were tested in the +600 -1000 µm
size fraction, based on the larger sodium form of the resins. Based on the size analysis presented in Table 1 of their work, 94% of the IRC748 resin beads tested would have been in the smaller portion of this size fraction (+600 - 710 μm). However, for the S930 only 49% were present in the smaller portion of the size fraction, and for the TP207 only 46% were present in the smaller portion of the size fraction. Since approximately half of the resin beads tested for the S930 and TP207 were in the larger (+710 - 1000 μm) portion of this size fraction, it is not surprising that the smaller IRC748 beads exhibited faster stripping.

Cumulative stripping curves for resins in the 710 – 850 micron size range are displayed in Figure 4.12.

**Figure 4.12: Cumulative Nickel Stripped from 710 – 850 Micron Beads**

*Iminodiacetic Chelating Resins, pH 4, 30°C*
Results in Figure 4.12 are generally in agreement with those previously reported in Figure 4.10. Once again a significant portion of nickel was observed to have been difficult to strip and required an acid hold step.

Cumulative stripping curves for the 1000 – 1180 micron size fraction are displayed in Figure 4.13. Note that there is a duplicate strip curve for the S930+/4888 resin, illustrating repeatability of this method. There is no duplicate strip curve for the XE818 resin, as the strip of the first load test was collected in a single flask and assayed using the procedures for the resins loaded at 500 ppm nickel to ensure both methods were yielding similar results.

**Figure 4.13: Cumulative Nickel Stripped from 1000 – 1180 Micron Beads**
*Iminodiacetic Chelating Resins, pH 4, 30°C*
4.4 CONCLUSIONS FROM RESIN COMPARISON

Loading rate and stripping rates of several large bead ion exchange resins designed for base metals RIP circuits have been compared. Each of the three new RIP grade resins excels in at least one area.

In terms of size, the large bead resin with the largest size distribution is the Ambersep XE818. The Purolite S930+/4888 resin is slightly smaller, while the Lewatit MonoPlus TP207XL is a significantly smaller product. The Ambersep XE818 also exhibits the smallest change in bulk volume during conversion from sodium to hydrogen form.

The large bead resin with the largest capacity is the Purolite S930+/4888. The Lewatit MonoPlus TP207XL resin has a slightly lower capacity, while the Ambersep XE818 has a significantly lower capacity.

The large bead resin with the fastest loading rate is the Lewatit MonoPlus TP207XL. This resin also has the tightest size distribution of resin bead diameters.

4.5 SELECTION OF RESIN FOR FURTHER WORK

The Lanxess Lewatit MonoPlus resins were selected for use in the remainder of this thesis. The rationale for this choice is that the MonoPlus resins have a narrow size distribution. Since resin bead diameter is known to have a significant impact on loading rates, using a resin with a narrow size distribution will allow for a better evaluation of other parameters impacting the system.
In order to develop an engineering model for RIP circuit design, it is important to have an understanding of the rate limiting mechanisms present in the system. As mentioned in Section 2.1.2, the three possible rate-limiting steps for ion exchange loading are: film diffusion, intraparticle diffusion, or the ion exchange process itself. Furthermore, intraparticle diffusion can be subdivided into two different processes. In the first case, a diffusion gradient exists across the resin bead, and intraparticle diffusion can be described using Vermeulen’s Approximation to the infinite series solution of the Nernst-Planck equation. In the second case, a sharp boundary exists within the resin bead where an unreacted core is surrounded by a shell of fully loaded resin.

Being aware of the rate-limiting step (or steps if under some form of mixed control) will help in the selection of the appropriate engineering model. However, it should be noted that the rate-limiting step may change as the resin bead loads. For example, all ion exchange processes start out film diffusion limited, although sometimes for only a very short (and hence negligible) period of time.

There are a number of experiments that can be conducted to qualitatively identify rate limiting steps. First of all, from the form of Equations 2.9, 2.14, and 2.18, it is clear that resin bead diameter plays an important role in loading rates when loading is diffusion controlled. For the case of film diffusion, loading rate is proportional to the resin bead diameter, whereas for both types of intraparticle diffusion, loading rate is proportional to the square of the resin bead diameter.

The concentration of the ion to be loaded in the bulk solution also has an impact on loading rate. This is true for all cases, except for the intraparticle diffusion described by Vermeulen’s Approximation.

Loading rate can also be affected by the rate of agitation. When the loading rate is film diffusion controlled, increasing the agitation rate can increase the rate of loading. Note that this only holds for a certain range, as there is an upper limit to the effect of agitation in the film diffusion limited regime. Increasing the agitation rate has no effect when the resin is being controlled by intraparticle diffusion or the exchange rate.
The interruption test is helpful for identifying processes that are intraparticle diffusion controlled. In an interruption test, the resin beads are separated from the solution mid-way through a test, left apart for a length of time, and then reintroduced to the solution. If a discontinuity is observed in the loading rate curve, then intraparticle diffusion is playing a significant role in the system.

The rate of complex formation / rate of ligand exchange could also be rate limiting. How the various parameters affect loading rate under the different rate-controlling regimes are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>Increasing Parameter</th>
<th>Film Diffusion</th>
<th>Intraparticle Diffusion (Vermeulen)</th>
<th>Shrinking Core Intraparticle Diffusion</th>
<th>Exchange Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin Bead Diameter: $d_p$</td>
<td>Rate $\propto d_p$</td>
<td>Rate $\propto d_p^2$</td>
<td>Rate $\propto d_p^2$</td>
<td>No Effect</td>
</tr>
<tr>
<td>Bulk Solution Concentration [M]</td>
<td>Increases</td>
<td>No Effect</td>
<td>Increases</td>
<td>Increases</td>
</tr>
<tr>
<td>Agitation Rate</td>
<td>Increases to a point</td>
<td>No Effect</td>
<td>No Effect</td>
<td>No Effect</td>
</tr>
<tr>
<td>Interruption Test</td>
<td>No Effect</td>
<td>Discontinuity</td>
<td>Discontinuity</td>
<td>No Effect</td>
</tr>
<tr>
<td>Rate of Complex Formation</td>
<td>No Effect</td>
<td>No Effect</td>
<td>No Effect</td>
<td>Increases</td>
</tr>
</tbody>
</table>

It has already been shown in Figure 3.4 that increasing the agitation rate from 300 to 450 RPM had no effect at a feed concentration of 250 ppm nickel. The effect of resin bead diameter, solution concentration, an interruption test, and the rate of complex formation on loading rate will each be discussed in turn.
5.1 EFFECT OF RESIN BEAD DIAMETER ON LOADING RATE

To determine the effect of resin bead diameter on loading rate, the Lewatit TP207 resin was used, since the MonoPlus products have such a narrow size distribution. Loading tests were conducted at 250 ppm nickel for the +500/-600, +600/-710, +710/-850, +850/-1000, and +1000/-1180 micron size fractions. Results showing the rate of loading are displayed in Figure 5.1.

As expected, the larger resin beads load more slowly than the smaller ones. However, Figure 5.1 also demonstrates that the final loading value for the large resin beads is significantly less than for the smaller resin beads. To ensure that this was not simply due to the fact that the larger resin beads did not have enough time to reach equilibrium, the test on the +710 -850 μm size fraction was run for 36 hours. During this extended run, the loading curve was observed to
level off at a value of 55 g Ni / L Resin—a value significantly lower than the observed loading of 60 g Ni / L Resin for the +500 – 600 μm size fraction at 20 hours.

The fact that the final capacity varies with resin bead diameter suggests that the large resin beads do not contain as high a concentration of functional groups as the small beads. Furthermore, it implies that the distribution of functional groups within a resin bead is not uniform, and that the outer surface of the bead may contain a higher concentration of functional groups than the centre of the bead. This is likely caused by the fact that the functionalization reagents need to diffuse into the bead during the manufacturing process. If such a diffusion process is intraparticle diffusion limited, it makes sense that the smaller beads contain a higher concentration of functional groups.

This raises a few practical issues of interest for RIP applications. Since RIP requires large beads to allow for the separation of pulp and slurry, these results highlight the fact that tests need to be conducted on only the portion of the beads that will be used. If scoping tests are conducted using the full size distribution of the resin, results could well overpredict the operating capacity of the resin being tested. Furthermore, it also suggests that variations in the size distribution during the resin manufacturing process could result in lot to lot variations in the operating capacity of the large bead fraction of the resin that will be used for RIP.

As was mentioned in Table 5.1, the loading rate is proportional to the resin bead diameter in film diffusion limited processes; it is proportional to the square of the resin bead diameter in intraparticle limited processes; and it is independent of the resin bead diameter in ion exchange limited processes. In order to determine the dependence of loading rate on particle diameter, the time required for each size fraction to reach a loading of 10, 15, 20, 25, 30, 35, 40, and 45 g Ni / L Resin was determined. To normalize the data, the time required to reach the target loading for each size fraction was divided by the time required for the 555 μm size fraction to reach the same target loading. This normalized loading time was plotted against the effective bead diameter (from Table 4.1) in Figure 5.2.
The power law fit to the data in Figure 5.2 suggests that the dependence of loading rate on particle diameter is best fit by raising $d_p$ to the 1.8 power. Note that there is a significant amount of spread in the results for the different final target loadings at the large bead diameters. To get a sense on the bounds, a power law was fit to the data at 10 g Ni/L Resin and at 45 g Ni/L Resin. Results from these fits yielded a fit of $d_p$ to the 1.5 power at 10 g Ni/L Resin, and a fit of $d_p$ to the 2.6 power at 10 g Ni/L Resin. Although there is a significant spread in the data (likely caused by the fact that the final capacity is also a function of resin bead diameter), these results suggest that intraparticle diffusion is the dominant process in the system being studied.
5.2 Effect of Bulk Solution Concentration on Loading Rate

To determine if solution concentration affects loading rate, a series of loading tests on the TP207MP resin were carried out at 50, 100, 250, 500, 1000, 2500, and 5000 ppm nickel. In order to better be able to see the various curves, results were filtered and only every 25th data point was plotted in Figure 5.3. Results clearly show that solution concentration has a significant effect on the overall loading rate. Thus, the loading rate is dependent on more than just the intraparticle diffusion process described by Vermeulen’s Approximation.

![Figure 5.3: Effect of Solution Concentration on Nickel Loading Rate](image)

**TP207MP**

<table>
<thead>
<tr>
<th>Feed Conc ppm Ni</th>
<th>Loaded g Ni / L R</th>
<th>Stripped g Ni / L R</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>49.0</td>
<td>50.1</td>
</tr>
<tr>
<td>100</td>
<td>52.0</td>
<td>47.6*</td>
</tr>
<tr>
<td>250</td>
<td>53.4</td>
<td>50.8*</td>
</tr>
<tr>
<td>500</td>
<td>55.6</td>
<td>54.8</td>
</tr>
<tr>
<td>1000</td>
<td>55.4</td>
<td>53.2*</td>
</tr>
<tr>
<td>2500</td>
<td>56.2</td>
<td>55.1</td>
</tr>
<tr>
<td>5000</td>
<td>57.7</td>
<td>59.2</td>
</tr>
</tbody>
</table>

*indicates sample without 20 hour acid hold step

5.3 Interruption Test

The interruption test started as a typical test at 250 ppm nickel; however, after one hour the resin was separated from the test solution using a 425 micron screen. The test solution was placed in a refrigerator for 68 hours, while the resin was kept in a sample vial at room
temperature. To resume the test, the solution was first placed in the hot water bath, heated to 30°C, and then the resin was reintroduced to the solution. Results are displayed in Figure 5.4, along with the baseline for 250 ppm. This figure clearly shows a discontinuity at 1 hour, confirming that intraparticle diffusion plays a significant role in this system.

**Figure 5.4: Interruption Test - 68 Hour Interruption After One Hour of Loading**

*TP207MP Resin, 250 ppm Nickel, pH 4, 30°C*

### 5.4 Effect of Complex Formation Rate

For this particular system, both the selectivity and the rate of ligand exchange are higher for copper than for nickel. Selectivity of iminodiacetic resins was discussed in Section 2.1.3, using the concept of decomplexing pH. The rate of ligand exchange for octahedral nickel complexes is typically slower than for the corresponding copper complexes. A study of the rate of exchange of water ligands from various transition metal ions showed that the exchange half-life
for nickel was on the order of $10^{-4} - 10^{-5}$ seconds; cobalt was on the order of $10^{-5} - 10^{-6}$ seconds; whereas copper was on the order of $10^{-8} - 10^{-9}$ seconds (119). Thus, running a series of tests for copper loading onto TP207MP should illustrate whether or not complex formation is affecting the overall rate of loading.

The copper loading tests were conducted at feed concentrations that would correspond to the equivalent molar concentration of the nickel feed concentrations used in Section 5.2. Results for the copper loading tests are displayed in Figure 5.5, and show that copper loaded much faster than nickel (Figure 5.3). Thus, the rate of complex formation appears to affect the overall loading rate.

![Figure 5.5: Effect of Solution Concentration on Copper Loading Rate](image)

**TP207MP Resin, pH 4, 30°C**

<table>
<thead>
<tr>
<th>Feed Conc ppm Cu</th>
<th>Loaded g Cu / L R</th>
<th>Stripped g Cu / L R</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>63.5</td>
<td>68.3</td>
</tr>
<tr>
<td>108</td>
<td>63.4</td>
<td>65.1</td>
</tr>
<tr>
<td>271</td>
<td>65.2</td>
<td>65.9</td>
</tr>
<tr>
<td>541</td>
<td>65.3</td>
<td>64.3</td>
</tr>
<tr>
<td>1082</td>
<td>66.2</td>
<td>66.4</td>
</tr>
<tr>
<td>2706</td>
<td>66.6</td>
<td>68.1</td>
</tr>
<tr>
<td>5412</td>
<td>66.6</td>
<td>69.2</td>
</tr>
</tbody>
</table>
5.5 CONCLUSIONS FROM QUALITATIVE TESTS

Results from the qualitative tests presented in this chapter, suggest that although the process must initially be film-diffusion limited, it is predominantly limited by some combination of intraparticle diffusion and exchange rate. For a fundamental loading rate model, the effect of selectivity and rate of complex formation would need to be quantified and separated from the intraparticle diffusion limitation. To separate out these effects, experiments on very small resin beads would be required to determine the fundamental kinetics of both the forward and reverse reactions at various pH values. Once the fundamental kinetics were determined, the detailed nature of the intraparticle diffusion mechanism would need to be ascertained. This would likely require isotopic tracer tests such as those previously presented for this purpose (11).

As mentioned in the literature review, such fundamental models typically require numerical solutions to partial differential equations. Such models tend to be cumbersome and overly detailed for most engineering design applications. Since the objective of this study is to develop an engineering model to quantify the effect of various parameters on an RIP circuit, such experiments are beyond the scope of the current work. To achieve the goal of developing an adequate loading rate model, the film diffusion limited regime will be defined separately from the intraparticle diffusion / exchange rate limited regime. An outline of the work necessary for developing a fundamental model can be found in the recommendations for future work.
6.0 QUANTITATIVE MODEL FOR FILM DIFFUSION COMPONENT

As previously mentioned, the rate limiting step often changes as a resin bead loads, and all exchange processes start out film diffusion limited (although sometimes for a negligible amount of time). The purpose of this chapter is to quantify the film diffusion component for the system being studied.

6.1 FILM DIFFUSION MODEL FIT

To quantify the effect of film diffusion, results from the copper and nickel tests are compared. Since the rate of diffusion across the film should be similar for the two metals, quantifying the film diffusion component of loading can be done for the region where the loading curves for the two metals overlap. The loading rates at 0.00085M (50 ppm nickel) and 0.0017M (100 ppm nickel) feed concentrations are plotted as fractional loading of resin in Figure 6.1.
Figure 6.1 shows that the two elements load at a similar rate early on, and then diverge. The engineering model most commonly applied to film diffusion limitation is the linear approach to equilibrium. This model is based on the analytical solution to isotopic exchange under infinite solution volumes and was described by Equations 2.7-2.9, repeated below:

\[
\frac{d}{dt} \langle \bar{M} \rangle = k_l ([\bar{M}]_{eqb} - \langle \bar{M} \rangle) \tag{2.7}
\]

\[
F = 1 - \exp(-k_l t) \tag{2.8}
\]

\[
k_f = \frac{6D_f[M]}{d_p \delta [M]_{max}} \tag{2.9}
\]

The linear approach to equilibrium was fitted to the first 0.2 hours of loading by adjusting the ratio of the film diffusion coefficient to the thickness of the boundary layer \((D_f/\delta)\) as a fitting parameter. The model fit \((D_f/\delta = 2.7 \times 10^{-5} \text{ m/s})\) is plotted in Figure 6.2 and shows good correlation at both 0.00085 M and 0.0017 M feed concentrations. Note how the rate of nickel loading deviates from the film diffusion model earlier than the rate of copper loading, which is in-line with the previous observations that the overall rate of nickel is much slower than the overall rate of copper loading.
6.2 THEORETICAL ESTIMATE OF FILM DIFFUSION COEFFICIENT

To confirm the validity of the fitting parameter, a rough set of diffusion calculations were performed to obtain an estimate of the film diffusion coefficient. These calculations involved estimating the Sherwood Number from the Frössling correlation for spheres, shown in Equation 6.1 (120). The various dimensionless numbers are defined in Equation 6.2, and the velocity of the particles was estimated using a large particle settling correlation (> 100 micron), shown in Equation 6.3 (121). Harriott has pointed out that using the terminal velocity is suitable for an order of magnitude estimate of the mass transfer coefficient (122). The diffusion coefficient was estimated at $8 \times 10^{-10} \text{ m}^2/\text{s}$, based on interpolation from the literature (123), and adjusted for temperature using the common correlation shown in Equation 6.4 (120).
\[ Sh = 2 + 0.6 \, Re^{1/2} \, Sc^{1/3} \]  

\[ Sh = \frac{k_m d_p}{D_f} = \frac{d_p}{\delta}; \quad Re = \frac{d_p u_p \rho}{\mu}; \quad Sc = \frac{\mu}{\rho D_f} \]  

\[ u_p = \left[ \frac{d_p^{1.6} (\rho_p - \rho)}{14 \rho^{0.4} \mu^{0.6}} \right]^{1/1.4} \]  

\[ D_{T2} = D_{T1} \frac{\mu_{T1} T_2}{\mu_{T2} T_1} \]  

Results from these calculations estimate the Sherwood Number to be approximately 23, giving an estimated film thickness of \(2 \times 10^{-3}\) cm. This is in good agreement with the observed fit parameter, which yields a film thickness of \(3 \times 10^{-3}\) cm for a diffusion coefficient of \(8 \times 10^{-10}\) m\(^2\)/s. These values are of the expected order of magnitude, reported as \(10^{-2}\) to \(10^{-3}\) cm (10). Therefore, the fit parameter was accepted as adequately representing the film diffusion component of the process.
As demonstrated during the qualitative tests, the rate of loading is predominantly controlled by some combination of intraparticle diffusion and exchange reaction. To determine whether it is possible to obtain an adequate fit to the system, four engineering models that are commonly applied to ion exchange systems were fitted to the data.

The four models evaluated were the linear approach to equilibrium, the quadratic approach to equilibrium, the shrinking core model, and the pseudo-second order reaction. Each of these models are fitted to the data for the loading of nickel onto TP207MP, presented in Figure 5.3, using the estimated resin bead diameter reported in Table 4.1. To obtain the fit parameters, the sum of the absolute values of the difference between the observed values and the model predictions was minimized.

Since many of the engineering models are written in terms of fractional approach to equilibrium, the nickel loading isotherm must first be defined. To achieve this, the final loading values obtained in each of the nickel loading tests were used. To describe the isotherm, the resin capacity and the selectivity coefficient, K, were taken as fitting parameters for the mass action law. Figure 7.1 displays the isotherm fit (K = 9.8 x 10^-5, capacity = 1.97 eq/L), drawn on a semi-log plot.
7.1.1 Linear Approach to Equilibrium

The linear approach to equilibrium is known to give a poor fit to intraparticle diffusion, but it is frequently selected over other models due to ease of application. Gluckauf and Coates first proposed applying the linear approach to equilibrium to intraparticle diffusion (21). Their model was described in Equations 2.7 – 2.9, which are repeated here. Note that the shape factor, $\eta$, is $< 0.5$.

\[
\frac{d}{dt} [\bar{M}] = k ([\bar{M}]_{eqb} - [\bar{M}]) \tag{2.7}
\]

\[
F = 1 - \exp(-k_1 t) \tag{2.8}
\]

\[
k_1 = k_g = \frac{D_p}{\eta d_p^2} \tag{2.9}
\]
The linear approach to equilibrium was fitted to three individual tests: 50, 500, and 5000 ppm nickel. The equilibrium loading values ([M]_{eqb}) at each concentration were based on the isotherm displayed in Figure 7.1, and the $k_l$ value adjusted to minimize the absolute value of the error between predicted and observed values. The individual model fits of the linear approach to equilibrium to the observed data are displayed in Figure 7.2, and the best fit parameters of the $k_l$ parameter are tabulated as an inset to this graph.

![Figure 7.2: Linear Approach to Equilibrium Fit to Individual Loading Curves](image)

**Figure 7.2: Linear Approach to Equilibrium Fit to Individual Loading Curves**

*Nickel Loading onto TP207MP at pH 4, 30°C, and constant nickel concentration*

Based on this figure, the linear approach to equilibrium provides a good fit at 50 ppm nickel, but the fit of the curve shape becomes poorer as the solution concentration of nickel increases. Furthermore, the inset table shows that the fitting parameter is not constant, but varies with the solution concentration. This suggests that the linear approach to equilibrium can not adequately model the full dataset.
7.1.2 **Vermeulen’s Quadratic Approach to Equilibrium**

As mentioned in the literature review, the exact solution to the differential equations for the case of infinite solution volume and constant diffusivities is the infinite series of Equation 2.10 (22), which can be approximated by Vermeulen’s Approximation, described in Equations 2.11 – 2.14 (23).

\[
F = 1 - \frac{6}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp \left( \frac{-4D_p \pi^2 j^2 t}{d_p^2} \right) \tag{2.10}
\]

\[
\frac{d}{dt} \left[ \bar{M} \right] = \frac{2k_v (\bar{M}_{eqb}^2 - \bar{M}^2)}{\bar{M}} \tag{2.11}
\]

\[
t = \frac{-1}{4k_v} \ln \left( \frac{[\bar{M}]_{eqb}^2 \bar{M}^2}{[\bar{M}]_{eqb}^2} \right) \tag{2.12}
\]

\[
F = \sqrt{1 - \exp \{-4k_v t\}} \tag{2.13}
\]

\[
k_v = \frac{\pi^2 D_p}{d_p^2} \tag{2.14}
\]

In order to determine whether or not Vermeulen’s approximation to the infinite series was adequate for modeling this system, both models were fitted to the curve generated at 250 ppm nickel, using the same fitted diffusion coefficient for both models. Figure 7.3 displays these results and demonstrates that the simpler Vermeulen approximation is adequate for describing this type of intraparticle diffusion.
Figure 7.3: Comparison of Vermeulen’s Approximation and Boyd’s Exact Solution

Nickel Loading onto TP207MP at pH 4, 30°C, 250 ppm Ni

Figure 7.4 displays the individual curve fits for Vermeulen’s quadratic approach to equilibrium for tests run at 50, 500, and 5000 ppm nickel. As before, the equilibrium resin loadings were taken from the isotherm generated in Figure 7.1, and the effective diffusion coefficient in the resin bead, $D_p$, was adjusted as a fitting parameter to each individual curve.

Fit parameter:

$$D_p = 8.9 \times 10^{-13} \text{ m}^2/\text{s}$$
Once again the fitted effective intraparticle diffusion coefficient, $D_p$, varies from test to test, suggesting that the Vermeulen model is not adequately describing the effect of solution concentration on nickel loading rate. However, the profile of the loading curves do match the shape of the Vermeulen model, suggesting that the Vermeulen model should make an excellent starting point for modeling nickel loading in this system. Figure 7.5 shows the best Vermeulen fit to the full set of test results, using only a single effective diffusion coefficient for the entire dataset. From this figure, it is clear that the Vermeulen model underpredicts the effect of solution concentration when using a single effective diffusivity coefficient ($D_p = 1.0 \times 10^{-12} \text{ m}^2/\text{s}$).
7.1.3 Shrinking Core Model

The shrinking core model was described in Chapter 2 using Equations 2.15-2.18:

\[
\frac{dF}{dt} = \frac{k_c d_c}{2(d_p - d_c)} [2.15]
\]

\[
t = \frac{1+2(1-F)-3(1-F)^{2/3}}{k_c} [2.16]
\]

\[
F = 1 - \left\{ \frac{1}{2} + \sin \left( \frac{\text{arcsin}[1-2k_c t]}{3} \right) \right\}^3 [2.17]
\]

\[
k_c = \frac{24D_s[M]}{d_p^2[M]_{\text{max}}} [2.18]
\]
Figure 7.6 displays the best fit of the shrinking core model to the individual loading curves at 50, 500, and 5000 ppm. Once again, the equilibrium resin loading values are based on the isotherm generated in Figure 7.1, and the effective diffusion coefficient through the reacted layer, $D_s$, was adjusted as a fit parameter for each individual curve. From this figure, it can be seen that the shape of the shrinking core model predicts the data very well for the first portion of loading, but overpredicts the data as the test nears equilibrium.

![Figure 7.6: Shrinking Core Model Fit to Individual Loading Curves](image)

**Table**: Nickel Loading onto TP207MP at pH 4, 30°C, and constant nickel concentration

<table>
<thead>
<tr>
<th>ppm Ni</th>
<th>$D_s$ [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>$4.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>500</td>
<td>$6.8 \times 10^{-13}$</td>
</tr>
<tr>
<td>5000</td>
<td>$1.5 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

Once again, the best fit effective diffusion coefficient through the reacted layer, $D_s$, is not constant. Figure 7.7 shows the best simultaneous fit to all the loading curves, using only a single diffusivity coefficient. From this figure, it is clear that the shrinking core model overpredicts the effect of solution concentration when using a single diffusivity coefficient ($D_s = 2.0 \times 10^{-10}$ m²/s).
7.1.4 SECOND ORDER RATE MODEL

As mentioned in the literature review, a second order chemical reaction is often used as an analogy for ion exchange. The Thomas model, described by Equations 2.1, 2.19, and 2.20, was used to fit the data presented in this work.

\[ 2R-H + M^{2+} \rightarrow R_2-M + 2H^+ \]  \hspace{1cm} [2.1]

\[ \frac{d}{dt} [\bar{M}] = k_{fwd}[M][\bar{H}] - k_{rev}[H][\bar{M}] \]  \hspace{1cm} [2.19]

\[ \frac{d}{dt} [\bar{M}] = \{k_{fwd}[M] + 2k_{rev}[H]\} [\bar{M}] - k_{fwd}[M][\bar{M}]_{max} \]  \hspace{1cm} [2.20]
Figure 7.8 shows the second order model fitted to the individual test data at 50, 500, and 5000 ppm nickel. The final equilibrium resin loadings were based on the isotherm presented in Figure 7.1 and the two empirical rate constants, $k_{\text{fwd}}$ and $k_{\text{rev}}$, were determined by trial and error for each curve. The differential equation 2.20 was solved numerically, using a fourth-order Runge-Kutta algorithm.

