REMOVAL OF IRON BY ION EXCHANGE FROM COPPER ELECTROWINNING ELECTROLYTE SOLUTIONS CONTAINING ANTIMONY AND BISMUTH

by

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ABSTRACT

In order to increase the current efficiency in copper electrowinning tankhouses, iron can be removed from the electrolyte using ion exchange. While this is a proven technology, very little data is available for the application of this technology to copper electrowinning electrolytes containing antimony and bismuth.

The feasibility of utilizing iron ion exchange for the removal of iron from copper electrowinning electrolytes containing antimony and bismuth was studied in the laboratory. A picolylamine, a sulphonated diphosphonic, an aminophosphonic and three sulphonated monophosphonic resins were tested. The picolylamine resin was found to be completely impractical as it loaded high levels of copper. All the phosphonic resins tested loaded an appreciable amount of antimony, however, only the aminophosponic resin loaded an appreciable amount of bismuth.

Tests to determine whether or not the sulphonated monophosphonic Purolite S957 resin would continue to load antimony with time and, hence, reduce the resin's ability to remove iron gave inconclusive results. In the event that the resin's ability to remove iron is hampered due to antimony loading, testing has shown that the resin performance may be restored via a regeneration with a solution containing sulphuric acid and sodium chloride.

A case study for the application of this technology to the CVRD Inco CRED plant has shown that, while iron removal by ion exchange is technically feasible, it will upset the plant's acid balance in electrolyte. Therefore, an acid removal process would need to be implemented in tandem with an iron ion exchange system. Additionally, preliminary calculations suggest that a system with a single ion exchange column may have difficulty removing sufficient iron for the CRED design conditions. Therefore, consideration should be given to the possibility of utilizing a two column system (one column loading, one column stripping).

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LIST OF ACRONYMS AND ABBREVIATIONS

APU	Acid Purification Unit
BFA	Basic Ferric Arsenate
BV	Bed Volumes
С	Concentration
C ₀	Initial Concentration
CE	Current Efficiency
CPT	Central Process Technology
CRED	Copper Refinery Electrowinning Department
CVRD	Companhia Vale do Rio Doce
EMEW	Electrometals Electrowinning
EW	Electrowinning
ENS	Electrowinning Nickel Slurry
EMS	Engineered Membrane Separation
FSC	First Stage Cake
IPC	Inco Pressure Carbonyl
IX	Ion Exchange
LIMS	Laboratory Information Management System
ORP	Oxidation Reduction Potential
PIMS	Process Information Management System
PMR	Precious Metals Refinery
SHE	Standard Hydrogen Electrode
SX	Solvent Extraction
TOL	Total Oxidative Leach
TUS	Tower Underflow Solids

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1.0 INTRODUCTION

The presence of soluble iron in copper electrowinning electrolytes significantly reduces the energy efficiency of a copper electrowinning operation. This is because iron is reduced from the ferric to ferrous species at the cathode, and then oxidized back from ferrous to ferric at the anode, creating a parasitic reaction in the tankhouse.

In order to address this loss of energy efficiency, many operations bleed a certain volume of electrolyte from the tankhouse. In many cases this is undesirable as it also results in the loss of cobalt sulphate (added to the electrolyte to reduce anode corrosion and lower the anodic overpotential), and can incur neutralization costs.

An alternative to the conventional iron bleed is the implementation of an iron ion exchange system. The Fenix Hydromet ion exchange system was implemented commercially at the Mount Gordon operation, Australia, in 2002. The Mount Gordon flowsheet utilizes solvent extraction to transfer copper from a leach solution to an electrolysis solution. Antimony and bismuth were not present in the leach solution at Mt. Gordon and therefore antimony and bismuth would not be expected to be present in their electrolyte solution. Operations that do not utilize solvent extraction between copper metal leaching and copper electrowinning may have these impurities (Sb, Bi) present in their electrolyte solution.

The purpose of this thesis is to investigate the applicability of iron ion exchange to copper electrowinning electrolytes containing appreciable amounts of bismuth and antimony. This is done through a case study evaluation of the iron ion exchange technology to the CVRD Inco CRED plant located in Copper Cliff, Ontario.

2.1 THE CVRD INCO CRED PLANT

The CRED Plant is part of the CVRD Inco Ontario Division and is located in Copper Cliff, Ontario. The name CRED is an acronym dating back to the days when Inco operated a copper electrorefining operation, known as the Copper Cliff Copper Refinery. Historically, the CRED plant was operated under the management of the Copper Refinery and was referred to as the "Copper Refinery Electrowinning Department" (CRED). The Copper Refinery was closed in December of 2005; however this did not affect the feed to the CRED plant, since it has always received feed from the Nickel Refinery.

CRED takes the residue from the Copper Cliff Nickel Refinery and separates it out into five streams:

- A precious metals concentrate (designated TOL Slurry) to feed the Port Colborne Precious Metals Refinery (PMR)
- 2) A nickel-cobalt slurry (designated ENS) to feed the Port Colborne Cobalt Refinery
- 3) Electrowon Grade B Copper Cathode for Market
- 4) A selenium and tellurium product (designated TUS). Historically, TUS was processed in the Silver Refinery
- 5) Stabilized iron-arsenic cake for disposal in the tailings area

Additionally, an intermediate product, First Stage Cake (FSC), is reverted upstream whenever the CRED Tankhouse is unable to process all the copper in the residue feeding the plant [1].

To properly understand the CRED process, it is helpful to have a basic understanding of where it fits in the overall Ontario Division flowsheet. This is shown in Figure 2.1, which shows CRED's position in the Ontario Division Flowsheet:



FIGURE 2.1: CVRD INCO ONTARIO DIVISION FLOWSHEET

As this flowsheet illustrates, the principal products from the Ontario Division are nickel products, copper products, cobalt, and precious metals. While copper cathodes are a product of the CRED plant, copper production is not the plant's principal objective. In fact, copper is generally considered to be a byproduct and the principal products are the feeds to the two Port Colborne Refineries.

Iron is removed throughout the Ontario Division flowsheet; however it can not all be removed upstream of the CRED plant. The three principal minerals in the Sudbury ore body are: chalcopyrite -CuFeS₂, pentlandite $-(Ni,Fe)_9S_8$ (~36 wt% Ni), and pyrrhotite $-(Fe,Ni)_8S_9$ (~0.8 wt% Ni). Clarabelle Mill removes iron from the flowsheet by rejecting most of the pyrrhotite. Pyrrhotite comes in two forms: hexagonal (for the low sulphur portions that approach FeS) and monoclinic (for the higher sulphur portions). Monoclinic pyrrhotite is strongly magnetic and can therefore be removed with magnetic separators before the flotation cells. The hexagonal pyrrhotite is depressed in the flotation cells through the addition of TETA (triethylene tetramine) and sulphite [2]. Even if complete rejection of pyrrhotite were obtained, there would still be a significant amount of iron reporting to the Bulk Smelter with the chalcopyrite and pentlandite.

The principal purpose of the Bulk Smelter is iron and sulphur removal. This is achieved in a two-step process: matte-making in the Inco Flash Furnaces, and converting in Pierce-Smith Converters. During these processes, sulphur reacts with oxygen to form SO_2 , and iron reacts with silica to form a Fayalite slag (2FeO·SiO₂) [3]. However, not all iron can be removed at this stage, as too much iron removal will result in cobalt losses (and to a lesser extent, nickel and copper losses). This can be illustrated by the fact that the slags from many copper refineries contain appreciable amounts of cobalt [4].

At the Copper Cliff Nickel Refinery, the Inco Pressure Carbonyl (IPC) process is used to refine the nickel. In this process, carbon monoxide is used to volatilize the nickel from the solid as nickel carbonyl, Ni(CO)₄. During this process, some iron carbonyl, $Fe(CO)_5$, also forms and this is separated from the nickel carbonyl using distillation. The carbonyls are then decomposed to form nickel and ferronickel pellets [5].

It is the residue from the IPC process that is the feed to the CRED plant, and it is essential that this residue contain sufficient iron to stabilize the arsenic present in this stream as basic ferric arsenate to allow for disposal to tailings [6]. An overview of the CRED Process is presented in the following block diagram:



FIGURE 2.2: CRED BLOCK DIAGRAM

IPC Residue enters the First Stage Leach, where nickel, iron, and cobalt are removed through acid dissolution (for oxides) and through cementation reactions with soluble cupric, Cu^{2+} , (for sulphides and metallics). At the end of this leaching process, most of the iron, nickel, and cobalt have been leached into solution, while most of the copper and precious metals remain in the solids.

The solids continue on to the Second Stage Leach, which is a Total Oxidative Leach. At the end of the Second Stage Circuit, most of the copper, selenium, and tellurium are present in the solution, while the precious metals remain in the solids. The solids are then shipped to the Port Colborne Precious Metals Refinery as TOL Slurry. The Second Stage Filtrate continues through the Selenium and Tellurium Removal Circuit to create an aqueous stream that is of

sufficient purity to be added to the Tankhouse electrolyte. There are two routes for iron to enter the Second Stage Circuit from the First Stage Circuit. First, any unleached iron will report to the solids. Secondly, some dissolved iron enters the Second Stage due to incomplete washing of the solids [1]. Most of the iron that reports to the Second Stage reports to the Second Stage Filtrate and hence ends up in the Tankhouse electrolyte.

Selenium and tellurium are removed from Second Stage Filtrate through the addition of copper shot in the Selenium and Tellurium Removal Circuit. The purified Second Stage Filtrate is mixed with Spent Electrolyte in the EW Mix Tank. It is then fed into the Tankhouse where copper is electrowon from solution into Grade B cathodes. The solution leaving the Tankhouse is the Spent Electrolyte and returns to the EW Mix Tank. A bleed stream of Spent Electrolyte is sent to the First Stage Leach to provide the cupric ions required in that processing step. This provides a bleed stream to allow for iron removal from electrolyte. However, it should be noted that the amount of Spent Electrolyte bled to the First Stage is dictated by the leaching chemistry and not by the levels of iron present in the electrolyte. Spent Electrolyte is also consumed in the Second Stage Leach; however, this does not provide a bleed for iron since the iron will simply recycle back to the electrolyte.

Several studies have been performed at the University of British Columbia pertaining to leaching at the CRED plant. These studies can be reviewed for more details of the two leaching circuits [7], [8], [9], [10].

The First Stage Filtrate contains most of the nickel, cobalt, and iron, as well as arsenic and some residual copper from the electrolyte. This moves on to the Iron – Arsenic Removal Circuit (or simply, the Iron Circuit). In this circuit, all iron is oxidized to ferric in a series of two autoclaves and is precipitated as a hydroxide with lime. The arsenic co-precipitates with the iron to form a stable basic ferric arsenate cake (BFA) that can be sent to the tailings area. This precipitate is sent to the Effluent Mix Tank where the pH is raised to precipitate any remaining metals before disposal in the tailings area. Most of the copper, nickel, and cobalt that were present in the First Stage Filtrate remain in solution and proceed to the Copper Clean-Up Circuit.

In the Copper Clean-Up Circuit, any copper present in the First Stage Filtrate is precipitated with soda ash. This precipitate is filtered and sent back to the Second Stage for reprocessing. This precipitate contains some iron and is a second source of iron getting into the electrolyte.

The filtrate from the Copper Clean-Up Circuit moves on to the Nickel – Cobalt Precipitation Circuit. In this circuit, nickel and cobalt are precipitated with soda ash and thickened. This slurry (designated ENS) is sent to the Port Colborne Cobalt Refinery for further processing. The thickener overflow is sent to the Effluent Mix Tank where it combines with the BFA from the iron circuit. Lime is added to the Effluent Mix Tank to precipitate any remaining trace metals, and the slurry is pumped to tailings for disposal.

As previously mentioned, the Tankhouse can not always process all of the copper present in IPC Residue, resulting in the practice of reverting some First Stage Cake upstream in the Smelter. If the throughput through the Tankhouse could be increased, then the reverting of First Stage Cake, and the associated reprocessing costs, could be eliminated.

2.2 BEHAVIOUR OF IRON IN AQUEOUS SOLUTIONS

2.2.1 Iron in Water

The best way to describe the behaviour of iron in water is to examine a Pourbaix diagram for iron. The following Pourbaix diagram was generated in HSC [11] for iron concentrations of 1 m, at 60°C and 1 atm. Sixty degrees Celsius was chosen as the temperature of interest since this is the temperature of Spent Electrolyte. Note that, for aqueous solutions, the area of interest is in the water stability zone (drawn on this diagram as two hatched lines):



FIGURE 2.3: POURBAIX DIAGRAM FOR IRON-WATER SYSTEM AT 60°C

This diagram clearly shows the areas of predominance for the two iron ions: ferric (Fe³⁺) and ferrous (Fe²⁺), and their half-cell potential of 0.8 V_{SHE}. This diagram also shows that iron will not remain in its pure form in water (i.e. it will rust) and that the two thermodynamically stable oxides at this temperature are Hematite, Fe₂O₃, and Magnetite, Fe₃O₄.

2.2.2 Iron in CRED Electrolyte

It is well known that the presence of iron in electrolyte reduces the current efficiency in a copper electrowinning tankhouse, and this phenomenon has been demonstrated in the laboratory at the CRED plant, under controlled test conditions [12]. This loss of current efficiency is because iron is involved in a parasitic reaction, taking away electricity from the plating of copper by being oxidized from Fe^{2+} to Fe^{3+} at the anode, and by being reduced from Fe^{3+} to Fe^{2+} at the cathode.

This loss of current efficiency (CE) due to the presence of iron in electrolyte can be seen by plotting current efficiency against concentration of iron in electrolyte. These parameters were both reported for many refineries around the world in the 2003 World Electrowinning Tankhouse Survey [13]. The reported current efficiencies and iron concentrations for electrowinning refineries that use permanent cathode technology are plotted in Figure 2.4:



Current Efficiency vs Iron in Electrolyte Based on 2003 World Tankhouse Survey

FIGURE 2.4: CURRENT EFFICIENCY VS. IRON CONCENTRATION IN ELECTROLYTE Based on Data from the 2003 World Electrowinning Tankhouse Survey (Robinson 2003)

The iron levels in the Spent Electrolyte at the CRED Tankhouse are the highest of all copper electrowinning tankhouses that responded to the 2003 World Electrowinning Tankhouse Survey [13]. Several refineries have installed an electrolyte bleed system which allows them to lower iron levels in electrolyte; however, CRED relies on the bleed of Spent Electrolyte to First Stage Leaching to control iron levels. Since the amount of Spent Electrolyte to the First Stage is dictated by the leaching chemistry of the IPC Residue, rather than by the iron levels in the Tankhouse electrolyte, CRED can not adjust electrolyte bleed volumes to lower iron levels. The following histogram uses the data from the 2003 World Tankhouse Survey to illustrate how the iron levels in CRED electrolyte compare to the rest of the world.

Iron Levels in Copper EW Tankhouses



FIGURE 2.5: IRON LEVELS IN COPPER ELECTROWINNING TANKHOUSES AROUND THE WORLD Based on Data from the 2003 World Electrowinning Tankhouse Survey (Robinson 2003)

The low current efficiency realized at CRED results in a high energy consumption per torne of copper produced. This loss in energy efficiency due to iron can best be seen in an Ettel Diagram. Ettel Diagrams were first developed in 1977 as a graphical means of evaluating the energy requirement of an electrometallurgical process. Ettel diagrams plot "Faradays per mol of metal" against cell voltages [14]. The ordinate is related to the amount of charge required in the electrometallurgical process, since a Faraday is defined as 96,487 Coulombs per mol electrons. These plots display energy consumption graphically since the amount of energy required per kg of metal [kWhr/kg metal] equals the area of the plot [C V/mol metal] divided by 3600 and by the molar mass of the metal.

The following Ettel diagrams for the CRED plant and for Codelco's Radimiro Tomic refinery were created using the approach described by Ettel. The data used to construct these plots came from the 2003 World Tankhouse Survey [13], published electrolyte conductivity data [15], published anode overpotential data [16], and Ettel's 1977 estimates for energy consumption due to cathodic overpotential, cell hardware, and reversible cell potential. Note that energy lost due to stray currents was not taken into account in the drawing of these diagrams, but was considered to be less than 1% of the total energy consumption by Ettel in 1977.





FIGURE 2.6: ETTEL DIAGRAMS FOR COPPER ELECTROWINNING AT CRED AND CODELCO U_E – Ohmic Drop Across Electrolyte; U_H –Ohmic Drop Across Electrical Hardware

The Ettel diagram clearly shows how the lower current efficiency realized at CRED (83% CE reported) results in a much higher energy consumption per kilogram of copper when compared to a refinery with a much higher current efficiency, such as the Radimiro Tomic Refinery (93% CE reported). Since iron is believed to be responsible for a large portion of the current efficiency losses at the CRED plant, removal of iron from electrolyte should result in lower energy consumption per pound of copper produced (i.e. a higher energy efficiency for the process).

In addition to affecting the current efficiency in the Tankhouse, the presence of iron in electrolyte also affects the copper shot consumption. Because of the oxidative nature of the Second Stage Leach, iron is present in solution as ferric. As the Second Stage Filtrate passes over the Copper Shot Column in the Selenium and Tellurium removal circuit, the iron is reduced to ferrous. Therefore, reducing the amount of iron present in CRED electrolyte will also result in reducing the copper shot consumption.

2.2.3 Benefits of Iron in the CRED Process

It should be noted that iron may have a positive impact in at least two locations in the CRED circuit: the Second Stage Leach and the Selenium and Tellurium Removal Circuit.

During the Second Stage Leach, copper is leached through oxidation. Second Stage Leaching tests done by Grewal on washed filter cake with a synthetic electrolyte containing no iron showed considerably slower leaching kinetics [7]. This was attributed to two factors. The first was that iron acts as a surrogate oxidant for the leaching of copper (i.e. oxygen oxidizes ferrous to ferric, and then the ferric oxidizes the copper sulphide). The second factor is that iron appears to affect the morphology of the basic copper sulphate formed in the leach. Without iron, much finer precipitates are formed. The finer precipitates create a more viscous slurry which interferes with gas-liquid mass transfer.

In the Selenium and Tellurium Removal Circuit, selenium and tellurium are removed in two steps. First, in the Copper Shot Tower, Se^{4+} and Te^{4+} are reduced, and this reduction is believed to be by Cu^+ . Next, in the Aging Towers, Se^{6+} and Te^{6+} are reduced, but the

mechanism of reduction is not very well understood. It is likely that these are also reduced by cuprous, Cu^+ , but thermodynamics indicate that this reduction could also occur by ferrous. A fundamental study of selenium and tellurium reduction in the Aging Towers would need to be conducted in order to rule out the fact that iron may be involved in this reaction.

Since iron may have a positive benefit on both Second Stage Leaching and on the Selenium and Tellurium Removal Circuit, further investigations should be carried out before making a decision to remove all iron from entering the Second Stage, or to remove all iron before the Copper Shot Column. However, if iron removal were to occur on a bleed stream of Spent Electrolyte, the iron would be removed after the Second Stage Leach and the Selenium and Tellurium Removal Circuit, so iron removal could be implemented with much less risk.

2.3 **OPTIONS FOR IRON REMOVAL**

There are several options available for iron removal from electrolyte. These are discussed below and critiqued for their applicability to the CRED Plant.

2.3.1 Washing / Repulping the First Stage Filter Cake

The simplest solution to the problem of high iron in CRED electrolyte is to reduce the amount of iron getting into the electrolyte in the first place. This could be achieved through better washing or repulping of the solids leaving the First Stage Circuit. However, only a limited amount of water can be added at this point due to water balance constraints in the Iron Circuit. Also, as mentioned in section 2.2.3, removing all iron from Second Stage could result in significantly longer Second Stage batch autoclave leach cycle times, and could potentially have a deleterious effect on the Selenium and Tellurium Removal Circuit. Therefore, it would be advantageous to be able to remove iron downstream of the Second Stage, so that the benefits of the iron on leach kinetics can be maintained.

2.3.2 Selective Precipitation

Controlling pH for the purpose of selective precipitation is often used as a separation technique between two aqueous ions. For example, at the CRED plant, iron in the First Stage Filtrate is removed in the Iron Circuit by first oxidizing all iron to ferric in the Iron Autoclaves and then precipitating the iron as a hydroxide with lime. This works well since the primary purpose of this step is to separate iron from nickel and cobalt. Several precipitation diagrams were presented by Monhemius in 1977 [17], and a hydroxide precipitation diagram for iron, copper, and nickel at 25°C is presented in Figure 2.7:



Hydroxide Precipitation Diagram 25C

FIGURE 2.7: HYDROXIDE PRECIPITATION DIAGRAM FOR FE, CU, NI AT 25°C (after Monhemius)

This diagram illustrates the precipitation curves for the various hydroxides, and indicates that precipitation is a function of both solution pH and metal ion concentration. For pHs and concentrations to the left of a line, the metal will remain in solution. Similarly, if the concentration and pH lie to the right of a line, the metal will precipitate out as a hydroxide.

This diagram shows that there is a large gap between ferric and nickel, illustrating why precipitation is a good method for separating these two ions out of CRED First Stage Filtrate. The diagram also shows that the starting point of copper precipitation is close to the end of the

ferric precipitation line, which is why copper often co-precipitates with ferric when trying to remove all ferric ions from a solution, as was observed by Zhang [18].

An option for iron removal from electrolyte would be to take a bleed stream of electrolyte and to precipitate out the ferric iron and copper. The great advantage of this scheme is that precipitate copper could be reverted to the Smelter instead of being plated in the Tankhouse. The amount of copper in this precipitate would then replace an equivalent amount of copper in First Stage Cake reverted to the Smelter. The reprocessing costs of a copper product precipitated from the Tankhouse Electrolyte would be lower than for the First Stage Cake Revert. Such a precipitation scheme was previously investigated as a possibility for eliminating the First Stage Cake recycle at CRED [19], [20]. Alternative precipitation schemes, such as using NaHS to form copper sulphides, were also investigated, but were deemed to be more expensive than hydroxide precipitation [21]. In the end, the hydroxide precipitation option was abandoned in favour of installing a copper crystallization circuit [22], due to cost considerations. Note, however, that this crystallization circuit has yet to be installed.

It should be noted that a large portion of the operating cost for the hydroxide precipitation scheme is the reagent required to neutralize the highly acidic Electrolyte. This could be mitigated through the application of an Acid Purification Unit (APU), which is able to separate acid from metal salts. The APU is fed with electrolyte and generates two streams: a Product stream which contains most of the acid and a Byproduct stream which contains most of the metal salts. At CRED, the Product would be recycled to the EW Mix Tank to maintain the acid balance and the Byproduct would be neutralized to create a copper-iron precipitate for reverting to the Copper Smelter. APUs have been implemented commercially in copper electrorefining operations to remove nickel from decopperized solution [23]. It should be noted that the amount of acid remaining in the Byproduct may need to be higher than the value of 4 g/L reported in the literature [24], and more in line with the 25 to 35 g/L reported by Sterlite Industries [25]. This is because the CRED electrolyte contains bismuth, antimony, and arsenic, which would likely hydrolyze and plug the APU resin bed at low acidities.

However, once the copper and iron hydroxide precipitates were filtered, the filtrate would still contain a significant amount of nickel and cobalt since the electrolyte at CRED contains these

elements in the g/L range. This makes sending the filtrate directly to the Effluent Disposal Circuit undesirable, and increasing the pH to precipitate out the nickel and cobalt is also undesirable since this precipitate would be reverted to the Smelter, where cobalt losses are quite high.

2.3.3 Change of Second Stage Leach Operation

Another option for iron removal would be to run the second stage autoclaves deficient in acid so that iron would precipitate out and report to the TOL Slurry. However, this is not desirable since it would also result in the formation of elemental sulphur in the autoclaves, rather than sulphate. Since TOL Slurry is the most valuable product produced at CRED, contamination of this slurry with iron and sulphur would be undesirable.

2.3.4 Solvent Extraction (SX)

Solvent Extraction is used pervasively throughout the Copper Industry as the primary form of purifying leach liquors before an electrowinning operation. In solvent extraction, the aqueous leach liquor is contacted with an "organic phase" which consists of an extractant chemical, that is usually mixed with an organic solvent diluent. The extractant chemical selectively removes the cupric ions from the leach liquor. The two phase mixture (aqueous and organic) is then allowed to settle, so that the two phases can disengage. The aqueous phase, known as the Raffinate, now contains most of the impurity ions, while the organic phase is loaded predominantly with copper ions.

The organic phase is then contacted, in a Stripping Circuit, with the aqueous Spent Electrolyte from the electrowinning operation. The operating conditions are engineered such that the reverse reaction takes place and the copper is stripped off the organic into the aqueous phase. After disengaging, the stripped organic is reused to extract more cupric ions, while the aqueous Tankhouse Feed (often referred to in the literature as "Pregnant Electrolyte") moves forward to copper electrowinning. This process is summarized in Figure 2.8:



FIGURE 2.8: SIMPLIFIED SOLVENT EXTRACTION FLOW DIAGRAM

Although most of the impurities remain in the Raffinate, some iron does get carried over into the electrolyte, and many SX-EW operations have had to implement an iron removal step to control iron levels in electrolyte. Iron can be transferred to the electrolyte by either aqueous entrainment in the Loaded Organic or by iron being picked up by the extractant.

The amount of iron transferred by aqueous entrainment can be minimized by the use of coalescers to reduce the amount of aqueous solution which proceeds to the stripping stage. Iron transfer can also be minimized by adding a wash stage for the loaded organic between the extraction and stripping stages.

The chemistry of the extractant and diluent can also impact the amount of iron transferred to the tankhouse electrolyte. A study of the effect of various diluents on the chemistry of a popular extractant, LIX 64N, showed that the diluent chosen has a significant impact on the amount of iron extracted [26]. A recent plant and laboratory study on the effect of adding different additional organic species, known as "modifiers" to another extractant, Acorga's P50, also influences the amount of iron extracted [27].

As already mentioned, many SX operations have had to implement an additional iron control bleed step, so it would not make sense to apply this technology to CRED for the purpose of iron removal.

2.3.5 Engineered Membrane Separation (EMS)

Engineered Membrane Separation allows for the separation of ions of different valencies by applying pressure to a solution passing over a membrane. The ions in the lower valence state would pass through the membrane into the Permeate Stream, and the ions in the higher valence state, as well as any solids would remain outside the membrane and find their way into the Concentrate Stream.

This technology has been developed by HW Process Technologies and has been implemented in commercial operations with feed rates at least as high as 4000 GPM [28].

Results for pilot testing of EMS to separate iron from commercial copper electrowinning electrolytes were presented at Copper '99 [29], and are displayed in Table 2.1:

Stream	Copper		Iron		Ec / Cu		Volume
	g/L	Split	g/L	Split	re/Cu	g/L H ₂ SU ₄	Fraction
Feed	38.7	1.00	1.14	1.00	0.029	199.9	1.00
Concentrate	48.1	0.32	2.89	0.69	0.060	196.0	0.25
Permeate	34.1	0.68	0.44	0.31	0.013	200.5	0.75

TABLE 2.1: ON-SITE FIELD PILOT PLANT DATA FOR AN EMS Data from Table II and Figure 3 in Copper 99 Paper (Bernard et al. 1999)

This table shows that the EMS is able to concentrate the iron in solution, relative to the copper, and that the acidity of both the Concentrate and the Permeate are approximately the same (less than 3% difference). The paper did not specify how much of the iron was present as ferric, so it may be that much of the iron in the Permeate was ferrous, since these tests were run with plant electrolyte, which would be expected to contain both ferric and ferrous.

The most logical way to apply EMS at the CRED plant would be to feed the EMS with Spent Electrolyte and to run sufficient volumes to allow the replacement of all Spent Electrolyte going to the First Stage with Concentrate from the EMS. If one were to speculate that all ferric remained in the Concentrate and that 1/3 of the ferrous remained in the concentrate (as appears to be the case for copper), then if the amount of iron present as ferric in Spent Electrolyte is approximately 40% [30], then approximately 60% of the iron and 33% of the copper would

report to the Concentrate. Since the amount of Spent Electrolyte bled from the Tankhouse to the First Stage is dictated by the amount of cupric required in the First Stage Leach, this would translate into bleeding almost double the amount of iron from the Tankhouse to the First Stage (~ 1.8 times more iron).

The EMS appears to hold promise as a potential technology for removing iron from CRED electrolyte and should be further investigated. Note that this investigation is beyond the scope of this thesis.

2.3.6 Ion Exchange (IX) and Molecular Recognition Technology (MRT)

Ion exchange allows for removal of specific ions from solution by attaching them with an ionic bond onto a resin surface. The bonded ions then need to be released from the resin into a separate process stream during an elution step, which allows the resin to be reused to remove more of the desired ion.

Molecular Recognition Technology is marketed by IBC Advanced Technologies as an alternative to ion exchange; however, it appears to simply be a particular type of IX resin. MRT is also implemented commercially in packed bed columns and eluted with similar reagents as other IX resins [31]. Therefore, in this review it will simply be considered as another type of IX resin.

In order to remove only iron from electrolyte, a specific/chelating ion exchange resin is generally used. Chelating ion exchange resins differ from standard ion exchange resins, (such as those used in water softening), in that the reactive portion of the resin binds ions through the formation of complexes, instead of just ionic bonds. This allows specific ion exchange resins to remove a specific ionic species (i.e. ferric), while excluding others (e.g. cupric). A detailed explanation of the different types of ion exchange resins has been published by Dorfner [32].

In a review of chelating resins available for iron ion exchange, five main resin types were identified: iminodiacetic, picolylamine, aminophosphonic, sulphonated phosphonic and sulphonated diphosphonic [33]. An example of a commercially available iminodiacetic resin is

Chelex 100; however, it is only rated for a pH range of 4 to 14 [34]. An example of a commercially available picolylamine resin is Dowex M4195. This resin is marketed as being effective at pH values less than 2, but it has an extremely strong affinity for copper at low pH [35]. Therefore, only the phosphonic resins (aminophosphonic, sulphonated monophosphonic, sulphonated diphosphonic) and the MRT resin (chemistry unknown) are suitable for iron removal from copper electrowinning solutions.

An early resin developed for removal of ferric from electrolyte was a sulphonated diphosphonic resin, marketed under the tradename of Diphonix [36], [37]. The loaded resin was then stripped with a solution containing 2 M H₂SO₄, 0.6-0.8 M H₂SO₃, and 1-2 g/L Cu²⁺ at 85°C. Under these stripping conditions, the stripping cycle was approximately twice as long as the loading cycle, and the design engineers were concerned that this may result in an inefficient use of resin volume if a two-column system were implemented. Therefore, piloting and full-scale implementation used thirty fixed-bed ion exchange columns, which were rotated on a carousel arrangement, in order to minimize the amount of resin required. This system was an "ISEP" continuous contactor and was supplied by Advanced Separations Technology [38].

The Diphonix resin is familiar to the CRED plant, as Inco was one of four companies which sponsored Eichrom's research in this area in the early 1990s. Tests were done at the University of British Columbia using Inco Spent Electrolyte and the Diphonix resin. Results showed that ferric could be loaded onto the Diphonix resin and could be eluted with a solution containing 2 M H₂SO₄, 0.65 M H₂SO₃, and 5 g/L Cu²⁺. However, after only 10 cycles of loading/elution, there was a significant amount of antimony and some bismuth bound to the Diphonix resin [39], suggesting that these impurities were being removed from the electrolyte by the resin, but were not being eluted with the iron. These results prompted Inco to withdraw from Eichrom's R&D program at that point. The following three reasons were cited for abandoning the project [40]:

- 1) Too large a volume of eluate for the First Stage Leach to be able to process.
- Reintroduction of SO₂ into the CRED plant. Sulphur dioxide use resulted in constant corrosion problems and leaks when it was used in the Selenium/Tellurium Removal Circuit in the early 1970s.
- A significant amount of antimony and some bismuth was left on the IX resin after only 10 cycles.

Since that time, further advances have been made in this field. The most notable improvement, from CRED's perspective, is the development of a process for eluting the bound iron using cuprous, Cu^+ , generated by copper cuttings in a column [41] (like the CRED Copper Shot Tower). This technology was implemented commercially at the Mount Gordon operation in September 2002 and operated until that refinery was shut down in July 2003 [42]. The use of cuprous as the eluant eliminates the need for the reintroduction of SO₂, and preliminary calculations suggest that the volume of Spent Electrolyte that is currently being sent to the First Stage Leach may be sufficient for the amount required for elution [43]. This addresses the first two of the three issues for applying this technology to CRED.

The outstanding issue of antimony and bismuth poisoning on the resin remains. However, it should be noted that the resin utilized at the Mount Gordon site was a sulphonated monophosphonic resin, and may well have a different selectivity with respect to impurity elements than the original Diphonix resin previously tested. It would be worthwhile to investigate the impurity selectivity of this resin, along with other available resins. The purpose would be to determine if a resin is currently available which would be able to remove the ferric without being poisoned by the impurities present in the CRED electrolyte.

An item of interest from the full-scale application of iron IX at Mount Gordon, is that oxidation reduction potential (ORP) probes were used to assist in the monitoring of the IX system. Although none of the data collected from the ORP probes was published, a discussion with Dr. D. Dreisinger revealed that the ORP probes were found to be quite useful in this application.

It should be noted that ion exchange has been implemented for the removal of bismuth and antimony from copper electrorefining tankhouses and could be considered for removing these elements before an iron IX column, if necessary. An extensive study of several resins for this purpose was conducted at the University of British Columbia in the early 1990s [44]. In this study, all tests used hydrochloric acid to elute the antimony and bismuth from the resin. As an alternative to hydrochloric acid, it may be possible to elute the antimony and bismuth using a solution containing sulphuric acid and sodium chloride, as was proposed by Fukui et al. in their patent for recovering antimony and bismuth from copper electrolytes [45].

If an acid and chloride wash were introduced at the CRED plant, care would need to be taken to ensure that no chlorides would be introduced into CRED electrolyte. This is because chlorides are known to damage stainless steel equipment. A chloride wash would need to be sent directly to the Effluent Mix Tank, and this tank would likely need to be reconstructed using a more corrosion resistant material before it would be able to handle large amounts of chlorides. Fortunately, soluble antimony and bismuth should precipitate out in the Effluent Mix Tank according to the following reactions:

Other options for antimony and bismuth removal from electrorefining tankhouse electrolytes include: electrodeposition in the liberator cathodes and/or increasing the concentration of arsenic(V) in the electrolyte to encourage precipitation of bismuth and antimony in the anode slimes [46] (not recommended for CRED since arsenic in electrolyte may adversely affect the kinetics in the Second Stage and since mudding of the cells only occurs periodically); electrodialysis [47], which can only remove antimony in the +5 valence state; alternate adsorbents, such as an antimony-barium sulphate adsorbent [48], which also requires the presence of chloride during the elution step; or, adsorption onto activated carbon. Activated carbon has shown some promise for antimony removal (the electrolyte tested had no bismuth), and can be stripped with a sulphuric acid solution [49]. This suggests that it should be possible to remove antimony and bismuth upstream using an adsorbent or ion exchange, if required; however, it is not simply a case of installing a known and proven technology.

For implementation of ion exchange at CRED, Spent Electrolyte could be used for both the loading and elution steps in an ion exchange system. Using Spent Electrolyte means that a new copper shot column would need to be introduced as a part of the iron IX circuit.

In conclusion, Ion Exchange appears to hold promise for iron removal at CRED. This thesis investigates the applicability of iron ion exchange to the CRED plant.

In order to assess the effect of adding an Iron Ion Exchange System to CRED, the 2005 plant operating data was downloaded from the plant databases (PIMS and LIMS)^{*} and used to create an Excel heat and mass balance model of the plant. The model was constructed from a template created by D. Dreisinger of the University of British Columbia. The model performs heat, mass, and element balances for each unit operation in the CRED plant. The enthalpy values from the heat balance were taken relative to 298K (H = $H_{298} + {}_{298}\int^{T} C_{p} dT$). The mass and element balances were only performed for the principal elements (Cu, Ni, Co, Fe, As, H, S, O); minor elements (Se, Te, Bi, Sb, Sn, Zn) and precious metals (Au, Ag, Pt, Pd, Rh, Ru, Ir) were not incorporated into the model.

Note that since plant operating data is sensitive information, only results essential to the development of an iron ion exchange system are reported in this thesis.

3.1 MODEL METHODOLOGY: BASE CASE

The model was programmed to take several operating parameters as inputs and to follow the chemistry through the various unit operations in the plant. The model was programmed to calculate intermediate stream flows and compositions as well as final product production rates and assays. Initial estimates for all internal recycle streams are inputs in the model, and a macro was developed which adjusts these values by iterating until the input and output values are within 0.1%. The recycle streams adjusted by the macro are: Spent Electrolyte, Pregnant Electrolyte, Copper Clean-Up Slurry, and two streams in the Iron Circuit. This programming method resulted in being able to close the overall plant mass balance, in the Base Case, to within 0.5%.

First Stage Batch Make-Up was programmed to take the volume of Pregnant Electrolyte per batch as an input, and then adds the required amount of Spent Electrolyte and New Acid in order to reach the target concentrations of copper and acid in the First Stage Filtrate.

^{*} PIMS = Process Information Management System: stores process data

LIMS = Laboratory Information Management System: stores assay data

In order to calculate the amount of First Stage Cake recycled to the Smelter, the model was programmed such that the total amount of copper cathode produced in the Tankhouse was held constant, based on an estimated current efficiency. The model then imposes the condition that the concentration of copper in Spent Electrolyte must remain between 40 g/L and 50 g/L. Whenever the concentration of copper in Spent Electrolyte is calculated to be greater than 50 g/L, the model increases the amount of First Stage Cake recycled to the Smelter by 0.25%. Similarly, whenever the concentration of copper in Spent Electrolyte is calculated to be less than 40 g/L, the model decreases the amount of First Stage Cake recycled to the Smelter by 0.25%.

The CRED 2005 operating data was used to create and debug the model. The following discrepancies in input values were introduced in order for the base case Spent Electrolyte assays to be in line with the operating data:

- 1) IPC residue sulphur assay increased by approximately 20%
- 2) IPC tonnage through plant increased by approximately 10%

It should be noted that this model does not represent the Iron Circuit very well. The flow through the Iron Autoclaves calculated by the model is only about 2/3 of what is measured in the plant, and the iron assays in the iron cake are quite low compared to plant assays (i.e. the model is calculating too much gypsum). Since the volumes and assays through the Nickel Precipitation Circuit are fairly close to plant operating data, it is believed that the errors in the Iron Circuit are primarily due to errors in a circulating loop within this circuit. Since there is very little monitoring in the plant of this stream, this circulating loop is difficult to debug. However, since this circulating loop has little impact on the Tankhouse electrolyte, these errors should not affect the Iron IX analysis significantly.

3.2 MODEL METHODOLOGY: IRON ION EXCHANGE

The iron IX system being considered removes ferric from electrolyte streams. There are three steps to iron IX: loading, generation of cuprous, and stripping. The chemistry for these three steps is summarized in equations 3.1 - 3.4:
Chemistry: Loading

 $[3.1] \quad \text{Fe}_2(\text{SO}_4)_3 + 6 \text{ (H-R)} \rightarrow 3\text{H}_2\text{SO}_4 + 2(\text{Fe-R}_3)$

Chemistry: Cu Shot Tower

 $[3.2] \quad Fe_2(SO_4)_3 + Cu \rightarrow 2FeSO_4 + CuSO_4$

 $[3.3] \quad Cu + CuSO_4 \rightarrow Cu_2SO_4$

Chemistry: Stripping

 $[3.4] \quad 2(Fe-R_3)+Cu_2SO_4+3H_2SO_4 \rightarrow 6 (H-R)+2FeSO_4+2CuSO_4$

While Spent Electrolyte would likely be used for loading of an iron IX system, the model was constructed such that Tankhouse Feed (lower ferric content) was used to load the IX column. This was done to simplify programming since Spent Electrolyte is adjusted by the model to determine the amount of First Stage Cake produced. This should not affect the key mass balance results: concentration of iron in eluate, concentration of copper in eluate, and total mass of iron removed per day.