![Figure 7.8 Thomas Model Fit to Individual Loading Curves](image)

**Figure 7.8 Thomas Model Fit to Individual Loading Curves**

*Nickel Loading onto TP207MP at pH 4, 30°C, and constant nickel concentration*

The shape of the Thomas model fits each individual dataset fairly well; however, when a single set of fitting parameters is used to model the various infinite solution volume tests run at different concentrations, the model overpredicts the system's dependence on solution concentration. This is illustrated in Figure 7.9, where the best fitting parameters to the entire dataset are plotted.
While it is possible to debate ad infinitum the best analogous chemical reaction model for ion exchange systems, it is doubtful that any model with integer coefficients would be able to fit the range of solution concentrations in this work. As was seen by the Vermeulen model, if the rate of loading is independent of nickel concentration (i.e. rate proportional to $[\text{Ni}]^0$), the family of curves will be too close together to represent the dataset for tests run at 50 – 5000 ppm nickel. On the other hand, the Shrinking Core model demonstrated that if the rate of loading is linearly dependent on nickel concentration (i.e. rate proportional to $[\text{Ni}]^1$), the family of curves will be spread too far apart to represent the dataset for tests run at 50 – 5000 ppm nickel.
7.2 Development of Hybrid Correlation

Since none of the standard engineering models used for ion exchange were able to adequately describe the system for the full range of concentration, a new correlation was developed. The approach taken to address the fact that the dependence of this system on solution concentration lies somewhere between $[\text{Ni}]^0$ and $[\text{Ni}]^1$ was to develop a hybrid correlation that combines the Vermeulen ($[\text{Ni}]^0$) and Shrinking Core ($[\text{Ni}]^1$) models. These models were chosen as the starting point for the hybrid correlation, in lieu of the second order rate analogy, because they both have relatively simple analytical solutions. Note that the physical significance of the various fit parameters in the hybrid correlation will be explored in Section 8.2.

Mathematically, the two models appear to be quite different, but both appear to fit the data quite well for the first portion of the loading curve. Therefore, an attempt was made to see whether or not a correlation between the two constants, $k_v$ and $k_c$, could be made that minimizes the error between the two models. It was found that the error is minimized when $k_v = 0.667 k_c$. Given that the Vermeulen model better fit the observed nickel loading data, it was decided that it would be better to approximate the Shrinking Core Model by a Vermeulen expression, rather than the other way around.

Figure 7.10 displays the shrinking core model as open circles for $k_c$ values of 0.05, 0.01, 0.005, 0.002, 0.001, 0.0005, and 0.0001. Lines corresponding to the best approximation of the Vermeulen model to these points (i.e. $k_v = 0.667 k_c$) are also drawn in. This graph shows good agreement between the two models up to a fractional conversion of 0.8, at which point the shrinking core model predicts higher values than the Vermeulen model. Since the Vermeulen approximation is underpredicting the shrinking core model, the approximation should result in conservative predictions if it were ever applied to a situation which followed true shrinking core behaviour.
Figure 7.10: Using Vermeulen Model to Approximate Shrinking Core Model

To combine the Vermeulen model and the Vermeulen approximation to the Shrinking Core model into a single hybrid correlation, a second fit parameter, $\alpha$, was introduced. The various constants in the expression were combined in such a way that as $\alpha \to 0$, the correlation becomes the Vermeulen model, and as $\alpha \to 1$, the correlation becomes the Vermeulen approximation to the shrinking core model.

The hybrid correlation results in a new constant, $k_h$ (Equation 7.1), which can then be used in the standard Vermeulen model to create the hybrid correlation. Note that $k_h$, like $k_f$ and $k_c$, varies with solution concentration.

$$k_h = \frac{\pi^2 D_{app}}{d_p^2} \left( \frac{16[M]}{\pi^2[M]_{max}} \right)^\alpha$$  \[7.1\]
The analytical solution to the Vermeulen model, using $k_h$ in lieu of $k_v$ is displayed in Equation 7.2. The steps used to derive the new constant are tabulated in Table 7.1.

$$F = \sqrt{1-\exp\{-4k_h t\}}$$  \[7.2\]

### Table 7.1: Development of Hybrid Correlation Equation

<table>
<thead>
<tr>
<th>Model</th>
<th>Standard Vermeulen</th>
<th>Vermeulen Approx to Shrinking Core</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>$k_v = \frac{\pi^2 D_p}{d_p^2}$</td>
<td>$k_v \approx \frac{2}{3} k_c$; $k_c = \frac{24D_s[M]}{d_p^2 [\bar{M}]_{max}}$</td>
</tr>
<tr>
<td>$F = \sqrt{1-\exp\left(\frac{-4\pi^2 D_p t}{d_p^2}\right)}$</td>
<td>$\sqrt{1-\exp\left(\frac{-4*\frac{2}{3}*24D_s[M]t}{[M]_{max} d_p^2}\right)}$</td>
<td></td>
</tr>
<tr>
<td>Collecting constants and pulling out $4\pi^2$</td>
<td>$\sqrt{1-\exp\left(\frac{4*\frac{\pi^2}{\pi^2} * 16(D_s[M]) t}{[\bar{M}]_{max} d_p^2}\right)}$</td>
<td></td>
</tr>
<tr>
<td>Hybrid Correlation</td>
<td>$\sqrt{1-\exp\left(\frac{4\pi^2 D_{\text{app}} \left(\frac{16 * [M]}{[\bar{M}]_{max}}\right)^\alpha}{d_p^2}\right)}$</td>
<td></td>
</tr>
<tr>
<td>Simplifying</td>
<td>$F = \sqrt{1-\exp(-4k_h t)}$, $k_h = \frac{\pi^2 D_{\text{app}}}{d_p^2} \left(\frac{16 [M]}{\pi^2 [\bar{M}]_{max}}\right)^\alpha$</td>
<td></td>
</tr>
</tbody>
</table>

The hybrid correlation was fitted to the set of curves in Figure 7.11. In this figure, the final resin loadings are all based on the isotherm presented in Figure 7.1, and both $D_{\text{app}}$ and $\alpha$ were adjusted as fitting parameters.
Figure 7.11 suggests that the hybrid correlation is able to adequately describe the set of curves, using the following fit parameters: \(D_{\text{app}} = 3.9 \times 10^{-12} \text{ m}^2/\text{s}, \alpha = 0.28\). The following chapter will investigate whether the hybrid correlation can be applied to the loading of nickel onto another iminodiacetic resin or to the loading of metals other than nickel. Once this has been explored, the significance of the two fit parameters can be discussed.
8.0 APPLICATION OF HYBRID CORRELATION TO OTHER BATCH SYSTEMS

In order to ensure that the hybrid correlation is flexible enough to be able to accommodate more than one set of conditions, it was fitted to several additional datasets. This also generates sufficient data to begin to understand the significance of the various fitting parameters.

8.1 FITTING THE HYBRID CORRELATION TO ADDITIONAL DATA SETS

The hybrid correlation was fitted to nickel loading onto TP207 and two lots of TP207XL (lot CHC 5034, which was used in the resin comparison and lot CHE 50019, which was used in the RIP miniplant –see Chapter 10). It is also fitted to cobalt and copper loading onto TP207MP, and to copper loading onto TP207XL (lot CHE 50019).

For each of these datasets, the equilibrium isotherm was first modeled using the mass action law, and then the predicted equilibrium values were used with the hybrid correlation. The full set of loading isotherms can be found in Appendix C.

Since TP207XL is considered a large bead version of TP207MP, a single selectivity coefficient, $K$, was used for the set of isotherms, but the resin capacity was left as a fitting parameter for each dataset. For loading of the various metals onto TP207MP, it was found that a single resin capacity value was insufficient to generate a good fit to the data. Therefore, the resin capacity was left as a fitting parameter for each individual dataset. It is interesting to note that the slight variation in resin capacity follows the resin selectivity: Cu > Ni > Co. Table 8.1 displays the isotherm model parameters from the various datasets.

<table>
<thead>
<tr>
<th>Resin</th>
<th>TP207</th>
<th>TP207XL CHC5034</th>
<th>TP207XL CHE50019</th>
<th>TP207MP</th>
<th>TP207MP</th>
<th>TP207MP</th>
<th>TP207XL CHE50019</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Ni</td>
<td>Ni</td>
<td>Ni</td>
<td>Ni</td>
<td>Co</td>
<td>Cu</td>
<td>Cu</td>
</tr>
<tr>
<td>$K$</td>
<td>$3.9 \times 10^{-5}$</td>
<td>$9.8 \times 10^{-5}$</td>
<td>$5.0 \times 10^{-5}$</td>
<td>$7.5 \times 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity [eq/L]</td>
<td>2.12</td>
<td>2.01</td>
<td>2.36</td>
<td>1.97</td>
<td>1.91</td>
<td>2.11</td>
<td>2.50</td>
</tr>
</tbody>
</table>
8.1.1 Nickel Loading onto TP207

A series of nickel loading tests were carried out on the +710 – 850 micron size fraction of the TP207 resin. The best fit parameters for this data set were $\alpha = 0.28$, and $D_{\text{app}} = 2.7 \times 10^{-12}$ m$^2$/s. Test results and the fit of the hybrid correlation can be found in Figure 8.1.

The hybrid correlation appears to fit reasonably well to this dataset. The fitting parameter $D_{\text{app}}$ is lower for TP207 than was found for the TP207MP resin. This makes sense since the TP207MP resin has been reported to have a porosity of 44%, while the TP207 resin’s porosity is reported to be 36% (118).
8.1.2 Nickel Loading onto TP207XL (Lot CHC 5034 – Resin Comparison)

The lot of TP207XL used in the resin comparison work reported in Chapter 4 (Lot CHC 5034) was evaluated at the +710 -850 micron size fraction for the full range of nickel feed concentrations. The fitting parameters for this data set were $\alpha = 0.32$, and $D_{app} = 4.5 \times 10^{-12}$ m$^2$/s. Test results and the fit of the hybrid correlation can be found in Figure 8.2.

Once again, the hybrid correlation was found to fit the data set quite well.

**Figure 8.2: Hybrid Correlation Fit to Nickel Loading onto TP207XL, Lot CHC 5034**

$pH$ 4, $30^\circ$C, constant nickel concentration

Once again, the hybrid correlation was found to fit the data set quite well.
8.1.3 Nickel Loading onto TP207XL (Lot CHE 50019 – Miniplant)

A second lot of TP207XL resin (lot CHE 50019) was also evaluated for the full range of nickel feed concentrations at the +710 -850 micron size fraction. This lot was ordered for use in the RIP miniplant (see Chapter 10). The fitting parameters for this data set were $\alpha = 0.36$, and $D_{\text{app}} = 4.4 \times 10^{-12} \text{ m}^2/\text{s}$. Test results and the fit of the hybrid correlation can be found in Figure 8.3.

![Figure 8.3: Hybrid Correlation Fit to Nickel Loading onto TP207XL, Lot CHE 50019](image)

The hybrid correlation was shown to provide an adequate fit to this data set. It is interesting to note that the best fit parameters for the two lots of TP207XL were different, particularly in the case of the reported alpha values. The principal difference in these two lots is their total capacities (2.36 for CHE 50019 vs. 2.11 for CHC 5034).
8.1.4 Cobalt Loading onto TP207MP

A series of cobalt loading tests were done on the +500 – 600 micron size fraction of the TP207MP resin. The best fit parameters for this data set were alpha = 0.25, and $D_{\text{app}} = 4.2 \times 10^{-12} \text{ m}^2/\text{s}$. Test results and the fit of the hybrid correlation can be found in Figure 8.4.

Once again, the hybrid correlation was shown to fit the data set quite well. The fit parameters for nickel and cobalt for this resin are quite similar; although, the cobalt alpha value (0.25) is slightly lower than the nickel alpha value (0.28).
8.1.5 Copper Loading onto TP207MP

The +500 – 600 micron size fraction of the TP207MP resin was also evaluated for copper loading. Loading was much faster with copper and the best fit parameters for this data set were $\alpha = 0.62$, and $D_{\text{app}} = 3.7 \times 10^{-11}$ m$^2$/s. Test results and the fit of the hybrid correlation for the first 12 hours of loading can be found in Figure 8.5.

![Figure 8.5: Hybrid Correlation Fit to Copper Loading onto TP207MP](image)

The hybrid correlation was found to fit copper loading quite well. It is very interesting to note that the fit parameters for copper loading differ significantly different from those for nickel and cobalt loading. The apparent diffusivity, $D_{\text{app}}$, is an order of magnitude larger, and the alpha fit parameter is approximately double what was reported for nickel and cobalt.
A series of copper loading tests were done on the +710 – 850 micron size fraction of the TP207XL resin, lot CHE 50019 (RIP miniplant). Note that due to the high capacity of this resin, only 4.4 mL of resin were used per test, in lieu of the typical 5 mL resin per test. The best fit parameters for this data set were \( \alpha = 0.62 \), and \( D_{\text{app}} = 2.8 \times 10^{-11} \text{ m}^2/\text{s} \). Test results and the fit of the hybrid correlation can be found in Figure 8.6.

The hybrid correlation was shown to fit the data set reasonably well. The fitting parameters for copper loading onto TP207XL are similar to the fitting parameters reported for copper loading onto TP207MP.
8.2 Physical Significance of Hybrid Correlation Fit Parameters

Ideally, even in the case of empirical correlations, the various fit parameters should trend with experimental observations, in order to allow one to estimate coefficients for similar systems. Table 8.2 displays the empirical fit parameters for the various systems studied.

Table 8.2: Summary of Hybrid Fit Parameters

<table>
<thead>
<tr>
<th>Resin</th>
<th>Metal</th>
<th>$D_{\text{app}}$ [m$^2$/s]</th>
<th>Alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP207MP</td>
<td>Cobalt</td>
<td>$4.2 \times 10^{-12}$</td>
<td>0.25</td>
</tr>
<tr>
<td>TP207 (+710 -850um)</td>
<td>Nickel</td>
<td>$2.7 \times 10^{-12}$</td>
<td>0.28</td>
</tr>
<tr>
<td>TP207MP</td>
<td>Nickel</td>
<td>$3.9 \times 10^{-12}$</td>
<td>0.28</td>
</tr>
<tr>
<td>TP207XL (CHC 5034)</td>
<td>Nickel</td>
<td>$4.5 \times 10^{-12}$</td>
<td>0.32</td>
</tr>
<tr>
<td>TP207XL (CHE 50019)</td>
<td>Nickel</td>
<td>$4.4 \times 10^{-12}$</td>
<td>0.36</td>
</tr>
<tr>
<td>TP207MP</td>
<td>Copper</td>
<td>$37 \times 10^{-12}$</td>
<td>0.62</td>
</tr>
<tr>
<td>TP207XL (CHE 50019)</td>
<td>Copper</td>
<td>$28 \times 10^{-12}$</td>
<td>0.62</td>
</tr>
</tbody>
</table>

8.2.1 Apparent Diffusivity

The first fit parameter, $D_{\text{app}}$, trends well with the rate of loading. From the experimental observations, the rate of loading onto TP207MP can be described as Cu > Ni ~ Co; which matches the magnitudes of the $D_{\text{app}}$ values. Furthermore, the resin comparison work for nickel in the +710 -850 micron size range showed that TP207XL > TP207, which is also reflected in the magnitude of the $D_{\text{app}}$ values. Comparing the nickel $D_{\text{app}}$ for the two lots of TP207XL suggests that for a given resin, $D_{\text{app}}$ is only accurate to one significant figure (i.e. $D_{\text{app}} = 4 +/- 1$ m$^2$/s).

To check whether the apparent diffusivities are of the correct order of magnitude, they were compared to resin diffusivities published in the literature. As a rule of thumb, diffusivities in non-selective ion exchangers, compared to diffusivities in water, are typically 1/10 for monovalent ions, 1/100 for divalent ions, and 1/1000 for trivalent ions (30). Diffusion coefficients for copper and nickel in water are reported as being of the order of $10^{-10}$ m$^2$/s (123), suggesting intraparticle diffusivities of the order of $10^{-12}$ m$^2$/s. In the case of copper and cobalt
loading onto the old Dowex A1 iminodiacetic chelating resin, self diffusion coefficients of 9.78 \times 10^{-12} \text{m}^2/\text{s} for copper, and 3.93 \times 10^{-12} \text{m}^2/\text{s} for cobalt are reported (9). While a self-diffusion coefficient for nickel loading onto an iminodiacetic resin was not found in the literature, nickel loading onto a macroporous aminophosphonic chelating resin was reported as 1.92 \times 10^{-13} \text{m}^2/\text{s} in the gel phase, and 6.35 \times 10^{-11} \text{m}^2/\text{s} in the internal pores, resulting in an overall effective diffusivity of 1.63 \times 10^{-12} \text{m}^2/\text{s} (12). Consequently, the empirical apparent diffusivity values (10^{-11} – 10^{-12} \text{m}^2/\text{s}), obtained with this correlation appear to at least be of the right order of magnitude.

### 8.2.2 Alpha

The second empirical fit parameter, \(\alpha\), can be considered a measure of how sharp a boundary exists between the loaded and unloaded portion of the ion exchanger. As \(\alpha\) approaches 1, the resin should be loading in a shrinking core fashion, whereas, when \(\alpha\) approaches 0, the resin should be loading in a Vermeulen intraparticle diffusion fashion. This means that it is reasonable to expect that a much sharper boundary would exist in systems with a high \(\alpha\) value.

To test this hypothesis, TP207MP beads were loaded to approximately 1 eq/L (50% capacity) with each metal from 0.0085M solutions (500 ppm nickel, 502 ppm cobalt, and 541 ppm copper). The resin was removed from the test solution, mounted using a rapid cold cure acrylic mount (Lecoset 100), polished to approximately 27 microns, and observed under an optical microscope to view whether or not a sharp boundary was present. Note that the time from removing the resin from solution to the time the resin was observed under the microscope was on the order of an hour.

Figure 8.7 shows photographs of the three resin beads loaded to 1 eq/L. Note that no boundary or gradient is visible for nickel or cobalt (under the microscope the beads simply had a greenish or pinkish hue), but that a clear ring can be seen for copper (strong blue ring could even be seen without any magnification). This is in agreement to what one would expect based on the values of the fit parameter \(\alpha\). It is interesting to note that the decomplexing pH for copper (1.0) is significantly lower than for nickel (2.1) or cobalt (2.6), as previously mentioned in Chapter 2 (32). Further work would be required to determine if a relationship exists between the decomplexing pH and the fit parameter \(\alpha\).
8.2.3 Qualitative Evaluation of Effect of pH on Alpha

To determine if the operating pH affects the fitting parameter $\alpha$, copper was loaded at pH 2 and pH 3 under semi-constant solution concentrations of 5412 ppm, 541 ppm, and 54 ppm. It should be noted that the pH controller used was factory set to turn on at 0.1 pH units below the set point and to turn off at 0.1 pH units above the set point. Because the copper stock solution is being added with the sodium hydroxide used to maintain constant pH, tests at lower pH values had larger swings in beaker copper concentration. At pH 3, the Jenco controller was used to maintain pH in the test beaker; however, at pH 2, the feed pump was manually turned on at a pH read-out of 1.99 and turned off at a pH read-out of 2.01. Additionally, the pH unit’s accuracy is only +/- 0.02 pH units, so additional noise in mass balances is expected at lower pH values. Therefore, these tests at lower pH are reported merely for qualitative purposes, not quantitative purposes. A summary of how test parameters were affected based on the target pH is presented in Table 8.3; data on observed solution concentrations and mass balances can be found in Appendix D.
To see if lowering the solution pH had a dramatic effect on the alpha parameter, the hybrid model was fit to the three datasets at pH 2 and 3. Since tests were only run at three solution concentrations, insufficient data was available to generate isotherms, and so the observed final resin loading was taken as the equilibrium loading. The one exception to this was the 54 ppm test at pH 2, where the equilibrium loading was allowed to vary as a fitting parameter since the resin had not reached equilibrium when the test was stopped.

The observed loading rates and best fit hybrid correlation curves are plotted in Figure 8.8. The top plot corresponds to tests at pH 4, the plot on the bottom left corresponds to tests at pH 3, and the plot on the bottom right corresponds to tests run at pH 2. In these curves, note how the final copper loading values drop significantly as the pH decreases.

![Table 8.3: Effect of Target pH on Test Conditions](image)

<table>
<thead>
<tr>
<th>Test pH</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Controller on/off</td>
<td>1.99 / 2.01</td>
<td>2.90 / 3.10</td>
<td>3.90 / 4.10</td>
</tr>
<tr>
<td>Corresponding variation in [Cu]</td>
<td>+/- 7 ppm</td>
<td>+/- 8 ppm</td>
<td>+/- 1 ppm</td>
</tr>
<tr>
<td>pH unit accuracy</td>
<td>+/- 0.02</td>
<td>+/- 0.02</td>
<td>+/- 0.02</td>
</tr>
<tr>
<td>Corresponding error in resin loading [g Cu / L Resin]</td>
<td>+/- 2</td>
<td>+/- 0.2</td>
<td>+/- 0.02</td>
</tr>
</tbody>
</table>
The best fit parameters for the hybrid correlation at the various pHs can be found in Table 8.4.

**Table 8.4: Hybrid Correlation Fit Parameters for Copper Loading at pH 4, 3, 2**

<table>
<thead>
<tr>
<th>pH</th>
<th>4</th>
<th>3</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>D&lt;sub&gt;app&lt;/sub&gt; [m&lt;sup&gt;2&lt;/sup&gt;/s]</td>
<td>2.8 x 10&lt;sup&gt;-11&lt;/sup&gt;</td>
<td>2.8 x 10&lt;sup&gt;-11&lt;/sup&gt;</td>
<td>2.2 x 10&lt;sup&gt;-11&lt;/sup&gt;</td>
</tr>
<tr>
<td>Alpha</td>
<td>0.62</td>
<td>0.59</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Results suggest that decreasing the pH from 4 to 2 resulted in a significant drop in the final resin loadings, and a slight drop in the alpha parameter. Understanding how the equilibrium resin loadings, the alpha values, and the decomplexing pH correlate is beyond the scope of this thesis, but would make an interesting study for future work.
8.3 EFFECT OF BEAD SIZE ON HYBRID CORRELATION

The Lewatit MonoPlus TP207XL ($d_p = 736 \mu m$) is a larger version of the Lewatit MonoPlus TP207 ($d_p = 552 \mu m$), so it would be reasonable to expect that the kinetic parameters for these two resins should be similar. Given that the observed capacity for TP207XL, Lot CHC 5034 (2.01 eq/L) is quite close to the observed capacity of the TP207MP lot tested (1.97 eq/L), these two resins were modeled as a single system to see if the hybrid correlation adequately captures the effect of resin bead diameter during nickel loading at pH 4. The best fit parameters to the combined system were $\alpha = 0.30$ and $D_{app} = 4.3 \times 10^{-12} \text{ m}^2/\text{s}$.

Figure 8.9 plots the hybrid correlation fit to the TP207MP data at 50, 500, and 5000 ppm nickel, and Figure 8.10 plots the hybrid correlation fit to the TP207XL data at the same concentrations. In these graphs, the hybrid correlation is plotted using the best fit parameters from the TP207MP dataset in blue ($\alpha = 0.28$ and $D_{app} = 3.9 \times 10^{-12} \text{ m}^2/\text{s}$), the best fit parameters from the combined dataset in black, and the best fit parameters from the TP207XL dataset in red ($\alpha = 0.33$ and $D_{app} = 5.0 \times 10^{-12} \text{ m}^2/\text{s}$).
Results show that there is very little difference between the three sets of best fit parameters, and both the TP207MP ($d_p = 552 \, \mu m$), and the TP207XL ($d_p = 736 \, \mu m$) are adequately described. Therefore, it would appear that the hybrid correlation is adequately capturing the effect of resin bead diameter.

### 8.4 Limitations of Hybrid Correlation

The hybrid correlation has been shown to be adaptable to model single element loading of nickel, copper, and cobalt from pure synthetic solutions onto iminodiacetic resins in the hydrogen form. Note that all experiments presented thus far to develop this correlation have been conducted under infinite solution volume conditions.
The next three chapters of this thesis explore whether the hybrid correlation can be extended to non-infinite solution volume conditions. This is achieved through running batch tests with variable solution concentration and through the operation of an RIP miniplant.

Application of the hybrid correlation to a system containing impurities is beyond the scope of this thesis. However, it is believed that the hybrid correlation should be able to provide bounds for loading a desired element (such as nickel) in the presence of impurities (such as manganese and calcium). The upper bound would be determined by applying the hybrid correlation to the loading of nickel onto the resin in the hydrogen form. To determine the lower bound, the resin would first need to be fully loaded with the impurities present in the feed stream. The impurity-laden resin could then be used in a series of nickel loading experiments. The hybrid correlation could be fit to the data from these experiments to determine the lower bound on loading. This should be explored in future work.

The effect of solids on the loading rate is also beyond the scope of this thesis. It is important to note that several researchers have observed the redissolution of various metals from the solid phase to the solution phase during the operation of RIP circuits (18,102,104,5,106), and this would need to be taken into account in a circuit model.
9.0 Verification of Hybrid Correlation (Batch Tests)

Based on the results presented thus far, base metal loading onto an iminodiacetic resin at pH 4 is initially film diffusion limited, but then becomes limited by some combination of intraparticle diffusion and/or the exchange process. In Chapter 6, a quantitative model was developed to describe the film diffusion limited regime, and in Chapter 7, a new correlation was developed to describe the intraparticle diffusion / exchange process limited regime. Since the film diffusion model is based on a linear approach to equilibrium and the intraparticle diffusion model is based on a non-linear approach to equilibrium, combining the two rate limiting regimes into a single equation with a combined constant would be highly complex.

In lieu of a combined model, a modified Helfferich number was developed to determine which process was rate-limiting at any given point in time. Furthermore, to determine whether or not an additional correlation was required to describe mixed control (i.e. both film diffusion and intraparticle diffusion / exchange process significant), a series of batch tests with changing solution composition were conducted and modeled.