Even though Tankhouse Feed was used to load the IX resin, instead of Spent Electrolyte, it was still more difficult to be able to close the overall plant mass balance. It was decided that iron was the most important element in this balance, and so the balance was set up so that the overall plant iron balance was within 0.5%. However, larger tolerances were used for the other elements: copper, nickel, and cobalt were balanced to within 2%, while arsenic was balanced to within 4%.

Iron is stripped from the IX column using cuprous sulphate, which is generated by running Spent Electrolyte over a column of Copper Shot. The operating temperature of this column was set at 90°C in the model. In the model, Spent Electrolyte was used in all cases for the eluate and the volume of eluate was fixed to ensure that the First Stage Leach would be able to consume all of the eluate.

The model was programmed to target a concentration of 2 g/L iron in Spent Electrolyte. To achieve this target, the concentration of iron required in the bleed eluate was increased. In terms of model programming, this was achieved by increasing the number of times the eluate recirculates through the Copper Shot Column before being bled to the First Stage. If the iron concentration in Spent Electrolyte was greater than 2.1 g/L, then the number of cycles before bleeding was increased by 0.5; if the concentration in Spent Electrolyte was < 1.9 g/L iron, then the number of cycles before bleeding was decreased by 0.5.

The model was also programmed to hold the volume in the First Stage Autoclaves constant through the addition of water when the volume was less than that used in the base case. This was a necessary condition since the bleed to the First Stage Autoclaves is dictated by the amount of cupric required in the reaction and the eluate is higher in copper sulphate than Spent Electrolyte due to being passed repeatedly over a bed of copper shot. If this condition were not in the model, the concentrations of all elements in the First Stage Filtrate would be higher and consequently more iron, nickel, and cobalt would be entrained in the First Stage Filter Cake than in the base case. This was deemed to be an unfair penalty, since a decrease in volume through the First Stage should allow for the washing of the First Stage Filter Cake, and hence result in less entrained metal ions going to the Second Stage.

The maximum possible reduction in the First Stage Cake was set at 80%. This constraint was added since the model was based on steady-state operation. In actual plant operating practice, the amount of First Stage Cake can vary considerably from day to day and week to week based on the composition of the IPC residue received and the availability of equipment in the plant.

The model was initially run using the same current efficiency as in the base case. Then, since removal of iron should increase the Tankhouse current efficiency, the model was run again with the estimated current efficiency increased by 5, 10, and 15%.

3.3 MODEL RESULTS AND DISCUSSION

Results from the various model runs are summarized in Table 3.1:

% Increase in CE	g/L Fe Spent	g/L Fe Eluate	g/L Cu in bleed to First Stage	% Reduction FSC [*]	% Reduction Cu Shot	% Reduction in kg Cu Shot per kg Cathode	Spent g/L H₂SO₄
BASE CASE							
N/A	11.0	N/A	45.0	N/A	N/A	N/A	227
ION EXCHANGE MODEL							
0%	2.0	20.2	55.7	12	24	23.9%	312
5%	2.0	21.7	56.5	42	18	23.5%	340
10%	2.0	23.3	57.6	68	13	23.1%	362
15%	1.9	24.8	58.3	80	9	22.5%	389

TABLE 3.1: MODEL RESULTS SUMMARY

 $[\]overset{\sim}{\sim}$ *FSC = First Stage Cake recycled to Smelter

The model results show that implementation of iron ion exchange results in a lower copper shot consumption per pound of cathode produced. It also shows that the amount of First Stage Cake recycled back to the Smelter should decrease appreciably, depending on the increase in current efficiency realized in the Tankhouse. Additionally, the model indicates that as a consequence of implementing iron IX a significant increase in electrolyte acidity may be realized. These points will be reviewed in more detail below.

3.3.1 Effect on Copper Shot Consumption

The model results indicate that the amount of copper shot consumed per pound of cathode will decrease by 23-24% However, the model also shows that the higher the current efficiency realized in the Tankhouse, the lower the actual savings in total copper shot consumed. This is because as the Tankhouse current efficiency increases, more copper is plated in the Tankhouse, requiring more material to be processed through Second Stage, and hence more copper shot is consumed.

3.3.2 <u>Reduction in First Stage Cake Recycle</u>

The model indicates that the amount of First Stage Cake recycle will decrease and the amount of this decrease will be dependant upon the current efficiency realized in the Tankhouse. Note that if a current efficiency increase of 15% is realized in the Tankhouse, then the model's maximum allowable decrease of 80% is achieved. Note also the decrease of 12% in First Stage Cake recycle realized if the current efficiency in the Tankhouse remains unchanged. This savings in First Stage Cake is the result of the fact that less copper shot is being consumed. (Note that the copper consumed in the copper shot column is later plated out in the Tankhouse).

It should also be noted that as the amount of First Stage Cake recycle decreases, the amount of iron required to be bled to the First Stage increases. This makes sense since more material (and hence more iron) is being processed through the Second Stage. Note that at the model's maximum allowable decrease of 80%, a concentration of ~25 g/L iron will be required in the IX eluate stream.

3.3.3 Increase in Electrolyte Acidity

An important result from the ion exchange model is the significant increase in the Spent Electrolyte acid concentration. The model shows that the amount of acid could increase from the base case value of 227 g/L to 312-389 g/L acid, depending on the current efficiency realized in the Tankhouse. Note that an increase in acidity from the current value to 350 g/L would be equivalent to adding an additional 6000 L per day of fresh acid to the electrolyte.

It makes sense that iron ion exchange causes the acid levels in the electrolyte to increase for two reasons. First of all, reducing the amount of First Stage Cake reverted to the Smelter results in an increase in the amount of copper plated in the Tankhouse, and hence the amount of acid produced at the anode. To maintain the same level of acid in electrolyte, this increase in acid production would need to be offset by an increase in acid consumption in the leach. However, at the CRED plant, the leaching is done in two stages, and both stages consume a significant amount of acid. Since all of the plant feed already goes through the First Stage Leach, the amount of acid consumed in the First Stage will not change. Therefore, it makes sense that the acid level in the electrolyte will increase. Figure 3.1 illustrates the various streams in the electrolyte acid balance for CRED.



FIGURE 3.1: STREAMS AFFECTING CRED ELECTROLYTE ACID BALANCE

The second reason for the acid level increasing in electrolyte due to iron ion exchange is the ion exchange stripping process itself. In order to increase the amount of iron being bled to the First

Stage Leach, a tank of bleed electrolyte that is used to strip the ion exchange resin several times would be required. This tank of bleed electrolyte would be expected to contain a constant volume of electrolyte by replenishing the volume bled to First Stage Leach with Spent Electrolyte. During the stripping process, the copper shot used to generate cuprous will become cupric in the bleed electrolyte after reacting with the iron on the resin. Since the volume of electrolyte bled to the First Stage Leach is dictated by the amount of cupric needed, increased cupric concentration results in a decrease in the electrolyte volume bled to the First Stage, and hence less acid bled from the main volume of recirculating electrolyte. However, this problem is compounded by the fact that the stripping solution is itself depleted in acid during the stripping process. As shown previously in Equations 3.1 and 3.4, the iron from solution is loaded onto the resin by displacing acid during the stripping cycle. While the acid consumed in loading is equal to the acid generated in stripping, the ion exchange column serves to transfer the acid from the reservoir of stripping electrolyte (the bleed to First Stage Leach) to the main volume of Tankhouse Electrolyte, as shown in Figure 3.2:



FIGURE 3.2 ACID TRANSFER FROM BLEED ELECTROLYTE VIA ION EXCHANGE

Such a large increase in electrolyte acidity could not be tolerated since it would result in increased acid misting in the Tankhouse and increased problems with copper sulphate precipitation around the plant. Therefore, an additional acid removal step would be required to be installed on a portion of the recirculating electrolyte, as part of the installation of an iron ion exchange circuit. Two possible options are the installation of an acid purification unit (APU) or the installation of a decopperizing step, such as standard liberator cells or Electrometals electrowinning (EMEW) cells.

3.4 MODEL CONCLUSIONS

- Lowering the concentration of iron in electrolyte will result in a lower consumption of copper shot per pound of cathode produced. However, depending on the increase in current efficiency realized in the Tankhouse, the total amount of copper shot consumed may not decrease appreciably over the base case since more material would be processed through the Second Stage, rather than being reverted as First Stage Cake.
- 2) The amount of First Stage Cake reverted to the Smelter should decrease significantly, and will depend on the actual current efficiency realized in the Tankhouse. If a current efficiency increase of 15% is achieved, then the amount of First Stage Cake recycle may be reduced by 80% and the concentration of iron in the IX eluate to First Stage will need to be ~ 25 g/L.
- 3) Installation of an iron ion exchange system will result in a significant increase in the acid concentration in electrolyte. Therefore, a process to control acid levels in the electrolyte would need to be installed at CRED in conjunction with an iron ion exchange system. Potential technologies to achieve this include an APU or a decopperizing process, such as liberator cells or EMEW cells.

The following experimental procedures are the default procedures used throughout the experimental work. If a variation on these procedures was used for a specific test, the exceptions will be noted in the discussion for that particular test.

4.1 RESIN CONDITIONING AND DETERMINATION OF RESIN VOLUMES

All resins were conditioned prior to testing to ensure that each resin was in the acidic (H^+) form. This was achieved in two steps. In the first step, the resin was placed in a solution of 50 g/L sulphuric acid and overhead stirring was provided. In the second step, the resin was placed in a glass column and approximately 5 Bed Volumes (BV) of 220 g/L sulphuric acid solution were passed over the resin. Finally, the resin was washed in the column with approximately 10 BV of deionized water to ensure any excess acid was removed.

After conditioning, the resin sample was poured into a graduated cylinder filled partially with deionized water. The graduated cylinder was vibrated until the settled volume of resin remained unchanged. This procedure was repeated twice for one resin sample and showed good repeatability. The resin was then poured into a container of known weight and the excess water removed by applying vacuum to a small porous cylinder placed in the container. The container of resin was then weighed and a bulk density calculated. All resin volumes reported in this thesis were obtained by weighing out an appropriate amount of resin based on this bulk density calculation.

4.2 Assay Analysis Procedures

All samples were analyzed at the CVRD Inco Central Process Technology (CPT) Laboratory.

Solution samples were analyzed using an in-house inductive coupled plasma procedure (ICP-PMET), which had been previously developed for analysis of bismuth, tin, and arsenic in copper refining electrolyte. To ensure that this procedure would be appropriate, three solutions were made up containing varying amounts of these impurities along with 40 g/L copper and 220 g/L sulphuric acid. A small amount of residue was observed and so these test solutions were filtered before being sent in for analysis. Results can be found in Appendix I, and showed a good correlation for arsenic and bismuth; however, the antimony levels reported were approximately 50% of what would have been expected given the amount of reagent added. Note that the antimony levels did appear to trend with the amount of antimony added (i.e. as more antimony was added, more antimony was reported), and that the small amount of residue would not likely account for such a large difference in antimony concentration. Initially, an attempt was made to use the ICP-PMET assays for antimony; however, mass balances for antimony showed large errors. After discussion with the analysts at the assay lab, it was decided that the best way to obtain accurate antimony assays in a solution so high in copper sulphate would be to run them through inductively coupled plasma mass spectrometry (ICP-MS). The results from the initial scoping tests and the equilibrium batch tests used the antimony values from ICP-PMET; all other antimony values reported are based on ICP-MS assays.

To determine the optimum procedure for iron analysis in solution, several samples of known concentration were submitted for both atomic absorption (AA) and ICP-PMET. The results from ICP-PMET showed slightly higher concentrations than the values obtained by AA (Fe by ICP-PMET ~ 1.04x Fe by AA –see Appendix I). Since ICP-PMET was already required for minor element analysis, it was decided that the ICP-PMET results for iron would be sufficient for this work. Therefore, all iron solution assays reported were obtained by ICP-PMET.

Determination of acid concentration was done by titration and values were reported in g/L H₂SO₄. Samples were diluted with deionized water, complexed with potassium oxalate and then titrated with 1.0 N sodium hydroxide solution.

To analyze the amount of material loaded on resin samples, a known mass was completely dissolved in nitric acid using microwave digestion. The solution was then analyzed using a standard ICP analysis and results were reported in mg/g resin. This could then be correlated back to the initial volume of resin by multiplying by the total weight of resin before analysis, and then dividing by the known initial resin volume, to obtain values of mg/mL resin. Iron, for example, would be calculated thus: mg Fe / mL resin = (mg Fe / g resin)(g resin / mL resin).

Note that in many cases, the resin loadings were simply calculated based on a simple mass balance using volumes and solution assays. The two methods were shown to correlate well for iron, as shown in Appendix II. Throughout this thesis, it will be noted if resin loadings are calculated, or whether they are based on an actual resin digestion.

4.3 EQUILIBRIUM LOADING EXPERIMENTS

A synthetic electrolyte solution was prepared by adding sulphuric acid, copper sulphate, nickel sulphate, cobaltous sulphate, ferric sulphate, bismuth trioxide, antimony sulphate, and arsenic pentoxide into an Erlynmeyer flask filled with $\frac{1}{2} - \frac{3}{4}$ L of water^{*}. The solution was heated until the copper sulphate was observed to have dissolved. This solution was then poured into volumetric flasks and deionized water was added until a total solution volume of 1.1 L was obtained. Some residue and/or precipitation was observed in the solution, so the solution was shaken and filtered through Whatman #5 filter paper (2.5 µm pore size). After filtration, the solution was shaken and a 25 mL sample was taken with a pipette. This 25 mL sample was weighed to determine the solution specific gravity, and then diluted with water in a 50 mL volumetric flask to provide a sample of the electrolyte feed. Note that the solution temperature was not measured when the specific gravity was taken and may have varied from test to test.

Based on the synthetic electrolyte specific gravity, a calculated mass of electrolyte was added to each of the six 250 mL Erlenmeyer flasks, with baffles embossed on their base. To these flasks, specific weights of resin were also added such that the following volume ratios were obtained: 100:1, 50:1, 25:1, 12:1, 6:1, 3:1 (mL electrolyte : mL resin).

The flasks were placed in a Lab-Line Orbit Environ Shaker for 24 hours to reach equilibrium loading. The speed setting on the shaker was held constant for all tests at approximately 175 RPM; the heater was adjusted to maintain the samples at 55°C. A series of tests with plant electrolyte at a volume ratio of 14:1 indicated that equilibrium was typically attained within 8 hours, so the 24 hour equilibration time is believed to have been more than adequate. Results from the initial scoping tests can be found in Appendix III. Since these tests have several

^{*} Note: actual solution assays can be found in the discussion sections of the various tests.

samples at equilibrium, these results can be used to estimate the amount of error associated with this procedure. The estimated error for ferric resin loading is $\pm 6\%$.

4.4 COLUMN KINETIC EXPERIMENTS

4.4.1 Loading Procedure

For loading, 25 mL of conditioned resin was weighed out, slurried with deionized water and charged into a 50 mL burette, partially filled with deionized water. The burette was placed inside a 35 mm diameter glass tube which was then sealed on both ends with rubber stoppers.

Water from a heated bath was circulated between the glass column and the burette to provide heating to the ion exchange resin. The recirculating water was overflowed through a small test tube prior to returning to the bath. Temperature was monitored in this test tube, and the amount of heating was adjusted to maintain this temperature at 50°C. This resulted in the temperature of the water in the bath being approximately 55°C.

A synthetic loading electrolyte solution was prepared, typically containing \sim 35 g/L copper, \sim 220 g/L acid, and \sim 1.2 g/L iron as ferric. The synthetic solution was sampled at the start of the experiment to determine specific gravity and for assay. The mass of prepared solution was determined at the start and end of each experiment, so that the total volume of solution passed through the column could be calculated based on the mass through the column and the solution specific gravity.

The loading solution was pumped at a flowrate of approximately 10 BV/hr down through the ion exchange resin, with a Masterflex #14 L/S peristaltic pump. As the electrolyte exited the burette it was either collected directly into a graduated cylinder, or collected in a small test tube that overflowed into a graduated cylinder. The purpose of the small test tube was to provide a reservoir of sample where the ORP was monitored using a silver/silver chloride electrode. Before each test, the calibration of the silver/silver chloride electrode was checked using an Orion ORP standard solution (420 \pm 3 mV_{SHE}). The ORP readings were adjusted based on this

calibration and hence all ORP values are reported against the standard hydrogen electrode (SHE).

Once the volume in the graduated cylinder reached a target number of BVs, the graduated cylinder collecting the loaded solution was changed and a sample of the loaded solution was taken for assay. The target number of BVs for loading samples were: 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, 60, and 80 BV. Note that the ion exchange column was initially filled with deionized water, so the first few samples contained a significant amount of water. To correct for this, copper was used as a tie element to determine the amount of dilution water contained in the first few samples. The use of copper as a tie element to determine dilution water volumes is discussed in more detail in Appendix IV.

After loading was completed, approximately 7-10 BVs of deionized water were passed through the column at slightly more than 10 BV/hr (the pump remained at the same speed as for loading, however calibration of 10 BV was based on electrolyte, not water). This solution was collected, weighed, sampled, and assayed as well. Once again, solution volume was calculated based on solution mass and specific gravity.

When a full loading curve was not required, all loaded solution was collected in a single vessel, rather than collecting samples at various BVs. In this case, the volume of loaded solution was calculated based on weights and specific gravities, rather than on the volumes collected in graduated cylinders.

The apparatus used for the loading experiments is depicted on the following page in Figure 4.1 (shown for the case with ORP monitoring):



FIGURE 4.1: APPARATUS FOR LOADING EXPERIMENTS

4.4.2 Stripping Procedure

For stripping, a second burette was filled with ~ 50 mL (~ 2 BV) of copper shot^{*} and placed in a second 35 mm diameter glass tube, in the same manner as the burette filled with the ion exchange resin. A glass reservoir with a bent outlet tube at the base (the "elution reservoir") was partially submerged in the hot water bath and the ion exchange column was placed directly above this reservoir. A lid to the elution reservoir was made from a rubber stopper with holes bored to allow for an inlet tube, a silver/silver chloride ORP probe, and a stopcock to be inserted. Norprene tubing (1/8") was used to connect the base of the ion exchange column to the inlet of the elution reservoir, the elution reservoir outlet through the peristaltic pump to the base of the copper shot column, and the top of the copper shot column to the top of the ion exchange and copper shot columns, and the tubing connecting the top of the ion exchange and copper shot columns, and the tubing connecting the formation of copper powder in the lines once cuprous was present in the recirculating electrolyte.

A synthetic solution of stripping electrolyte was prepared by the addition of sulphuric acid and copper sulphate crystals to deionized water. Stripping solutions typically consisted of \sim 220 g/L acid and \sim 45 g/L copper. To fill the system with stripping electrolyte, a syringe was used to fill both the copper shot column and the ion exchange column from the base of the appropriate burette. Once each column was filled, the stopcock on the burettes was closed. The elution reservoir was filled from the base by having the venting stopcock in the open position and using the syringe to transfer the electrolyte through the tubing used to connect the outlet of the reservoir to the base of the copper shot column. The total mass of stripping electrolyte was weighed before and after filling the system, and the specific gravity measured in order to calculate the volume of stripping electrolyte in the system. Typically, the volume of recirculating electrolyte was approximately 150 mL.

The recirculating loop of heated water was set up with 3/8" Norprene tubing. The path was from the hot water bath, up around the copper shot column, up around the ion exchange column

^{*} Copper Shot was fairly coarse: 92% retained on a Tyler #10 mesh screen (openings 1.68mm diameter)

and then back to the hot water bath. As the water in the water bath was heated, it was circulated through the two columns. Temperature was measured on the return water line and logged every 30 seconds, by inserting a TPS-90P temperature probe into a glass tube with an overflow. To reduce heat losses, the two glass columns were wrapped in towels, and the temperature in the hot water bath was typically 5-7 °C warmer than the temperature recorded on the return water line. While the system was coming up to temperature, the elution reservoir venting stopcock was left open, the peristaltic pump was left open, the stopcocks on the two burettes remained closed, and the connection from the copper shot column to the ion exchange column was left loose to allow for venting as the stripping electrolyte heated up.

Once the system was at temperature (85°C), the venting stopcock on the reservoir was closed and covered with a septum, the connection from the copper shot column to the ion exchange column was firmly seated, the peristaltic pump was turned on, and the stopcocks on the burettes were opened. The electrolyte began to recirculate through the system from the elution reservoir, up through the copper shot column, down through the ion exchange column and back to the elution reservoir. During the stripping cycle, ORP readings were logged every 30 seconds using a TPS 90-P meter. For some tests, samples of the stripping electrolyte were taken every half hour through the venting stopcock on the elution reservoir.

Sampling was performed by attaching a piece of plastic tubing to the end of a syringe and inserting the plastic tubing through the septum on the elution reservoir venting stopcock. Then, the venting stopcock was opened and the plastic tubing was threaded through the venting stopcock orifice into the elution reservoir, and a 2-3 mL sample was drawn. The weight of the removed solution was taken and a 2 mL sub-sample was taken to measure the specific gravity and then placed in a 10 mL volumetric flask. This flask was filled with deionized water and the diluted sample was submitted for assay.

The stripping electrolyte was recirculated until shortly after an appreciable drop in ORP was observed. At the end of the test, the septum on the venting stopcock was removed and the vent was opened. The stopcocks on the copper shot column and ion exchange column were closed and the tubing connecting the outlet of the elution reservoir to the copper shot column was disconnected from the copper shot column and was placed in a 500 mL volumetric flask. The

pump was used to empty out most of the recirculating electrolyte from the elution reservoir. When the elution reservoir was almost empty, it was removed from the hot water bath and rinsed out with deionized water into the volumetric flask. The tubing connecting the tops of the two columns was removed and rinsed out into the volumetric flask. The volumetric flask was then placed under the copper shot column, the stopcock on the column was opened and deionized water was rinsed through the column until the solution leaving the copper shot column appeared clear. The ion exchange column was rinsed by pumping approximately 8-10 BV of deionized water through the column at just under 10 BV/hr, in the same fashion as the loading wash cycle. Once all the recirculating electrolyte and wash rinsings were collected in the volumetric flask, deionized water was added to fill the flask to the 500 mL mark. This final strip solution was then sampled and submitted for analysis.

The apparatus used for the stripping tests is displayed, on the following page, in Figure 4.2:



FIGURE 4.2: APPARATUS FOR STRIPPING EXPERIMENTS

Six ion exchange resins were evaluated in these preliminary tests, and are listed in Table 5.1 More detailed information for the various resins can be found in Appendix V. Note that the MRT resin was not tested as IBC Technologies did not think that CVRD Inco had the ability to properly test their resin, and felt that an evaluation performed by CVRD Inco personnel may yield erroneous results.

Manufacturer	Resin Name	Resin Type	
Eichrom	Dinhoniy	Sulphonated	
	Diphomx	Diphosphonic	
Purolite	\$057	Sulphonated	
	3937	Monophosphonic	
Lanxess	Lewatit Monoplus TP 260	Aminophosphonic	
Generic	D416	Sulphonated	
(Chinese)	(Chinese) D416		
Eichrom	Mananhagnhania	Sulphonated	
	Monophospholite	Monophosphonic	
Dow	Dowex M4195	Picolylamine	

TABLE 5.1: IRON ION EXCHANGE RESINS EVALUATED

All phosphonic resins were conditioned and had their volumes determined, as described in section 4.1. No precipitates were observed during the conditioning of any of the monophosphonic resins; a white precipitate was observed during the conditioning of the Diphonix resin and is believed to have been gypsum (CaSO₄), since this resin is provided in the calcium form. The picolylamine resin only had its volume determined, as it was provided from the manufacturer in a "ready-to-use" state.

A series of equilibrium loading experiments was performed on each resin, using the procedure described in section 4.3. The purpose of the experiments performed was to determine the extent to which the various impurities would co-load onto the resin with ferric iron. These experiments were performed using a synthetic electrolyte containing iron(III), antimony(III), bismuth(III), and arsenic(V) in a solution of copper sulphate, nickel sulphate, cobalt sulphate

and sulphuric acid. The decision was made to not add any ferrous sulphate to this electrolyte in order to simplify the iron balance calculations.

The composition of the synthetic electrolyte feed solutions is displayed in Table 5.2. Note that the Dow test was run at 9.6 g/L acid, while all other tests were run at approximately 220 g/L acid. Note that antimony values were obtained by ICP-PMET and not by ICP-MS.

g/L	Cu	Ni	Co	As	Fe	Sb	Bi
Diphonix	33.0	13.6	10.0	2.6	2.0	0.12	0.29
Purolite	38.8	15.6	12.0	2.9	2.3	0.29	0.44
Lewatit	37.0	15.2	11.6	2.8	2.3	0.19	0.46
Generic	35.4	14.4	10.8	2.9	2.2	0.29	0.38
Eichrom	33.2	13.6	10.2	2.7	2.1	0.19	0.38
Dow	38.8	16.4	12.2	2.5	1.7	< 0.015	< 0.03

TABLE 5.2: FEED COMPOSITION OF SYNTHETIC ELECTROLYTE FOR BATCH TESTS

The ideal resin would have a high iron loading capacity and a greater selectivity for iron than for either antimony or bismuth. These two characteristics for the tests run at ~220 g/L acid will be explored, in the following sub-sections, followed by a discussion of the test run at ~10 g/L acid.

5.1 RESIN SELECTIVITY

To determine the selectivity of a resin, the concentration of an element in the final solution (C), divided by the concentration of that element in the initial solution (C₀) is plotted against the volume ratio for the various flasks (C/C₀ vs. volume ratio). A C/C₀ value equal to one would indicate that there is no interaction of the element with the resin. If an element loads onto the resin, then the C/C₀ value would be less than one. Similarly, if an element is displaced from the resin, then the C/C₀ value would be greater than unity. Therefore, a resin is considered to have a higher selectivity for elements which appear lower on the graph (i.e. lower C/C₀ values). Resin selectivity graphs for the 5 phosphonic resins tested can be seen in Figures 5.1-5.5:



FIGURE 5.2: PUROLITE SELECTIVITY

Ratio Electolyte: Resin (v/v) → Fe(III) → · · Sb(III) → · · Bi(III)



FIGURE 5.3: LEWATIT SELECTIVITY



FIGURE 5.4: GENERIC SELECTIVITY



FIGURE 5.5: EICHROM SELECTIVITY

Note from these five graphs that all resins show a preference for antimony over iron, suggesting that poisoning of all resins with antimony is likely. The only resin to show a preference for bismuth over iron is the aminophosphonic resin (Lewatit).

5.2 FERRIC LOADING

In addition to selectivity, the iron loading capacity of a resin is also a key parameter for determining the optimum resin for a given application. Iron loading capacity, for the sake of this work, is measured in mg Fe / mL resin in the H^+ state (i.e. conditioned resin volume at the start of the test). The ferric loading capacity, for these specific test conditions, is the maximum amount of ferric that can be loaded onto the resin. It can be determined by plotting iron loading against the volume ratio of the various flasks. The ferric loading should initially increase with increasing volume ratio, since more iron is available to load onto the resin. Once the resin is

fully loaded, the ferric loading will reach a plateau. This plateau corresponds to the ferric loading capacity.

Ferric loading for the various resins is plotted in Figure 5.6. Note that the loading values in these graphs are calculated based on the solution assays, and are not the result of resin digestion.



FIGURE 5.6: FERRIC LOADING OF VARIOUS RESINS

This graph shows that the ferric loading capacity of the Purolite, Generic and Lewatit resins are very similar at ~23 mg Fe / mL resin. It also shows that the ferric loading capacity of the Eichrom monophosphonic is significantly higher (capacity is greater than or equal to ~35 mg Fe / mL resin, since this resin did not plateau) and that the capacity of the Diphonix resin is significantly lower at ~14 mg Fe / mL resin. It is interesting to note that the loading of the Lewatit resin appears to have decreased as the volume ratio increased beyond 25:1, suggesting that the iron may be being displaced from the resin by another element. Note that, on this graph, the calculated iron loading for the Generic resin is ~30 mg Fe / mL resin at a volume ratio of 100:1. This is believed to be due to an erroneous assay result as the resin digestion

results for this sample, which will be presented in the following section, shows that the total iron loaded onto the resin was ~ 25 mg Fe / mL resin.

5.3 RESIN LOADINGS –100:1 VOLUME RATIO

Resin digestion was performed on all samples with a volume ratio of 100:1. These results provide an insight into the loading of antimony and bismuth onto the resins, in addition to the ferric loading. Note that no antimony or bismuth was detected in samples of conditioned, unloaded resin (i.e. resin blanks) and only minimal amounts of iron (< 0.2 mg Fe / mL resin). Results are displayed in Figure 5.7:



BATCH TESTS

FIGURE 5.7: RESIN LOADING AT A VOLUME RATIO OF 100:1

This chart suggests that the Lewatit resin will be unsuitable for the CRED application because of the significant amount of bismuth loaded. It also suggests that the Diphonix resin would be undesirable for the CRED application because of the low iron loading. This leaves the three sulphonated monophosphonic resins. Note that of these resins, the Eichrom monophosphonic resin loads significantly more iron than the Purolite and Generic resins, while loading a similar amount of antimony, making this resin desirable for the CRED application.

5.4 PICOLYLAMINE RESIN

The CRED mass balance, presented in chapter three, showed that the acid levels in electrolyte would be expected to increase significantly if an iron ion exchange system were installed at CRED. Therefore, an acid removal system (e.g. APU, EMEW) would be required to be installed as part of an iron ion exchange project.

If an APU were installed, a byproduct stream would be generated that would contain most of the base metal salts and be low in acid (expect ~ 10-30 g/L acid). This could provide an opportunity to feed the ion exchange system with a low-acid electrolyte. An acidity of 10 g/L H_2SO_4 would correspond to a pH of ~0.7, which may make the use of a picolylamine resin possible. Recall from Chapter 2 that picolylamine resins are supposed to be stable at pH < 2, but are known to have a strong affinity for copper at low pH.

A quick batch test was done with a low acid electrolyte and the Dowex M4195 resin. Selectivity results (C/C_0) for iron and copper are presented in Figure 5.8. Note that the effect of low acid levels on the Purolite resin will be presented later in Section 8.1.1.



FIGURE 5.8: SELECTIVITY FOR PICOLYLAMINE RESIN

This graph shows a slightly higher selectivity for copper over iron for this resin under these conditions. Of interest, though, is that even at a solution : resin volume ratio as low as 6:1, the iron C/C_0 value is as high as ~0.95. Also note how the iron curve reaches a plateau by a volume ratio of 12:1. This suggests that this resin has a very low capacity for iron under these conditions and hence is not suitable for this application.

5.5 IMPLICATIONS FOR CRED APPLICATION

Based on the results presented in this chapter, the Eichrom Monophosphonic resin appears to have the best combination of properties for the CRED application. It appears to have the highest capacity for iron, and loads a similar amount of antimony as the other resins. Unfortunately, this resin is from a developmental batch and is not currently commercially available. The next best resin performance appears to be shared by both the Purolite resin and

the Generic resin, which appear to have very similar performance. These resins are both commercially available.

The Lewatit resin does not appear to be suitable to the CRED application because it appears to have a high affinity for bismuth. The Dow resin is unsuitable for the CRED application because it has such a low capacity for iron. The Diphonix resin is undesirable in the CRED application because it also has a relatively low capacity for iron, compared to the Generic and Purolite resins.

These results are only a reflection of equilibrium loading conditions. Loading and stripping kinetics are also key parameters for the selection of an optimum resin. These will be investigated in the following chapter for the five phosphonic resins.

A series of column experiments were performed on each of the five phosphonic resins to evaluate each resin with respect to both ferric loading and stripping. Loading tests were performed using a synthetic electrolyte solution of approximately 35 g/L copper, 1.2 g/L ferric, and 220 g/L sulphuric acid. Two types of stripping electrolyte solutions were tested for each resin. Both contained approximately 45 g/L copper and 220 g/L sulphuric acid. The "low iron" stripping solution had no iron added, while the "high iron" stripping solution had approximately 25 g/L ferrous added. No impurity elements were added to these synthetic electrolyte solutions.

The most salient points for the various tests are discussed in the following subsections. More detailed results from each test can be found in Appendix VI.

6.1 FERRIC LOADING

The loading curves for the various resins depict the concentration of ferric left in the solution after passing through the ion exchange column. As the resin becomes saturated, the concentration of ferric left in solution increases. The ferric loading curves for the various IX resins are depicted in Figure 6.1. Note that the ordinate displays the concentration of ferric present as a fraction of the feed concentration; therefore, all curves should approach unity as the resin becomes saturated.

FERRIC LOADING -COLUMN TESTS



FIGURE 6.1: FERRIC LOADING CURVES FOR THE VARIOUS ION EXCHANGE RESINS

These results clearly show that the diphosphonic resin (Diphonix) removes significantly less ferric from solution than the monophosphonic resins. Loading kinetics for the various monophosphonic resins appear to be quite similar, with perhaps the Eichrom monophosphonic resins removing slightly more iron from solution than the other monophosphonic resins. To determine whether or not this was the case, mass balances were performed on all loading tests to calculate an approximate resin loading value (mg Fe/mL resin). These results are summarized in Table 6.1:

FEED	Strip Test	g/L Cu	g/L Fe
Purolite	Low Fe	32.8	1.37
	Low Fe	33.1	1.36
	High Fe	33.9	1.39
Lewatit	Low Fe	32.7	1.36
	High Fe	32.7	1.38
	Low Fe	34.8	1.44
Generic	Low Fe	31.2	1.33
	High Fe	30.5	1.25
Eichrom	Low Fe	30,3	1.31
	High Fe	30.3	1.35
Diphonix	Low Fe	30.1	1.31
	Low Fe	29.4	1.32
	High Fe	29.0	1.27

Fe loaded	mg/mL Resin*	BV Soln	
Purolite	22.2	76	
	22.4	78	
	24.2	76	
Lewatit	24.8	81	
	17.8	74.9	
	24.8	86.1	
Generic	23.9	81	
	20.3	72	
Eichrom	27.5	82	
	27	78	
Diphonix	9.9	82	
	10.8	90	
	12.1	85	

TABLE 6.1: FEED ASSAYS AND FERRIC LOADING FOR THE VARIOUS LOADING TESTS

* mg/mL Resin Calculated from Solution Assays

This table confirms that the capacity of the Diphonix resin was significantly lower (roughly one half) than all the other resins. It also shows that the values for the Purolite, Generic, and Lewatit resins are roughly the same and that the Eichrom Monophosphonic resin may have a slightly higher capacity. Note that the calculated loading value from the loading portion of the Lewatit high iron stripping test is significantly lower than for the other two cases. This is believed to be because the resin was not fully stripped after the first low iron test, evidenced by the fact that there was a 12% overall iron mass balance error for this test.

6.2 LOADING CORRELATION WITH ORP

During the Diphonix loading test, the ORP of the loaded solution was monitored. The ORP results are plotted in the Figure 6.2, along with the iron loading curve:

DIPHONIX LOAD



FIGURE 6.2: LOADING CURVE FOR DIPHONIX TEST: ORP AND IRON CONCENTRATION

This graph illustrates how ORP could be useful for determining the point at which a resin is loaded. Note how the ORP reaches a plateau at approximately the same time as the iron in solution approaches the feed concentration. It should be noted that this curve was obtained for a feed solution containing only ferric and that the shape of the curve may be slightly different for an electrolyte containing high levels of ferrous.

6.3 FERRIC STRIPPING WITH NO FERROUS IN INITIAL ELECTROLYTE

The set-up for stripping the ferric from the resin is a closed loop system, which means that the concentration of iron in the recirculating electrolyte solution will increase with stripping time and will reach a plateau when all the iron has been stripped. Results from the stripping tests performed with no iron in the initial electrolyte are shown in Figure 6.3:



FIGURE 6.3: IRON STRIPPING WITH NO IRON IN INITIAL ELECTROLYTE

This graph shows that the stripping results for the Purolite and Generic resins are virtually identical. It also shows that the stripping rate for the Eichrom resin is approximately the same as for the Purolite and Generic resins, but that it continues for significantly longer, indicating that the Eichrom resin has a higher loading capacity for iron. The stripping rate for the Lewatit resin is significantly lower than the Purolite and Generic resins, however the concentration finishes at approximately the same value, indicating that this resin has a similar loading capacity for iron. The low final iron concentration for the Diphonix resin indicates that this resin has a much lower loading capacity for iron.

6.4 STRIPPING CORRELATION WITH ORP

During the low iron stripping tests, ORP was measured continuously and samples of the recirculating strip solution were taken approximately every half hour. A plot of ORP and iron concentration in the strip solution is plotted in Figure 6.4. Note that this graph is from the test run with the Generic resin, similar graphs for all other resins can be found in Appendix VI.



GENERIC LOW IRON COLUMN TEST

FIGURE 6.4: IRON CONCENTRATION AND ORP VS. STRIPPING TIME

This graph shows quite clearly the sudden drop in ORP associated with cuprous breakthrough from the ion exchange column between 2 and 2.5 hours. Note that this also corresponds to approximately the same time as the concentration of iron in solution reaches a plateau. This is a classic example of an ORP titration curve for an ORP reaction that has gone to completion [50], and illustrates that ORP can be used to detect the stripping endpoint.

It should be noted that in Figures 6.3 and 6.4 straight lines have been drawn through the iron concentration points and that, in most cases, the points lie above the line early in the stripping test and below the line later in the stripping test. This would indicate that these points follow a

curve, rather than a straight line; however, lines have been drawn for simplicity's sake, since a detailed investigation into the stripping kinetics is beyond the scope of this thesis.

6.5 EFFECT OF HIGH FERROUS CONCENTRATION ON FERRIC STRIPPING

As discussed in Chapter 3, the model of the CRED plant showed that iron levels in the strip solution bled to First Stage Leach would need to be around 25 g/L in order to achieve the desired target of 2 g/L Fe in the plant electrolyte. Therefore, a second column test was run on all resins, and stripping was performed with a solution containing \sim 23-25 g/L Fe (actual assay results in Appendix VI).

Sampling was attempted during a trial column test, however, it was difficult to extract any value in the iron concentration results since the relatively small increases in iron concentration were masked by the large dilution errors incurred with a sample with such a high initial concentration. Since ORP is able to give an indication of the stripping endpoint, it was decided to run the high ferrous stripping tests with ORP monitoring alone (i.e. no sampling).

To see the effect of the high ferrous concentration in strip solution, the ORP curves from the low iron and the high iron stripping tests are plotted on the same graph. A typical curve is shown in Figure 6.5; the complete set of curves can be found in Appendix VI.

PUROLITE COLUMN: STRIPPING ORP



FIGURE 6.5: EFFECT OF IRON CONCENTRATION ON STRIPPING ORP CURVE

This graph shows that the high ferrous concentration in the strip solution drops the initial ORP of the solution significantly. It also shows that the sudden drop in ORP, characteristic of cuprous breakthrough, occurs later in the test (approximately 30-45 minutes later). This suggests that the presence of the extra iron in solution is somehow slowing the stripping kinetics.

It should be noted that, in the case of the Eichrom monophosphonic resin, the sudden drop in ORP actually occurred sooner in the case of the high iron electrolyte. This was surprising, so the experiment was repeated and the same result was obtained. A third loading cycle and strip was then performed with low iron strip solution to determine whether perhaps the resin itself was degrading. The ORP from this third cycle was almost identical to the first cycle strip (low Fe). The reason the ORP drop occurs sooner in the case of high iron electrolyte for the Eichrom monophosphonic resin remains unknown.