9.1 Modified Helfferich Number

In order to qualitatively determine whether an ion exchange process was predominantly film diffusion limited or intraparticle diffusion limited, Helfferich developed a criterion, now referred to as the Helfferich number. This criterion was developed by taking the ratio of the predicted time to reach 50% loading under film diffusion conditions to the predicted time to reach 50% loading under intraparticle diffusion control.

The Helfferich number was defined for the case of complete conversion of an ion exchange resin initially fully loaded with ion A to being fully loaded with ion B. Furthermore, it was defined assuming that the two ions were of equal mobility and equal valence, and that the reaction was carried out under infinite solution volume conditions. Helfferich’s criterion for finding the overall rate determining step is described in Equations 9.1 and 9.2 (10). Note that the separation factor, \( S^A_B \), is only equal to the selectivity coefficient, \( K \), for the exchange of ions of unit valence.
For film diffusion: \[ \frac{2[A]_{\max}D_p \delta}{[A]D_t d_p} (5 + 2S_B^A) \gg 1 \] \[9.1\]

For intraparticle diffusion: \[ \frac{2[A]_{\max}D_p \delta}{[A]D_t d_p} (5 + 2S_B^A) \ll 1 \] \[9.2\]

where: \[ S_B^A = \frac{[A][B]}{[A][B]} \] \[9.3\]

As proposed by Helfferich, this criterion only gives the rate limiting step at the moment that the resin is loaded to 50% capacity. For the ion exchange process being studied, the resin initially starts out film-diffusion controlled, goes through a zone of mixed control, and then ends up controlled by intraparticle diffusion and/or the exchange reaction. For development of an RIP circuit model, there would be value in modifying the Helfferich criterion so that it is able to track the rate limiting step as the resin loads. To achieve this goal, the ratio of the time it would take to load a resin to any given fraction of loading, \( F \), under film diffusion control (\( t_f \)) over the time to achieve the same loading using the hybrid correlation (\( t_h \)) was taken. This is illustrated in Equations 9.4 – 9.6; a full derivation of the modified Helfferich Number can be found in Appendix E.

**Film Diffusion Control:** \[ t_f = -\ln(1-F) \]

**Hybrid Correlation:** \[ t_h = -\ln(1-F^2) \]

**Modified Helfferich No:** \[ \frac{4k_h \ln(1-F)}{k_t \ln(1-F^2)} \]

The same criteria for determining rate limiting step can be used as are used with the original Helfferich criterion (i.e. film diffusion if \( \gg 1 \), intraparticle diffusion if \( \ll 1 \), mixed control if \( \approx 1 \)). For the overall loading rate model, film diffusion control will be used for modified Helfferich values \( > 1 \), and the hybrid correlation will be used for modified Helfferich values \( < 1 \). Therefore, by examining test results where the modified Helfferich number is \( \approx 1 \), it will be possible to determine whether an additional model is required to describe mixed control.


9.2 **Batch Tests with Changing Solution Concentrations**

In Chapter 7, the hybrid correlation was developed under conditions where the concentration of nickel is held constant over the course of the test. For the ion exchange process being studied, each resin bead will be exposed to more than one solution concentration during loading. Therefore, a series of tests to see how the model performs under varying nickel solution concentrations were conducted. In this section, the hybrid correlation fit to the combined TP207MP/TP207XL dataset developed in Section 8.3 is being used for modeling.

9.2.1 **Dual Concentration Test**

To see if the overall loading model is expected to perform under conditions reflective of an RIP circuit, a dual concentration batch test was conducted. In this test, TP207XL resin (lot CHC 5034) was placed in a beaker held at constant nickel concentration of 50 ppm for 2.6 hours. The resin was then separated from the test solution using a screen and introduced into a second beaker held at a constant nickel concentration of 2500 ppm for the remainder of the test (total duration 21 hours). The objective of this test was to determine whether the overall loading model could account for the loading rate when resin from one tank is moved upstream to a higher concentration nickel tank, as would be expected in a counter-current RIP circuit.

The first portion of the model uses either the lower of the two values calculated from the film diffusion model and the hybrid correlation for this resin at 50 ppm for the first 2.6 hours. The final predicted loading from the hybrid correlation is 27.9 g Ni / L Resin. To model the second portion of the curve, one must take into account that the time required to achieve a given resin loading at 2500 ppm is less than the time required to reach the same resin loading at 50 ppm. In this case, it takes 2.59 hours to load the resin to 27.9 g Ni / L Resin at 50 ppm, but it would have only taken 0.53 hours to reach this same loading if the feed composition had been 2500 ppm. This equivalent loading time was calculated using Equation 9.7, which is a slight variation on Equation 2.12, where the Vermeulen constant \( k_v \) is replaced by the hybrid correlation constant, \( k_h \).

\[
t_r = -\frac{1}{4k_h} \ln\{1 - F^2\} \quad [9.7]
\]
Therefore, the time used in the model to calculate the resin loading during the 2500 ppm portion of the curve has to be adjusted by subtracting a value of 2.06 hours. Results from the dual concentration test are plotted in Figure 9.1.

**Figure 9.1: Dual Concentration Test**

*TP207XL Resin (Lot CHC5034), pH 4, 30°C*

Figure 9.1 shows good correlation between the predicted and observed values. In particular, there does not seem to be any discrepancy at the point when the resin is transferred from the beaker at 50 ppm to the beaker at 2500 ppm, suggesting that the model should be appropriate for modeling a counter-current RIP circuit.
9.2.2 Test with Increasing Solution Composition

A test was run with TP207MP (kinetic parameters used: $D_f = 2.7 \times 10^{-5} \text{ m/s}$, $D_{app} = 4.3 \times 10^{-12} \text{ m}^2/\text{s}$, $\alpha = 0.30$, $d_p = 5.52 \times 10^{-4} \text{ m}$), where the solution nickel concentration was increased over the course of the test. This was achieved by adding an overly-strong nickel stock solution, so that as the resin loaded, the concentration of nickel in the beaker increased. The test started at 50 ppm nickel, and reached nearly 500 ppm nickel when the resin was fully loaded.

To model the changing solution composition, the same approach was taken as with the dual concentration test. To model the constantly changing solution environment, a finite difference approach was taken where resin loadings were calculated as if the resin was moved to a new solution every 30 seconds (i.e. $\Delta t = 30 \text{ s}$). To ensure that this time step was sufficiently small, a single run with a time step of 10 seconds was also conducted and found to yield the same results. Thus the mathematical solution to the loading rate problem becomes an initial value problem, based on the initial solution concentration (50 ppm), the initial resin loading (0 g Ni/L Resin), and the initial volume of solution present in the beaker (495 mL).

At any given time $t$, the solution concentration $[M]$, and resin loading $[\bar{M}]$, are known from the previous time step calculation. The model then calculates the equilibrium resin loading $[\bar{M}]_{eqb}$, using the equilibrium isotherm presented in Section 7.1 ($K = 9.8 \times 10^{-5}$, capacity = 1.97 eq/L). The fractional attainment of equilibrium $F$, the constant for the film diffusion model $k_f$, and the constant for the hybrid correlation $k_h$, are calculated and used to determine the modified Helfferich number. The equivalent time required to reach the current resin loading $t_r$ is calculated using Equation 9.8 for modified Helfferich numbers $> 1$, or Equation 9.7 for modified Helfferich numbers $\leq 1$.

\begin{align*}
\text{For film diffusion:} & \quad t_r = \frac{-1}{4k_f} \ln\{1 - F\} \quad [9.8] \\
\text{For hybrid correlation:} & \quad t_r = \frac{-1}{4k_h} \ln\{1 - F^2\} \quad [9.7]
\end{align*}

The predicted resin loading at time $t + \Delta t$, can now be calculated. This loading should be the same as that which would have been achieved under infinite solution volume conditions after a time $t_r + \Delta t$. The resin loading is calculated using either the film diffusion model (Equation 9.9;
a slight variation on Equation 2.8) for modified Helfferich numbers less than one, or the hybrid correlation (Equation 9.10; a slight variation on Equation 7.2) for modified Helfferich numbers greater than or equal to one.

For film diffusion:

\[
[M]_{t+\Delta t} = [M]_{eqb} (1 - \exp(-k_f(t_r + \Delta t)))
\]  

[9.9]

Hybrid correlation:

\[
[M]_{t+\Delta t} = [M]_{eqb} \sqrt{1 - \exp(-4k_h(t_r + \Delta t))}
\]  

[9.10]

In order to determine the predicted solution concentration at time \( t + \Delta t \), both a volume balance and a nickel mass balance are required. The general balance equation can be described in words as: acc\( \text{cumulation} = \text{inputs} - \text{outputs} + \text{generation} \).

For the volume balance, the inputs correspond to the amount of stock solution added. Since the volume of resin used in the test is known (5 mL) and each mole of nickel that loads onto the resin should displace 2 moles of hydrogen ions (see Equation 2.1), the number of moles of sodium hydroxide required to neutralize this displaced acid can be calculated. This value can then be converted into a volume of 0.25M sodium hydroxide solution that would be added. For the particular set of pumpheads used in this particular test, the two pumpheads delivered solution to the test beaker at essentially the same rate, so the volume of nickel stock solution added was equal to the volume of sodium hydroxide solution added.

The outputs in the volume balance correspond to water lost due to evaporation, and volume lost due to solution sampling. To estimate the rate of evaporation, a test was run at 500 ppm nickel and no ion exchange resin was added to the beaker. Samples were taken over the course of the test and assayed. Based on the assay results, an approximate solution evaporation rate of 2.8 mL/hr was obtained. In terms of sampling, a 5 mL sample of the feed solution was taken before the start of the test (i.e. an initial volume of 495 mL), and subsequent samples taken were 4 mL in volume.

It was assumed that the rate of resin swelling was negligible in this test and that the rate of volume generation from the loading reaction could be ignored. This assumption is investigated in detail in Section 11.5. Therefore, the expected solution volume in the beaker at time \( t + \Delta t \) can be calculated as the volume at time \( t \) plus the increase due to stock addition less the volume lost to samples and evaporation.
For the nickel mass balance, the inputs correspond to the nickel added in the stock solution. The stock solution was made up to target 0.225 M, and this value was confirmed by AA assay. The nickel outputs correspond to the nickel lost in the solution samples. The generation term in the nickel mass balance corresponds to nickel that is produced as a result of a reaction. Since the nickel is loading from the solution onto the resin, this is a negative value and it corresponds to the amount of nickel that is predicted to load onto the resin between time $t$ and $t + \Delta t$. Thus the total amount of nickel present in the beaker at time $t + \Delta t$ can be taken as the amount of nickel present at time $t$ plus the nickel added in stock less the nickel lost to samples less the nickel loaded onto the resin. Once both the predicted volume and predicted total amount of nickel are calculated, the predicted solution concentration at time $t + \Delta t$ can be calculated.

A comparison of the model predictions to the actual observed test data are plotted in Figure 9.2.

**Figure 9.2: Loading While Nickel Concentration Increases with Time**

*TP207MP Resin, pH 4, 30°C, 50 ppm Ni at $t=0$, 0.225M Ni stock solution*
The fit of the model to the observed data indicates that the model captures the rate of loading adequately. Figure 9.3 plots the modified Helfferich number against time to illustrate how the rate limiting step changes over the course of the test. For this test, the loading rate is initially film-diffusion limited, as expected. The mixed control portion of the curve is around the region where the modified Helfferich number is $\approx 1$, which occurs around 8 minutes, and it appears that minimal error is introduced by not having a separate model to describe mixed control. Most of the test occurs under intraparticle diffusion control (modified Helfferich number $<< 1$).

**Figure 9.3: Modified Helfferich Number for Increasing Nickel Concentration Test**

*TP207MP Resin, pH 4, 30°C, 50 ppm Ni at t=0, 0.225M Ni stock solution*
9.2.3 Tests with Decreasing Solution Composition

Two tests were run with TP207MP using sodium hydroxide to maintain the solution pH, but no nickel stock solution was added. The first test was run with an initial solution concentration of 500 ppm nickel; the second test was run with an initial solution concentration of 250 ppm nickel. The finite difference model presented in Section 9.2.2 was used to predict solution concentration and resin loadings over the course of the tests.

Results for the first test, run at 500 ppm nickel are displayed in Figure 9.4.

![Graph showing nickel loaded on resin versus solution concentration over time](image)

**Figure 9.4: Loading from Solution with Initial Concentration of 500 ppm Nickel**

*TP207MP Resin, pH 4, 30°C, 500 ppm Ni at t=0, No nickel stock solution*

The model was found to predict the observed values quite well. Of note is that near the end of the test, the observed resin loading (based on the amount of sodium hydroxide added to the beaker) is significantly higher than the model prediction. This is likely due to the fact that at such a low nickel concentration in the beaker (final assay 16.5 ppm), sodium co-loads onto the
resin, as discussed in Section 2.1.3. To confirm this hypothesis, the final resin loading value from the strip assay is also plotted on this graph. Since the strip value lines up better with the model values than the values calculated from sodium hydroxide addition, it is reasonable to conclude that the discrepancy is due to sodium co-loading.

To get a sense of rate-limiting step over the course of the test, the modified Helfferich number is plotted in Figure 9.5, along with the solution assays. The test began with a modified Helfferich number of 0.97, suggesting mixed control. As the resin bead loads, the modified Helfferich number decreased to a value of 0.26. However, since the solution concentration in the beaker was depleting over the course of the test, the modified Helfferich number increased back to a value of 0.5. These values suggest that particle diffusion / exchange reaction was the dominant mechanism in this test.

**Figure 9.5: Modified Helfferich Number – No Nickel Stock Solution, 500 ppm Ni Initial TP207MP Resin, pH 4, 30°C, 500 ppm Ni at t=0, No nickel stock solution**
Results for the second test are displayed in Figure 9.6.

**Figure 9.6:** Loading from Solution with Initial Concentration of 250 ppm Nickel

TP207MP Resin, pH 4, 30°C, 250 ppm Ni at t=0, No nickel stock solution

Results from the second test once again show reasonable correlation between model predictions and experimental observations. It is interesting to note that the observed loading is once again significantly higher than the predicted value, or the final strip assay. This discrepancy was larger in this test than in the previous test. Since the final nickel assay in the previous test was 16.5 ppm nickel, and the final nickel concentration in this test was 0.5 ppm, it makes sense that the effect of sodium co-loading would be more prominent in this test.
The plot of the modified Helfferich number is plotted with the solution concentrations for the first hour of the test in Figure 9.7.

![Graph](image)

**FIGURE 9.7: MODIFIED HELFFERICH NUMBER – NO NICKEL STOCK SOLUTION, 250 ppm Ni INITIAL TP207MP Resin, pH 4, 30°C, 250 ppm Ni at t=0, No nickel stock solution**

This plot shows that the test begins in the film diffusion limited regime, with a modified Helfferich number of 2.9. However, the modified Helfferich number drops to a value of 0.8, before increasing back to a value of 3.8. Most of the loading occurs in the time period where the modified Helfferich number is close to one, suggesting that mixed control is predominant in this test. Although the assay taken at 0.5 hours is slightly higher than that predicted by the model, the overall fit of the model to the test data appears to be adequate.
9.2.4 Summary of Batch Test Results and Assessment of Mixed Control Regime

The results from the batch tests carried out with changing nickel concentration indicate that the overall loading rate model developed in Chapters 6 and 7 should be adequate for modeling a counter-current RIP circuit. In particular, the test run with an initial solution concentration of 250 ppm without any stock solution being added suggests that the overall loading rate model is adequate, even when most of the test is carried out under mixed control conditions. Therefore, no further work was done to develop a more rigorous model for mixed control, and the research focus shifted to model verification with a continuous counter-current RIP miniplant.
10.0 Development of RIP Circuit Models

In order to verify the hybrid correlation with an RIP miniplant, a five stage countercurrent circuit model was developed. This chapter provides a step-by-step description of the methodology and assumptions used in the development of the five stage cascade circuit model and the five stage carousel circuit model. Recall that the differences in cascade and carousel operation were discussed in Section 2.2.1.

10.1 Cascade Circuit Model

The cascade circuit model developed calculates the steady-state solution profile and the steady-state resin profile across the circuit. In order to achieve this, the following inputs are required:

- Working volume of each contactor
- Flowrate and metal concentration of feed stream
- Resin volume in each contactor
- Resin transfer rate between contactors (constant for circuit)
- Factor for estimating solution transferred with resin
- Initial metal loading on resin entering circuit
- Metal concentration in solution coming into circuit with resin
- Resin isotherm parameters: $K$, capacity
- Resin kinetic parameters: $d_p \frac{D_I}{\delta}$, $\alpha$, $D_{app}$

The circuit model is calculated by providing an initial guess for the concentration of metal leaving the circuit in the tails stream. Assuming perfect mixing in the contactor, the concentration of metal in the contactor is the same as the concentration of the stream exiting the contactor. The average resin loading in the tank, $(F)$, is calculated using the Segregated Flow model, and then the concentration of nickel in the stream feeding the tank can be obtained by mass balance. This procedure is repeated until the overall concentration of metal in the feed is obtained. This value is compared to the input value, and the guess for the tails value changed until the calculated feed value matches the model’s input feed value. With Microsoft Excel, this can be automated using the program’s Solver routine.
The fractional resin loading function, $F(t)$, for each tank was based on either the film diffusion model of Chapter 6 or the hybrid correlation of Chapter 7, depending on which calculation gave a lower value for $\langle F \rangle$. Since the concentration of metal in the tank is known, the equilibrium loading value for the resin, $[M]_{eqb}$, can be calculated from the mass action isotherm. Furthermore, since the resin enters each tank partially loaded, the time it would have taken the resin to achieve this loading, $t_r$, if it had entered the tank fully stripped is required. This is calculated for the film diffusion model using Equation 10.1, and for the hybrid correlation using Equation 10.2.

**Film Diffusion:**

$$t_r = \frac{-1}{k_f} \ln \left( 1 - \frac{[M]}{[M]_{eqb}} \right) \tag{10.1}$$

**Hybrid Correlation:**

$$t_r = \frac{-1}{4k_h} \ln \left( \frac{[M]_{eqb}^2 - [M]^2}{[M]_{eqb}^2} \right) \tag{10.2}$$

The Segregated Flow Model was selected for calculating $\langle F \rangle$, since it is reasonable to assume that there is no significant interaction between resin beads that have been in the RIP contactor for different lengths of time. It was also assumed that, from the resin bead’s point of view, each contactor behaved as an ideal stirred tank reactor with an average resin residence time of $\tau_r$. This can be summarized by Equations 10.3 – 10.4 (120). Note that the integrals for average resin loading were solved numerically using the trapezoidal rule.

$$\langle F \rangle = \int_0^\infty F(t+t_r)E(t)dt \tag{10.3}$$

$$E(t) = \frac{1}{\tau_r} \exp \left( -t/\tau_r \right) \tag{10.4}$$

A simple mass balance is used to solve for the metal concentration of the solution entering each contactor. Figure 10.1 provides a block diagram of a single stage in the circuit.
The first step in the contactor balance is to calculate the volumetric flowrates of the solution in and out of the contactor. The volumetric flowrates of the resin transfer and the solution transferred with the resin are known from the model inputs. The flowrate of the feed to the circuit is also known, and so the flowrate of the solution exiting each contactor can be calculated by a simple flow balance. The implicit assumption in this calculation is that there is no change in resin volume as the beads load.

Once the volumetric flowrates are all known, the mass balance across the contactor can be completed. At this point in the calculation, the concentration of metal on the resin entering and exiting the contactor is known, as well as the concentration of metal in solution exiting the contactor. Assuming perfect mixing, the metal concentration within the contactor is equal to that exiting the contactor. Therefore, it is a matter of simple algebra to calculate the concentration of metal in the solution feeding the contactor.

The output for an example run with this model is displayed in Figures 10.2 and 10.3. All input cells are in grey, all other values are calculated. Note that the model also includes a Mix Tank (contains no resin), whose purpose is to combine the recycled solution from Stage 1 with the fresh feed. Figure 10.2 displays the inputs and outputs of the model; Figure 10.3 displays the actual flow and mass balances for each individual stream.

![Diagram](image-url)
**Solution Side**

- Tot Vol: 600 mL per tank
- Flow Rate: 20 mL/min FRESH FEED
- molar Ni: 58.71 g/mol

**Resin Side**

- TP207XL
- K: 9.78E-05
- Df/delta: 2.73E-05 m/s
- alpha: 0.36

**Kinetics**

- Cap: 2.36
- Dapp: 4.43E-12 m²/s
- Resin Rate: 2 mL/min bead dp: 736 µm
- gP Ni in resin feed solution: 0.000736 m

**TOTAL IN CIRCUIT**

- Resin Volume [mL]: 250
- % Resin: 8.3%
- Airlift total flow to upstream tank [mL/min]: 36.0

**Segregated Flow Model, OUTPUTS:**

- Soln (gP L): 4.000
- Mix Tk: 2.733
- 1
- 2.030
- 1.286
- 0.611
- 0.137
- 0.012
- 3.0

- Resin [g Ni / L R]:
  - 0.03
  - 0.05
  - 0.10
  - 0.39
  - 3.74

- Eqbm Load [g Ni / L R]:
  - 67.57
  - 67.13
  - 66.19
  - 62.92
  - 49.96
  - quadratic “a”: 1.35E-05
  - quadratic “b”: -3.2E-05
  - quadratic “c”: 1.88E-05

- Hybrid Correlation
  - kf: 0.006521
  - tr [s]: 116

- Film Diffusion Model
  - kf: 0.006521
  - tr [s]: 116

**FIGURE 10.2: CASCADE CIRCUIT MODEL INPUTS & OUTPUTS**
Figure 10.3: Flow and Mass Balance for Cascade Circuit Model
### 10.2 Carousel Circuit Model

The computer model of a five stage carousel circuit was programmed such that feed is directed to the lead contactor, which overflows to the high centre contactor (“HC”), the centre contactor (“C”), the low centre contactor (“LC”), the lag contactor, and finally overflows to tails.

The carousel circuit model consists of a pair of coupled ordinary differential equations. The first differential equation is the mole balance for the metal in the solution phase and the second differential equation is the mole balance for the metal in the resin phase. In words, the mole balances can be written as: \( \text{INPUTS} - \text{OUTPUTS} + \text{GENERATION} = \text{ACCUMULATION} \).

For a single contactor, assuming perfect mixing and minimal change in resin and solution volumes, the system balance for the solution phase is expressed by Equation 10.5, where \( Q \) is the solution flowrate through the contactor, \( V_s \) is the volume of solution in the contactor, and \( V_r \) is the volume of resin in the contactor. Note that the validity of the constant volume assumption will be explored in Section 11.5.

**Solution Phase**

\[
Q[M]_{\text{feed}} - Q[M] - V_r \frac{d}{dt}[M] = V_s \frac{d}{dt}[M] \tag{10.5}
\]

The mole balance for the resin phase is trivial, since no resin is being added or removed from the contactor. Therefore, the rate of loading is described by Equation 2.7 when the resin is loading under film diffusion control (modified Helfferich number greater than one), and a slight variation on Equation 2.11 (\( k_v \) replaced here with \( k_h \)) when loading under intraparticle diffusion / exchange reaction limited control (modified Helfferich number less than or equal to one).

**Mod He > 1:**

\[
\frac{d}{dt}[M] = k_f ([M]_{eqb} - [M]) \tag{2.7}
\]

**Mod He \leq 1:**

\[
\frac{d}{dt}[M] = 2k_h \left( \frac{[M]_{eqb}^2 [M]^2}{[M]} \right) \tag{2.11}
\]

To solve the set of coupled ordinary differential equations, a finite difference approach was taken. Euler’s method (1st order Runge-Kutta) was selected for ease of application, and is described by Equation 10.6.

**Euler’s Method:**

\[
[M]_{t+\Delta t} = [M]_t + \Delta t \frac{d}{dt}[M] \tag{10.6}
\]
The initial concentrations of the metal in both the resin and solution phases for each contactor must be input into the model. The model uses these initial conditions for $t = 0$, and works through a time-step sequence, calculating all subsequent resin and solution values at time $t + \Delta t$, based on the previous values. The time step, $\Delta t$, used in this model was 0.24 minutes. To confirm that this time-step was sufficiently small, a single run of the model was made with a time step of 0.06 minutes and was found to yield the same steady-state results. Note that for the carousel circuit, the concentrations in each contactor are always a function of time and steady-state occurs when the same solution and resin profile repeat with each operating cycle.

The following inputs are required for this circuit model:

- Working volume of each contactor
- Flowrate and metal concentration of feed stream
- Resin volume in each contactor
- Carousel cycle time (how often contactor positions change)
- Initial solution concentration in each contactor at time $t = 0$
- Initial metal loading on resin in each contactor at time $t = 0$
- Metal loading on resin entering the circuit from elution
- Resin isotherm parameters: $K$, capacity
- Resin kinetic parameters: $d_p$, $D_f$, $\alpha$, $D_{app}$

The outputs of the circuit model are the solution concentration and metal concentration within each contactor as a function of time. At the end of each cycle (i.e. when the lead contactor is taken offline and the role of the contactors changes), the model assumes an instantaneous switch of contactor position, and then continues.

At any given time $t$, the current concentration of metal in the contactor solution phase $[M]$, and the current resin loading $[\bar{M}]_t$ are known. The current solution concentration is used to calculate the equilibrium resin loading value. From this information, the fractional attainment of equilibrium, the modified Helfferich number, and the time it would have taken the resin to reach the current loading $t_r$, can be calculated.
To obtain the resin loading for the next time step \([\mathcal{M}]_{t+\Delta t}\), the analytical solution to the film diffusion model (modified He > 1) or the analytical solution to the hybrid correlation (modified He ≤ 1), is calculated using \(t = t_r + \Delta t\), as per Equation 9.9 and 9.10.

For film diffusion:
\[
[\mathcal{M}]_{t+\Delta t} = [\mathcal{M}]_{eq} (1 - \exp\{-k_f(t_r + \Delta t)\}) \quad [9.9]
\]

Hybrid correlation:
\[
[\mathcal{M}]_{t+\Delta t} = [\mathcal{M}]_{eq} \sqrt{1 - \exp\{-4k_h(t_r + \Delta t)\}} \quad [9.10]
\]

To obtain the solution concentration at the next time step \([\mathcal{M}]_{t+\Delta t}\), one must first estimate the rate of resin loading in the “generation” term. This is achieved with Equation 10.7.

\[
\frac{d}{dt} [\mathcal{M}] = [\mathcal{M}]_{t+\Delta t} - [\mathcal{M}]_t \quad [10.7]
\]

Rearranging Equation 10.5, substituting in Equation 10.7, and applying Euler’s method, the concentration of solution in the contactor at time \(t + \Delta t\) can be expressed using Equation 10.8.

\[
[\mathcal{M}]_{t+\Delta t} = \left[\frac{Q \Delta t ([\mathcal{M}]_{feed} - [\mathcal{M}]_t) - V_f ([\mathcal{M}]_{t+\Delta t} - [\mathcal{M}]_t)}{V_S} \right] \quad [10.8]
\]

For modeling the full set of five reactors, it is important to realize that the concentration of metal entering each subsequent reactor, \([\mathcal{M}]_{feed}\), is the concentration of metal exiting the previous reactor. Thus, the finite differences model was solved for all reactors using the same time step sequence.