6.6 LANXESS LEWATIT RESIN

The shape of the stripping curve of the Lanxess Lewatit Monoplus 260 resin was significantly different than for the other resins. A typical stripping curve is shown in Figure 6.6:



LEWATIT COLUMN -LOW IRON

FIGURE 6.6: STRIPPING CURVE FOR LEWATIT COLUMN

Note the sudden drop in ORP at around 30 minutes for this resin. This sudden drop was observed in all three tests performed with the Lewatit resin, and was not observed for any other resin. Recall from Section 5.3, that during the equilibrium batch testing, the Lewatit resin was loaded with more bismuth than iron, whereas no other resin showed any appreciable amount of bismuth loading. These two observations suggest that the behaviour of the aminophosphonic resin is significantly different than the behaviour of the sulphonated monophosphonic resins.
6.7 EFFECT OF STAINLESS STEEL RESERVOIR ON STRIPPING ORP

A single test was run with the Diphonix resin in which the glass elution reservoir was replaced with a slightly different style of elution reservoir, built from 316 stainless steel. A synthetic electrolyte solution was circulated through the stainless steel reservoir for \sim 3 hours prior to the experiment in order to attempt to passivate the vessel prior to the experiment starting. The two different styles of elution reservoir are depicted in Figure 6.7:



FIGURE 6.7: ELUTION RESERVOIRS. (a) GLASS RESERVOIR, (b) STEEL RESERVOIR

The ORP curve for the test run with the steel reservoir was quite different from the ORP curve for the test run with the glass reservoir. This is shown in Figure 6.8:

DIPHONIX COLUMN -STEEL RESERVOIR



FIGURE 6.8: EFFECT OF STEEL ELUTION RESERVOIR ON ORP CURVES

Note how the ORP from the steel elution reservoir starts much lower than for the glass reservoir. This seems to suggest some sort of corrosion reaction occurring in the vessel, which generates cuprous ions. Approximately 20 minutes into the test, the ORP shoots up suddenly, likely depicting the presence of some ferric iron reaching the elution reservoir and reacting with the small amount of cuprous present to form ferrous iron. The drop in ORP, typically representative of cuprous breakthrough, is not as sharp as in the case with the glass vessel, however, the two curves do reach approximately the same final level, at approximately the same time.

To determine whether or not stripping occurred at approximately the same time, the concentration of iron in solution was plotted for the two tests. This is shown in Figure 6.9:



FIGURE 6.9: EFFECT OF STEEL RESERVOIR ON SOLUTION SAMPLES

This graph shows that the concentration of iron in solution reached a plateau by 1.5 hours in both tests. This suggests that, despite the difference in shape of the ORP curves, stripping is occurring at approximately the same time. Therefore, in a full scale operation where stainless steel may be used as the material of construction, the ORP curves should still give valid indications to determine the end of stripping, even if the shape of the curve is not as sharp as those observed in the laboratory with the glass vessels.

It is interesting to note that, in Figure 6.9, the concentration of iron in the solutions from the steel vessel are much higher than in those from the glass vessel. This is surprising since the volume of recirculating electrolyte added to the two systems was approximately the same (158 mL and 160 mL, respectively). This same effect is observed if the Fe/Cu ratio is plotted, suggesting that the difference can not be due to dilution error in the preparation of the sam ples. Perhaps this difference is due to corrosion of the vessel, indicating that passivation of the vessel was not complete prior to running the stripping experiment. This supposition is supported by

the fact that much more iron was observed to have been "stripped" from the resin, than loaded onto the resin during this test (see Appendix VI).

6.8 SELECTION OF OPTIMUM RESIN FOR CRED

As previously mentioned in section 5.0, the ideal resin would have a high iron loading capacity and a greater selectivity for iron than for either antimony or bismuth. Figure 6.10 summarizes the iron loading of the various resins for all batch and column tests run.



Iron Loadings on Resins

FIGURE 6.10: SUMMARY OF FERRIC LOADINGS OF VARIOUS RESINS

The ferric capacities obtained from the column tests simply reiterate the conclusions drawn from the equilibrium batch tests. This graph clearly shows that the Diphonix resin has a low iron loading capacity, the Purolite, Lewatit, and Generic resins have similar iron loading capacities, and the Eichrom Monophosphonic resin has the highest loading capacity.

Recall from section 6.1 that the column loading kinetics were similar for all monophosphonic resins. Recall from section 6.3 that the stripping kinetics showed slower kinetics for the aminophosphonic resin (Lewatit), giving yet another reason why this resin is not ideally suited for the CRED application.

As mentioned in section 5.5, the Eichrom Monophosphonic resin is not currently commercially available, so the resin of choice for CRED would be either the Purolite S957 resin or the Generic D416 resin.

All further testing was performed on the Purolite S957 resin. This resin was chosen over the Generic D416 resin for the simple reason that there was a large volume of this resin already available at the CRED laboratory.

7.0 STRIPPING RATE SERIES

A series of stripping rate tests were performed on a single 25 mL sample of Purolite resin. In these experiments, the resin was loaded as described in section 4.4.1, using the case where only one sample of loaded solution was taken and with ORP monitoring in place. The ORP curves for the various loading experiments can be found in Appendix VII.

Stripping was performed as described in section 4.4.2, using the case where samples were not taken through the septum over the course of the test. The only exception was that the stripping temperature and concentration of copper in the synthetic strip electrolyte was varied for these tests. The time taken to strip the resin was defined as the time taken for the ORP to reach a value of 500 mV_{SHE} (near the middle of the sharp drop of the stripping ORP curve).

7.1 EFFECT OF TEMPERATURE ON STRIPPING RATE

A series of stripping tests were performed at various temperatures. Note that the temperature reported is the temperature of the heating water returning from the ion exchange column and that the heating water temperature at the inlet to the copper shot column is typically $\sim 6^{\circ}$ C hotter.

Figure 7.1 displays the stripping ORP curves obtained at the various temperatures:



FIGURE 7.1: STRIPPING ORP CURVES AT VARIOUS WATER BATH TEMPERATURES

This graph shows that as the stripping temperature increases, the sudden drop in ORP characteristic of cuprous break-through occurs sooner, suggesting that the stripping rate has increased. It is interesting to note that the stripping curves for 85°C and 88°C are essentially overlapping in this graph.

7.2 EFFECT OF TOTAL COPPER CONCENTRATION ON STRIPPING RATE

Two additional tests were run at 75°C at different copper concentrations to determine the effect of cupric concentration on stripping rate. These results are shown in Figure 7.2:



FIGURE 7.2: EFFECT OF TOTAL COPPER CONCENTRATION ON STRIPPING RATE

This graph shows that as the concentration of copper increases, the stripping rate appears to increase. Note that for the test run at 80 g/L, some copper sulphate was observed to precipitate in the base of the burette while the system was being brought up to temperature; therefore, it was decided not to run any tests at a higher concentration of copper sulphate. Instead, a final test was run at a concentration of copper ~60 g/L and a temperature of 85°C. These results are shown in Figure 7.3:

STRIPPING ORP CURVES



FIGURE 7.3: EFFECT OF INCREASING TEMPERATURE OR CONCENTRATION FROM STANDARD STRIP CONDITIONS

This graph shows that no significant change in stripping rate was observed by increasing either the temperature or the concentration of copper over the standard stripping conditions of 45 g/L copper at 85°C. Since stripping rate is being estimated by a change in ORP, this suggests that the generation rate of cuprous is approximately constant for these three tests. (Note that if cuprous was present in excess, it would be present in the solution leaving the ion exchange column and hence the ORP would change sooner).

7.3 EFFECT OF CUPROUS CONCENTRATION ON STRIPPING RATE

Since the stripping reaction requires cuprous, it is interesting to take the data from the previous sections and plot the time required for stripping against the calculated theoretical cuprous concentration in the solutions. Note that all stripping tests were run with the recirculating

electrolyte flowing through the ion exchange column at a rate of approximately 10 BV/hr, and the effect of changing recirculation rate of electrolyte was not included in this study.

For the purposes of this graph, stripping time was defined as the time taken until the ORP reached a value of 500 mV_{SHE}. This ORP value typically occurs in the middle of the large ORP drop associated with cuprous breakthrough, and provides a time for the test run at 50°C, even though this particular test never actually reached cuprous breakthrough. Theoretical cuprous concentrations were calculated using HSC data for the equation: $Cu + Cu^{2+} \rightarrow 2Cu^{+}$. Sample calculations can be found in Appendix VIII, and the results are displayed in Figure 7.4:



TIME TO CUPROUS BREAKTHROUGH

FIGURE 7.4: EFFECT OF THEORETICAL CUPROUS CONCENTRATION ON STRIPPING TIME

This graph shows that the time to cuprous breakthrough appears to trend well with the theoretical concentration of cuprous available in solution between theoretical cuprous concentrations of 0.4 and 0.8 g/L Cu^+ . At higher theoretical concentrations of cuprous, the time

to cuprous breakthrough appears to plateau, and at lower theoretical concentrations of cuprous, the time to cuprous breakthrough increases significantly more than expected.

The point in the top left corner of the graph corresponds to the temperature test run at 50°C. This test never exhibited the sudden drop in ORP corresponding to cuprous breakthrough (it approached the value of 500 mV_{SHE} gradually), and so the temperature of the water bath was increased to 85°C at the end of the test to ensure complete stripping of the resin. Samples were taken over the course of this test and by comparing the concentration of iron in solution to the final concentration of iron, it is possible to estimate how close this test was to complete stripping. These results are plotted in Figure 7.5:



Iron Stripped at 50C

FIGURE 7.5: IRON STRIPPED WITH TIME FOR STRIPPING TEMPERATURE OF 50C

This graph confirms that stripping was occurring for the test run at 50°C, and that it had nearly reached completion when the test was ended after 8 hours. Complete stripping corresponds to the "X" in the top right corner of the graph, obtained by increasing the temperature in the

recirculating solution to 85° C. Based on these results, the stripping done at 50° C can be estimated as having been ~ 90 % complete.

7.4 APPLICATION OF RESULTS TO A FULL SCALE UNIT

The theoretical equilibrium concentration of cuprous appears to trend well with stripping rate. This means that in a full scale unit, increasing the stripping rate could be achieved by either increasing the temperature or the cupric concentration in the recirculating electrolyte. Stripping rate is also likely to be affected by the recirculation rate of the stripping electrolyte; however, this parameter was not included in this study.

A major operating expense for a full scale system would be the regular replacement of the ion exchange resin. High operating temperatures could potentially cause thermal degredation of ion exchange resins and may result in frequent replacement of the resin. Extensive piloting would be required to determine the effect of temperature on resin life. If a full-scale unit were installed and the resin were found to require frequent replacement, consideration should be given to lowering the temperature during the stripping cycle as this may result in significantly increasing the resin life. Therefore, the ion exchange vessel(s) should be designed with excess capacity, in case the size of the ion exchange bed needs to be increased in the future, to allow for removal of the same amount of iron with extended stripping times.

It is important to note that, at 50°C, the stripping rate is much longer than what would be expected, based on the theoretical equilibrium concentration of cuprous. Also note that the time to cuprous breakthrough reaches a plateau and does not decrease beyond a theoretical equilibrium cuprous concentration of ~0.8 g/L Cu⁺. Therefore, if piloting were to occur at CRED, tests should be run at various stripping temperatures to further investigate this phenomenon.

A series of tests were performed to better understand the effect of antimony on the ion exchange resin, and to try and determine whether or not iron ion exchange would still be feasible in an electrolyte with high antimony levels. These tests were all performed on the Purolite S957 resin, and are described in the following sections.

8.1 ANTIMONY EQUILIBRIUM SERIES

Two sets of batch equilibrium experiments were performed and are described below.

8.1.1 Effect of Acidity

To determine the effect of acid concentration on the loading of antimony and iron, an additional two sets of batch equilibrium tests were performed using a similar procedure as that described in section 4.3. The only difference was that no flask was prepared using a 3:1 volume ratio, and the acidity of the synthetic electrolyte was different. In the first set of tests the acidity was \sim 10 g/L acid and in the second set of tests the acidity was \sim 350 g/L acid. As mentioned in Chapter 3, running a tankhouse with an electrolyte acid concentration of \sim 350 g/L is impractical; however, this test was included for academic interest.

The reason for the acid concentrations chosen goes back to the CRED mass balance described in Chapter 3. If no acid is removed, the acidity of the Tankhouse is predicted to increase to 350 g/L acid, so a test was performed to determine how an acid concentration this high would affect an ion exchange system. If an APU is used to create an acid bleed from the Tankhouse, the APU Byproduct stream (typically 10 - 30 g/L acid) could be used to feed the ion exchange unit.

The actual feed composition of the two test series is displayed in Table 8.1, along with the feed composition from the original equilibrium batch test performed with the Purolite resin.

FEED g/L	ACID	COPPER	NICKEL	COBALT	ARSENIC	IRON(III)	ANTIMONY	BISMUTH
LOW ACID	9.4	38.8	16.4	12.2	2.5	1.7	< 0.015	< 0.03
PUROLITE	235.6	38.8	15.6	12.0	2.9	2.3	0.29	0.44
HIGH ACID	357.5	38.6	16.7	12.4	2.9	2.4	0.24	0.46

 TABLE 8.1:
 FEED COMPOSITION FOR ACID TESTS

Note that the same amount of antimony and bismuth were added to the low acid test series electrolyte as the other two tests. The reason the concentrations were below the detection limit for the low acid test series is that insufficient antimony and bismuth dissolved due to such low acid levels.

Resin selectivity graphs (solution C/C_0 vs. volume ratio) are shown in Figure 8.1 for the iron selectivity of the Purolite resin at the various acidities.



EFFECT OF ACIDITY ON IRON REMOVAL

FIGURE 8.1: EFFECT OF ACIDITY ON PUROLITE SELECTIVITY FOR FERRIC IRON

This graph clearly shows that the Purolite has a higher affinity for iron at a lower acidity. It also shows that if the acidity of the electrolyte were to increase from ~ 240 to ~ 360 g/L, this should not have too deleterious of an effect on the resin performance.

The resin samples from the 100:1 test were digested to determine the resin loadings of iron, antimony, and bismuth. These results are displayed in Figure 8.2:



FIGURE 8.2: RESIN DIGESTION OF 100:1 SAMPLES

This bar chart clearly shows that at very low acidity, the resin capacity for iron appears to be almost twice the resin capacity at 240 g/L. It is interesting to note that, at low acidity, the resin digestion indicates the presence of a small amount of antimony on the resin, even though the antimony levels in the synthetic electrolyte were below detection limits.

8.1.2 Effect of Iron to Antimony Ratio

A batch equilibrium series was performed in a solution of ~220 g/L acid, following a similar procedure as described in section 4.3. The main deviations from this procedure were that a constant electrolyte: resin volume ratio of 100:1 was maintained in all flasks and the ratio of iron to antimony in the feed electrolyte was varied. 2.1 L of base electrolyte was prepared, containing antimony, but no iron. This base electrolyte was then divided into eight 250 mL flasks, into which varying amounts of iron was added. Finally, a 250 mL electrolyte sample was prepared containing iron, but no antimony. The composition of the various feed samples can be found in Table 8.2:

FEED g/L	IRON(III)	ANTIMONY	Fe/Sb	COPPER	NICKEL	COBALT	ARSENIC	BISMUTH
"A"	< 0.01	0.22	0	41.6	10.4	9.5	2.7	0.36
"B"	0.13	0.22	0.59	40.6	10.3	9.4	2.7	0.37
"C"	0.23	0.23	0.97	40.6	10.2	9.3	2.7	0.35
"D"	0.41	0.23	1.75	39.4	10.0	9.2	2.6	0.33
"E"	0.86	0.24	3.55	41.2	10.5	9.6	2.7	0.38
"F"	2.10	0.25	8.54	40.6	10.2	9.4	2.7	0.37
"G"	4.28	0.25	17.0	41.6	10.5	9.6	2.7	0.38
"H"	8.68	0.24	35.9	41.0	10.5	9.6	2.7	0.39
In	2.10	< 0.01	0	39.2	15.2	11.2	2.7	0.15

Table 8.2: FEED COMPOSITION FOR RATIO EQUILIBRIUM TESTS

Since flasks F and I both contain the same amount of iron, and only flask F contains antimony, comparing the results from these two flasks gives an indication as to whether or not the presence of antimony affects the amount of iron loaded onto the resin. Although the solution iron C/C_0 values were the same for both tests, the resin digestion results show a slightly higher iron loading when no antimony was present in the electrolyte (30.6 mg Fe / mL resin for I vs. 27.6 mg Fe / mL resin for F). This suggests that antimony may have an adverse effect on iron loading.

Results from flasks A-H are displayed in Figures 8.3 and 8.4 . Figure 8.3 shows the resin selectivity (C/C₀ vs. Fe/Sb in feed), and Figure 8.4 shows the resin loading results (mg/mL resin) based on resin digestion (mg/mL resin).



FIGURE 8.3 SELECTIVITY OF RESIN VS. IRON / ANTIMONY RATIO



RESIN LOADINGS

Note from the resin loading curve (Figure 8.4) that in a solution with no iron (iron/antimony ratio = 0), the resin loaded the most antimony. Based on the resin digestion results, the amount of antimony loaded onto the resin decreased at a fairly steady rate, indicating that the iron was competing favourably with the antimony, until the iron / antimony ratio reached a value of 1.75. From this point on, the amount of antimony loaded onto the resin only decreased very slightly as the iron/antimony ratio continued to increase, indicating that increasing the iron / antimony ratio beyond 1.75 has very little effect on the antimony loading. Note the extremely low antimony loaded at an iron/antimony ratio of 17. This is believed to be the result of a poor assay as there is no evidence of lower antimony present in the corresponding solution sample. Unfortunately, there was insufficient resin available to re-assay this sample.

In reading the selectivity graph, recall that the resin preference is for the element with the lower C/C_0 value. In Figure 8.3, iron has a significantly lower C/C_0 value than antimony at iron / antimony ratios ≤ 1.75 , indicating selectivity of iron over antimony. At iron / antimony ratios \geq 8.5, the iron has a significantly higher C/C_0 value than antimony, indicating selectivity of antimony over iron.

8.2 ANTIMONY COLUMN EXPERIMENTS

A series of column tests were performed to investigate the kinetics of antimony loading. These are described in the following sections.

8.2.1 Iron-Antimony Displacement Test

A column displacement test was performed to determine whether iron would tend to displace antimony off the resin, or whether antimony would displace iron off the resin. If iron were to be able to displace antimony off the resin, increasing the flow rate through the column may be able to significantly reduce the amount of antimony loaded onto the resin.

A synthetic electrolyte loading solution, similar in composition to that used in the initial equilibrium batch tests (Chapter 5), was prepared. This solution was placed in a hot-water bath

at 50°C, in order to minimize copper sulphate crystallization. The test was run for longer than a standard loading test (130 BV vs. 80 BV) in order to try and determine which element would displace the other off the resin. Otherwise, the solution loading was performed as described in section 4.4.1, for the case with ORP monitoring.

The composition of the synthetic electrolyte is shown in Table 8.3.

TABLE 8.3: FEED COMPOSITION FOR DISPLACEMENT TEST

g/L	COPPER	NICKEL	COBALT	ARSENIC	IRON (III)	ANTIMONY	BISMUTH
FEED	39.2	13.6	10.9	2.5	2.1	0.18	0.33

Determination of whether or not an element will displace another element can be seen from a loading curve where the relative concentration of the loaded solution to the feed solution for the various elements is plotted (C/C₀). While an element is being loaded onto the resin, the C/C₀ value will be < 1. If there is no interaction between an element and the resin, the C/C₀ value will remain at 1. If an element is being displaced from the resin, the C/C₀ value will be > 1. Such a loading curve for antimony and iron is displayed is Figure 8.5:



FIGURE 8.5: DISPLACEMENT TEST LOADING CURVE

This graph shows that neither the antimony nor the iron appear to equilibrate with C/C_0 values greater than one. It also shows that the breakthrough point for antimony is significantly later than the breakthrough point for iron, providing yet more evidence that the resin is selective for antimony over iron.

In addition to the column test, three batch equilibrium tests were run using the same synthetic electrolyte. Two of these flasks contained a volume ratio of 100:1, and the third flask contained a volume ratio of 200:1. This was done to provide a baseline for resin loading. These three samples, as well as a resin sample from the loaded column were digested to determine iron and antimony loadings in mg/mL resin.

If, after an extended loading cycle, element "A" were to displace element "B" from the resin, then the loading of element "A" should increase and the loading of element "B" would decrease. Therefore, one way to determine whether or not this has occurred would be to look at the resin loading ratio: mg A / mg B. If "A" has displaced "B", then the ratio of mg A / mg B would increase, if "B" has displaced "A", then the ratio would decrease.

Table 8.4 displays the resin digestion results, the ratio of mg Fe / mg Cu and the ratio of mg Fe / mg Sb:

Sample	mg Fe/mL	mg Sb/mL	mg Cu/mL	mg Fe/mg Cu	mg Fe/mg Sb
100:1 A	31.1	1.85	7.53	4.13	16.8
100:1 B	33.2	1.42	7.09	4.69	23.3
200:1	34.7	2.39	9.57	3.62	14.5
COLUMN	31.2	2.31	3.62	8.61	13.5

 TABLE 8.4:
 RESIN DIGESTION RESULTS FROM DISPLACEMENT TEST

This table shows that the ratio of mg Fe / mg Cu was significantly higher for the resin that came from the ion exchange column after the extended loading test, indicating that iron had displaced copper off of the ion exchange resin. The ratio of mg Fe / mg Sb is slightly lower than the values reported for the three equilibrium loading tests. This suggests that the

possibility of iron displacing antimony off of the resin is extremely low. Therefore, no testing was performed to determine the effect on increasing the flow rate through the column.

8.2.2 Antimony-Only Tests

A set of column tests was performed using a loading electrolyte containing sulphuric acid, and saturated in antimony sulphate. To obtain this solution, an excess amount of antimony sulphate was added to the acid mixture and then filtered through Whatman #5 filter paper. Solutions were analyzed using the general ICP task, since extremely large dilutions of the sample were not required before analysis, (typically the high copper sulphate levels require that samples be diluted significantly before analysis).

For these tests, a smaller volume of resin was used (10 mL) and the flowrate ended up being increased to \sim 15 BV/hr as the peristaltic pump was unable to reliably deliver a flowrate of 10 BV/hr. Approximately 150 BV of solution were passed through the columns during loading, and were sampled every 10 BV. Otherwise the column loading procedure followed that described in section 4.4.1.

Two tests were performed, on two separate resin samples. In the first test, samples were taken to generate the loading curve and the strip was performed using a solution containing only sulphuric acid. In the second test, samples were only taken of the feed, loaded solution, and wash water during the load, and the strip was performed using a solution containing both sulphuric acid and sodium chloride (salt).

The stripping procedure was different from that described in section 4.4.2, in that the stripping solution was not recirculated through the system. Instead the strip was performed in the same fashion as a typical loading curve; i.e. the solution was passed through the column and samples collected in 10 BV aliquots. Stripping temperature was set at 50°C for both tests.

Table 8.5 shows the composition of the feed solution for both the loading and stripping tests.

g/L	ACID	COPPER	IRON (III)	ANTIMONY	SODIUM
LOADI	219.3	0.00	0.00	0.45	0.00
LOAD II	218.5	0.00	0.00	0.47	0.00
STRIP I (Acid Only)	177.8	0.00	0.00	0.00	0.00
STRIP II (Salt and Acid)	169.9	0.00	0.00	0.00	79.2

 TABLE 8.5:
 FEED COMPOSITION FOR ANTIMONY-ONLY TESTS

A mass balance performed on the solution samples from the loading tests showed antimony loadings of 43.6 mg Sb/mL resin for test one and 41.4 mg Sb/mL resin for test two. The loading curve for antimony, plotted as C/C_0 against BV passed is presented in Figure 8.6:



ANTIMONY LOADING CURVE

FIGURE 8.6: LOADING CURVE FOR ELECTROLYTE CONTAINING ONLY ANTIMONY

This graph shows that the resins were not fully loaded, since the antimony concentration in the solution that passed out of the resin column never reached the initial antimony concentration in the feed solution (i.e. C/C_0 never reached 1).

Based on the assays of the stripping samples, and on the calculated Sb loaded onto the resin, cumulative percent antimony stripped was calculated for each sample. These results are plotted against BV of stripping solution in Figure 8.7:



CUMULATIVE % ANTIMONY STRIPPED

FIGURE 8.7: CUMULATIVE % ANTIMONY STRIPPED

This graph shows that antimony appears to strip slowly when the resin is washed with sulphuric acid, and that it strips very quickly when washed with both sulphuric acid and salt. Further testing would need to be performed to determine whether or not complete antimony stripping would be possible using a solution containing only sulphuric acid.

It should be noted that as the strip with acid and salt started, a white precipitate was observed in the strip solution, which then subsequently redissolved by the time 5 BV of solution had been collected. The white precipitate was not collected but it is possible that SbOCl may have formed, since the initial sample of strip solution collected would have low acidity due to displacing the deionized water remaining in the column from the load wash step. This suggests that flushing the ion exchange bed with water prior to a salt and acid wash to remove antimony may not be desirable, as it may lead to SbOCl precipitation in the ion exchange bed. Further work would be required to test this hypothesis.

8.3 IMPLICATIONS FOR CRED APPLICATION

These tests have confirmed that the ion exchange resin has an affinity for antimony under the expected operated conditions in the CRED plant. Therefore, a method of antimony removal from the resin will likely be required.

A quick test has shown that antimony can be removed from the resin with salt and acid. If this type of a resin regeneration process were employed at CRED, then the stripping solution would need to be directed to the Effluent Mix Tank, in order to avoid contaminating the CRED electrolyte with chlorides. The antimony in the rinse solution should precipitate out as the pH is increased with lime in the Effluent Mix Tank, according to the following reaction:

$$2 \text{ Sb}^{3+} + 3 \text{ CaO} + 2\text{HCl} \rightarrow 2 \text{ SbOCl}_{(s)} + 3 \text{ Ca}^{2+} + \text{H}_2\text{O}$$

The performance of the resin over a series of load-strip cycles will be investigated in the following chapter.

A series of column tests were performed on the same resin sample, where both antimony and iron were present in the feed and stripping solutions. The purpose of these tests was to observe how antimony loading onto the resin would affect the performance of the resin, and to determine whether the resin performance could be restored with a salt and acid wash, as the results from section 8.2.2 suggest.

Ten cycles of column loading and stripping were performed, using the procedures from section 4.4.1 and 4.4.2. This was followed by a column wash with salt and acid (NaCl and H_2SO_4), where 50 BV of wash solution was passed over the column at 50°C. A final column loading and stripping cycle was then performed to determine whether or not this wash had been able to restore the performance of the ion exchange column.

Antimony was added to both the loading and ferric stripping solutions, all of which contained approximately 220 g/L acid. The compositions of the various feed solutions are displayed in Table 9.1.

		LOAD			STRIP	
Cycle #	g/L Cu	g/L Fe	g/L Sb	g/L Cu	g/L Fe	g/L Sb
1	31.8	1.39	0.200	41.0	< 0.01	0.234
2	31.1	1.35	0.241	42.5	<0.01	0.263
3	31.5	1.37	0.252	41.6	<0.01	0.260
4	31.9	1.39	0.245	41.6	<0.01	0.268
5	31.6	1.38	0.232	42.4	<0.01	0.296
6	32.6	1.40	0.247	42.2	< 0.01	0.206
7	33.6	1.42	0.177	45.4	0.03	0.260
8	34.2	1.45	0.208	45.8	0.04	0.236
9	34.0	1.43	0.237	46.6	0.02	0.268
10	34.1	1.43	0.239	46.2	0.02	0.274
11	32.9	1.40	0.261	44.2	< 0.01	0.324

TABLE 9.1: FEED COMPOSITIONS FOR COLUMN CYCLE SERIES

9.1 FERRIC LOADING IN THE PRESENCE OF ANTIMONY

To determine whether the iron loading performance of the resin was significantly impacted by the presence of antimony in electrolyte, a solution mass balance was performed to determine the amount of iron loaded and the amount of iron stripped for each cycle. These results are plotted in Figure 9.1:



Iron Loading vs. Cycle Number

FIGURE 9.1: IRON LOADED ONTO RESIN VS. CYCLE NUMBER

This graph shows that the amount of iron loaded onto the resin stayed approximately constant over the course of the tests, suggesting that the effect of antimony on iron loading is not deleterious over ten cycles. Note that the total amount of iron loaded in these tests (typically 20 - 21 mg Fe/mL resin), is approximately the same as the values obtained in Chapter 6 for the Purolite tests performed with no antimony present (20-22 mg Fe / mL resin). Also note that there is significantly more scatter in the mg Fe / mL resin calculated from the loading mass balance than the stripping mass balance, likely indicating sampling error of the fully loaded solution.

To more precisely determine the effect of antimony on iron loading, the stripping time required was plotted against cycle time. As in Chapter 7, stripping time was defined as the time required to reach an ORP of 500 mV_{SHE}. The plot of stripping time against cycle number is found in Figure 9.2:



STRIPPING TIME OVER REPEATED CYCLES

FIGURE 9.2: STRIPPING TIME VS. LOAD/STRIP CYCLE WHEN ANTIMONY PRESENT IN ELECTROLYTE

Note how, in Figure 9.2, the stripping time tends to decrease with cycle number, for cycles 1 through 10. This suggests that the antimony is loading onto the resin, thus reducing the number of sites available for iron to load. Note that after the salt wash, the stripping time increases in cycle 11, indicating that after the antimony is removed, ion exchange sites are once again freed up to load more iron.

It is interesting to note that the results from cycle 3 and cycle 6 fall significantly off the general trend line. During cycle 3, the loading cycle was not stopped after 8 hours (approximately 80 BV), and 110 BV of loading solution were passed over the resin. The fact that this cycle took longer to strip may be an indication that the resin was not fully loaded after 8 hours. The reason for cycle 6 stripping much sooner than expected in unknown. It may be that some of the cuprous from the previous stripping cycle formed copper powder and found its way into the ion

exchange column. The mass balance for this test does not give any indication that this occurred, however if this were to have happened, then less iron would have loaded onto the resin since some of the ferric would have been reduced to ferrous during the loading cycle.

9.2 ANTIMONY LOADING OVER REPEATED CYCLES

A solution mass balance was performed to determine the amount of antimony that loaded onto the resin during each load and each strip cycle. From these values, the cumulative antimony loaded onto the resin was calculated. These results are based on ICP-MS assays and are plotted in Figure 9.3. Full mass balance results can be found in Appendix IX:



Cumulative Antimony Loaded on Resin

FIGURE 9.3: CUMULATIVE ANTIMONY LOADED OVER REPEATED CYCLES

This figure shows that the amount of antimony loaded onto the resin tends to increase over the course of the repeated cycles. This is in line with the observation that the ferric stripping time is decreasing with time, since more antimony loaded onto the resin would result in less available loading sites for ferric. Note that the cumulative amount of antimony loaded after 10

cycles (~9 mg Sb / mL) is much less than ten times the amount of antimony loaded after 1 cycle (~4 mg Sb / mL x 10 cycles = ~40 mg Sb / mL). Also of note is that the amount of antimony removed in the salt and acid wash (circle) is very close to the predicted cumulative amount of antimony loaded over the course of the ten cycles.

It is interesting that in cycles 4, 5, and 7, the cumulative amount of antimony loaded is lower than for the previous cycle. This is due to the fact that the mass balance based on the loading assays for these cycles indicates that antimony is stripping. However, this could be due to sampling error, supported by the fact that the iron balance based on loading solutions showed significantly more scatter than the balance based on stripping solutions (see Figure 9.1). If stripping of antimony is, in fact, occurring, then it may be possible that the resin may reach an equilibrium level of antimony loading and that a salt and acid wash may not be required. Pilot testing with an electrolyte containing a significant amount of antimony is recommended.

During loading cycle 10, samples were taken to generate a loading curve. As in section 8.2.1, the relative concentration of the loading solution to the feed solution (C/C_0) for both iron and antimony is plotted against BV of solution passed. This is displayed in Figure 9.4:



Cycle 10 Loading Curve

FIGURE 9.4: CYCLE 10 LOADING CURVE

It is interesting to note that in cycle 10, the breakthrough of antimony appears to occur slightly before the breakthrough of ferric. This is the complete opposite of what was observed during the displacement test (section 8.2.1), however, it supports the observation that the amount of antimony loaded during the first cycle is much greater than the amount of antimony loaded during subsequent cycles.

Also note that the final C/C_0 value for antimony is greater than unity, which would indicate that some antimony is being displaced from the resin as the ferric loads. However, given that the stripping time is continually decreasing (fig. 9.2) and that the cumulative amount of antimony loaded tends to increase (fig. 9.3), it is possible that this may simply be due to a low initial concentration value for antimony (i.e. sampling / assay error). Alternatively, it may be an indication that once the resin has loaded an appreciable amount of antimony, ferric is able to displace antimony from the resin. Further testing to determine whether ferric is able to displace antimony from the resin once the resin has already loaded an appreciable amount of antimony is recommended.

9.3 REPEAT CYCLE TEST CONCLUSIONS

Results are inconclusive as to whether or not the antimony will continue to load onto the resin to the point where the loaded antimony would significantly impede iron loading. On the one hand, the iron loading capacity does not appear to have decreased over the ten cycles, and some of the mass balance data indicates that some stripping of antimony from the resin may have occurred during some cycles. On the other hand, the required stripping time appears to have decreased steadily as the number of cycles increased, indicating the possibility of continuous antimony loading on the resin. Pilot testing is recommended to determine the long-term behaviour of the resin in a solution containing both antimony and iron.

The salt and acid wash appears to be able to restore resin performance, indicating that iron ion exchange is technically feasible in electrolyte solutions containing antimony, even if antimony continuously loads on the resin.

Ion exchange systems can be set up using a variety of different column configurations. Each ion exchange column used needs to cycle between loading and stripping. In situations where the ion exchange resin needs to be able to completely remove a certain species from a stream, this requires the use of multiple columns (either two columns running side-by-side or a set of columns in a lead-lag configuration). However, in situations where ion exchange only needs to remove a portion of the species from a stream, then it is possible to use a single ion exchange column. This section investigates the merits of utilizing various column configurations (single column, two columns, three columns: lead-lag, and four columns: lead-lag).

All calculations are based on the experimental results for the Purolite resin presented in Chapters 6 and 7, where no antimony was present in the electrolyte solutions. All bench tests were conducted with a solution flowrate through the columns of 10 BV/hr.

The loading solution used to generate the design data contained 30 g/L copper, 220 g/L acid, and 1.4 g/L ferric. It was assumed that a fully loaded Purolite resin would hold 21 mg Fe / mL resin.

The initial stripping solution contained 45 g/L copper, 0 g/L iron, and 220 g/L acid. The stripping solution differs from the expected stripping electrolyte in that the iron concentration is much lower than the expected value of 20 - 25 g/L iron. As shown in Chapter 6, the presence of large amounts of ferrous in the electrolyte results in slower stripping times for this resin. To account for this, the assumption was made that the required stripping time would be 20% longer than those observed in the tests conducted with no iron in electrolyte (see Appendix X).

It is important to note that changing of any of the experimental parameters would be expected to result in different results than those presented here. (e.g. changing solution flowrate through the IX column, concentration of ferric in loading solution, and / or loading solution temperature). Note also that no design margin is included in these calculations.

In a commercial installation, care would need to be taken to use air to displace the remaining electrolyte to the elution reservoir before starting the next loading cycle to avoid contamination of the plant electrolyte with high iron solution. Such a displacement with air was performed in the commercial installation at Mount Gordon. It was followed by a rinse in which electrolyte was used to displace the final traces of high iron solution from the column. Care would need to be taken during the design of a full scale system for CRED that the amount of rinse solution does not exceed the amount of eluate bled to the First Stage. Note that the time required for air displacement and rinsing was not included in any column sizing calculations.

10.1 SINGLE ION EXCHANGE COLUMN

In a single ion exchange column system, no eluate is circulated during the loading cycle, and the main volume of loading electrolyte bypasses the ion exchange column during the stripping cycle. The main advantage to a single column system is that it generally lowers the initial capital cost because only one set of pumps, columns, et cetera are required.

To determine the size of ion exchange column required, the data from the loading curve for the Purolite resin was used (Chapter 6), as well as the stripping times at 45 g/L copper and various temperatures (Chapter 7). It was assumed that all resins had been fully loaded with 21 mg Fe / mL of resin, the stripping rate was constant with time and the stripping rate under the CRED operating conditions was 120% of the values obtained in the tests in Chapter 7. The rationale for these assumptions can be found in Appendix X.

Using this data and these assumptions, the flowrate of electrolyte and the amount of resin required per tonne of iron removed per day, was calculated at the various stripping temperatures, as described in Appendix X. These calculations were performed for various degrees of resin loading (i.e. stripping performed on a resin that is only partially loaded). The reason for this is that the loading curves presented in Chapter 6 show that the rate of resin loading decreases as more and more ferric is loaded in the column. This may indicate that as the loading cycle progresses, the resin at the top of the ion exchange column is fully loaded, so only the resin at the bottom of the column is removing ferric. Therefore, stripping a partially

loaded resin allows for iron removal to always occur at the high iron loading rates. Further work should be performed to determine if increasing the flowrate of electrolyte through the ion exchange column during the loading cycle could reduce / eliminate this phenomenon.

In practice, automatically switching the column from loading to stripping after a designated number of BVs could easily be achieved by programming a process logic controller (PLC).

The results for the required electrolyte flowrate and volume of resin required through a single ion exchange column as a function of BVs of loaded solution passed through the resin bed before stripping is shown in Figure 10.1:



SINGLE ION EXCHANGE COLUMN: DESIGN FLOWS 45 g/L Cu; 1.4 g/L Ferric; 10 BV/hr

FIGURE 10.1: REQUIRED ELECTROLYTE FLOWS THROUGH A SINGLE IX COLUMN

This graph can be read to determine the required electrolyte flowrate and resin volumes at a given stripping temperature. For example, for a daily iron removal rate of 1 tonne of iron, if the loading cycle is set at 60 BV long, and a stripping temperature of 85C is used, then a flowrate of 3000 L/min of electrolyte and a single column with 18 m³ of resin would be required. Alternatively, if 1.5 tonnes of iron need to be removed per day, this would result in a

flowrate requirement of 3000 x 1.5 = 4500 L/min of electrolyte, and a required resin volume of $1.5 \times 18 = 27 \text{m}^3$ of resin.

The percentage of time the column spends in the stripping cycle is plotted against the required resin volume in Figure 10.2. (N.B. The time for air displacement and rinsing of solutions are unknown and so are not included in the total time / cycle calculation).



SINGLE ION EXCHANGE COLUMN

FIGURE 10.2: FRACTION OF TIME SPENT STRIPPING VS. COLUMN SIZE

This graph illustrates that in order to be able to operate a column with minimal resin volume at a loading flowrate of 10 BV/hr, the ion exchange operating time will be dominated by stripping.

10.2 TWO ION EXCHANGE COLUMNS

In a two ion exchange column system, one ion exchange column strips while the other ion exchange column is loading. If the time required to strip the resin is the same as the time required to load the resin then there is always a continuous stripping of iron into the eluate and a continuous removal of iron from electrolyte. In the case of iron ion exchange with cuprous stripping, it is possible to adjust the stripping time by adjusting the stripping temperature, as shown in Chapter 7. As previously mentioned, decreasing the stripping temperature may well extend resin life, so it would make sense to operate the stripping cycle at the minimum temperature required to be able to keep up with the loading cycle.

In order to determine the optimum operating conditions to allow for balancing the time for the loading and stripping cycles at various temperatures, the time required for stripping of a resin under various amounts of loading was calculated. These results are displayed graphically, in Figure 10.3; calculation results can be found in Appendix XI.





FIGURE 10.3: STRIPPING DESIGN CURVES FOR TWO IX COLUMNS AT 10 BV/HR

Note that the line for optimal use of two ion exchange columns is drawn on this graph (load time = strip time). If a curve lies above and to the left of this line, then the ion exchange process will be dominated by stripping time (i.e. a fully loaded column will remain in standby as it waits for the other column to finish stripping). Conversely, if a curve lies below and to the right of this line, then the ion exchange process will be dominated by loading time (i.e. a fully stripped column will remain in standby as it waits for the other column to finish stripping).