The output for a single run of the carousel model would be over one thousand pages long. Appendix F displays the output for the first 0.072 hours for the lead, high centre, and centre contactors.
11.0 Verification of Circuit Models (RIP Miniplant)

A five stage RIP miniplant (working volume: 560 mL / stage) was constructed for the purpose of circuit model verification for both nickel and copper loading onto Lewatit MonoPlus TP207XL, lot CHE 50019. Five litres of resin were converted to the hydrogen form and wet-screened to the +710 -850 size fraction. The miniplant was designed to operate in a continuous cascade mode, although it was also used in a carousel fashion.

During cascade operation, fresh feed was pumped to the Feed Mix Tank and then was fed by gravity through the five RIP loading stages. Resin was fed continuously from the Resin Feed Tank to the final RIP stage using an airlift pump. In order to maintain the resin inventory in the Resin Feed Tank, fresh resin was manually added every 15 minutes. The resin was moved countercurrently through the circuit using airlift pumps. Note that some solution was also transferred with the airlift pumps, and no attempt was made to separate the solution from the resin feeding the five RIP contactors. However, resin exiting the first RIP stage was passed over a screen to remove the excess solution prior to the resin being transferred to the elution columns. The excess solution was pumped to the Feed Mix Tank, where it was combined with the fresh feed prior to being returned to the first RIP contactor. The pH in each contactor was held constant at 4.0 +/- 0.1 pH units through the addition of 1M sodium hydroxide, and temperature controllers held each stage at 30 +/- 1 °C.

Elution was done in columns at approximately 2 BV/h. Stripping consisted of 10 BV of 100 g/L sulphuric acid, followed by 5 BV water wash. At the end of elution, the resin retained a greenish hue, suggesting incomplete stripping of nickel. For the miniplant, the decision was made to run with a recycle load of nickel on the resin to avoid an acid hold step. Samples of resin returning to the circuit were taken and stripped with a full 20 hour acid hold step to determine the level of recycle load. Results indicated that the resin was returning to the circuit with a loading of approximately 3 g Ni / L Resin, and there was no indication of the amount of nickel left on the resin increasing after five cycles. At the end of the run, the total resin volume in each contactor was recorded and a 5 mL subsample of the resin was taken and stripped to determine the resin loading in each contactor.

A flowsheet of the cascade circuit can be found in Figure 11.1; photographs of the circuit can be found in Figure 11.2, and detailed operating procedures can be found in Appendix G.
**Figure 11.1: RIP Miniplant Flowsheet (Cascade Operation)**

- **Mix Tank**
- **Resin Tank**
- **Feed**
- **Recycle**
- **Water**
- **Air Compressor**

**Legend:**
- **TC** = Temperature Control (30°C)
- **AC** = pH Control (4.0 with 1M NaOH)
- **X** = Solution Sample Point
- **--- ---** = Air Flow
- **---** = Solution Flow
- **--- --- ---** = Continuous Resin Flow
- **--- --- --- ---** = Periodic Manual Resin Transfer

**Key Reagents:**
- 100 g/L H₂SO₄
- Elution Column (Batch Step)

**Notes:**
- Eluate
- Effluent
Figure 11.2: Photographs of RIP Miniplant (Cascade Operation)
11.1 NICHEL CASCADE RUNS

Three continuous cascade runs were performed with nickel. In the first run (Run A), fresh resin was used, but in all other runs recycled resin (~ 3 g Ni / L resin) was used. Maintaining constant resin inventories in all the tanks with the airlifts was found to be difficult. Since the objective of the exercise was model verification, the decision was made that it was more important to reach a steady-state condition rather than to try and hold the total resin inventories constant. Therefore, no adjustments were made to resin addition rates or the airflow pumps after the first two hours of the test. Note that the effect of solution back-mixing with the airlifts will be investigated in Section 12.1, and the effect of operating the circuit with a recycle load of nickel on the resin will be investigated in Section 12.6.4.

Inputs to the cascade circuit model developed in Chapter 10 include the resin equilibrium and kinetic parameters for TP207XL, lot CHE50019 reported in Chapter 8 and the film diffusion model parameters reported in Chapter 6. Additional inputs to the model included: feed flowrate (15 mL/min), resin flowrate (1.5 mL/min), initial resin loading (0 or 3 g Ni/L resin), final measured resin volume in each tank, total airlift flowrates, and the measured nickel concentration exiting the Mix Tank. Note that the assay concentration of solution exiting the Mix Tank was used in lieu of the concentration of the feed solution (5 g/L) since some solution was removed from the circuit with the resin exiting the circuit, and the exact amount was not measured. For the total airlift flowrate, the total volume was not recorded for all tests and an estimate was required for the first two tests. Details on how this estimate was calculated can be found in Appendix H.

The model inputs for each run are tabulated in Table 11.1, and the model results are compared to the observed values in Figure 11.3. Note that the two model lines in Figure 11.3 correspond to the model being run once using the highest observed mix tank assay, and again using the lowest observed mix tank assay. The three charts on the left side of Figure 11.3 correspond to the steady-state solution profile across the circuit, while the figures on the right side of Figure 11.3 display the steady-state resin loading profile across the circuit. Appendix I contains the detailed model results.
<table>
<thead>
<tr>
<th>TEST</th>
<th>Nickel A</th>
<th>Nickel B</th>
<th>Nickel C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Flowrate [mL/min]</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Mix Tank Assay [g/L Ni]</td>
<td>3.5 / 3.7</td>
<td>3.5 / 3.4 / 3.2</td>
<td>4.3 / 4.0 / 3.8</td>
</tr>
<tr>
<td>Resin Flowrate [mL/min]</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Resin Loading Entering Circuit [g Ni / L Resin]</td>
<td>0</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Tank 1</th>
<th>Tank 2</th>
<th>Tank 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Resin Volumes in Each Tank [mL] (volume %)</td>
<td>40½ (7.2%)</td>
<td>63 (11.2%)</td>
<td>92 (16.3%)</td>
</tr>
<tr>
<td></td>
<td>Tank 2</td>
<td>Tank 3</td>
<td>Tank 4</td>
</tr>
<tr>
<td>Airlift Flowrate Exiting Contactor [mL]</td>
<td>31*</td>
<td>22*</td>
<td>25*</td>
</tr>
<tr>
<td></td>
<td>Tank 5</td>
<td>Resin Feed Tank</td>
<td></td>
</tr>
<tr>
<td></td>
<td>61 (10.8%)</td>
<td>120* (21.3%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tank 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61 (10.8%)</td>
<td>120* (21.3%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tank 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61 (10.8%)</td>
<td>120* (21.3%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tank 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61 (10.8%)</td>
<td>120* (21.3%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tank 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61 (10.8%)</td>
<td>120* (21.3%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tank 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61 (10.8%)</td>
<td>120* (21.3%)</td>
<td></td>
</tr>
</tbody>
</table>

* indicates estimated values

Resin Isotherm Parameters: $K = 9.8 \times 10^{-5}$, capacity = 2.36 eq/L

Resin Kinetic Parameters for Ni: $D_t/\delta = 2.7 \times 10^{-5} \text{m/s}$, $D_{app} = 4.4 \times 10^{-12} \text{m}^2/\text{s}$, $\alpha = 0.36$, $d_p = 7.36 \times 10^{-4} \text{m}$
ASSAYS: $\triangle \rightarrow 14 \text{ h}$  $\times \rightarrow 15 \text{ h}$  $\diamond \rightarrow 16 \text{ h}$

Lines are model predictions based on the highest and lowest observed Mix Tank Solution Assay

RESIN STRIP ASSAYS: $\triangle$
While there is some deviation in the model predictions from observed values, the overall model appears to be adequate, given the amount of uncertainty that is associated with miniplant scale testwork. In particular, no section of the circuit appears to consistently be overpredicted or underpredicted, suggesting that the deviations do not highlight a major model deficiency. Therefore, the Segregated Flow Model selected in Chapter 10 for modeling resin movement through the circuit appears to be adequate for this application.

In terms of the modified Helfferich numbers, most of the circuit is observed to be predominantly rate-limited by intraparticle diffusion / exchange reaction, rather than by film diffusion. The only tank predicted to be under film diffusion control was the final tank in the second nickel run. The calculated modified Helfferich numbers, based on the observed solution assays and observed resin loadings are displayed in Table 11.2.

<table>
<thead>
<tr>
<th>TEST</th>
<th>Nickel A</th>
<th>Nickel B</th>
<th>Nickel C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank 1</td>
<td>0.025-0.026</td>
<td>0.027-0.029</td>
<td>0.026-0.027</td>
</tr>
<tr>
<td>Tank 2</td>
<td>0.035-0.037</td>
<td>0.041-0.043</td>
<td>0.046-0.048</td>
</tr>
<tr>
<td>Tank 3</td>
<td>0.055-0.057</td>
<td>0.131-0.138</td>
<td>0.10-0.11</td>
</tr>
<tr>
<td>Tank 4</td>
<td>0.094</td>
<td>0.57-0.94</td>
<td>0.28-0.29</td>
</tr>
<tr>
<td>Tank 5</td>
<td>0.22-0.23</td>
<td>9.6-11</td>
<td>0.76-0.84</td>
</tr>
</tbody>
</table>

### 11.2 Copper Cascade Run

A cascade run was conducted for loading copper onto TP207XL using a solution feed flowrate of 18.5 mL /min. This test was run for 11 hours, and solution samples were taken after 8, 9, 10, and 11 hours. The recirculating load of copper on the resin appears to have been negligible (resin samples only showed differences of +/- 0.2 g Cu / L Resin when assayed with and without an acid hold step). The model inputs for this test are summarized in Table 11.3, and the observed values are compared to the model predictions in Figure 11.4. As was the case for the nickel cascade run, two model lines are generated, correspond to the highest and lowest observed mixed tank assay being used as a model input parameter.
**Table 11.3: Summary of Model Inputs and Sampling Times for Copper Cascade Test**

<table>
<thead>
<tr>
<th>Feed Flowrate [mL/min]</th>
<th>18.5</th>
<th>Resin Flowrate [mL/min]</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed Mix Tank Assays [g/L Cu]</td>
<td>3.9 / 3.7 / 3.8 / 3.9</td>
<td>Resin Loading Entering Circuit [g Cu/L Resin]</td>
<td>0</td>
</tr>
<tr>
<td>Solution Assays at [h]</td>
<td>8 / 9 / 10 / 11</td>
<td>Resin Assays at [h]</td>
<td>11</td>
</tr>
<tr>
<td>Airlift Flowrates [mL/min]</td>
<td>Final Resin Volumes in Tanks [mL] (volume %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tank 1</td>
<td>28½</td>
<td>Tank 1</td>
<td>43  (7.6%)</td>
</tr>
<tr>
<td>Tank 2</td>
<td>23</td>
<td>Tank 2</td>
<td>73½  (13.1%)</td>
</tr>
<tr>
<td>Tank 3</td>
<td>14</td>
<td>Tank 3</td>
<td>39  (6.9%)</td>
</tr>
<tr>
<td>Tank 4</td>
<td>21</td>
<td>Tank 4</td>
<td>63  (11.2%)</td>
</tr>
<tr>
<td>Tank 5</td>
<td>21</td>
<td>Tank 5</td>
<td>54  (9.6%)</td>
</tr>
<tr>
<td>Resin Feed Tank</td>
<td>40</td>
<td>Resin Feed Tank</td>
<td>120* (21.3%)</td>
</tr>
</tbody>
</table>

*indicates estimated values

Resin Isotherm Parameters: K = 7.5x10^-4, capacity = 2.5 eq/L

Resin Kinetic Parameters for Cu: D_f/δ = 2.7x10^-5 m/s, D_app = 2.8x10^-11 m^2/s, α = 0.62, d_p = 7.36x10^-4 m

**Figure 11.4: Copper Cascade Miniplant Results – Model vs Actual**

*TP207XL Resin (Lot CHE 50019), 30°C, pH 4*
In terms of the modified Helfferich numbers, the first three tanks are expected to be intraparticle diffusion limited / exchange reaction limited, and the final tank is expected to be film diffusion limited. The calculated modified Helfferich numbers, based on the observed solution and resin assays are tabulated in Table 11.4.

**Table 11.4: Modified Helfferich Numbers for Copper Cascade Test**

<table>
<thead>
<tr>
<th>Tank 1</th>
<th>Tank 2</th>
<th>Tank 3</th>
<th>Tank 4</th>
<th>Tank 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.069-0.071</td>
<td>0.10-0.11</td>
<td>0.22</td>
<td>0.66-0.78</td>
<td>9.1-10.3</td>
</tr>
</tbody>
</table>

It is interesting to note that the tank with a modified Helfferich number closest to one (i.e. the tank most likely to be affected by mixed control) is the fourth tank in this test, and the model underpredicts the resin loading in this tank. This is in direct contrast to the results from the nickel cascade tests, where the fourth tank in Run B (modified Helfferich value of 0.57-0.94) overpredicts the resin loading. Furthermore, the observed resin loading is within the model predictions for the fifth tank in Run C (modified Helfferich value of 0.76-0.84). Since the model overpredicts in one case, underpredicts in another, and predicts the observed value in the third case, it is unlikely that this error is due to the fact that there is no separate model for mixed control.

**11.3 Nickel Carousel Run**

The miniplant configuration was slightly modified to run as a five stage carousel circuit, and a 36 hour nickel carousel test was conducted. In carousel mode, feed was pumped to the lead contactor, and then overflowed to the high centre contactor (“HC”), the centre contactor (“C”), the low centre contactor (“LC”), the lag contactor, and finally overflowed to the tails bucket. In these tests, the role of the contactors was changed each hour. To change the role of the contactors, the physical position of the feed line was moved from contactor to contactor. When necessary, a pump was used after the lowest contactor to direct the overflow from this contactor back to the highest contactor. The time required to take the lead contactor off-line and put a new contactor in the lag position could be achieved in less than three minutes. Therefore, feed was pumped to the circuit for 57 minutes, the roles of the contactors was adjusted, and then the
feed was turned back on at 60 minutes, in order to create a constant one hour cycle time. Detailed operating procedures for the carousel runs can be found in Appendix J.

To determine the feed flow rate, the total tails volume collected each hour was measured. It was noticed that the flow rate fluctuated considerably over the course of this test and varied from 13 – 22 mL / min. Consequently, the test never reached steady-state.

Solution samples were taken for assay at 34.75, 35.25, 35.5, 35.75, and 36 hours. The physical circuit configuration chosen for sampling is shown in Figure 11.5. This physical configuration was typically the point in time at which the feed flow rate had been most steady, based on the tails volumes collected each cycle.

![Figure 11.5: Physical Circuit Configuration During Sampling - Carousel](image)

**Figure 11.5: Physical Circuit Configuration During Sampling - Carousel**
The carousel finite difference model developed in Chapter 10 was run using the resin equilibrium and kinetic parameters listed for TP207XL, lot CHE50019 reported in Chapter 8 and the film diffusion model parameters reported in Chapter 6. Additional inputs to the model included: the measured hourly feed flowrate (13-22 mL/min), resin volume (40 mL/stage), initial resin loading (3 g Ni/L resin), contactor working volume (560 mL), and the average nickel feed assay (4.14 g/L Ni). Note that in this model, it is assumed that the circuit operates for 60 minutes in each position and that the contactor change is instantaneous. These model input values are summarized in Table 11.5. Note that the sample calculations provided in Appendix F were based on this experimental run.

**Table 11.5: Summary of Model Inputs and Sample Times for Nickel Carousel Test**

<table>
<thead>
<tr>
<th>Contactor Volume [L]</th>
<th>0.56</th>
<th>Resin per Stage [mL],(%)</th>
<th>0.40 (7.1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate [mL/min]</td>
<td>13-22</td>
<td>Contactor Cycle Time [min]</td>
<td>60</td>
</tr>
<tr>
<td>Feed Assay [g/L Ni]</td>
<td>4.14</td>
<td>Eluted Resin [g Ni/L Resin]</td>
<td>3</td>
</tr>
<tr>
<td>Solution Samples at [h]</td>
<td>34.75, 35.25, 35.5, 35.75, 36</td>
<td>Resin Samples at [h]</td>
<td>36</td>
</tr>
</tbody>
</table>

Resin Isotherm Parameters: \( K = 9.8 \times 10^{-5} \), capacity = 2.36 eq/L

Resin Kinetic Parameters for Ni: \( D_f/\delta = 2.7 \times 10^{-5} \text{m/s}, D_{app} = 4.4 \times 10^{-12} \text{m}^2/\text{s}, \alpha = 0.36, d_p = 7.36 \times 10^{-4} \text{m} \)

Results comparing the circuit model with the actual solution assays indicate that the circuit model is significantly over-predicting circuit performance. However, the results are still within test error bounds, as the assays are still greater than the predicted values at the lowest feed rate (13 mL/min). Figure 11.6 displays the circuit model, the circuit model lower error bound, and the actual solution assays. Note that this graph plots the solution assays for the various tanks against time for the last six hours, since during carousel operation the solution composition in each contactor is continually changing.
The resin in each contactor was sampled and stripped at the end of the run. These final strip assays are compared to the model values in Figure 11.7. Once again the model is over-predicting resin loadings, although the final strip assays are again within error bounds.
11.4 COPPER CAROUSEL RUN

A 30 hour copper carousel test was conducted, using 40 mL fresh resin per stage (no initial loading). As in the case of nickel, feed was directed to the circuit for 57 minutes. After shutting off the feed pump, the lead contactor was taken off-line and a new contactor was placed in the lag position. The circuit was always restarted at the end of three minutes, so that the total cycle time was one hour. More care was taken as to the placement of the various lines during this test and the feed flow rate was kept between 14 and 17 mL/minute. The average feed assay for this run was 4.4 g/L copper.

Solution samples were taken from each contactor at 24.75, 29.25, 29.5, 29.75, and 30 hours. The physical circuit configuration at the time of the sampling was the same as that shown in Figure 11.6. This means that there was a plug flow component (not included in the model)
between the lead and the high centre contactors. At the end of the run, resin samples were taken from each contactor and stripped. Table 11.6 summarizes the model inputs for this test. Results comparing the solution assays to the model predictions can be found in Figure 11.8.

**TABLE 11.6: SUMMARY OF MODEL INPUTS AND SAMPLE TIMES FOR COPPER CAROUSEL TEST**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contactor Volume [L]</td>
<td>0.56</td>
</tr>
<tr>
<td>Resin per Stage [mL],(%)</td>
<td>0.40 (7.1%)</td>
</tr>
<tr>
<td>Feed Rate [mL/min]</td>
<td>14-17</td>
</tr>
<tr>
<td>Contactor Cycle Time [min]</td>
<td>60</td>
</tr>
<tr>
<td>Feed Assay [g/L Cu]</td>
<td>4.4</td>
</tr>
<tr>
<td>Eluted Resin [g Cu/L Resin]</td>
<td>0</td>
</tr>
<tr>
<td>Solution Samples at [h]</td>
<td>24¾, 29½, 29¾, 30</td>
</tr>
<tr>
<td>Resin Samples at [h]</td>
<td>30</td>
</tr>
</tbody>
</table>

Resin Isotherm Parameters: \( K = 7.5 \times 10^{-4} \), capacity = 2.5 eq/L

Resin Kinetic Parameters for Cu: \( D_f/\delta = 2.7 \times 10^{-5} \text{ m/s} \), \( D_{app} = 2.8 \times 10^{-11} \text{ m}^2/\text{s} \), \( \alpha = 0.62 \), \( d_p = 7.36 \times 10^{-4} \text{ m} \)

**FIGURE 11.8: COPPER CAROUSEL MINIPLANT RESULTS - SOLUTION**

*TP207XL Resin (Lot CHE 50019), 30 °C, pH 4*
Figure 11.8 shows a good fit between the observed and predicted values in the lead contactor. In the high centre contactor, the observed values are slightly below the predicted value, which makes sense since the solution from the lead contactor had to be pumped all the way back to the high centre contactor, creating a plug-flow component that the model does not account for.

Results comparing the final resin strip assays with predicted model loadings are presented in Figure 11.9.

![Figure 11.9](image)

**Figure 11.9: Copper Carousel Miniplant Results – Resin**

*TP207XL Resin (Lot CHE 50019), 30°C, pH 4*

Results from the final resin loadings show fairly good correlation with the predicted model values. Consequently, the results from Figures 11.8 and 11.9 suggest that the overall circuit model adequately describes copper loading under carousel operating conditions.
11.5 VALIDITY OF CONSTANT VOLUME ASSUMPTION

In the development of both circuit models, the implicit assumption was made that the volumes of the resin and solution do not change with time. However, it is well known that there is a significant change in resin volume for iminodiacetic resins when converted from the sodium form to the hydrogen form, as was seen in Figure 4.1 in the comparison of resins. Therefore, the validity of this assumption to the RIP circuit studied must be scrutinized.

In terms of the rate of metal loading onto the resin, the change in resin volume is irrelevant. This is because both the film diffusion model and the hybrid correlation were defined with respect to the original bead diameter, in the hydrogen form. Thus, as the resin swells, the only error that is incurred in the model is the change in the solution volume present in the contactor (i.e. since the resin takes up more volume, there is slightly less room for solution).

To determine how much resin swelling occurred during these tests, the resin volumes exiting the circuit in the carousel tests can be examined. In these tests, 40 mL of resin were added to the offline contactor, and was removed when the contactor had cycled through all positions and was taken offline. These results are displayed in Figure 11.10.

![Figure 11.10: Measured Wet-Settled Resin Volumes During Carousel Tests](image)
From Figure 11.10, it is clear that some resin swelling is occurring. Ignoring the first three measurements, when the resin may not have yet swelled completely, the average resin volume exiting the circuit was 42.6 mL. This corresponds to a resin volume change of only 6.1% between the loaded form of the resin and the hydrogen form of the resin. This is significantly less than the observed volume change of 27% for the TP207XL reported in Chapter 4 when converted from the sodium form to the hydrogen form.

The percent resin during the carousel tests was 7.1%, so the corresponding error in solution volume estimate is only 0.5% (negligible). If the circuit were run with a higher percent resin, the expected error would increase, but is still fairly low, as is tabulated in Table 11.7. Thus, the constant volume assumption appears to be adequate for this application.

**Table 11.7: Estimate of Solution Volume Errors**

<table>
<thead>
<tr>
<th>% Resin</th>
<th>1</th>
<th>5</th>
<th>7.1</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Error</td>
<td>0.07%</td>
<td>0.3%</td>
<td>0.5%</td>
<td>0.7%</td>
<td>1.2%</td>
<td>1.6%</td>
<td>2.2%</td>
</tr>
</tbody>
</table>

**11.6 Conclusions from Miniplant Testwork**

Results from the miniplant testwork suggest that the film diffusion model from Chapter 6 and the hybrid correlation model from Chapter 7 are adequate for describing loading of a single element RIP circuit. Both the results for nickel (low alpha) and for copper (high alpha) appear to be adequately described.

The segregated flow model appears to be adequate for describing loading under cascade operating conditions. While the finite differences model for carousel operation did not provide a very good fit to the nickel carousel run, results are within error bounds and the discrepancy between the model and observations is believed to be due to the poor feed rate control experienced during this run. In the copper carousel run, much tighter control of the feed rate was achieved and there was good agreement between observations and the finite differences model.

Therefore, both the cascade and carousel models appear to be adequate at predicting circuit operation, and are, therefore, believed to be suitable for simulating the effect of various parameters on circuit performance.
12.0 RIP Circuit Simulation and Results

In this chapter, a number of different RIP operating scenarios are evaluated. The RIP circuit simulation is based on the circuit models verified in the previous chapter. For these simulations, the base case consists of five 20 m$^3$ RIP loading tanks fed with 5 g/L solution (either nickel or copper) at 30 m$^3$/hour, and a circuit recovery of 99.5%. To determine total resin volume, it is assumed that the resin feed tank is the same size as a loading tank, but holds twice the resin volume. Furthermore, it is assumed that resin spends six hours in the elution circuit (5 BV wash @ 10 BV/hr, 5 BV acid strip @ 2 BV/hr, 10 BV strip wash @ 10 BV/hour + 1.5 hours for resin transfer and/or acid hold step). In terms of resin properties, the kinetic parameters for the TP207XL, lot CHE 50019, were used, except that the manufacturer specification for resin capacity (2.0 eq/L) was used in lieu of the observed capacity for the particular lot tested.

12.1 Effect of Resin Volume in Tanks and Solution Backflow on Cascade Circuit

The cascade RIP circuit model was used to determine how the amount of resin in the loading tanks affects overall circuit performance. In these runs, the total resin volume present in the loading circuit (5 loading tanks + resin feed tank) was modeled at 5 m$^3$, 10 m$^3$, 15 m$^3$, 20 m$^3$, 25 m$^3$, 30 m$^3$, and 35 m$^3$ (corresponds to 3.6%, 7.1%, 10.7%, 14.3%, 17.9%, 21.4%, and 25.0% resin in each loading contactor). To ensure that the target recovery of 99.5% was achieved, the rate of resin transfer between the tanks was adjusted. Circuit performance was evaluated in terms of final resin loading exiting the circuit and the total resin inventory required.

The set of scenarios were run twice to determine the effect of solution back-mixing during resin transfer. In the first set, it was assumed that there was no solution back-mixing occurring (i.e. perfect separation of resin and solution when resin is transferred between contactors). In the second set, it was assumed that all solution in the airlift with the resin was back-mixed (i.e. no interstage screening on airlift discharges).

Removal of interstage screening during resin transfer could have significant benefits to an RIP operation. During the original resin evaluations for continuous uranium RIP circuits in the 1950s, it was the vibrating interstage screens that were expected to produce the largest amount
of resin attrition in the circuit (52). In modern RIP circuits, sieve-bend screens are often used, but can cause operational concerns due to fouling of the screens in some environments. Note that interstage screening can only be removed on the resin transfer stream; interstage screening (internal or external) on pulp transfer is still required.

12.1.1 RESIN VOLUMES & SOLUTION BACK-MIXING: NICKEL CASCADE

All six resin volume scenarios were run for nickel loading with no solution back-mixing, but only four resin volume scenarios were run for nickel loading with solution back-mixing. This was because at 3.6% and 7.1% resin volumes, so much dilution was occurring that the circuit could not achieve the target 99.5% recovery.