To determine the electrolyte flow and volume of resin required, calculations were performed using the data from the loading curve for the Purolite resin, as described in Appendix XI. The results of these calculations, are plotted as a function of the number of bed volumes per cycle, in Figure 10.4:



FIGURE 10.4: RESIN AND ELECTROLYTE FLOWRATE REQUIREMENTS: LOADING OF TWO COLUMN SYSTEM

Figure 10.4 reads in the same fashion as Figure 10.1, for a single column system. Therefore, if one tonne of iron is to be removed per day, then for a loading cycle that is 60 BV long, an electrolyte flowrate of 2000 L/min and a resin volume of 12 m^3 / column is required.
In order to determine the amount of resin and electrolyte required at the optimum operating point for various temperatures, the results from Figures 10.3 and 10.4 need to be combined. The requirements for the optimum operating point, at the various stripping temperatures, are summarized in Table 10.1.

Strip Temp	BV Loaded	m' Resin / Column per tonne Fe	L/min Spent per tonne Fe
85	25	5.6	925
80	36	7.2	1200
75	42	8.3	1375
70	50	9.9	1650
65	52	10.2	1700

TABLE 10.1: OPTIMUM TOWER SIZING AND OPERATION, BASED ON STRIPPING TEMPERATURES

As expected, this table shows that a larger tower would be required for optimum operation at a lower stripping temperature. Note also that at each stripping temperature the total volume of resin required for a two column system is approximately the same as would be required in a single column when stripping time is approximately 50% the total cycle time (Figure 10.2). The required flowrate for a two column system, on the other hand, is approximately 50% of the required flowrate of a single column system when stripping time is approximately 50% the total cycle time (Song the total cycle time) is approximately 50% the total cycle time (Song the total cycle time) is approximately 50% of the required flowrate of a single column system when stripping time is approximately 50% the total cycle time.

The selection of operational stripping temperature (and hence column size) would be based on an economic analysis based on the cost of the resin and the expected resin life at the various stripping temperatures. It is recommended that resin life as a function of stripping temperature be studied in order to be able to determine whether it would be economically beneficial to build a larger tower and operate it at a lower stripping temperature.

If an iron IX system were to be installed, the results from Figure 10.2 also give an indication of how to troubleshoot a two column commercial system, assuming that an ORP probe is present

on the elution recirculating line to give an indication of cuprous breakthough. Some potential operating issues and their solutions are displayed in Table 10.2:

Operating Condition	Strip Temp		# BV in Load Cycle
Iron in Electrolyte too High	Increase ↑	AND	Decrease ↓
Cuprous Breakthrough before Load Cycle complete	Decrease ↓	OR	Decrease ↓
Cuprous Breakthrough does not occur before Load completes	Increase ↑	OR	Increase 1
Resin Life is Short	Decrease ↓	AND	Increase 1

TABLE 10.2: TROUBLESHOOTING OF A TWO-COLUMN SYSTEM

Note that there is currently no data to quantify how much reducing stripping temperature will improve resin life. Decreasing the stripping temperature and increasing the number of BVs per cycle will result in an increase in iron in electrolyte unless more resin is installed in the ion exchange columns and the electrolyte flowrate is also increased.

10.3 THREE ION EXCHANGE COLUMNS: LEAD - LAG CONFIGURATION

In a three column ion exchange system, electrolyte would pass through two columns in series for loading in a lead – lag configuration, while the third column would be stripping. In this configuration each column would be used first in the lag position (second column in series), followed by the lead position (first column in series), followed by the stripping position. This is summarized in Table 10.3:

 TABLE 10.3:
 COLUMN Assignments for a Three Column Lead-Lag Configuration

CYCLE #	COLUMN 1	COLUMN 2	COLUMN 3
1, 4, 7	LAG	LEAD	STRIP
2, 5, 8	LEAD	STRIP	LAG
3, 6, 9	STRIP	LAG	LEAD

The main advantage to a lead-lag configuration is that it is possible to remove all iron from a stream. (i.e. no iron is present in the electrolyte leaving the lag column). However, for iron removal from copper electrowinning electrolytes, this is typically unnecessary as the objective is to remove a certain quantity of iron, not to create an iron-free stream.

Column sizing calculations were performed, as described in Appendix XII. Note that in order to model the loading rate on the resin in the lag column, a model of ferric loading rate as a function of ferric concentration in the feed solution would be required. Since this type of data was not collected as a part of this study, the model assumed that ferric loading rate is independent of ferric concentration in the feed. While this assumption is very likely erroneous, these calculations do provide for a general sizing estimate of a 3 column configuration.

Results for the loading portion of the lead-lag system are displayed, on the following page, in Figure 10.5. Note that the abscissa represents the number of bed volumes per cycle (i.e. the number of bed volumes loaded before column assignments are switched). This is important because the resin loading after 10 BVs of a column with 20 BVs per cycle does not equal the resin loading after 10 BVs for a column with 10 BVs per cycle since the amount of iron present on the resin when the column switches from the lag position to the lead position differs. In this graph, the resin loadings and column size read off the left axis, while the concentration of iron in the stream leaving the lag column reads off the right axis.

LEAD-LAG CONFIGURATION



FIGURE 10.5: LOADING COLUMN RESULTS FOR A LEAD-LAG CONFIGURATION

From this graph, it can be seen that stripping of a fully loaded column would be possible if the columns were switched every 20 BVs. This graph also shows that the predicted size of resin volume per column remains constant until after the breakthrough of iron from the lag column, which occurs after approximately 10 BVs.

In order for the three column lead-lag configuration to be implemented, the third column must be able to strip the total amount of iron loaded on the resin of the lead column before the column assignments are switched. The following graph displays the required stripping rate for the three column system at the various number of BVs per cycle, along with the iron stripping rate at the various temperatures. For the system to be practical at a given temperature, the required stripping rate must appear below that temperature's stripping rate. It also shows the required flowrate of electrolyte and the total available electrolyte at CRED. These results are presented in Figure 10.6:



FIGURE 10.6: STRIPPING GRAPH FOR A THREE COLUMN LEAD-LAG SYSTEM

This graph shows that the required strip rate is significantly higher than the possible stripping rate at the various temperatures, making the three column lead-lag configuration impractical.

10.4 FOUR ION EXCHANGE COLUMNS: LEAD - LAG CONFIGURATION

In the four column lead – lag configuration, two columns would be used for loading and the other two columns for stripping. As a result, the loading and column sizing calculations would be identical for those presented for the three column lead – lag configuration. On the other hand, the available time for stripping is twice that in the three column figuration. The column assignments for a four column lead-lag configuration is displayed, in Table 10.4:

CYCLE #	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4
1, 5, 9	LAG	LEAD	STRIP	STRIP
2, 6, 10	LEAD	STRIP	STRIP	LAG
3, 7, 11	STRIP	STRIP	LAG	LEAD
4, 8, 12	STRIP	LAG	LEAD	STRIP

 TABLE 10.4:
 COLUMN ASSIGNMENTS FOR A FOUR COLUMN LEAD-LAG CONFIGURATION

The stripping graph for the four column lead-lag system is presented in Figure 10.7:



STRIPPING FOR A FOUR COLUMN LEAD-LAG SYSTEM 10 BV/hr Recirculation, 45 g/L Copper

FIGURE 10.7: STRIPPING GRAPH FOR A FOUR COLUMN LEAD-LAG SYSTEM

This graph shows that a four column lead-lag system would be possible, when stripping occurs at 85°C. Five possible design configurations are presented, in Table 10.5.

BV per Cycle	Strip Temp	mg Fe / mL Resin Lead Column	m ³ Resin / Column per tonne Fe Removed per Day	Electrolyte L/min per tonne Fe Removed per Day
2	85	2.7	3.0	507
6	85	8.2	3.0	507
10	85	13.7	3.0	507
15	85	18.6	4.9	817
20	85	20.0	8.7	1453

TABLE 10.5: COLUMN SIZING BASED ON FOUR COLUMN CONFIGURATION

This table shows that the main effect of increasing the BV / cycle is that it increases the final iron loading on the lead column resin. This could potentially be advantageous if iron is demonstrated to be able to displace antimony from the resin.

10.5 COMPARISON OF THE VARIOUS COLUMN CONFIGURATIONS

E.

In order to compare the merits of the various column configurations, the lowest practical resin volume for each column configuration was selected. These results are summarized in Table 10.6:

No of Columns	Resin Volume per tonne Fe removed per day [m ³]	Load BV / Cycle	Electrolyte Flow per tonne Fe removed per day [L / min]	mg Fe / mL resin / day
1	9	10	1500	110
2	10	25	925	100
4	12	10	500	83

TABLE 10.6: COMPARISON OF VARIOUS COLUMN DESIGN CONFIGURATIONS WHEN STRIPPING AT 85°C

This table illustrates that a single column configuration offers the best resin utilization (highest mg Fe / mL resin / day). This, combined with the fact that a single column system requires less capital cost due to the fact that only one column, one set of pumps, etc. are required, is likely why a single column system was implemented at Mount Gordon. It also shows that increasing the number of columns significantly reduces the flowrate of electrolyte required to pass through the columns.

10.6 IMPLICATIONS FOR CRED

The best way to apply any technology to a mining operation often varies from site to site. Therefore, just because a single column performed extremely well at Mount Gordon does not necessarily mean that it would be the best choice for CRED. Using published data on the CRED plant [1], Mount Gordon's responses to the 2003 World Tankhouse Survey [13], and data reported on the operation of iron IX at Mount Gordon [38], the following table was generated to highlight how the CRED application differs significantly from the Mount Gordon application.

		Electrolyte	Total Electrolyte	Design Iron
Plant	# EW Cells	Flowrate per Cell	Flowrate	Removal
		[L/min]	[L/min]	[Tonne Fe / day]
Mt. Condon	96 old	260 old	24 580	0.22
Mt. Gordon	74 new	130 new	34,380	0.22
CRED	40	40	1.060	1 - 1.5
CKED	+7	+0	1,900	(Estimate)

TABLE 10.7: RELEVANT DIFFERENCES BETWEEN MOUNT GORDON AND CRED

This table clearly shows that an iron ion exchange system at the CRED plant will need to remove significantly more iron than at Mt. Gordon, and that the circulating volume of electrolyte through the Tankhouse is significantly lower.

Given that the lowest calculated flowrate for a single column system is 1500 L / min / tonne Fe removed, this means that at the current flowrate through the CRED Tankhouse (1960 L/min), an iron IX system would only be able to remove a maximum of 1.3 tonne Fe per day.

While it may be possible to increase the flowrate through the CRED Tankhouse, this would result in a higher concentration of copper in the Spent Electrolyte leaving the Tankhouse. As mentioned in section 3.3.3, the bleed volume of Spent Electrolyte to First Stage is dictated by the amount of cupric required in the leach, and a higher copper concentration in Spent Electrolyte would result in less volume being bled to the First Stage. This would cause a further increase in Tankhouse acidity and a higher required ferrous concentration in the Eluate being bled to the First Stage. Even if the IX and acid removal systems were designed to be able to accommodate these factors, plant tests would need to be performed to ensure that a higher flowrate through the Tankhouse would not stir up cell mud and have a deleterious impact on cathode quality.

Even if a higher flowrate were attained through the Tankhouse, the iron removal capability of a single column system would not be able to be easily increased in the future, if required. Therefore, a two column system would offer much more operational flexibility, including:

- Ability to lower stripping temperature to increase resin life, if found to be economical.
- Ability to design the system for a lower operating temperature which may make it feasible to utilize some plastics (e.g. CPVC) as a material of construction.
- Ability to significantly increase the amount of iron removed, if required
- Ability to significantly increase the loading flowrate through columns, if desired
- More consistent concentration of iron and copper in eluate being bled to the First Stage Leach since stripping of a column would always be taking place.

Consequently, serious thought should be given to the possibility of a two column system at CRED, and these points should be taken into consideration before a final decision is made regarding column configuration.

The experimental work presented in this thesis has shown that it is technically feasible to remove iron with ion exchange from copper electrolyte solutions containing antimony and bismuth.

Only the aminophosphonic resin loaded an appreciable amount of bismuth; however, all resins tested loaded an appreciable amount of antimony. An investigation into the antimony loading of the sulphonated monophosphonic Purolite S957 resin yielded inconclusive results as to whether antimony would continuously load onto the resin or whether it would reach an equilibrium level of loading on the resin. Either way, the ion exchange process could still be implemented as it has been shown that the performance of the resin can be restored by passing a solution containing sodium chloride and sulphuric acid through the ion exchange column.

Ferric stripping with cuprous was investigated, using an electrolyte that contained no antimony or bismuth. Results showed that the presence of high levels of ferrous in the electrolyte solution reduced stripping rate for all resins except the Eichrom Monophosphonic resin, where high levels of ferrous resulted in an increased stripping rate. With a constant recirculation rate of eluate, stripping rate was found to trend with the theoretical equilibrium concentration of cuprous for theoretical cuprous concentrations between 0.35 and 0.75 g/L Cu⁺, in a test series where copper concentration and temperature were varied.

Unfortunately, mass balance calculations have shown that the application of iron ion exchange to the CRED plant would result in an unacceptably large increase in acid level in the Tankhouse electrolyte. In order to address this large increase in acid level, an acid removal system, such as an Acid Purification Unit (APU) or a decopperizing step, such as conventional liberator cells or an Electrometals Electrowinning (EMEW) cell, would be required. The acid rich stream would then need to be redirected to somewhere in the CRED flowsheet as it would contain a significant amount of cobalt and nickel, since there is a significant amount of these elements present in the CRED electrolyte. The most appropriate place to reintroduce a nickel and cobalt rich acid stream back into the CRED process is the First Stage Leach. Note, however, that this may not be possible due to water balance constraints. Based on these results, the following process flowsheet, displayed in Figure 11.1, would be required for the implementation of iron IX at the CRED plant. Note that individual flowsheets for each individual step are available in Appendix XIII.



FIGURE 11.1: PROCESS FLOWSHEET FOR IRON ION EXCHANGE AT CRED

11.1 RECOMMENDATIONS FOR FURTHER WORK: IRON IX

- Determine Resin Life as a Function of Stripping Temperature. The results in this thesis have shown that satisfactory stripping occurs, albeit at a lower rate, at temperatures below 85°C. Consideration should be given to whether or not longer resin life could be achieved if stripping occurred at a lower temperature, and an economic evaluation performed to determine whether longer resin life could offset the initial capital cost required for a larger resin volume due to the reduced stripping rate.
- Determine Whether Resin Antimony Loadings Will Reach an Equilibrium Level. The data collected in the antimony investigation was inconclusive as to whether the resin will continue to load with antimony or whether the antimony loading on the resin will reach a plateau.

First of all, it is recommended that a lab test be performed to determine whether ferric will displace antimony from the resin. This could be achieved by running an extended loading cycle (150 BV) with an electrolyte containing antimony but no iron. This would result in a high loading of antimony on the resin. Next, an extended load with an electrolyte containing only ferric, and no antimony should be performed. If an appreciable amount of antimony were to be found in the electrolyte that passed through the column, then this would provide evidence of ferric being able to displace antimony.

If the lab test demonstrates that ferric is able to displace antimony, piloting with an antimony rich electrolyte should occur to determine whether or not a salt and acid washing step would be required. During piloting, resin samples should be taken every 25 cycles for 200 cycles to determine whether or not the antimony loading on the resin remains constant or whether it increases with time. Being able to design the system without the salt and acid wash step would result in a large savings in construction costs since the equipment would be able to be made out of stainless steel. On the other hand, if the salt and acid wash is required, much of the equipment would need to be constructed out of a more corrosion resistant material, such as titanium due to the introduction of chloride ions.

- 3) Determine the Effect of Loading Flowrate. All the tests performed in this thesis used an electrolyte loading rate of 10 BV/hr. Tests should be done to determine the effect of loading rate on the shape of the ferric loading curve. It may be possible to build smaller ion exchange columns if a reduced flowrate results in ferric breakthrough occurring when the resin has a higher loading of ferric.
- 4) Determine the Effect of Eluate Recirculation Rate During Stripping. This thesis investigated the effect of changing stripping temperature and the concentration of copper in the stripping solution on the time required for stripping to occur. In these tests, the eluate was recirculated at a rate of 10 BV/hr. Further testing should be done to determine how recirculation rate affects stripping times.
- 5) Determine Iron Loading as a Function of Initial Ferric Concentration. The lead lag calculations performed in this thesis assumed that the rate of iron loading was independent of the initial ferric concentration in electrolyte. While this is clearly an erroneous assumption, no data was available to determine the effect of initial ferric concentration. This data should be generated in order to be able to properly design lead-lag systems.
- 6) Investigate Reasons for Time to Cuprous Breakthrough Reaching Plateau. It is interesting that in the experiments at various stripping temperatures and copper concentrations, the stripping rate reached a plateau once theoretical cuprous concentrations reached ~ 0.8 g/L Cu⁺. Further work should be done to see if changing the size of the copper shot in the copper shot column, or if changing the total volume of copper shot available can eliminate this plateau.

11.2 RECOMMENDATIONS FOR FURTHER WORK: CRED APPLICATION

 Perform Sample Surveys for % Iron as Ferric. The percentage of the iron in the electrolyte in the ferric state is a key design parameter. Sampling surveys should be performed to determine the amount of iron present in the ferric form in the plant electrolyte streams. Given that the concentration of total iron in electrolyte fluctuates at CRED, surveys should be performed at various total iron concentrations to determine whether or not the fraction of iron present as ferric remains unchanged.

- 2) Investigate the Possibility of Engineered Membrane Separation for Iron Removal. As mentioned in the literature review, Harwest Technologies have developed an Engineered Membrane Separation system (EMS) that allows for the separation of divalent ions from trivalent ions in copper electrolyte solutions. This technology should also be investigated and evaluated as an alternative to iron ion exchange.
- 3) Investigate How to Address an Increase in Acidity in the Tankhouse. If further work on iron ion exchange is desired, it should start with an investigation into how best to deal with the increased acidity in the Tankhouse. During the evaluation of decopperizing technologies, consideration should be given to the possibility of arsine gas formation since arsenic is present in CRED electrolyte. During the evaluation of an Acid Purification Unit, consideration should be given to the fact that there will be an appreciable amount of copper, nickel, cobalt, and iron (both ferrous and ferric) present in the acid rich stream produced.

Once a solution to the problem of high acid levels in electrolyte is found, further work should focus on whether or not ferric is able to displace antimony from the resin, as discussed in item #2 for iron IX recommendations.

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MINOR ELEMENTS ANALYZED BY ICP-PMET

ARSENIC

Target100020003000Result105820603126

ANTIMONY

Target50100200Result36.7861.31100.9

BISMUTH

Target150300500Result196.6345.3493.8





IRON ASSAYS mg Fe/L



The best way to determine resin loading is by resin digestion. However, resin loading can also be easily determined by performing a simple mass balance using the assays from solution samples. Assuming that the amount of an element in the feed solution and the amount of the same element in the final solution is known, then the amount of the element on the resin must be the difference of these two values. In these tests, initial solution volume and both initial and final concentrations are known; only an estimate of the final solution volume is unknown.

To determine the final volume of solution, a tie element that does not bond onto the resin would ideally be required. While no such ion was present in our solution, calculations using copper, nickel, and cobalt as tie elements were found to yield approximately the same final solution volume. Therefore, in the mass balance, the volume of final solution was taken as the average of the volume calculated using copper, using nickel, and using cobalt.

Ferric loading for several samples was determined both by the mass balance method and by resin digestion. If both methods yield similar results, then the assay techniques used for both the solution assays and the resin digestion are likely valid. On the following page two graphs are plotted. In the first graph, the ferric loading by resin digestion is compared to the resin loading by mass balance, using the procedure described above. In the second graph, the ferric loading by resin digestion is compared to the resin loading by mass balance, assuming that no change in solution volume occurs. These graphs clearly show a much tighter correlation when the final solution volume is estimated by tie elements.



RESIN DIGESTION vs SOLUTION MASS BALANCE <u>Tie Element Correction</u>

Tests were performed with plant electrolyte, and ferrous iron was determined using $K_2Cr_2O_7$ titration. All flasks contained a volume ratio of 14:1 (plant electrolyte : resin). Only solution assays were performed; resin concentrations were calculated using the solution assays.