The solution profile and resin profile across the circuit have been plotted in Figures 12.1 and 12.2 for the case of no solution back-mixing; and in Figures 12.3 and 12.4 for the case of solution back-mixing. Work done at Mintek on the optimization of carbon-in-pulp plants in the 1980s was based on a linear approach to a linear isotherm (109,110). If this assumption were applied to an RIP circuit, it would result in an exponential decrease in solution concentration across a multi-stage circuit with equal resin distribution in each stage. However, when the hybrid correlation is used to predict loading rates, a very different solution profile across the circuit is observed, as can be seen in Figures 12.1 and 12.3. Thus, the conclusions from the CIP optimization study may or may not hold true for a base metal RIP circuit.
**Figure 12.1: Solution Profile Across Circuit – Nickel Cascade, No Back-Mixing**

**Figure 12.2: Resin Profile Across Circuit – Nickel Cascade, No Back-Mixing**
**Figure 12.3: Solution Profile Across Circuit – Nickel Cascade, With Back-Mixing**

**Figure 12.4: Resin Profile Across Circuit – Nickel Cascade, With Back-Mixing**
The effect of resin volume per stage on final resin loading is plotted in Figure 12.5. This graph shows that the final resin loading increases with the amount of resin in each tank, but the incremental benefit of increasing the resin volume diminishes. In order to reach the target of 99.5% recovery when less resin was present in the tank, the resin had to be cycled through the circuit more quickly. Thus, these predictions are in agreement with those reported by researchers at the Tshwane University of Technology, who found that the final resin loading increased with the residence time of the resin in the circuit (105).

**FIGURE 12.5: FINAL RESIN LOADING VS. PERCENT RESIN IN TANK – NICKEL CASCADE**
The total circuit resin inventory (loading circuit + elution circuit) is plotted against the percent resin in each tank in Figure 12.6. This graph shows that the minimum total resin inventory is achieved near 10% resin volume for the case of no solution back-mixing and somewhere between 10-15% for the case of complete back-mixing of airlift solution. Furthermore, this graph suggests that separation of the solution and resin has minimal benefit on the overall resin inventory. In fact, at the point where the discrepancy between the two models is greatest (10% resin volume), the total resin inventory differs by only 3 m³ (approximately 10% difference in total resin inventory).

**Figure 12.6: Total Resin Inventory vs. Percent Resin in Tank – Nickel Cascade**
To further understand the effect of solution back-mixing, the final resin loading value was plotted against the total resin residence time in the five RIP loading contactors. These results are plotted in Figure 12.7 and show that the two curves (solution recycle and no solution recycle) are almost overlapping. This suggests that very similar circuit performance can be achieved under both operating conditions and that it is simply necessary to increase the resin transfer rate when solution back-mixing is occurring.

![Figure 12.7: Effect of Resin Residence Time on Final Resin Loading](image)

Figure 12.8 compares the two metrics used to evaluate circuit performance against each other. Ideally, an RIP circuit will have a high resin loading and a low total resin inventory. In an industrial RIP circuit high resin loading results in more concentrated eluate with fewer impurities, while lowering the total resin inventory results in cost savings. Ultimately, the selection of optimum conditions will vary from system to system, and one will need to take the eluate processing steps into consideration when designing the loading circuit.
12.1.2 RESIN VOLUMES & SOLUTION BACK-MIXING: COPPER CASCADE

The same six scenarios were run for a copper RIP circuit. The solution and resin profiles for these simulations can be found in Appendix K. Note that for copper loading, all six resin volume scenarios were able to be evaluated for the case of solution back-mixing.

The final resin loadings under various resin volume fractions are displayed in Figure 12.9. Note that the final resin loading reaches a maximum at 14% resin volume and then decreases with increasing resin volume. This illustrates that too much resin in a circuit can lead to decreased circuit performance, and in an industrial RIP plant this would translate into increased impurity loadings on the resin exiting the circuit.
Since copper has a much higher alpha value than nickel (0.62 vs 0.36) it is reasonable to expect that the effect of solution back-mixing should be more pronounced. However, from the column graph in Figure 12.9, it only appears that this is the case at low resin concentrations. Figure 12.10 plots the total resin inventory against final resin loading to further investigate this point.
Figure 12.10: Total Resin Inventory vs. Final Resin Loading – Copper Cascade

Results from Figure 12.10 illustrate that at low final resin loadings, the discrepancy in total resin inventory is much greater for copper than for nickel. However, it is unlikely that a copper RIP circuit would be operated in this regime, since low loadings would result in high levels of impurities co-loading onto the resin. Thus, as in the case of nickel, it would appear that separation of resin from the pulp on the resin transfer streams may be unnecessary.

12.2 Effect of Size and Number of Tanks on Cascade Circuit Performance

Since the cascade circuit simulation assumes perfect mixing and no short-circuiting of solution in the contactors, the only effect tank size has on circuit performance is in the amount of solution transferred with the resin in the airlifts. Thus, if one assumes no solution back-mixing, the simulation results are independent of tank size. Note that this was also true of the
simulation results presented in the work of Zainol and Nicol, for their simulation based on a linear approach to equilibrium (3).

To determine the effect of the number of stages on cascade circuit performance, a series of scenarios were run for both nickel and copper recovery. In these scenarios 5 g/L feed was modeled through a three tank cascade circuit, a four tank cascade circuit, and a five tank cascade circuit. For this evaluation, it was assumed that there was no solution back-mixing, and the recovery target of 99.5% was used once again.

12.2.1 Nickel Cascade Circuit

To determine the effect of the number of contactors for nickel, the amount of resin in each circuit was adjusted to achieve the target loadings of 45, 48, 50, and 52 g Ni / L Resin. Note that the three stage circuit could not achieve a loading target of 46 g Ni / L Resin or greater, and the four stage circuit could not attain a resin loading of 52 g Ni / L Resin. In order to achieve the target of 99.5% recovery, the rate at which the resin was moved through the circuit was adjusted.

Results showed that to achieve a higher resin loading and still maintain the same circuit recovery, one needs to slow down the rate of resin transfer and increase the amount of resin present in the circuit. Assuming, once again, that 6 hours worth of resin are required outside the loading circuit (elution, resin transfer steps), increasing the total number of stages results in lower total resin inventories. This is illustrated in Figure 12.11.
For copper, the target final resin loadings were: 57, 58.5, 60, and 61.5 g Cu / L Resin. Note that the four tank circuit could not achieve a resin loading of 60 g Cu / L Resin, and the three tank circuit could not achieve resin loadings of 60 or 61.5 g Cu / L Resin.

Results for copper showed the same general trend as those previously reported for nickel, namely that more stages resulted in a lower total resin inventory. However, in the case of copper, higher resin loadings were achieved and the amount of resin inventory required is significantly less than that required for nickel. This is illustrated in Figure 12.12.

**Figure 12.11: Effect of Number of Stages on Total Resin Inventories –Nickel Cascade**

### 12.2.2 Copper Cascade Circuit

For copper, the target final resin loadings were: 57, 58.5, 60, and 61.5 g Cu / L Resin. Note that the four tank circuit could not achieve a resin loading of 60 g Cu / L Resin, and the three tank circuit could not achieve resin loadings of 60 or 61.5 g Cu / L Resin.

Results for copper showed the same general trend as those previously reported for nickel, namely that more stages resulted in a lower total resin inventory. However, in the case of copper, higher resin loadings were achieved and the amount of resin inventory required is significantly less than that required for nickel. This is illustrated in Figure 12.12.
To determine the process sensitivity of a cascade operation, various parameters were adjusted and the resulting effect on circuit recovery was calculated by the model. Three of the nickel circuit models with no back-mixing presented in Section 12.1.1 were evaluated for each parameter: 5 m$^3$, 20 m$^3$, and 35 m$^3$ resin volume in the loading circuit.

**12.3 Process Sensitivity of a Cascade Circuit**
12.3.1 Effect of Uneven Resin Distribution

To determine the effect of an uneven resin profile across the RIP circuit, the distribution of resin across the circuit was adjusted, and both the total resin inventory and the rate of resin movement through the circuit were held constant. In this simulation, the case of complete solution back-mixing with the resin transfer was considered.

Four resin distribution profiles for each scenario were investigated. For the base case, an even resin distribution was considered. Three additional resin profiles were considered: a resin profile decreasing across the RIP circuit, a resin profile increasing across the RIP circuit, and finally a resin profile where it was assumed that the middle tank lost most of its’ resin inventory and the upstream tank had almost twice the normal resin inventory. Figure 12.13 displays the resin profiles across the circuit for the four cases being evaluated.

![Figure 12.13: Resin Profile Across RIP Circuit – Uneven Resin Distribution Scenarios](image)

**Figure 12.13: Resin Profile Across RIP Circuit – Uneven Resin Distribution Scenarios**
To get a sense of how the overall resin distribution affects the solution profile across the RIP circuit, results for the four cases when the average resin volume per tank is 18% (25 m$^3$ resin in loading circuit) are displayed in Figure 12.14.

![Figure 12.14: Solution Profile Across Circuit – Uneven Resin Distribution](image)

This graph suggests that an RIP circuit should have the ability to somewhat compensate for uneven resin distributions. This has been observed in miniplant testwork on laterite pressure acid leach tailings by Nicol and Zainol when they experienced higher resin concentrations in the final three stages of their circuit (18).

However, different resin distribution patterns do affect the overall circuit recovery. In the case of gold CIP circuits (110), the highest circuit recovery is expected when there is an even resin distribution across the circuit. Figure 12.15 plots the overall circuit recovery for each resin
distribution profile for each of the three scenarios investigated: 15 m$^3$, 25 m$^3$, and 35 m$^3$ resin inventory in loading circuit.

![Graph showing circuit recovery for different resin distribution profiles](image)

**Figure 12.15: Circuit Recovery for Different Resin Distribution Profiles**

This graph shows that the highest circuit recoveries are typically achieved with an even distribution of resin across the circuit, as is the case for gold CIP. The one exception to this is at 15 m$^3$ total resin inventory, where a very slight increase in recovery was observed when more resin is placed in the front end of the circuit (i.e. tanks 1 and 2). To determine if a higher recovery could be expected in a circuit operated with a very high resin transfer rate with more resin in the front end, a simulation was run with no solution back-mixing and a total resin inventory of 5 m$^3$ in the circuit. Results indicated a noticeable increase in predicted recovery in this case: 99.8% vs. 99.5%.
More importantly, this graph shows the process sensitivity to fluctuations in resin distribution across the circuit. In the case of low resin volumes in the loading tanks and a high resin feed rate (15 m$^3$), the process is relatively robust with respect to fluctuations in resin distribution across the circuit. On the other hand, at high resin volumes and a low resin feed rate (35 m$^3$), the circuit is much more sensitive to fluctuations in resin distribution across the circuit.

### 12.3.2 Effect of Losing Resin Volume in Loading Circuit

To determine the process sensitivity to losing resin volume in the loading portion of the RIP circuit, four scenarios were then run for each base case. In each scenario, the resin volume in the loading portion of the circuit was decreased, but the rate of resin transfer was held constant. The model was run using resin volumes of 95%, 80%, 67%, and 50% of the base case values.

Figure 12.16 plots the overall circuit recovery against the resin volume in the loading section of the circuit.

![Figure 12.16: Effect of Losing Resin Volume in Loading Section of RIP Circuit](image)

Results from Figure 12.16 suggest that a loading circuit with a high resin content and a low resin transfer rate is much more robust to variance in the total amount of resin present in the
loading section of the circuit. It is important to point out that the changes in resin volumes in Figure 12.16 refer to percent variation from the base case (i.e. poorer recoveries are observed when a circuit decreases from 5 m$^3$ of resin to 2.5 m$^3$ resin than when a circuit decreases from 35 m$^3$ of resin to 17.5 m$^3$ resin). Thus, the circuit with a low resin volume and a high resin transfer rate is much more sensitive to losing a particular volume of resin (say 1 m$^3$ of resin) than a circuit with a high resin content and a low resin transfer rate.

### 12.3.3 Effect of Swings in Feed Concentration

To determine the process sensitivity to spikes in feed concentration, the model was run with higher concentrations of nickel in the feed. In addition to the base case of 5000 ppm nickel, the model was run at 5263, 6250, and 7500 ppm nickel in the feed. As would be expected, if one makes no changes to circuit operation, the process recoveries drop significantly (in a real operation one could increase the speed of resin transfer to compensate for this). Results are plotted in Figure 12.17 and show that the scenario with high resin volumes is most sensitive to swings in feed concentration.

![Figure 12.17: Effect of Increased Feed Concentration on Circuit Recoveries](image)
12.3.4 SUMMARY: CASCADE CIRCUIT PROCESS SENSITIVITY

Based on the modeling scenarios presented above, there is no one optimum circuit operating strategy that is robust under all process variations. A circuit operated with a low resin concentration in each tank and a high resin flowrate is more sensitive to fluctuations in the total resin volume present in the circuit, the effect of slurry back-mixing with resin transfer, and is expected to have higher levels of impurities reporting to elution. On the other hand, if a circuit is operated with a high resin concentration in each tank and low resin flowrate, it is predicted to be more sensitive to fluctuations in feed concentration and to variations in the resin distribution profile across the circuit.

12.4 RESIN UTILIZATION: CASCADE VS. CAROUSEL OPERATION

Carousel operations have the advantage of eliminating solution back-mixing and allowing for much tighter control of resin inventory. In order to determine how the two modes of operation compare in terms of resin utilization, the cascade case with 25 volume percent of resin and no solution back-mixing was taken as a base case. To obtain the same 99.5% recovery with a five stage carousel circuit and 25% resin volume, the time interval between changing the position of the contactors was varied. Furthermore, it was assumed that when the lead contactor came offline, all the solution in that contactor was recycled back to the feed tank, and that the new contactor coming online in the lag position was full of water.

Results from the circuit simulation showed that the carousel mode of operation is more efficient in terms of resin utilization. To achieve 99.5% recovery with the cascade circuit, the resin needs to be transferred at a rate of 3 m³/hr, giving a total circuit resin residence time of 8.3 hours and a final resin loading of 52.9 g Ni/L Resin. However, to achieve this same recovery with a carousel circuit, the contactor positions need to cycle every 2.3 hours, yielding a total circuit resin residence time of 11.5 hours and a final resin loading of 57.3 g Ni/L Resin. This suggests that the optimum resin residence time for a circuit running in cascade mode is not the same as for a circuit running in carousel mode. This is important, as previous researchers have concluded that either operating strategy will yield the same results, but in their work the same
resin residence time was used to experimentally compare circuit performance under the two operating strategies (105).

Furthermore, it is interesting to note that very little loading occurs in the lead contactor of the carousel arrangement, suggesting that the carousel circuit may be able to operate with fewer contactors than the cascade circuit. This will be further explored in Section 12.5.3.

The significant disadvantage of the carousel arrangement is the logistics of taking the lead contactor offline, moving the resin through the elution process, and then bringing a fresh contactor back online in the lag position. For base metals, the required cycle times are quite fast: 2.3 hours in this particular simulation. Practically speaking, the amount of time required to drain the lead contactor and separate the resin from the slurry could be greater than the optimum cycle time calculated by a process model. Thus, practical materials handling constraints must be evaluated as part of a carousel circuit evaluation.

The simulation results for two cycles of the carousel circuit are displayed in Figures 12.18 (solution) and 12.19 (resin). Note that the solution and resin profiles for the cascade circuit are flat with respect to time (assuming steady-state) and the values at 25% resin volume were previously reported in Figures 12.1 and 12.2.
Figure 12.18: Carousel Solution Profile at 25 Volume Percent Resin

Figure 12.19: Carousel Resin Profile at 25 Volume Percent Resin
12.5 **Effect of Contactor Size, Cycle Time, and Number of Contactors – Carousel**

In terms of carousel circuit design, the cycle time between tanks coming offline, the size of the contactors and the number of contactors all play a significant role. For this exercise, the target of 99.5% recovery was once again used, and for each scenario the amount of resin in the loading circuit or the carousel cycle time was adjusted to ensure that this target was achieved.

**12.5.1 Effect of Contactor Size**

To determine the effect of contactor size, a resin volume of 5 m$^3$ per contactor was used in all scenarios, the size of the contactor was varied, and the cycle time was adjusted to achieve the target of 99.5% recovery. Results from this simulation showed that increasing the contactor size had negligible impact on the solution and resin profiles across the circuit; although increasing contactor size does result in an increased cycle time, as shown in Figure 12.20.

![Figure 12.20: Effect of Contactor Volume on Carousel Cycle Time](image-url)
Figure 12.20 suggests that increasing contactor volume results in a linear increase in cycle time. However, by increasing the size of the contactor, the time required to drain the contactor also increases. If one compares the results from the simulation run at 15 m$^3$ and 30 m$^3$, the cycle time only increases from 2.2 to 2.7 hours, even though the volume of the contactor has doubled. Therefore, large contactors are not necessarily beneficial for reducing the minimum allowable cycle time for practical purposes (i.e. the minimum cycle time that can accommodate the logistics of resin movement).

12.5.2 Effect of Cycle Time

To evaluate the effect of cycle time, the circuit with five 20 m$^3$ tanks was used. The cycle time of 1, 1.5, 2, 2.5, and 3 hours was input into the model and the resin volume in the contactors was adjusted to achieve the target of 99.5% recovery. Results in Figure 12.21 show that for the simulations performed, as the cycle time increased, the amount of resin required in each contactor increased linearly.

![Figure 12.21: Resin Required Per Stage vs. Carousel Cycle Time](image-url)
The effect of carousel cycle time on resin loading is displayed in Figure 12.22. Note that the resin loading values plotted in these curves are the final resin loadings at the end of a cycle (i.e. the resin in the lead contactor is about to be transferred to elution).

It is interesting to note that at a resin cycle time of one hour, most of the tanks are loading approximately the same amount of nickel. However, as the cycle time increases, most of the loading is taking place in only the last few tanks. This suggests that perhaps not as many tanks are needed when the amount of resin present in each contactor is high.
12.5.3 Effect of the Number of Contactors

To investigate the effect of the number of contactors in a carousel RIP circuit, the case of 5 m³ resin in 20 m³ contactors was once again selected for evaluation. The resin cycle time was adjusted until the circuit recovery was 99.5%. Figure 12.23 shows that the number of contactors in series is predicted to have minimal effect on the circuit cycle time.

![Figure 12.23: Effect of Number of Contactors on Carousel Cycle Time](image)

The other significant variable being affected by the number of contactors is the final resin loading. The circuit resin distribution at the end of a cycle is plotted in Figure 12.24. Note that there is minimal variation in resin loading in the third tank (52.4 – 53.0 g Ni / L Resin), regardless of the number of contactors in use. For the sake of comparison, the resin loading for the five stage cascade circuit was 52.9 g Ni / L Resin with no back-mixing and 52.5 g Ni / L Resin with back-mixing. This suggests that, for this particular case study, a three stage carousel circuit would provide similar metallurgical performance as a five stage cascade circuit.
In Chapter 4, a number of different iminodiacetic resins were evaluated. In terms of the loading curves generated for resins of the same size, the most significant difference between resins was the final loading capacity. There was also a slight difference in resin loading rate, where the Lanxess MonoPlus products were observed to have slightly faster loading rates than the other resins. The five stage cascade model with no back-mixing was used to evaluate how these differences in resin properties may affect circuit performance. Once again, the five cascade model was evaluated at 3.6, 14.3, and 25 vol% resin.

**Figure 12.24: Effect of Number of Stages on Carousel Resin Loadings**

12.6 Effect of Resin Properties on Circuit Performance

In Chapter 4, a number of different iminodiacetic resins were evaluated. In terms of the loading curves generated for resins of the same size, the most significant difference between resins was the final loading capacity. There was also a slight difference in resin loading rate, where the Lanxess MonoPlus products were observed to have slightly faster loading rates than the other resins. The five stage cascade model with no back-mixing was used to evaluate how these differences in resin properties may affect circuit performance. Once again, the five cascade model was evaluated at 3.6, 14.3, and 25 vol% resin.
12.6.1 Effect of Resin Capacity

In the resin comparison work, results for the final loading values at 2500 ppm nickel were reported in Table 4.3. If these values are converted from g Ni / L Resin to eq/L, the capacity of these resins varied from approximately 0.75 – 2.0 eq/L. The second lot of TP207XL used in the miniplant had an even higher capacity of 2.4 eq/L. Therefore, for the circuit simulations, capacity values of 0.75, 1, 1.5, 2, and 2.5 eq/L were used.

In these simulations, the flowrate of resin through the circuit was adjusted to achieve the target recovery of 99.5%. The final adjusted tank resin residence times are plotted in Figure 12.25. Note that many of the required resin flowrates at 3.6 volume percent are unrealistically fast—the point plotted at 1.5 eq/L required that the resin residence time per tank be just over 2 minutes; the point at 1 eq/L would require a tank resin residence time of about 12 seconds.

![Figure 12.25: Effect of Resin Capacity on Total Resin Residence Time](image)
It is interesting to note that in Figure 12.25, while the three curves appear to be approximately linear, the slopes are quite different, depending on the resin volume present in the circuit. For all three scenarios, doubling the resin capacity resulted in a reduction of the required residence time by more than a factor of two.

Assuming, once again, that 6 hours worth of resin flow are required for elution and resin transfer steps, the resulting total resin inventories are plotted in Figure 12.26:

![Graph](image)

**Figure 12.26: Effect of Total Resin Capacity on Total Resin Inventory**

The results in Figure 12.26 show that when a circuit is operated at low resin volume and high transfer rate, the circuit performance is more sensitive to variations in resin capacity. This is important to be aware of when operating an RIP circuit and replacing resin inventory, as there can be variation in capacity between lots of the same resin (as was experienced in this work with the two lots of TP207XL), and there can certainly be large differences with resins from
different manufacturers. Furthermore, Figure 12.26 also indicates that the relationship between total resin inventory and resin capacity is non-linear. Therefore, using a resin with double the capacity does not necessarily mean that only half the resin inventory is required.

To get a sense of how different resin capacities could affect the amount of impurities reporting to elution, the final resin loading was examined. It is reasonable to assume that most of the capacity unused by nickel would be occupied by impurities in an operating circuit. Therefore, the resin with the lowest fractional nickel loading (nickel loaded / nickel loaded at capacity), would be expected to load the highest amount of impurities. The results for fractional nickel loading are plotted in Figure 12.27.

![Figure 12.27: Effect of Capacity on Fractional Nickel Loading](image)

Results from Figure 12.27 re-iterate the fact that when the circuit is operated with low resin volumes and high resin transfer rates greater levels of impurities are expected to report to
elution. The general trend is that, assuming no difference in resin selectivities, and that the circuit is optimized to achieve the same recoveries at the different resin capacities, resins with higher capacities should load less impurities.

To see how resin capacity affects carousel circuits, a single simulation of a five tank circuit with five cubic meters of resin in each tank was run with a resin capacity of 1.0 eq/L and was compared to the base case simulation presented in Section 12.4 (2.0 eq/L). Results showed that the carousel cycle time dropped from approximately 2.3 to 1.3 hours and the final resin loading dropped from 98% to 95% of the resin capacity. This suggests that using a resin with high capacity is beneficial in carousel operation as well.

### 12.6.2 Effect of Variation in $D_{app}$ on Nickel Loading

In the resin comparison work, the loading rates of the Lanxess Lewatit MonoPlus TP207 products were noticeably faster than for the other resins evaluated. In Chapter 8, the hybrid correlation was fitted at the +710-850 μm size fraction to both the regular TP207 product and the TP207XL product (lot CHC 5034). The fit parameters for these two resins were reported in Table 8.2, and the $D_{app}$ value for the MonoPlus TP207XL ($5.0 \times 10^{-12} \text{ m}^2/\text{s}$) was significantly higher than the $D_{app}$ value for the TP207 product ($2.7 \times 10^{-12} \text{ m}^2/\text{s}$). As was previously mentioned, the MonoPlus products are reported to have a more porous structure than the heterodispersed product (118), and so this increase in apparent diffusivity makes sense.

To see how this variation in apparent diffusivity could affect RIP circuit performance, the 5 stage circuit simulation was run with the two $D_{app}$ values, assuming a constant $\alpha$ factor of 0.3, and a constant resin capacity of 2.0 eq/L. Once again, the target of 99.5% recovery was used, and the rate of resin movement was adjusted to ensure this target was reached. Note that these simulations are not a direct comparison of the TP207 and TP207XL resins since the TP207 resin has a higher capacity than the TP207XL, but the model is holding the capacity constant to better see the effect of the variance in $D_{app}$ values.

Results show that to compensate for a lower $D_{app}$ value, the resin must be moved through the circuit more quickly. Again, assuming that there are six hours of resin in the elution circuit,
Figure 12.28 plots the total resin inventory against the resin volume in each tank for both the high and low $D_{app}$ values.

![Figure 12.28: Effect of Apparent Diffusivity on Total Resin Inventory](image)

Results from this simulation show that increasing the $D_{app}$ parameter results in a lower overall resin inventory. This is particularly pronounced when the circuit is being operated with low volumes of resin in the tanks and a high resin recirculation rate.

The effect of the apparent diffusivity on final resin loadings is displayed in Figure 12.29. Results suggest that a higher apparent diffusivity results in higher final resin loading values, and hence lower levels of impurities reporting to the elution circuit.
To see how the apparent diffusivity affected carousel circuit performance, a single simulation of a five cell circuit, with five cubic meters of resin in each tank was run using the low apparent diffusivity of $2.7 \times 10^{-12}$ m$^2$/s. Results were compared to the base case simulation presented in Section 12.4 ($D_{app} = 4.4$ m$^2$/s). The carousel cycle time decreased slightly from approximately 2.33 to 2.25 hours and the final resin loading dropped from 57.3 to 55.2 g Ni / L Resin. This suggests that having a high apparent diffusivity is beneficial in carousel circuits as well.

### 12.6.3 Effect of Resin Bead Diameter on Nickel Loading

The effect of resin bead diameter on nickel loading rate was evaluated using the five stage cascade simulation, assuming no solution back-mixing. The simulation was run at 3.6, 14.3,
and 25 volume percent resin in each tank for resin diameters of 600, 710, 850, 1000, and 1180 μm.

The effect of resin bead diameter on total resin inventory, assuming 6 hours of resin present in the elution circuit, is plotted in Figure 12.30. Note how the resin inventory required increases with the resin bead diameter, and that this effect is much more pronounced when the circuit is run with low resin concentrations in the tanks.

![Figure 12.30: Effect of Resin Bead Diameter on Total Resin Inventory](image)

The effect of resin bead diameter on final resin loading is plotted in Figure 12.31. This plot indicates that the final resin loading decreases as the size of the resin bead increases, even though the resin capacity was assumed to be constant in this simulation. This suggests that the higher loading rate associated with the smaller resin beads should result in fewer impurities
reporting to elution. However, large resin beads are still beneficial in RIP circuits to aid in the separation of the resin beads from the solids present in the feed slurry.

![Figure 12.31: Effect of Resin Bead Diameter on Final Resin Loading](image)

**Figure 12.31: Effect of Resin Bead Diameter on Final Resin Loading**

### 12.6.4 Effect of Recirculating Load of Nickel on Circuit Performance

During the resin comparison work, it was observed that an acid hold step was required to obtain complete stripping of nickel from some of the resin beads. During the operation of the RIP miniplant, the decision was made to recycle the resin to the circuit without using an acid hold step, resulting in a recirculating load of approximately 3 g Ni / L Resin. To quantify how such a recirculating load impacts circuit performance, simulations were run with resin recirculating loads of 0, 0.5, 1, 3, and 5 g Ni / L Resin.

In these simulations, the resin flowrate through the circuit was adjusted to ensure the target recovery of 99.5% was achieved in all cases. In order to attain the target recovery with higher
initial loadings on the resin, the rate of resin transfer through the circuit needed to be increased. Note that 99.5% recovery at a feed rate of 5 g/L nickel corresponds to a tails concentration of 25 ppm nickel. At 25 ppm nickel, the equilibrium capacity of the resin is still quite high (> 40 g Ni / L Resin) and so incomplete stripping would be expected to have minimal effect on the final attainable equilibrium concentration exiting the circuit. From Figure 9.6, at a solution concentration of 0.5 ppm nickel, the equilibrium capacity of the resin was 24 g Ni / L Resin. Thus, one would have to be targeting an extremely low concentration of nickel in the tails for these levels of recirculating loads to be equal to or lower than the equilibrium loading of the resin.

Figure 12.32 displays the expected final resin loading values for simulations run at 3.6, 14.3 and 25 volume percent. This graph shows that the presence of a recirculating load on the resin beads results in slightly lower final resin loadings at low resin concentration, but the effect is hardly noticeable in the simulation run at 25 volume percent.

![Figure 12.32 Effect of Resin Recirculating Load on Final Resin Loadings](image-url)
The effect of the resin recirculating load on total resin inventory was also investigated. Results show that at high resin volume concentrations, there is only a slight increase in inventory requirements if resin is returned to the circuit with a recirculating load of nickel. However, at low resin volume concentrations, returning resin to the circuit without complete stripping results in a significantly higher resin inventory. This is displayed in Figure 12.33.

![Figure 12.33: Effect of Incomplete Stripping on Resin Inventory Requirements](image)

**12.6.5 Summary of Effect of Resin Properties on Circuit Performance**

It is not surprising that the results on the effect of resin properties on metallurgical performance can be summarized by saying that the best resin will have both a high capacity and a fast loading rate (high $D_{app}$, and small $d_p$). The circuit simulation predicts that increasing either the capacity or the loading rate will result in lower total resin inventories and lower impurity levels reporting to elution.
The simulation also predicts that a circuit operated with low resin volumes in the contactors and at a high resin transfer rate will be particularly sensitive to variation in these parameters. However, it is important to reiterate that other factors not included in this evaluation, such as resin durability, may drive the selection criteria of the resin for a particular application.

### 12.7 Resin Comparison: Lewatit TP207 vs Lewatit MonoPlus TP207XL

Although insufficient tests were conducted to determine the hybrid correlation parameters for all the resins tested in Chapter 4, a full set of loading tests were conducted on the +710 -850 μm size fraction of the Lewatit TP207 and the Lewatit MonoPlus TP207XL. These results were reported in Chapter 8, and the key resin properties required for circuit simulation are reported in Table 12.2 (note that the results for TP207XL, lot CHC 5034 were used in this comparison).

**Table 12.1: Key Parameters for Nickel Loading onto TP207 and MonoPlus TP207XL**

<table>
<thead>
<tr>
<th>Property</th>
<th>TP207</th>
<th>MonoPlus TP207XL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_p$ [μm]</td>
<td>770</td>
<td>736</td>
</tr>
<tr>
<td>$K$ [-]</td>
<td>$3.9 \times 10^{-5}$</td>
<td>$9.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Capacity [eq/L]</td>
<td>2.12</td>
<td>2.01</td>
</tr>
<tr>
<td>Alpha [-]</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td>$D_{app}$ [m²/s]</td>
<td>$2.7 \times 10^{-12}$</td>
<td>$5.0 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

From Table 12.2, it can be seen that this size fraction of this lot of TP207 has a greater capacity than this lot of TP207XL. On the other hand, the TP207XL has a larger apparent diffusivity, and a slightly smaller typical resin bead diameter. To compare the performance of these two resins, the five stage nickel cascade circuit simulation was used. The circuit was simulated for each resin at 3.6, 7.1, 10.7, 14.3, 17.9, 21.4, and 25 volume percent resin. As before, the target recovery of 99.5% was achieved by varying the resin flowrate through the circuit.

In order to compare the amount of impurities that would report to elution with the two resins, the final nickel loading was calculated as fractional attainment of resin capacity. These results are plotted in Figure 12.34, which shows that, for the scenarios simulated, the TP207XL resin should have fewer impurities reporting to elution than the same size fraction of TP207.
Assuming that six hours of resin inventory is present in the elution circuit, the total resin inventory is plotted against the percent resin volume in each tank in Figure 12.35. This graph shows that at low resin concentrations in the tanks, the same recovery can be achieved using less TP207XL resin than TP207 resin. At higher resin concentrations in the tanks, the resin inventory for the two resins is approximately the same.
This resin comparison suggests that the loading properties of the TP207XL resin should be superior to the loading properties of the TP207 resin. The TP207XL product is superior in terms of the amount of impurities reporting to elution and in term of requiring less total resin inventory. However, note that other properties, such as resin durability were not evaluated in this work.
Key findings from the circuit simulations are presented in bullet form below, and the cascade circuit sensitivity analysis results are tabulated in Table 12.2.

- The same recovery from an RIP circuit can be achieved in many ways. If the resin volume in each tank is reduced, it is possible to compensate for this by increasing the resin flowrate through the circuit.

- There is a minimum resin inventory that can be achieved for a given recovery. However, this minimum resin inventory may not occur at the ideal operating point, in terms of process robustness.

- Optimum results are achieved when the resin is distributed evenly in all loading tanks.

- The total resin inventory required in a cascade circuit decreases with the number of stages used. Furthermore, the amount of impurities reporting to elution also decreases with the number of stages.

- For the case of both nickel and copper, the deleterious effect of solution back-mixing when transferring resin to the upstream contactor is minimal, if the circuit is operated with high resin volumes and a low resin flowrate.

- A resin with high capacity and fast loading rates results in lower total resin inventories and fewer impurities reporting to elution, especially when operating with low resin volumes and a high resin flowrate.

- The optimum resin residence time for a circuit running in cascade mode is not the same as for a circuit running in carousel mode. Results from these simulations suggest that if the optimum resin residence time is used in both cases, the carousel arrangement results in higher final resin loadings due to a longer resin residence time. Alternatively, it may be possible to reduce the number of contactors in a carousel circuit and still achieve a similar final resin loading as occurs in a cascade circuit.
Base metal circuit operation in carousel mode is probably going to be limited by the logistics of taking the lead contactor offline and transferring resin to and from the elution circuit. In order to increase the carousel cycle time, the circuit should use a high capacity resin and be operated with high resin volumes in each tank.

Process sensitivity of a cascade operation varies depending on whether the circuit is operated with high resin volumes and a low resin transfer rate or with low resin volumes and a high resin transfer rate. Process sensitivity is summarized in Table 12.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>More Sensitive When…</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Resin Volume in Tank and Low Resin Transfer Rate</td>
</tr>
<tr>
<td>Total resin volume variations in loading circuit</td>
<td>X</td>
</tr>
<tr>
<td>Uneven resin distribution across loading circuit</td>
<td>X</td>
</tr>
<tr>
<td>Solution back-mixing, especially at high α</td>
<td>X</td>
</tr>
<tr>
<td>Swings in feed concentration</td>
<td>X</td>
</tr>
<tr>
<td>Impurities reporting to elution</td>
<td>X</td>
</tr>
<tr>
<td>Changes in Resin Loading Capacity</td>
<td>X</td>
</tr>
<tr>
<td>Changes in Resin Apparent Diffusivity</td>
<td>X</td>
</tr>
<tr>
<td>Changes in Resin Bead Diameter</td>
<td>X</td>
</tr>
<tr>
<td>Incomplete Stripping of Resin Beads</td>
<td>X</td>
</tr>
</tbody>
</table>
13.0 CONCLUSION

The three objectives for this research program have been met. The conclusions from this work and how they relate to the research objectives will be presented. This will be followed by recommendations for further work.

13.1 CONCLUSIONS FROM RESEARCH

The three objectives for this research program were to adequately describe the rate of nickel loading by examining data obtained under infinite solution volume conditions, verify the developed loading model under non-infinite solution volume conditions, and then use the model to quantify the effect of various RIP operating configurations. Conclusions from this research program can be grouped according to these three objectives.

13.1.1 ADEQUATELY DESCRIBE LOADING UNDER INFINITE SOLUTION VOLUME CONDITIONS

1) In order to obtain laboratory data that could be analyzed under infinite solution volume conditions, the pH-stat method was modified to minimize the effect of sodium co-loading onto an iminodiacetic acid resin. The modified method held the concentration of the pay metal (nickel, cobalt, or copper) approximately constant over the course of the test, in addition to the solution pH. For the specific case of nickel loading, the method was shown to have good repeatability with a maximum error of +/- 2 g Ni / L Resin.

2) The modified pH-stat method was used to compare the performance of three new large bead resins that have been manufactured specifically for RIP. Each of the three new RIP grade resins excels in at least one area:

- In terms of size, the large bead resin with the largest size distribution is the Ambersep XE818. The Purolite S930+/4888 resin is slightly smaller, while the Lewatit MonoPlus TP207XL is a significantly smaller product. The Ambersep XE818 also has the least bulk volume change when converted from sodium form to hydrogen form.
• The large bead resin with the largest capacity is the Purolite S930+/4888. The Lewatit MonoPlus TP207XL resin has a slightly lower capacity, while the Ambersep XE818 has a significantly lower capacity.

• The large bead resin with the fastest loading rate is the Lewatit MonoPlus TP207XL. This resin also has the tightest size distribution of resin bead diameters. Since resin bead diameter is known to have a significant impact on loading rates, using a resin with a narrow size distribution will allow for a better evaluation of other parameters affecting the system. Therefore, the Lewatit MonoPlus resins were selected for use in this research program.

3) Qualitative tests were conducted to determine the predominant rate-limiting step. Results suggest that the process is initially film-diffusion limited, and then becomes limited by some combination of intraparticle diffusion and ion exchange rate. The portion of loading that is film diffusion limited was able to be described by a linear approach to equilibrium – the standard engineering model for this scenario. The portion of loading that is limited by intraparticle diffusion and/or ion exchange rate could not be adequately modeled by a standard engineering model. In particular, the dependence on solution concentration could not be adequately described by any model.

4) A hybrid correlation was proposed to describe the loading rate in the intraparticle diffusion / ion exchange limited regime. The hybrid correlation combines the Vermeulen Approximation to intraparticle diffusion limited loading and an approximation to the shrinking core model. A new model fit parameter, $\alpha$, was introduced to describe the dependence of the system on solution concentration. As $\alpha$ approaches zero, the model predicts standard intraparticle diffusion limitation, as described by the Vermeulen Approximation. As $\alpha$ approaches one, the hybrid correlation predicts shrinking core type intraparticle diffusion. Thus, $\alpha$ can be taken as a measure of how strong a boundary is present between the reacted and unreacted portion of a resin bead during loading. The hybrid correlation was fit to experimental results for copper, nickel, and cobalt loading. The hybrid correlation was found to adequately describe the loading rate of nickel over the range of 50 – 5000 ppm, meeting the first objective of this work. The alpha parameter for copper (0.62) was much higher than that for nickel and cobalt (0.28 & 0.25
respectively). When resin beads loaded to approximately 50% of capacity were placed under the microscope, a distinct shell and core structure was observed for copper, but not for nickel or cobalt.

13.1.2 Verification of Engineering Models

5) Three batch loading tests were conducted with non-constant nickel concentrations in solution. The early portion of loading was modeled using the film diffusion model and the latter portion of loading was modeled using the hybrid correlation. To determine the rate-limiting step as the resin loaded, a modified Helfferich number was developed. This modified Helfferich number yields a value greater than one during film diffusion control and a value less than one during intraparticle diffusion/ion exchange reaction limited control. Results showed that the two models provided an adequate fit to the experimental data, without an additional model being required to describe mixed control. In particular, a test was carried out without any stock solution being added, and the modified Helfferich number suggests that most of this test was carried out under mixed control conditions.

6) A five stage RIP miniplant was constructed and operated in both cascade and carousel modes for both nickel loading and copper loading. Loading rates were predicted using the film diffusion model, the hybrid correlation, and the modified Helfferich number. A cascade circuit model was assembled, assuming perfect mixing in each reactor and using the segregated flow model for the resin beads. This model was verified with experimental data for both nickel and copper. A carousel model was assembled using finite differences to calculate the changes in reactor solution concentrations and metal loadings with time. This model was verified experimentally for copper; the results from the nickel run were within error bounds; however the error bounds for this test were large due to fluctuations in solution feed rate during circuit operation. Results from the RIP miniplant suggest that both the hybrid correlation and the circuit models generated are adequately describing observations so that the second objective of model verification was met.
13.1.3 **Quantify Effect of Various Operating Conditions on Circuit Performance**

7) The circuit models were used to simulate various scenarios for a potential RIP plant. Key results from these simulations are:

- The same recovery from an RIP circuit can be achieved in many ways. If the resin volume in each tank is reduced, it is possible to compensate for this by increasing the resin flowrate through the circuit.

- There is a minimum resin inventory that can be achieved for a given recovery. However, this minimum resin inventory may not occur at the ideal operating point, in terms of process robustness.

- Optimum results are achieved when the resin is distributed evenly in all loading tanks.

- The total resin inventory required in a cascade circuit decreases with the number of stages used. Furthermore, the amount of impurities reporting to elution also decreases with the number of stages.

- For the case of both nickel and copper, the deleterious effect of solution back-mixing when transferring resin to the upstream contactor is minimal, if the circuit is operated with high resin volumes and a low resin flowrate.

- A resin with high capacity and fast loading rates results in lower total resin inventories and fewer impurities reporting to elution, especially when operating with low resin volumes and a high resin flowrate.

- The optimum resin residence time for a circuit running in cascade mode is not the same as for a circuit running in carousel mode. Results from these simulations suggest that if the optimum resin residence time is used in both cases, the carousel arrangement results in higher final resin loadings due to a longer resin residence time. Alternatively, it may be possible to reduce the number of contactors in a carousel circuit and still achieve a similar final resin loading as occurs in a cascade circuit.
- Base metal circuit operation in carousel mode will probably be limited by the logistics of taking the lead contactor offline and transferring resin to and from the elution circuit. In order to increase the carousel cycle time, the circuit should be operated with high resin volumes in each tank a resin with a high capacity should be used.

- Process sensitivity of a cascade operation varies depending on whether the circuit is operated with high resin volumes in the contactors and a low resin transfer rate, or operated with low resin volumes in the contactors and a high resin transfer rate. Table 12.2 is reprinted here to summarize which operating situations are more likely to affect a circuit, depending on which resin transfer strategy is used.

**Table 13.1: Sensitivity of Cascade Circuits (Repeat of Table 12.2)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>More Sensitive When…</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Resin Volume in Tank and Low Resin Transfer Rate</td>
</tr>
<tr>
<td>Total resin volume variations in loading circuit</td>
<td></td>
</tr>
<tr>
<td>Uneven resin distribution across loading circuit</td>
<td>X</td>
</tr>
<tr>
<td>Solution back-mixing, especially at high $\alpha$</td>
<td></td>
</tr>
<tr>
<td>Swings in feed concentration</td>
<td>X</td>
</tr>
<tr>
<td>Impurities reporting to elution</td>
<td></td>
</tr>
<tr>
<td>Changes in resin loading capacity</td>
<td></td>
</tr>
<tr>
<td>Changes in resin apparent diffusivity</td>
<td></td>
</tr>
<tr>
<td>Changes in resin bead diameter</td>
<td></td>
</tr>
<tr>
<td>Incomplete stripping of resin beads</td>
<td></td>
</tr>
</tbody>
</table>
13.2 RECOMMENDATIONS FOR FURTHER WORK

As with most research projects, several interesting areas and questions arose over the course of this work that were not critical to achieving the research objectives and so were not explored in detail. Recommendations for further work can be grouped into three research areas, and each will be discussed in turn.

13.2.1 FUNDAMENTAL LOADING MODEL FOR IMINODIACETIC RESINS IN HYDROGEN FORM

In the hybrid correlation, both the intraparticle diffusion and ion exchange reaction components of the process are grouped together. Separating out these effects could provide valuable insight for manufacturers of resin beads. In order to be able to separate out these effects, fundamental kinetic studies are recommended to model the ion exchange reaction component, and isotopic tracer tests are recommended to model the intraparticle diffusion component. A good reference in the literature that could help to plan such a fundamental study is the work of Price et al. for the study of nickel loading onto an aminophosphonic resin in the sodium form (12).

When developing such a fundamental model, it will be important to remember that the loading capacity of a resin typically varies with manufacturing lot, and the work done with the heterodispersed TP207 product suggests that loading capacity can vary with resin bead diameter within the same lot of resin. Therefore, it is recommended that sufficient resin of a single size fraction from the same lot be on hand to run the full set of fundamental tests.

To obtain the fundamental kinetics, the resin beads will need to be crushed to eliminate mass transfer effects. It is recommended that loading rate kinetics be determined at various pH values, feed metal concentrations, and temperatures. Past work on fundamental models for the iminodiacetic resin have typically been done using resin in the sodium form, and development of fundamental loading kinetics for a resin in the hydrogen form should be interesting.

To obtain the intraparticle diffusion coefficients, isotopic tracer tests can be done to obtain the diffusivities of individual components, and these can then be used to estimate a system’s overall diffusivity by use of the Nernst-Planck equation, as other researchers have done for iminodiacetic resins in the sodium form (11,9).
13.2.2 Application of Hybrid Correlation to Actual Slurries

The hybrid correlation developed in this work was only applied to the case of a single metal loading onto an iminodiacetic resin in the hydrogen form. In an actual application, it is expected that the resin will first load predominantly with impurities (calcium, magnesium, manganese, et cetera) and that these impurities will then be displaced by the pay metal. Thus, running a series of experiments to determine how the hybrid correlation’s fit parameters ($D_{\text{app}}$ and $\alpha$) change depending on the initial form of the resin (hydrogen form vs saturated with impurities) would be useful. Furthermore, determining how the hybrid correlation’s fit parameters vary with temperature and feed pH would also provide insight into the expected behaviour of an actual RIP system.

When the linear approach to equilibrium is used to model the loading of a base metal circuit in the intraparticle diffusion limited regime, the implicit assumption is that the intraparticle diffusion follows Gluckauf’s model. Strictly speaking, Gluckauf’s model was derived for the case of single element loading; however, engineers often use the model in more complex situations. This is also true for the application of all other engineering models: Vermeulen’s Approximation, the Shrinking Core Model, and even the linear approach to equilibrium for film diffusion control. Therefore, while the hybrid correlation was developed and proven for the case of single element loading, it may be possible to use it to model the loading of base metals from some slurries.

To investigate this possibility, the hybrid correlation should first be fit to loading tests conducted with synthetic solutions containing only one pay metal, and various common impurities. Next, the hybrid correlation should be fit to tests run with the filtrate from actual slurries, in order to determine if the loading rates can be described without the additional complication of solids redissolving as the resin loads. Note that if the filtrate contains both copper and nickel / cobalt, then tests should first be run at a low pH to only recover only the copper, and then repeated at a higher pH to recover the nickel and cobalt. Tests could also be run with the complete filtrate at higher pH to determine whether the hybrid correlation fails when trying to model the loading of two pay metals with such different loading behaviour. From a practical stand-point, it is interesting to note that the Brown’s Oxide RIP Flowsheet contained two RIP circuits: the first RIP circuit to recover copper and the second RIP circuit to recover nickel and cobalt.
13.2.3 Circuit Modeling With Variations in Resin Diameters

In this thesis, the RIP miniplant was operated with screened Lewatit MonoPlus resin, which has quite a narrow size distribution. Since resin bead diameter plays a significant effect on loading rate, it would be beneficial to extend the circuit models to be able to account for variations in resin bead diameters. This work is complicated by the fact that, even within a single manufacturing lot, the capacity of the resin can vary with resin bead diameter.

To account for a distribution of resin bead sizes, a statistical approach will likely be required. Such statistical methods have been applied to hydrometallurgical leaching systems and are reviewed in the literature (124). For CIP circuits, population balance models (125) have been used to simulate the counter-current movement of carbon through multiple tanks (126,127). Since CIP can be described in terms of a linear approach to equilibrium, the population model can be reduced to a set of coupled ordinary differential equations. However, since the hybrid correlation is based on a non-linear approach to equilibrium, a population balance model will result in a set of coupled partial differential equations. In this regard, it is interesting to note that a population balance model has been used with a non-linear approach to equilibrium to model the continuous ion exchange system at Rossing Uranium in Namibia (128).
REFERENCES


112. Mikhaylenko M. (2010) Solution Purification III -IX from Solution (from ISR) and RIP. Canadian Institute of Mining Short Course held in conjunction with U2010, August 14-15.


**APPENDIX A: BLANK BATCH TEST CHECK SHEET**

<table>
<thead>
<tr>
<th>Resin:</th>
<th>Size:</th>
<th>Ni Conc:</th>
<th>Date:</th>
</tr>
</thead>
</table>

**LOADING RATE TEST**

- **Prep Test Solution:** 500mL in 1L beaker. Place into hotwater bath to bring up to 30°C
  - Target g NiSO₄: ________  
  - Actual g NiSO₄ added: ________

- **Prep stock sol’n:** 0.25M NaOH, NiSO₄. Accuracy very important.
  - NiSO₄: ________ g into a 50 mL flask  
  - NaOH: ________ 25 mL into a 100 mL flask  
  - Actual g = ________

- **Measure SG** to three decimal places by pipetting 10 mL into flask on scale. Take 4-6 measurements.
  - SG of NaOH: ________  
  - SG of NiSO₄: ________  
  - Calc SG ________

- **Prep Equipment:** Turn on scales, calibrate pH probe (stand = pH 7, slope = pH 4)
  - Flush stock sol’n addition lines. Use solutions of appropriate pH so controller turns pump on and off
  - Weigh stock sol’n: Weights with no stoppers, tubing connected to flask. Record min. three decimal places.
    - Gross weight NaOH: ________  
    - Gross weight NiSO₄: ________

- **Prep resin:** 5mL in H⁺ form, place in beaker and fill to 15 mL with DI water. Initial resin pH = ________
  - pH adjust with NaOH to target 3.9-4.1 when stirred. Actual resin pH= ________

- **pH adjust** test solution in beaker to target 3.9 - 4.1. Beaker intial pH = ________  
  - Final pH = ________
  - Take sample #1. (Approx 5 mL)
  - Prep beaker for test: check pH probe, stock addition lines in place, pump is on "auto"
  - Measure rpm on motor. Target is 275-325 rpm; note that some fluctuation is normal. RPM = ________
  - Prep Scale: Zero scale with nothing on it. Replace flasks and record initial weight
  - Start Windmill Logger. **N.B. Parsing of data requires that a “+” sign preceeds all data -> else get “error 114”**
  - File> Restore logger setup: RIPBatch. Enter a file name & start logging data:
  - Start test: Transfer resin to test beaker and record start time as displayed on logger:
  - Sampling: Take sample after 1 hr, 4hrs, end of test
    - Time of Samples:
  - Ending Test: Shut off controller, mixer, stop data-logging. Record final wt on recording scale ________
    - Measure gross weights stock sol’n, no stoppers, tubing:  
      - Gross NaOH: ________  
      - Gross NiSO₄: ________
  - Take sample of NiSO₄ stock solution for assay

**RESIN ELUTION**

- Transfer resin into stripping column and change the DI water in the stripping flask (want NO ACID)
- Pass at least 5 BV DI water over resin at 10BV/hr (~0.8 mL/min). Solution to waste
- Pass 5 BV 100 g/mL sulphuric acid over resin and collect in 100 mL volumetric flask
- Leave resin in column 20 hours for acid hold step. Close stopcock at base of burette
- Pass 10 BV DI water over resin and collect in the same 100 mL flask
- Make up volume in flask, ready for assay
APPENDIX B: MANUFACTURER PROVIDED RESIN PROPERTIES

The following resin properties are taken from the published data sheets from the various resin manufacturers. Note that all resins tested were macroporous resins with iminodiacetic acid functional group and were shipped in the sodium form.

TABLE B.1: RESIN PROPERTIES FROM MANUFACTURER DATA SHEETS

<table>
<thead>
<tr>
<th>Resin</th>
<th>Amberlite IRC748</th>
<th>Ambersep XE818</th>
<th>Lewatit MonoPlus TP207</th>
<th>Lewatit MonoPlus TP207XL</th>
<th>Lewatit TP207</th>
<th>Purolite S930</th>
<th>Purolite S930 Plus</th>
<th>Purolite S930 Plus /4888</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot Tested</td>
<td>(92) 78544</td>
<td>6605081</td>
<td>CHT 5007</td>
<td>CHC 5034 CHE 50019</td>
<td>CHK 00444</td>
<td>107-92</td>
<td>SR 602078/1</td>
<td>SR 602078/2</td>
</tr>
<tr>
<td>Total exchange capacity</td>
<td>≥ 1.35 eq/L (Naform)</td>
<td>-</td>
<td>≥ 2.0 eq/L (H form)</td>
<td>≥ 2.0 eq/L (H form)</td>
<td>≥ 2.2 eq/L (H form)</td>
<td>-</td>
<td>≥ 2.9 eq/L</td>
<td>-</td>
</tr>
<tr>
<td>Reversible Swelling</td>
<td>30% typical</td>
<td>-</td>
<td>25% max</td>
<td>25% max</td>
<td>30% max</td>
<td>-</td>
<td>35% max</td>
<td>-</td>
</tr>
<tr>
<td>Size Range [mm]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&gt;90% 0.4-1.25</td>
<td>-</td>
<td>0.425 – 1.000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mean Size [mm]</td>
<td>0.50-0.65</td>
<td>-</td>
<td>0.61 ± 0.05</td>
<td>0.79 ± 0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Effective Size [mm]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.55 ± 0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fines Content [mm]</td>
<td>max 1% &lt; 0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>max 2% &lt; 0.425</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Coarse Beads [mm]</td>
<td>max 5% &gt; 1.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Uniformity Coefficient</td>
<td>≤ 1.7</td>
<td>-</td>
<td>≤ 1.1</td>
<td>≤ 1.1</td>
<td>≤ 1.7</td>
<td>-</td>
<td>≤ 1.5</td>
<td>-</td>
</tr>
<tr>
<td>Data Source</td>
<td>[B1]</td>
<td>[B2]</td>
<td>[B3]</td>
<td>[B4]</td>
<td>[B5]</td>
<td>[B6]</td>
<td>[B7]</td>
<td>[B8]</td>
</tr>
</tbody>
</table>

Data Sources

[B6] Historical Purolite Product. Unsure as to appropriate datasheet.
APPENDIX C: LOADING ISOTHERMS

The equilibrium isotherms in this appendix were generated from the resin final loading values obtained during the laboratory batch tests. For completeness, both the loading value and the stripping value are included on the curves (note: strip values for tests run before the 20 hour acid hold step was introduced are not plotted on the graphs). The mass action law was fit to the final loading values. The best fit parameters were reported in Table 8.1, and are repeated here:

<table>
<thead>
<tr>
<th>Resin</th>
<th>TP207</th>
<th>TP207XL</th>
<th>TP207XL</th>
<th>TP207MP</th>
<th>TP207MP</th>
<th>TP207MP</th>
<th>TP207XL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Ni</td>
<td>Ni</td>
<td>Ni</td>
<td>Ni</td>
<td>Co</td>
<td>Cu</td>
<td>Cu</td>
</tr>
<tr>
<td>K</td>
<td>3.9 x 10^{-5}</td>
<td>9.8 x 10^{-5}</td>
<td>5.0 x 10^{-5}</td>
<td>7.5 x 10^{-4}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity [eq/L]</td>
<td>2.12</td>
<td>2.01</td>
<td>2.36</td>
<td>1.97</td>
<td>1.91</td>
<td>2.11</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Nickel loading onto TP207 (+710 / -850 um size fraction):

![Isotherm for TP207](image-url)
Nickel loading onto TP207XL, lot CHC 5034 (Resin Comparison Work):

Note that no acid hold step was conducted to predict recirculating load on resin.

Nickel loading onto TP207XL, lot CHE 50019 (RIP Miniplant):

*Note that no acid hold step was conducted to predict recirculating load on resin*
Nickel loading onto TP207MP:

Cobalt loading onto TP207MP:
Copper loading onto TP207MP:

![Isotherm for TP207MP](image1.png)

Copper loading onto TP207XL, lot CHE 50019 (RIP Miniplant):

*Note that no acid hold step was conducted to predict recirculating load on resin*

![Isotherm for TP207XL (RIP Miniplant)](image2.png)
APPENDIX D: QUALITATIVE TESTS ON EFFECT OF pH (COPPER ALPHA VALUE)

Qualitative tests were run at 54, 541, and 5412 ppm copper at pH 2, 3, and 4. Mass balances for these tests are displayed in the table below:

<table>
<thead>
<tr>
<th>Target pH</th>
<th>4</th>
<th>3</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution ppm Cu</td>
<td>5412</td>
<td>541</td>
<td>54</td>
</tr>
<tr>
<td>Copper Loaded</td>
<td>80.3</td>
<td>78.6</td>
<td>72.5</td>
</tr>
<tr>
<td>Copper Stripped</td>
<td>81.2</td>
<td>80.2</td>
<td>72.8</td>
</tr>
</tbody>
</table>

Ideally, the solution composition for these tests was to be held constant over the course of the test. The following graph plots the measured solution composition (analyzed by AA) over the duration of the test. Results show that solution composition was held fairly constant for most tests (an exception being the 54 ppm test at pH 3).
APPENDIX E: DERIVATION OF MODIFIED HELFFERICH NUMBER

The Helfferich number, is a dimensionless number used to predict the nature of the rate controlling step in an ion exchange reaction. It was defined for the case of complete conversion of an ion exchange reaction for two ions of equal mobility and equal valence, under infinite solution volume conditions.

E.1 DERIVATION OF STANDARD HELFFERICH NUMBER

The following section summarizes the key steps Helfferich used in developing his criterion for the rate determining step. The full derivation can be found on page 277 of his text on ion exchange (10).

Given:

Ion exchange reaction: \( \bar{A} + B \rightarrow A + \bar{B} \), \( F = \frac{[B]}{[B]_{eq}} \)

Fractional Attainment of Equilibrium (equal valence ions, equal mobilities, ISV conditions):

Film Diffusion Control: \( \ln\left(1-F\right)+\left(1-\frac{1}{S_B}\right) = -\frac{6D_f[A]}{d_p [\bar{A}]_{eq} S_B} t \)

Intraparticle Diffusion Control: \( F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left\{ \frac{1}{n^2} \exp\left(-\frac{4D_p \pi^2 n^2}{d_p^2} t\right) \right\} \)

Half-time for exchange:

For film diffusion control: \( t_{1/2} = \left(0.167 + 0.064 \frac{S_B^A}{d_p [\bar{A}]_{eq}} \right) \frac{d_p [\bar{A}]_{eq}}{2D_f [A]} \)

For intraparticle diffusion control: \( t_{1/2} = 0.030 \frac{d_p^2}{4D_p} \)
Calculate:

\[
\text{Helfferich Number}= \frac{t_{1/2}^{\text{film}}}{t_{1/2}^{\text{particle}}}
\]

\[
\text{Helfferich Number}= (0.167+0.064 S_B^A)\frac{d_p\delta[A]^{\text{eqb}}}{2D[A]} \div 0.030 \frac{d_p^2}{4D_p}
\]

\[
\text{Helfferich Number}= \frac{2[A]^{\text{eqb}}D_p\delta}{[A]D_p d_p} (5.57+2.13S_B^A)
\]

Compare to Helfferich’s Criterion:

For film diffusion:

\[
\frac{2[A]^{\text{eqb}}D_p\delta}{[A]D_p d_p} (5+2S_B^A) \gg 1
\]

For intraparticle diffusion:

\[
\frac{2[A]^{\text{eqb}}D_p\delta}{[A]D_p d_p} (5+2S_B^A) \ll 1
\]

E.2 DERIVATION OF MODIFIED HELFFERICH NUMBER

The modified Helfferich number used in this thesis was derived using a similar approach. In lieu of assuming equal valence, equal mobility ions for film diffusion control, the simpler case of isotopic exchange that is typically used in engineering models was considered. In lieu of the exact solution to the differential equation for intraparticle diffusion, the hybrid correlation presented in this thesis for approximating intraparticle diffusion control was used.

Since it is reasonable to expect that the initial loading of the resin will be film diffusion controlled, while most of the loading will be intraparticle diffusion controlled, it was desired to derive the modified Helfferich number to be a function of the current fraction reacted. Under such a scheme, the Helfferich number will decrease as the reaction progresses, illustrating how
the mechanism changes from initial film diffusion control to finally being intraparticle diffusion controlled.

Given:

Ion exchange reaction: \( \tilde{A} + B \rightarrow A + \tilde{B} \), \( F = [\tilde{B}] / [\tilde{B}]_{eqb} \)

Fractional Attainment of Equilibrium (isotopic exchange, infinite solution volume):

Film Diffusion Control: \( F = 1 - \exp(-k_f t) \)

Intraparticle Diffusion Control: \( F = \sqrt{1 - \exp(-4k_h t)} \)

Time required to achieve fractional loading of \( F \):

Film Diffusion Control: \( t_f = \frac{-\ln(1-F)}{k_f} \)

Intraparticle Diffusion Control: \( t_p = \frac{-\ln(1-F^2)}{4k_h} \)

Definitions of diffusion constants:

Film Diffusion Control: \( k_f = \frac{6D_f [B]}{d_p \delta [\tilde{B}]_{eqb}} \)

Intraparticle Diffusion Control: \( k_h = \frac{\pi^2 D_{eff} (1.622 [B] / [\tilde{B}]_{eqb})^a}{d_p^2} \)

Calculate:

Modified Helfferich Number: \( \frac{t_f}{t_p} \)

Modified Helfferich Number: \( \frac{4k_h \ln(1-F)}{k_f \ln(1-F^2)} \)

\[
\text{Modified Helfferich Number} = \frac{2\pi^2 (1.622)^a D_{eff} \delta \left( \frac{[B]}{[\tilde{B}]_{eqb}} \right)^{a-1} \ln(1-F)}{3 D_f d_p \left( \frac{[B]}{[\tilde{B}]_{eqb}} \right)^a \ln(1-F^2)}
\]
APPENDIX F: CAROUSEL FINITE DIFFERENCE MODEL

The output from a single run of the carousel finite difference model would be over one thousand pages long. Consequently, only the output for the first few minutes of the first three contactors from the nickel run have been printed out for inclusion in this appendix.

The model starts at $t = 0$ and assumes that all the contactors contain no metal ions in solution (they were filled with water), and all the resin starts with the recirculated load from elution (i.e. 3 g Ni / L Resin or 0 g Cu / L Resin). The model then works through a time-step sequence, calculating all subsequent resin and solution values at time $t + \Delta t$, based on the previous values.

To determine the resin loading in each time step, $[\bar{M}]_{t+\Delta t}$, the equilibrium resin loading value, and the equivalent resin loading times, $t_r$, for both the film diffusion model and hybrid correlation are calculated based on the previous resin loading, $[\bar{M}]_t$, and the previous solution concentration, $[M]_t$. The resin loading value is then calculated at time $t_r + \Delta t$, using both the film diffusion model and the hybrid correlation. The lower of these two values is then taken for the resin loading $[\bar{M}]_{t+\Delta t}$.

The amount of metal in the contactor at time $t + \Delta t$ can be expressed as the amount of metal present at time $t$, plus the amount of metal that entered the system in the feed stream, less the amount of metal that overflowed the reactor. For a feed flowrate of $Q$, and a reactor containing a volume $V_R$ of resin and $V_S$ of solution, this is expressed as:

$$V_R[\bar{M}]_{t+\Delta t} + V_S[M]_{t+\Delta t} = V_R[\bar{M}]_t + V_S[M]_t + Q\Delta t[M]_{\text{feed}} - Q\Delta t[M]_t$$

Rearranging, the solution concentration at time $t + \Delta t$ can then be calculated using the following formula:

$$[M]_{t+\Delta t} = \frac{V_S[M]_t + Q \Delta t ([M]_{\text{feed}} - [M]_t) - V_R([\bar{M}]_{t+\Delta t} - [\bar{M}]_t)}{V_S}$$
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**Kinetics**

- alpha 0.36
- Dapp 4.43E-12 m/s
- Df/delta 2.73E-05 m/s
- Ni 58.71 g/mol

**Initial Nickel Concentrations:**

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EMERGENCY SHUT-DOWN INSTRUCTIONS:

***See next page for photographs of all key shut-offs***

1. SHUT OFF AIR COMPRESSOR –off switch at unit & unplug at South Wall. Open tank drain valve to bleed air.

2. SHUT OFF TEMPERATURE CONTROLLERS –unplug YELLOW extension cord on North Wall

3. SHUT OFF MOTORS –unplug orange extension cord on North Wall

4. SHUT OFF PUMPS –use power bar switch on wall just to the left of sink

5. SHUT OFF pH CONTROLLERS –use switch or unplug power bar on East Wall

6. SHUT OFF SCALES & COMPUTER –use switch or unplug power bar on East Wall
SOUTH WALL FOR OUTLET:

1) AIR COMPRESSOR:

On/off switch

Bleed Valve

Outlet: Panel#1 Circuit 2

NORTH WALL:

2) TEMPERATURE CONTROLLERS:

3) MOTORS:

Outlet: Panel 1 Circuit 9

EAST WALL:

4) PUMPS:

5,6) pH CONTROLLERS and SCALES:

Fed from Panel 1 Circuit 13

Outlet: Panel 1 Circuit 11
SYSTEM START UP:

☐ 1. Calibrate the pH probes on each controller using the Temperature Probe. When calibration is complete, switch for a 0.1% 111.7 ohm resistor (except for the resin feed tank which is calibrated with and keeps any other resistor)

☐ 2. Mount contactors to frame and connect tubing between them. Do not connect feed to first tk.

☐ 3. Place heaters with cages, airlifts, pH probes, and temperature sensors into each contactor

☐ 4. Measure out and add desired wet-settled resin volumes for each contactor

☐ 5. Add water and lower agitators into each contactor. Start mixing at 300 RPM.

☐ 6. Submerge NaOH addition lines into each contactor (must be below solution level!!)

☐ 7. Turn on and tare all scales with NaOH containers on them

☐ 8. Start feed pump with water. Adjust speed to get desired flowrate for test.

☐ 9. Turn off feed pump and connect to feed mix tank

☐ 10. Start overflow recycle pump with water. Adjust speed to desired flowrate.

☐ 11. Turn off recycle pump and place into feed mix tank

☐ 12. Start flow of water through circuit. Check for any leaks

☐ 13. Check that temperature controllers are in contactors and are not touching contactor walls

☐ 14. Plug in yellow extension cord on North wall to provide power to temperature controllers

☐ 15. Plug heaters into temperature controllers and turn on individual heater power bars

☐ 16. Check that temperature control is set to 30C and then initiate heaters by pressing the hand on the temperature controller.

☐ 17. Turn on the water feed pump to the resin feed tank (labeled “carousel recycle”)

☐ 18. Check that all airlifts are recycling back to the tank that they sample from

☐ 19. Start air compressor and connect to air manifold. Open manifold valves if necessary.

☐ 20. Measure rate of RESIN transfer for each contactor. Adjust valves to attain a value of 1.5 mL resin per minute through each airlift.

☐ 21. Once resin transfer is balanced, adjust airlifts so feeding to previous (higher) contactor.

☐ 22. Check resin flows via airlifts again, and make adjustments as necessary.

☐ 23. Re-tare all scales, turn on computer and start datalogging using Windmill.

☐ 24. When ready to start the test, place feed line into nickel feed solution. RECORD TIME OF STARTING!!!! Switch Loaded Resin Screen.

☐ 25. Monitor test –see circuit performance monitoring checklist
CASCADE CIRCUIT MONITORING:

1. DATALOGGING:
   - Is windmill recording the data?
   - Are the scale weights dropping as the NaOH pumps turn on?

2. RESIN FEED TANK:
   - Is water flowing into and out of the Resin Feed Tank?
   - Is there still water in the fresh water bucket?
   - Does the water overflow bucket need changing? If so, pH adjust overflow water to 6-10 and dispose of down sink. NOTE: DO NOT REUSE THIS WATER TO FEED THE RESIN FEED TANK AS IT WILL CONTAIN SODIUM FROM THE CAUSTIC ADDED – as sodium levels increase, the sodium will react with the ion exchange resin!
   - Is the airlift transferring resin to Tank #5 as per usual?

3. CONTACTORS:
   - Check that there is good mixing of resin within contactor
   - Check that airlift is moving resin appropriately
   - Check that the overflow screen is not plugging
   - Check no resin is breaking through overflow screen (fines okay)
   - Check temperature in tank is 28-32C
   - Check that heater is not too close to tank walls and is not smoking
   - Check that pH is between 3.8-4.2. (Ideally between 3.9-4.1). Adjust speed of motor on NaOH pumps as needed to avoid overshooting / undershooting

4. SOLUTION FLOW:
   - Is there still plenty of fresh feed?
   - Does the tails bucket need changing?

5. OTHER:
   - Is the Resin Overflow Screen plugging with resin?
   - How is the oil level in the air compressor?
   - Are the pH controllers reading okay? Is the resistor still firmly in place?
SYSTEM SHUT-DOWN AT END OF RUN:

1. Take any required samples from contactors before starting shut-down!
2. Turn off heaters using switch at individual power bars. Unplug yellow extension cord at north wall. Check lights off at all temperature controllers.
3. Turn off sodium hydroxide addition to all 7 tanks (feed tank, 5 RIP contactors, resin prep tank), by switching off the appropriate Masterflex drive units.
4. Turn off air compressor. Use switch at unit, unplug from extension cord, bleed air.
5. Turn off feed pumps at appropriate Masterflex drive units: fresh feed, recirculating solution to feed tank, water to resin prep tank
6. Stop windmill logger software on logging computer
7. Turn off individual agitators for each contactor

REMOVAL OF RIP CONTACTOR:

- Put on chemical goggles in addition to safety glasses.
- Remove feedline into contactor, if necessary (use container to catch spills!)
- Unhook airline to contactor’s airlift
- Raise & Rinse Agitator
- Remove from contactor and rinse the following:
  - Resin transfer tube from airlift feeding this contactor
  - Immersion heater & cage
  - pH probe & holder
  - airlift & holder
  - NaOH feedline
- Remove outlet hose to next contactor (use container to catch spills!)
- Unscrew the three screws holding contactor onto frame
- Drain tank. Use outlet hose for first portion, then tip contactor sideways towards you. Use deionized water to rinse out and collect the resin.
- Separate nickel solution and resin. Nickel solution to go to waste drum, resin to be rinsed with deionized water. Measure resin volume, keep and label sample.
CASCAD E OPERATING SHEET

**TEST START TIME:**

- **Add 22.5 mL resin at:** (15 mins)
- **Change screen at:** (30 mins)
- **Sampling at:**

**target ~45**

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**NaOH Weights**

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<th>Tank 1</th>
<th>Tank 2</th>
<th>Tank 3</th>
<th>Tank 4</th>
<th>Tank 5</th>
</tr>
</thead>
</table>

**Final Resin Volumes**

- Tank 1
- Tank 2
- Tank 3
- Tank 4
- Tank 5
APPENDIX H: ESTIMATE OF AIRLIFT TOTAL FLOWRATES

During the first few cascade runs, the total airlift volumetric flowrate was not recorded. However, the total resin volume in each tank was measured, as well as the rate of resin transfer. Thus, an empirical calculation was needed to estimate the total volumetric flowrate from these two measured values. The proposed empirical correlation was:

\[
\text{Total Airlift Flowrate} = \frac{\text{Resin Flowrate}}{\text{Volume Fraction Resin in Tank}} \times \text{Empirical Factor}
\]

The proposed empirical correlation was fit to all the measured total airlift flowrates, and the empirical factor adjusted to a value of 1.13, in order to get an appropriate fit to the data. The predicted vs. actual values are plotted in the graph below, and the diagonal line corresponds to a 1:1 correlation between predicted and actual.
APPENDIX I: RIP MINIPLANT CASCADE CIRCUIT MODEL OUTPUT

This appendix contains the Excel print outs for the cascade circuit models presented in Chapter 10. The first page contains all the inputs (outlined cells) and key outputs. The second page contains the flows and mass balances.

On the first page, the solution and resin calculations printed out in the vicinity of the circuit are the outputs from the segregated flow model. The actual integrals were evaluated using the trapezoidal rule.

To provide a check for the segregated flow model, the equivalent loading that would be experienced if all the resin in the tank moved in a plug flow fashion through each contactor with a residence time equal to $t_{\text{mean}}$ was calculated. These calculations are done using both the film diffusion model and the hybrid correlation, and the outputs are lower down on the spreadsheet, under the headings “film diffusion” and “hybrid correlation”. Since these calculations are sufficiently close to the values obtained with the segregated flow model, the calculations for the segregated flow model are believed to be programmed correctly.
**Solution Side**

- **Tot Vol:** 563 mL per tank
- **Flow Rate:** 15 mL/min FRESH FEED
- **molar Ni:** 58.71 g/mol

**Resin Side**

- **Resin Volume [mL]:** 228
- **% Resin:** 7%
- **Airlift total flow to upstream tank (estimated):** 31.3

**Resin Rate:** 1.5 mL/min

**Kinetics**

- **Df/delta** 0.0000273 m/s
- **K** 0.0000978
- **Kappa** 0.36
- **Cap** 2.36
- **Dapp** 4.43E-12 m²/s
- **bead dia** 736 μm

- **Initial Load:** 0 g Ni / L Resin

**Cap** 2.36

**Dapp** 4.43E-12 m²/s

**Flow Rate** 15 mL/min

**Film Diffusion**

- **kf** 0.009466
- **eqv s already loaded** 97
- **total eqv time in this tank (s):** 1,717
- **resin loading moving forward at tmean:** 67.85

**Hybrid Correlation**

- **kh** 3.08E-05
- **eqv s already loaded** 3,657
- **total eqv time in this tank (s):** 5,277
- **resin loading moving forward at tmean:** 46.93

**Segregated Flow Model, OUTPUTS:**

<table>
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<tr>
<th>Soln (gpl)</th>
<th>4.800</th>
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<th>2.947</th>
<th>1.978</th>
<th>1.115</th>
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**Eqbm Load [g Ni / L R]**

- 67.85
- 66.98
- 66.63

**Mod He #**

- 0.02
- 0.03
- 0.06
- 0.10
- 0.47

**Eqbm Load [g Ni / L R]**

- 67.85
- 66.98
- 66.63

**Hybrid Correlation**

- **kh** 3.08E-05
- **eqv s already loaded** 3,657
- **total eqv time in this tank (s):** 5,277
- **resin loading moving forward at tmean:** 46.93

**Flow Rate** 15 mL/min

**Film Diffusion**

- **kf** 0.009466
- **eqv s already loaded** 97
- **total eqv time in this tank (s):** 1,717
- **resin loading moving forward at tmean:** 67.85

**Hybrid Correlation**

- **kh** 3.08E-05
- **eqv s already loaded** 3,657
- **total eqv time in this tank (s):** 5,277
- **resin loading moving forward at tmean:** 46.93
### Table: Mass Flow and Assays

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<th>STREAM</th>
<th>FLOWS: mL/min</th>
<th>Ni mass flow: gNi/min</th>
<th>Assays</th>
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</thead>
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<td>soln flow</td>
<td>resin flow</td>
</tr>
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<td>15.00</td>
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<td>5 o/f (tails)</td>
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<td>1.50</td>
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**Balance by Stage:**

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<tr>
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<th>Mass Flow</th>
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<tr>
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<td>44.82</td>
</tr>
<tr>
<td>OVERALL</td>
<td>25.56</td>
<td>25.56</td>
</tr>
</tbody>
</table>
## Solution Side

| Tot Vol | 563 mL per tank |
| Flow Rate | 15 mL / min |
| molar Ni | 58.71 g/mol |

## Resin Side

### TP207XL

| K | 0.0000978 |
| Cap | 2.36 |
| Resin Rate | 1.5 mL/min |
| Initial Load | 0 g Ni / L Resin |

### Kinetics

| Df/delta | 0.0000273 m/s |
| alpha | 0.36 |
| bead dia | 4.43E-12 m2/s |
| nickel in resin feed solution | 0.000736 m |

## Tot Vol

563 mL per tank

## Flow Rate

15 mL / min • FRESH FEED

## molar Ni

58.71 g/mol

## TOTAL IN CIRCUIT

| Resin Volume [mL] | 228 |
| % Resin | 7% |
| Airlift total flow to upstream tank (estimated) | 31.3 |

## Segregated Flow Model, OUTPUTS:

### Soln (gpl)

| 4.986 | 3.738 | 3.139 | 2.163 | 1.276 | 0.984 | 0.166 |

### Mix Tk

| 47.2 | 1 | 2 | 3 | 4 | 5 | 0.0 |

### Mod He #

| 0.02 | 0.03 | 0.05 | 0.09 | 0.33 |

### Eqbm Load [g Ni / L R]

| 67.90 | 67.62 | 67.12 | 66.83 | 63.47 |

### quadratic “a”

| 2.09E-05 | 1.44E-05 | 8.5E-06 | 6.56E-06 | 1.106E-06 |

### quadratic “b”

| -4.9E-05 | -3.4E-05 | -2.01E-05 | -1.55E-05 | -2.62E-06 |

### quadratic “c”

| 2.91E-05 | 2.01E-05 | 1.18E-05 | 9.13E-06 | 1.54E-06 |

### Film Diffusion

| kf | 0.010084 | 0.00695 | 0.004098 | 0.003161 | 0.000533 |
| eqv s already loaded | 95 | 97 | 103 | 97 | - |
| total eqv time in this tank (s) | 1,715 | 2,417 | 2,103 | 837 | 2,440 |
| resin loading moving forward at tmean | 67.90 | 67.62 | 67.11 | 62.09 | 46.20 |

### Hybrid Correlation

<p>| kh | 3.15E-05 | 2.76E-05 | 2.28E-05 | 2.08E-05 | 1.094E-05 |
| eqv s already loaded | 3,815 | 2,479 | 1,383 | 874 | - |
| total eqv time in this tank (s) | 5,435 | 4,799 | 3,383 | 1,614 | 2,440 |
| resin loading moving forward at tmean | 47.83 | 43.35 | 34.59 | 23.67 | 20.20 |</p>
<table>
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<tr>
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<th>Assays</th>
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<tr>
<td>5 o/f (tails)</td>
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<td>24.06</td>
<td>0.00</td>
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|                | soln rec'c    |          |           | 98.19 | 98.19 |       | 3.14   |             |
|                | resin exit    | 1.50     | 0.00      |      70.79 |       | 70.79 |       | 47.19   |             |
|                | airlift to 1  | 21.84    | 20.34     | 1.50  | 106.95| 44.00 | 62.94  | 2.16    | 41.96    |
|                | airlift to 2  | 25.34    | 23.84     | 1.50  | 80.02 | 30.40 | 49.62  | 1.28    | 33.08    |
|                | airlift to 3  | 68.47    | 66.97     | 1.50  | 100.56| 65.90 | 34.66  | 0.98    | 23.11    |
|                | airlift to 4  | 20.77    | 19.27     | 1.50  | 29.73 | 3.20  | 26.53  | 0.17    | 17.68    |
|                | airlift to 5  | 10.56    | 9.06      | 1.50  | 0.00  | 0.00  | 0.00   | 0.00    | 0.00     |

**Balance by Stage:**

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**CIRCUIT RECOVERY** 94.66%
### Solution Side
- **Tot Vol**: 563 mL per tank
- **Flow Rate**: 15 mL/min \( \text{FRESH FEED} \)
- **Molar Ni**: 58.71 g/mol

### Resin Side
- **TP207XL**
- **Kinetics**
  - **Df/delta**: 0.0000273 m/s
  - **K**: 0.0000978
  - **alpha**: 0.36
- **Cap**: 2.36
- **Resin Rate**: 1.5 mL/min
- **Bead dia**: 736 um
- **Dapp**: 4.43E-12 m²/s
- **Initial Load**: 3 g Ni/L Resin

### Toral IN Circuit
- **Resin Volume [mL]**
  - **Mix Tk**: 322
  - **Resin Fd Tk**: 75
- **% Resin**
  - **Mix Tk**: 11%
- **Airlift total flow to upstream tank (estimated)**
  - **Mix Tk**: 20.1

### Segregated Flow Model, OUTPUTS:
- **Soln (gpL)**
  - **4.308**
  - **3.208**
  - **2.388**
  - **1.479**
  - **0.498**
  - **0.038**
- **Resin [g Ni/L R]**
  - **Mix Tk**: 46.0
  - **1**: 38.1
  - **2**: 27.8
  - **3**: 13.5
  - **4**: 3.8
  - **5**: 3.0
- **Mod He #**
  - **0.03**
  - **0.04**
  - **0.11**
  - **1.00**
  - **10.45**

### Film Diffusion
- **kf**
  - 0.007672
  - 0.004753
  - 0.001599
  - 0.000122
  - 1.054E-05
- **eqv s already loaded**
  - 108
  - 112
  - 144
  - 558
  - 7,907
- **Total eqv time in this tank (s)**
  - 2,628
  - 2,632
  - 3,144
  - 3,118
  - 10,187
- **Resin loading moving forward at tmean**
  - 67.70
  - 67.28
  - 65.86
  - 57.73
  - 37.53

### Hybrid Correlation
- **kh**
  - 2.86E-05
  - 2.41E-05
  - 1.63E-05
  - 6.44E-06
  - 2.665E-06
- **eqv s already loaded**
  - 3,332
  - 1,948
  - 663
  - 169
  - 601
- **Total eqv time in this tank (s)**
  - 5,852
  - 4,468
  - 3,663
  - 2,729
  - 2,881
- **Resin loading moving forward at tmean**
  - 47.28
  - 39.77
  - 30.32
  - 15.05
  - 6.53
<table>
<thead>
<tr>
<th>STREAM</th>
<th>FLOWS: mL/min</th>
<th>Ni mass flow: gNi/min</th>
<th>Assays</th>
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**Balance by Stage:**

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<td>69.11</td>
<td>69.11</td>
</tr>
</tbody>
</table>

**CIRCUIT RECOVERY** 99.88%
### Solution Side
- **Tot Vol**: 563 mL per tank
- **Flow Rate**: 15 mL/min FRESH FEED
- **molar Ni**: 58.71 g/mol

### Resin Side
- **TP207XL Kinetics**
  - \( \frac{Df}{\delta t} \): 0.0000273 m/s
  - K: 0.0000978
  - \( \alpha \): 0.36

- **Cap**: 2.36
- **Resin Rate**: 1.5 mL/min bead dia: 736 um
- **Initial Load**: 3 g Ni/L Resin

### TOTAL IN CIRCUIT
- **Resin Volume [mL]**: 322
- **% Resin**: 11%
- **Airlift total flow to upstream tank (estimated)**: 20.1

### Segregated Flow Model, OUTPUTS:

<table>
<thead>
<tr>
<th>Soln (gpl)</th>
<th>4.573</th>
<th>3.525</th>
<th>2.744</th>
<th>1.844</th>
<th>0.790</th>
<th>0.140</th>
<th>0.010</th>
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</thead>
<tbody>
<tr>
<td>Mix Tk</td>
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<td>41.4</td>
<td>32.1</td>
<td>18.7</td>
<td>6.0</td>
<td>5</td>
<td>3.0</td>
</tr>
<tr>
<td>Resin [g Ni / L R]</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
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<th>0.04</th>
<th>0.08</th>
<th>0.35</th>
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<tbody>
<tr>
<td>Eqbm Load [g Ni / L R]</td>
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<td>1.23E-05</td>
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<td>9.33E-07</td>
<td>6.53E-08</td>
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<tr>
<td>quadratic &quot;b&quot;</td>
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<td>-2.9E-05</td>
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<tr>
<td>quadratic &quot;c&quot;</td>
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<td>1.71E-05</td>
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<td>9.092E-08</td>
</tr>
</tbody>
</table>

- **Film Diffusion**
  - kf: 0.008814
  - eqv s already loaded: 107
  - total equiv time in this tank (s): 2,627
  - resin loading moving forward at tmean: 67.80

- **Hybrid Correlation**
  - kh: 3E-05
  - eqv s already loaded: 3,892
  - total equiv time in this tank (s): 6,412
  - resin loading moving forward at tmean: 49.70

### RUN B: High Feed Assay

- **Feed Assay**
- **model mix tank exit**: 3.525
- **observed mix tank assay**: 3.525
- **0.000**
<table>
<thead>
<tr>
<th>STREAM</th>
<th>FLOWS: mL/min</th>
<th>Ni mass flow: gNi/min</th>
<th>Assays</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total flow</td>
<td>soln flow</td>
<td>resin</td>
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<tr>
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<td>4 o/f</td>
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<td>0.00</td>
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<tr>
<td>resin exit</td>
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Balance by Stage:

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<th>mass flow</th>
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<td>Balance by Stage:</td>
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<td>Mix Tank</td>
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<tr>
<td>OVERALL</td>
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CIRCUIT RECOVERY 99.66%
<table>
<thead>
<tr>
<th>Solution Side</th>
<th>Resin Side</th>
<th>Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tot Vol</td>
<td>TP207XL</td>
<td>Df/delta</td>
</tr>
<tr>
<td>563 mL per tank</td>
<td>0.0000978</td>
<td>0.000273 m/s</td>
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<tr>
<td>Flow Rate</td>
<td>Cap</td>
<td>alpha</td>
</tr>
<tr>
<td>15 mL / min</td>
<td>2.36</td>
<td>0.36</td>
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<tr>
<td>molar Ni</td>
<td>Resin Rate</td>
<td>bead dia</td>
</tr>
<tr>
<td>58.71 g/mol</td>
<td>1.5 mL/min</td>
<td>736 um</td>
</tr>
<tr>
<td></td>
<td>Initial Load</td>
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<td>0.000736 m</td>
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### Run C: Low Feed Assay

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<tr>
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<td>14</td>
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<td>48.96</td>
</tr>
<tr>
<td>52.0</td>
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<td>21%</td>
<td>14</td>
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<tr>
<td>2%</td>
<td>3.757</td>
</tr>
<tr>
<td>0.000</td>
<td>82.56</td>
</tr>
<tr>
<td>9%</td>
<td>48.96</td>
</tr>
<tr>
<td>7%</td>
<td>38.4</td>
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<td>2%</td>
<td>12.0</td>
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<tr>
<td>21%</td>
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<tr>
<td>7%</td>
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<tr>
<td>21%</td>
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### Segregated Flow Model, OUTPUTS:

<table>
<thead>
<tr>
<th>Soln (gpl)</th>
<th>Resin (g Ni / L R)</th>
<th>Mod He #</th>
<th>Eqbm Load (g Ni / L R)</th>
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<tbody>
<tr>
<td>4.641</td>
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<td>67.78</td>
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<tr>
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### Film Diffusion

<table>
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<tr>
<th>kf</th>
<th>eqv s already loaded</th>
<th>total equiv time in this tank (s)</th>
<th>resin loading moving forward at tmean</th>
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<tbody>
<tr>
<td>0.008515</td>
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### Hybrid Correlation

<table>
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<tbody>
<tr>
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<td>1.6E-05</td>
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<td>1,792</td>
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<td>Ni mass flow: gNi/min</td>
<td>Assays</td>
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<tr>
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<td>--------------</td>
<td>----------------------</td>
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</tr>
<tr>
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<td>soln flow</td>
<td>resin flow</td>
</tr>
<tr>
<td>feed</td>
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<td>15.00</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
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<tr>
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<td>4 o/f</td>
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</tr>
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<td>airlift to 5</td>
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<tr>
<td>Balance by Stage:</td>
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</tr>
<tr>
<td>Flow in</td>
<td>Flow out</td>
<td>in</td>
<td>out</td>
</tr>
<tr>
<td>Mix Tank</td>
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<td>12.53</td>
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<tr>
<td>OVERALL</td>
<td>40.00</td>
<td>40.00</td>
<td>74.12</td>
</tr>
</tbody>
</table>
### Solution Side
- Tot Vol: 563 mL per tank
- Flow Rate: 15 mL/min, FRESH FEED
- molar Ni: 58.71 g/mol

### Resin Side
- TP207XL
- Kinetics
  - Df/delta: 0.0000273 m/s
  - K: 0.0000978
  - Cap: 2.36
  - Dapp: 4.43E-12 m²/s
  - Resin Rate: 1.5 mL/min
  - bead dia: 736 μm
  - Initial Load: 0 g Ni / L Resin

### TOTAL IN CIRCUIT
- Resin Volume [mL]: 276.08
- % Resin: 92.16
- Airlift total flow to upstream tank (measured): 12.0

### Segregated Flow Model, OUTPUTS:
- Soln (gpL): 5.163
- Resin [g Ni / L R]:
  - Mix Tk: 51.0
  - 1: 41.5
  - 2: 29.2
  - 3: 19.1
  - 4: 9.1
  - 5: 3.0
- Mod He #:
  - 0.02
  - 0.04
  - 0.08
  - 0.20
  - 0.67
- Eqbm Load [g Ni / L R]:
  - 67.91
  - 67.46
  - 66.62
  - 65.13
  - 63.04
  - quadratic "a":
    - 2.15E-05
  - quadratic "b":
    - -5.1E-05
  - quadratic "c":
    - 2.99E-05
- Film Diffusion:
  - kf:
    - 0.010345
  - eqv s already loaded:
    - 91
  - total equiv time in this tank (s):
    - 3,778
  - resin loading moving forward at tmean:
    - 67.91
- Hybrid Correlation:
  - kh:
    - 3.18E-05
  - eqv s already loaded:
    - 3,673
  - total equiv time in this tank (s):
    - 7,359
  - resin loading moving forward at tmean:
    - 52.96
<table>
<thead>
<tr>
<th>STREAM</th>
<th>FLOWS: mL/min</th>
<th>Ni mass flow: gNi/min</th>
<th>Assays</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total flow</td>
<td>soln flow</td>
<td>resin flow</td>
</tr>
<tr>
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<td>15.00</td>
<td>0.00</td>
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<td>38.50</td>
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<td>airlift to 2</td>
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<td>airlift to 4</td>
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</tr>
<tr>
<td>airlift to 5</td>
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<td>1.50</td>
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**Balance by Stage:**

<table>
<thead>
<tr>
<th></th>
<th>Flow in</th>
<th>Flow out</th>
<th>in</th>
<th>out</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix Tank</td>
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<td>OVERALL</td>
<td>40.00</td>
<td>40.00</td>
<td>81.95</td>
<td>81.95</td>
</tr>
</tbody>
</table>

**CIRCUIT RECOVERY** 92.91%
Solution Side

- Tot Vol: 563 mL per tank
- Flow Rate: 18.5 mL/min, FRESH FEED
- Molar Cu: 63.55 g/mol

Resin Side

- TP207XL Kinetics
  - K: 0.000745
  - Cap: 2.5
  - Resin Rate: 1.5 mL/min
  - Initial Load: 0 g Cu / L Resin
  - Cu in resin feed solution: 0.000736 m

- Df/delta: 0.000273 m/s
- Dapp: 2.8E-11 m²/s
- Bead dia: 736 μm

- Cap: 2.5
- Dapp: 2.8E-11 m²/s
- Bead dia: 736 μm

- Initial Load: 0 g Cu / L Resin

- Resin Fd Tk
  - Resin Volume [mL]:
    - 272.5
    - 43
    - 73.5
    - 39
    - 63
    - 54
    - 120
  - Resin Volume [%]:
    - 8%
    - 13%
    - 7%
    - 11%
    - 10%
    - 11%
    - 21%
  - Airlift total flow to upstream tank (measured): 28.5

Segregated Flow Model, OUTPUTS:

- Soln (gpl):
  - 5.153
  - 3.725
  - 2.798
  - 1.508
  - 0.387
  - 0.020
  - 0.001

- Resin [g Cu / L R]:
  - Mix Tk: 63.5
  - 1
  - 2
  - 3
  - 4
  - 5

- Mod He #:
  - 0.07
  - 0.10
  - 0.30
  - 2.33
  - 100.80

- Eqbm Load [g Cu / L R]:
  - 78.82
  - 78.60
  - 77.79
  - 72.49
  - 55.69
  - 9.54E-07
  - 6.274E-06
  - 6.274E-06

- Quadratic "a":
  - 0.0000131
  - 7.07E-05
  - 1.82E-05
  - 9.54E-07
  - 6.274E-08

- Quadratic "b":
  - 0.000032
  - 4.54E-05
  - 2.4E-06
  - 8.03E-07

- Quadratic "c":
  - 0.0000205
  - 2.84E-05
  - 1.49E-06
  - 9.80E-08

- Film Diffusion
  - Kf: 0.00784
  - 0.004224
  - 0.001085
  - 5.7E-05
  - 3.749E-06

- Eqv s already loaded:
  - 142
  - 104
  - 120
  - 109
  - 2

- Total eqv time in this tank (s):
  - 1,862
  - 3,510
  - 2,629
  - 2,160

- Resin loading moving forward at tmean:
  - 78.82
  - 78.60
  - 77.79
  - 72.49

- Hybrid Correlation
  - Kh: 8.65E-05
  - 5.89E-05
  - 2.54E-05
  - 4.09E-06
  - 7.556E-07

- Eqv s already loaded:
  - 1,736
  - 3,510
  - 2

- Total eqv time in this tank (s):
  - 3,456
  - 1,708
  - 2,522

- Resin loading moving forward at tmean:
  - 65.83
  - 58.97
  - 31.03

Copper: Low Feed Assay

- Feed Assay: Low

- Model mix tank exit:
  - 3.725

- Observed mix tank assay:
  - 3.725

- Components:
  - Molar Cu: 63.55 g/mol
  - Cu in resin feed solution: 0.000736 m
  - Eqbm Load:
    - 8%
    - 13%
    - 7%
    - 11%
    - 10%
    - 11%
    - 21%
  - Flow Rate:
    - 18.5 mL/min
  - Resin Rate:
    - 1.5 mL/min
  - Initial Load:
    - 0 g Cu / L Resin
<table>
<thead>
<tr>
<th>STREAM</th>
<th>FLOWS: mL/min</th>
<th>Cu mass flow: gCu/min</th>
<th>Assays</th>
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<tbody>
<tr>
<td></td>
<td>total flow</td>
<td>soln flow</td>
<td>resin</td>
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<tr>
<td>feed</td>
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<td>18.50</td>
<td>0.00</td>
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<tr>
<td>mix o/f</td>
<td>47.00</td>
<td>47.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1 o/f</td>
<td>40.00</td>
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<td>4 o/f</td>
<td>38.00</td>
<td>38.00</td>
<td>0.00</td>
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<tr>
<td>5 o/f (tails)</td>
<td>57.00</td>
<td>57.00</td>
<td>0.00</td>
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<td>28.50</td>
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<td>1.50</td>
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<tr>
<td>airlift to 1</td>
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<td>airlift to 2</td>
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<td>1.50</td>
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<td>airlift to 3</td>
<td>21.00</td>
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<td>airlift to 4</td>
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<tr>
<td>airlift to 5</td>
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<td>38.50</td>
<td>1.50</td>
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Balance by Stage:

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<tr>
<th>Flow in</th>
<th>Flow out</th>
<th>in</th>
<th>out</th>
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<tbody>
<tr>
<td>Mix Tank</td>
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<td>175.08</td>
<td>175.08</td>
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<td>286.93</td>
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<td>2</td>
<td>54.00</td>
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<td>78.00</td>
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OVERALL 58.50 58.50 95.32 95.32

CIRCUIT Recovery 99.92%
<table>
<thead>
<tr>
<th>Solution Side</th>
<th>Resin Side</th>
<th>Kinetics</th>
<th>Df/delta</th>
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<tbody>
<tr>
<td>Tot Vol</td>
<td>TP207XL</td>
<td>K</td>
<td>0.000745</td>
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<tr>
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<td></td>
<td>Cap</td>
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<tr>
<td>molar Cu</td>
<td>1.5</td>
<td>Resin Rate</td>
<td>1.5 mL/min</td>
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<tr>
<td></td>
<td></td>
<td>I</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Dapp</td>
<td>2.8E-11 m2/s</td>
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<tr>
<td></td>
<td></td>
<td>bead dia</td>
<td>736 um</td>
</tr>
<tr>
<td></td>
<td>0.000273 m/s</td>
<td>Initial Load</td>
<td>0.00736 m</td>
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<table>
<thead>
<tr>
<th>TOTAL IN CIRCUIT</th>
<th>Resin Volume [mL]</th>
<th>% Resin</th>
<th>Airlift total flow to upstream tank (measured)</th>
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<tr>
<td></td>
<td>272.5</td>
<td>8%</td>
<td>28.5</td>
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<table>
<thead>
<tr>
<th>Segregated Flow Model, OUTPUTS:</th>
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<tbody>
<tr>
<td>Soln (gpl)</td>
</tr>
<tr>
<td>Mix Tk</td>
</tr>
<tr>
<td>Resin [g Cu / L R]</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>Mod He #</td>
</tr>
<tr>
<td>Eqbm Load [g Cu / L R]</td>
</tr>
<tr>
<td>quadratic “a”</td>
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<tr>
<td>quadratic “b”</td>
</tr>
<tr>
<td>quadratic “c”</td>
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</tbody>
</table>

**Copper: High Feed Assay**

- model mix tank exit: 3.910
- observed mix tank assay: 3.910

**Film Diffusion**

- kf 0.008453 0.004884 0.001493 8.14E-05 5.133E-06
- eqv s already loaded 143 105 123 108 -
- total eqv time in this tank (s) 1,863 3,045 1,683 2,628 2,160
- resin loading moving forward at tmean 78.84 78.66 71.70 14.17 0.65

**Hybrid Correlation**

- kh 9.06E-05 6.45E-05 3.09E-05 5.09E-06 9.182E-07
- eqv s already loaded 1,877 678 229 4 -
- total eqv time in this tank (s) 3,597 3,618 1,789 2,524 2,160
- resin loading moving forward at tmean 67.30 61.27 34.78 16.47 5.21
<table>
<thead>
<tr>
<th>STREAM</th>
<th>FLOWS: mL/min</th>
<th>Cu mass flow: gCu/min</th>
<th>Assays</th>
<th>g/L Cu</th>
<th>g Cu / L R</th>
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<td>resin flow</td>
<td>total</td>
<td>soln</td>
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<td>120.68</td>
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<td>38.00</td>
<td>38.00</td>
<td>0.00</td>
<td>20.25</td>
<td>20.25</td>
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<td>4 o/f</td>
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<td>0.00</td>
<td>1.10</td>
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<tr>
<td>5 o/f (tails)</td>
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<td>0.04</td>
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<td>38.50</td>
<td>1.50</td>
<td>0.00</td>
<td>0.00</td>
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**Balance by Stage:**

<table>
<thead>
<tr>
<th></th>
<th>Flow in</th>
<th>Flow out</th>
<th>in</th>
<th>out</th>
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</thead>
<tbody>
<tr>
<td>Mix Tank</td>
<td>47.00</td>
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<td>183.76</td>
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<td>1.10</td>
<td>1.10</td>
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<tr>
<td>OVERALL</td>
<td>58.50</td>
<td>58.50</td>
<td>97.78</td>
<td>97.78</td>
</tr>
</tbody>
</table>

**CIRCUIT RECOVERY** 99.89%
EMERGENCY SHUT-DOWN INSTRUCTIONS:

***See next page for photographs of all key shut-offs***

1. SHUT OFF TEMPERATURE CONTROL – unplug yellow extension cord on North Wall
2. SHUT OFF MOTORS – unplug orange extension cord on North Wall
3. SHUT OFF PUMPS – use power bar switch on wall just to the left of sink
4. SHUT OFF pH CONTROLLERS – use switch or unplug power bar on East Wall
5. SHUT OFF SCALES & COMPUTER – use switch or unplug power bar on East Wall
NORTH WALL:

3) TEMPERATURE CONTROLLERS:  

2) MOTORS:

Outlet: Panel 1 Circuit 9

EAST WALL:

3) PUMPS:  

4,5) pH CONTROLLERS and SCALES:

Fed from Panel 1 Circuit 13

Outlet: Panel 1 Circuit 11
SYSTEM START UP:

☐ 1. Calibrate the pH probes on each controller using the Temperature Probe. When calibration is complete, switch for a 0.1% 111.7 ohm resistor (except for the resin feed tank which is calibrated with and keeps any other resistor)

☐ 2. Mount contactors to frame and connect tubing between them. Do not connect feed to first tk.

☐ 3. Place heaters with cages, pH probes, and temperature sensors into each contactor

☐ 4. Measure out and add desired wet-settled resin volumes for each contactor

☐ 5. Add water and lower agitators into each contactor. Start mixing at 300 RPM.

☐ 6. Submerge NaOH addition lines into each contactor (must be below solution level!!)

☐ 7. Turn on and tare all scales with NaOH containers on them

☐ 8. Start feed pump with water. Adjust speed to get desired flowrate for test.

☐ 9. Turn off feed pump and connect to feed mix tank

☐ 10. Start flow of water through circuit. Check for any leaks

☐ 11. Check that temperature controllers are in contactors and are not touching contactor walls

☐ 12. Plug in yellow extension cord on North wall to provide power to temperature controllers

☐ 13. Plug heaters into temperature controllers and turn on individual heater power bars

☐ 14. Check that temperature control is set to 30C and then initiate heaters by pressing the hand on the temperature controller.

☐ 15. Turn on motors to NaOH pumps so they control on pH

☐ 16. Re-tare all scales, turn on computer and start datalogging using Windmill.

☐ 17. When ready to start the test, place feed line into nickel feed solution. RECORD TIME OF STARTING!!!!
CAROUSEL SWITCHING OF CONTACTORS:

Lead – High Centre – Centre – Low Centre – Lag   (“Lead – H.C. – C – L.C. – Lag”)

- Take samples from all contactors 45 minutes into cycle  
  
  Label: Circuit Position – Hour – Physical Position (e.g. H.C. – 2 - F)

- Record NaOH Weights from Logger onto Test Sheet 55 minutes into cycle

- Three minutes before hour ends (i.e. 57 minutes into cycle), turn off Feed Pump and Carousel Recycle Pumps at Power Bar by Sink. Manually turn on/off Carousel Recycle Pump if necessary.

- Remove Feed Line to Lead Contactor and place into High Centre Contactor. Disconnect lead o/f.

- Place bucket under Lag Contactor and disconnect Tails line. Attach tail line to offline contactor

- Connect Lag overflow line to offline contactor. Switch and adjust position of Tails bucket.

- Turn on NaOH pump to offline contactor.

- Add ____ mL resin to each contactor in use. Turn Pumps back on at Power Bar. Contactors are all now in new circuit positions!

- Switch off power bar for heater to new offline contactor (formerly Lead Contactor)

- Switch off NaOH pump to offline contactor. Direct offline contactor O/F to bucket

- Remove and Rinse: pH probe, heater, temp sensor, agitator, NaOH line at offline contactor

- Remove offline contactor from frame. Use Caution. Do not handle contactor by overflow or inlet. Be careful around screens

- Mount spare contactor with ____ mL resin onto frame. Have overflow directed to a water rinse bucket. Lower agitator into contactor. Place pH probe, temp sensor, NaOH line into contactor.

- Double check position of heater. Point the sealed edge of the screen towards the contactor wall. Ensure that there is sufficient space between heater screen and contactor. Turn powerbar back on

- Clean-Out the offline contactor (formerly Lag Contactor)
  
  ***Use Caution. Do not handle contactor by overflow or inlet. Be careful around screens*** Rinse out Resin Fines Separately into Fines Container.

- Measure out and Record Final Resin Volume. Keep Resin Sample. Record volume of tails.
CAROUSEL CIRCUIT MONITORING:

1. **DATALOGGING:**
   - Is windmill recording the data?
   - Are the scale weights dropping as the NaOH pumps turn on?

2. **CONTACTORS:**
   - Check that there is good mixing of resin within contactor
   - Check that the overflow screen is not plugging
   - Check no resin is breaking through overflow screen (fines okay)
   - Check temperature in tank is 28-32C
   - Check that heater is not too close to tank walls and is not smoking
   - Check that pH is between 3.8-4.2. (Ideally between 3.9-4.1). Adjust speed of motor on NaOH pumps as needed. Check solution levels of NaOH and replenish with 1M solution as needed. If pH reading stuck ~ pH 7, check resistor.

3. **SOLUTION FLOW:**
   - Is there still plenty of fresh feed?
   - Does the tails bucket need changing?

SYSTEM SHUT-DOWN AT END OF RUN:

1. Take any required samples from contactors before starting shut-down!
2. Turn off heaters using switch at individual power bars. Unplug yellow extension cord at north wall. Check lights off at all temperature controllers.
3. Turn off sodium hydroxide addition to all 7 tanks (feed tank, 5 RIP contactors, resin prep tank), by switching off the appropriate Masterflex drive units.
4. Turn off feed pumps at appropriate Masterflex drive units: fresh feed, recirculating solution to F
5. Stop windmill logger software on logging computer
6. Turn off individual agitators for each contactor
REMOVAL OF RIP CONTACTOR:

- Put on chemical goggles if using safety glasses for PPE. MUST USE GOGGLES FOR THIS STEP!!!
- Remove feedline into contactor, if necessary (use container to catch spills!)
- Remove from contactor and rinse the following:
  - Immersion heater & cage & temperature probe
  - pH probe & holder
  - NaOH feedline
  - Raise & Rinse Agitator
- Remove outlet hose to next contactor (use container to catch spills!)
- Unscrew the three screws holding contactor onto frame
- Drain tank. Use outlet hose for first portion, then tip contactor sideways towards you. Use deionized water to rinse out and collect the resin.
- Separate feed solution and resin. Feed solution to go to waste drum, resin to be rinsed with deionized water. Measure resin volume, keep and label sample.
**RIP MINIPLANT OPERATING SHEET**

**Sample at:** ______________  
**Weights at:** ______________  
**Turn pump off at:** ___________  
**Pump on:** ______________

<table>
<thead>
<tr>
<th>Hour</th>
<th>Time for Change</th>
<th>Tank Order</th>
<th>Tails</th>
<th>Resin Volume</th>
<th>NaOH Scale Weights</th>
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<td></td>
</tr>
<tr>
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**FINAL TANK RESIN VOLUMES:**

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**During 36th hour:**

Sample all contactors at:

- 15 mins
- 30 mins
- 45 mins
- 60 mins (start of 37th hour)
APPENDIX K: COPPER RESIN VOLUME OPTIMIZATION

![Graph showing copper in solution and copper loaded on resin vs tank number.](image)

No Back-Mixing

- 3.6%
- 7.1%
- 10.7%
- 14.3%
- 17.9%
- 21.4%
- 25.0%