Ferric Iron vs. Time for 4 resins:

• Note that Purolite and Generic Results overlap (i.e. virtually identical)





Generic Resin Results:



GENERIC SCOPE TEST: mg/mL Resin







PUROLITE SCOPE TEST: mg/mL Resin



Lewatit Resin Results:



LEWATIT SCOPE TEST: mg/mL Resin



Diphonix Resin Results:



DIPHONIX SCOPE TEST: mg/mL Resin



During the preparation of a column tests, the ion exchange column is settled through a volume of deionized water in order to reduce the amount of air entrainment in the ion exchange bed. During the column loading test, this water is displaced by the electrolyte. In order to estimate the amount of water diluting the first few loading samples, copper was used as a tie-element. The problem with this method is that if copper is being loaded onto the ion exchange resin, this calculation will <u>overestimate</u> the amount of dilution water.

To check the validity of the copper tie-element method, acid titrations were performed on the loading samples during the Purolite column loading test. This meant that acid could also used as a tie element to determine the amount of dilution water. It should be noted that acid will be displaced from the resin during the loading of iron, therefore, using acid as a tie-element will <u>underestimate</u> the amount of dilution water. Therefore, using both methods will at least provide an upper and lower bound for dilution water estimation. Results comparing the results from both methods can be found in the following table:

Sample	Water based on Copper	Water based on Acid
1 BV	25.0 mL	24.9 mL
2 BV	20.4 mL	15.5 mL
3 BV	1.8 mL	1.3 mL

Given that the largest difference in values between the two methods is ~ 5 mL, which corresponds to a difference of ~ 0.2 BV, the use of copper as a tie-element was deemed satisfactory for estimating dilution volumes of water for this work.

Company	Resin Name	Resin Type (Colour)	Lot #/ Code	Description as per MSDS
Eichrom	Diphonix	Sulphonated	01261DP	Phosphonic Acid, Ethenylidene
		Diphosphonic	DP-B01	bis-, tetrakis (1-methylethyl)
		(Dark Brown -		ester, polymer with ethenyl
		Black)		benzene,
				2-propenenitrile, and
				diethenylbenzene, dibenzoyl
				peroxide initiated, sulfonated and
				hydrolized
Eichrom	Mono-	Sulphonated	JW-81-026	
	phosphonic	Monophosphonic		
		(Reddish-Brown)		
Purolite	S957	Sulphonated	SR600825/1	Macroporous crosslinked
1		Monophosphonic	6439Q/06/6	polymer with phosphonic +
		(Dark Brown with		sulphonic acid functional groups
		some Cream-		
		Coloured Beads)		
Generic	D416	Monophosphonic		Functionalized polymer with
(Chinese		(Dark Brown with		ethynyl benzene and
Company)		some Cream-		ethylethenylbenzene,
		Coloured Beads		chloromethylated, sulfonated and
				hydrolized
Lanxess	Lewatit	Aminophosphonic	CHC0589	Styrene-divinylenzene-
	MonoPlus	(Cream)	03750608	copolymer with phosphonic acid
	TP-260			groups in sodium form
Dow	Dowex	Picolylamine	UB03012DJ1	Bis-picolylamine functionalized,
	M4195			chloromethylated polymer of
				styrene and divinylbenzene



N.B. Load and Strip Solutions were both 40 g/L Cu; had problems with bluestoning Strip Assays plotted as Fe/Cu as had water in-leakage to reservoir Copper powder observed to have formed in lines at end of strip test



DIPHONIX LOAD

DIPHONIX COLUMN -LOW IRON



DIPHONIX COLUMN -ORP



LOADING RESULTS

	Test 1	Test 2	Test 3
% Shrinkage	16	14	-
Breakthrough BV	1	-	-
mg Fe / mL Resin	9.9	10.8	12.1
BV Solution Passed	82.1	90.1	84.6

STRIPPING RESULTS

	Test 1	Test 2	Test 3
Time to ORP switch	-	1:30	1:40
Initial g/L Fe in Strip	-	<0.007	27.4
mg / mL Resin	-	8.6	-

MASS BALANCE (g)

COPPER	Test 1	Test 2	Test 3
Load Feed	61.8	66.2	61.5
Loaded Solutions	60.5	65.6	62.3
Strip Feed	-	6.0	7.0
Strip Solutions	-	5.6	7.0
Mass Balance Error	N/A	1%	-1%

IRON	Test 1	Test 2	Test 3
Load Feed	2.7	3.0	2.7
Loaded Solutions	2.4	2.7	2.4
Strip Feed	-	0.0	4.1
Strip Solutions	-	0.2	4.1
Mass Balance Error	N/A	2%	6%

Purolite:



PUROLITE LOAD

PUROLITE COLUMN -LOW FE STRIP



PUROLITE COLUMN: STRIPPING ORP



LOADING RESULTS

	Test 1	Test 2	Test 3
% Shrinkage	13	-	22
Breakthrough BV	4	-	-
mg Fe / mL Resin	22.2	22.4	24.2
BV Solution Passed	76.4	77.6	75.6

STRIPPING RESULTS

	Test 1	Test 2	Test 3
Time to ORP switch	-	2:21	2:48
Initial g/L Fe in Strip	-	< 0.007	25.6
mg Fe / mL Resin	-	19.7	-

MASS BALANCE (g)

COPPER	Test 1	Test 2	Test 3
Load Feed	62.7	64.2	64.1
Loaded Solutions	62.7	64.6	63.0
Strip Feed	-	6.4	5.9
Strip Solutions	-	6.7	6.4
Mass Balance Error	N/A	-1%	1%

IRON	Test 1	Test 2	Test 3
Load Feed	2.6	2.6	2.6
Loaded Solutions	2.1	2.1	2.0
Strip Feed	-	0.0	3.5
Strip Solutions	-	0.5	3.8
Mass Balance Error	N/A	2%	4%

Lewatit:



LEWATIT LOADING

LEWATIT COLUMN -LOW IRON



LEWATIT COLUMN



Note: Problems observed with cuprous forming in line after High Fe Lewatit test.

LOADING RESULTS

	Test 1	Test 2
% Shrinkage	-1	-
Breakthrough BV	7	-
mg Fe / mL Resin	24.8	17.8
BV Solution Passed	81.4	74.9

MASS BALANCE (g)

COPPE	Test 1	Test 2
Load Feed	66.5	61.2
Loaded Solutions	65.2	61.3
Strip Feed	6.4	-
Strip Solutions	7.3	-
Mass Balance Error	0%	N/A

STRIPPING RESULTS

iiiiiiiiiiiiiiiiiiiiiiiiiiiiiiii	Test 1	Test 2
Time to ORP switch	0:15	0:20
Initial g/L Fe in Strip	< 0.007	-
mg Fe / mL Resin	11	-

IRON	Test 1	Test 2
Load Feed	2.8	2.6
Loaded Solutions	2.1	2.1
Strip Feed	0.0	-
Strip Solutions	0.3	-
Mass Balance Error	12%	N/A
	*	

Could this indicate not fully stripped? Note really low mg / mL stripped...



LEWATIT COLUMN -LOW IRON

LOADING RESULTS

	Test 1
% Shrinkage	-
Breakthrough BV	-
mg Fe / mL Resin	24.8
BV Solution Passed	86.1

MASS BALANCE (g)

COPPER	Test 1
Load Feed	74.9
Loaded Solutions	74.4
Strip Feed	6.9
Strip Solutions	7.5
Mass Balance Error	0%

STRIPPING RESULTS

	Test 1
Time to ORP switch	3:32
Initial g/L Fe in Strip	< 0.007
mg Fe / mL Resin	21

IRON	Test 1
Load Feed	3.1
Loaded Solutions	2.5
Strip Feed	0.0
Strip Solutions	0.5
Mass Balance Error	3%
Generic:



GENERIC LOADING

GENERIC -LOW IRON STRIP







LOADING RESULTS

	Test 1	Test 2
% Shrinkage	12	13
Breakthrough BV	4	-
mg Fe / mL Resin	23.9	20.3
BV Solution Passed	80.5	71.9

STRIPPING RESULTS

	Test 1	Test 2
Time to ORP switch	2:15	2:35
Initial g/L Fe in Strip	<0.007	22.8
mg Fe / mL Resin	17.8	-

MASS BALANCE (q)

COPPER	Test 1	Test 2
Load Feed	62.8	54.8
Loaded Solutions	61.7	53.8
Strip Feed	5.8	5.3
Strip Solutions	5.7	5.6
Mass Balance Error	2%	1%

IRON	Test 1	Test 2
Load Feed	2.7	2.2
Loaded Solutions	2.1	1.7
Strip Feed	0.0	3.0
Strip Solutions	0.4	3.4
Mass Balance Error	6%	2%

EICHROM



EICHROM LOADING CURVE

EICHROM COLUMN -LOW IRON



EICHROM COLUMN



LOADING RESULTS

	Test 1	Test 2
% Shrinkage	1	0
Breakthrough BV	3	-
mg Fe / mL Resin	27.5	27.0
BV Solution Passed	81.6	78.1

STRIPPING RESULTS

	Test 1	Test 2
Time to ORP switch	3:20	2:50
Initial g/L Fe in Strip	< 0.007	24.2
mg Fe / mL Resin	26.9	-

MASS BALANCE (g)

COPPER	Test 1	Test 2
Load Feed	61.8	59.1
Loaded Solutions	61.2	59.2
Strip Feed	6.1	6.3
Strip Solutions	6.9	6.8
Mass Balance Error	0%	-1%

IRON	Test 1	Test 2
Load Feed	2.7	2.6
Loaded Solutions	2.0	2.0
Strip Feed	0.0	3.9
Strip Solutions	0.7	4.5
Mass Balance Error	1%	1%



EICHROM COLUMN (REPEAT)

- Run #1: Low Iron Strip Solution
- Run #2: High Iron Strip Solution
- Run #3: Low Iron Strip Solution \rightarrow ORP almost identical to Run #1

N.B. ORP Data Only for Test #3 –Did not submit samples for assay.

LOADING RESULTS

	Test 1	Test 2	Test 3
% Shrinkage	-	-	-
Breakthrough BV	-	-	-
mg Fe / mL Resin	27.6	27.2	-
BV Solution Passed	117.3	117.3	112.5

MASS BALANCE (g)

COPPER	Test 1	Test 2	Test 3
Load Feed	90.0	91.5	-
Loaded Solutions	93.0	90.6	-
Strip Feed	6.2	6.1	-
Strip Solutions	6.8	6.6	-
Mass Balance Error	-4%	0%	N/A

STRIPPING RESULTS

	Test 1	Test 2	Test 3
Time to ORP switch	2:57	2:44	2:57
Initial g/L Fe in Strip	< 0.007	•	< 0.007
mg Fe / mL Resin	26.4	-	-

IRON	Test 1	Test 2	Test 3
Load Feed	4.0	4.0	-
Loaded Solutions	3.3	3.3	-
Strip Feed	0.0	3.7	-
Strip Solutions	0.7	4.2	-
Mass Balance Error	1%	2%	N/A



DIPHONIX COLUMN -STEEL RESERVOIR

Loading Balance:



Loading ORP Curves:



The curves for the various tests are not easily distinguishable one from another on this graph. However, this graph illustrates that loading was performed well past the initiation of a loading ORP plateau, suggesting that the resin was fully loaded for all stripping tests. Note that for the first two tests (65C Strip and 70C Strip), the ORP curves do not dip as much as for all other tests (see curves in the top left corner). This is likely because the ORP probe was replaced after running these two tests. Example Calculation: 45g/L Cu

Cu + Cu²⁺ ↔ 2 Cu⁺

$$\Delta G = \Delta G^{\circ} + 2.303 \text{RT log K}$$

K = $(aCu^{+})^{2}/(aCu^{2+})$

Use <u>unit molality</u> convention for activity calculations. Therefore,

$$aCu^{+} = mol Cu^{+} / kg H_{2}O = (mol Cu^{+} / L soln)(L soln / kg H_{2}O)$$

Define:
$$[Cu^{+}] = (mol Cu^{+} / L soln)$$

 $X = (L \operatorname{soln} / \operatorname{kg} H_2 O)$

So,

$$K = ([Cu^{+}]^{2} / [Cu^{2+}]) (X)$$

Rough Estimate of X:

Only have $CuSO_4$ and H_2SO_4 in solution, so

g H₂O / L \approx g soln / L – g H₂SO₄ / L – g CuSO₄ / L :

Rough Molality Correction: Want L Soln / kg H2O

g/L H2SO4 g/L Cu g/L CuSO4 SOLN SG	220 45 113 1.21	220 60 151 1.24	220 80 201 1.27	98.1 g/mol H2SO4 63.55 g/mol Cu 159.7 g/mol CuSO4
g/L Soln	1210	1240	1270	
g water / L Soln	877	869	849	
L Soln / kg H2O	1.14	1.15	1.18	

Used HSC data to determine delta G, and then used spreadsheet to find cuprous concentration:

X = L soln/kg water = 1.14

Cu + Cu(+2) --> 2 Cu(+) 63.5 molar mass Cu Delta G = Delta Go + 2.303RT log(K) K = [Cu+]^2/[Cu+2] X

TEMP [C]		DELTA G0	g/L Cu 2+	mol Cu 2+	logK	ĸ	mol Cu +	g/L Cu(+)	g/L Cu	ERROR
25	298.15	34414	44.95	0.71	-6.03	1.07E-06	0.00	0.06	45.0	9.19E-03
30	303.15	33684	44.93	0.71	-5.80	1.79E-06	0.00	0.07	45.0	4.71E-03
35	308.15	32947	44.91	0.71	-5.58	2.97E-06	0.00	0.09	45.0	4.80E-03
40	313.15	32202	44.88	0.71	-5.37	4.86E-06	0.00	0.12	45.0	1.79E-04
45	318.15	31451	44.85	0.71	-5.16	7.83E-06	0.00	0.15	45.0	2.57E-04
50	323.15	30690	44.81	0.71	-4.96	1.25E-05	0.00	0.19	45.0	2.20E-04
55	328.15	29924	44.76	0.70	-4.76	1.97E-05	0.00	0.24	45.0	7.96E-04
60	333.15	29153	44.71	0.70	-4.57	3.07E-05	0.00	0.30	45.0	5.64E-04
65	338.15	28374	44.63	0.70	-4.38	4.73E-05	0.01	0.37	45.0	6.21E-04
70	343.15	27587	44.55	0.70	-4.20	7.21E-05	0.01	0.45	45.0	4.54E-03
75	348.15	26795	44.45	0.70	-4.02	1.09E-04	0.01	0.55	45.0	7.25E-03
80	353.15	25998	44.32	0.70	-3.84	1.63E-04	0.01	0.68	45.0	1.91E-03
85	358.15	25193	44.18	0.70	-3.67	2.42E-04	0.01	0.82	45.0	2.52E-03
90	363.15	24384	44.01	0.69	-3.51	3.55E-04	0.02	1.00	45.0	6.46E-03
95	368.15	23568	43.81	0.69	-3.34	5.17E-04	0.02	1.20	45.0	9.69E-03
100	373.15	22744	43.56	0.69	-3.18	7.47E-04	0.02	1.44	45.0	6.18E-07
105	378.15	21917	43.29	0.68	-3.03	1.07E-03	0.03	1.72	45.0	1.04E-02
110	383.15	21082	42.96	0.68	-2.87	1.52E-03	0.03	2.04	45.0	1.27E-04
115	388.15	20242	42.59	0.67	-2.72	2.15E-03	0.04	2.41	45.0	3.52E-03

Target Cell. This is sum of errors. Use solver to change grey cells to minimize this cell. 6.78E-02

Target Copper Concentration: 45

CYCLE	1	2	3	4	5	6
BV Loaded	85.0	80.4	108.0	82.1	83.1	85.7
g Fe loaded	0.533	0.389	0.485	0.437	0.466	0.642
mg Fe/mL loaded	21.3	15.6	19.4	17.5	18.6	25.7
g Sb loaded	0.097	0.051	0.030	-0.028	-0.036	0.019
Strip Time	2:25:32	2:25:23	2:29:50	2:20:13	2:19:46	2:11:54
g Fe stripped	0.515	0.500	0.505	0.500	0.520	0.495
mg Fe / mL stripped	20.6	20.0	20.2	20.0	20.8	19.8
g Sb stripped	-0.010	-0.012	-0.008	-0.006	-0.013	0.002
Total g Sb Loaded	0.107	0.063	0.038	-0.022	-0.023	0.017
mg Sb/mL Loaded	4.3	2.5	1.5	-0.9	-0.9	0.7
Cumulative mg Sb/mL	4.3	6.8	8.3	7.4	6.5	7.2

CYCLE	7	8	9	10	SALT	11
BV Loaded	83.9	83.3	81.0	81.9	WASH	85.7
g Fe loaded	0.525	0.570	0.572	0.516		0.577
mg Fe/mL loaded	21.0	22.8	22.9	20.6		23.1
g Sb loaded	-0.034	0.010	0.031	0.009		0.144
Strip Time	2:18:47	2:16:53	2:14:52	2:14:39		2:22:52
g Fe stripped	0.515	0.519	0.473	0.507	0.007	0.515
mg Fe / mL stripped	20.6	20.8	18.9	20.3	0.3	20.6
g Sb stripped	-0.006	-0.004	-0.013	-0.008	0.189	-0.017
Total g Sb Loaded	-0.028	0.014	0.044	0.017	-0.189	0.161
mg Sb/mL Loaded	-1.1	0.6	1.7	0.7	-7.6	6.4
Cumulative mg Sb/mL	6.1	6.6	8.4	9.1	1.5	7.9

The following calculations were performed to size a single ion exchange column:

Loaded Soln g/L Fe:

This is the weighted average concentration of solution that would be expected if all bed volumes of solutions up to this point were collected in a single container.

Note that the calculated value of 1.10 g/L Fe after 73 BVs is very close to the actual concentration of 1.06 g/L Fe obtained during the second load (test 2) with the Purolite resin.

Strip Time:

This is the time it takes to remove the amount of iron loaded on the resin at a given temperature. As defined in Chapter 7, this is the time taken for the ORP to reach a value of 500 mV_{SHE} .

To estimate the longer stripping time expected at 25 g/L iron, the stripping time was multiplied by 120%. This is based on the Purolite stripping time results (Ch. 6):

0 g/L Fe	\rightarrow 2:21 stripping time =	141 mins	
25 g/L Fe	\rightarrow 2:48 stripping time =	168 mins	168/141 = <u>119%</u>

Stripping Rate (mg Fe / mL Resin / min):

Stripping rate of resin at various temperatures uses the total stripping time and assumes that fully loaded Purolite resin holds 21 mg Fe / mL resin and that stripping occurs linearly. A linear function was used since only the stripping time is available for most of the temperatures. Note that for 85C, a full data set is available, and the linear function correlates fairly well with the observed samples taken during this test:

IRON STRIPPED FROM PUROLITE RESIN AT 85C



Bed Volumes of Stripping Solution:

BV of stripping solution is calculated from the stripping time by assuming a recirculating flowrate of 10 BV/min.

g/L Iron to Resin

This is the weighted average concentration of iron that is loaded from the solution onto the resin during the loading cycle.

g/L Iron to Resin = g/L Iron in Feed – g/L Iron in Loaded Soln

g/L Iron "Idle"

This refers to the amount of iron that is loaded onto the resin during the stripping portion of the cycle. This number is set to zero.

g/L Iron Total

This is the time weighted average of iron loaded from electrolyte onto the resin.

Electrolyte Flowrate Required (L/min):

This is the minimum flowrate of electrolyte through the column to remove a tonne of iron per day:

L/min Electrolyte = (g/L Iron to Resin)/1000 * (1000 kg/day Fe Removed)/(24*60)

Volume of Resin Bed Required (m³):

The volume of resin bed (1 BV) required is based on a flowrate of 10 BVs per hour:

 m^{3} Resin = (L/min Electrolyte) * (60 min/hr) / { (10 BV /hr) * (1000 L / m^{3}) }

CALCULATION RESULTS:

ION EXCHANGE -SIZING COLUMNS 1000 kg/day iron bleed From Purolite Column Load Curve Test Data: 1.37 g/L Ferric in Feed 21 mg Fe/mL resin fully loaded

LOADING CALCULATIONS

BV	g/L Fe	cum Fe	cum Fe	mg	loaded	g/L Fe to
Passed	Sample	in	out	Fe/mL	soln fe g/L	Resin
0.0		0.000	0.000	0.0	0.0	1.4
0.2		0.006	0.000	0.3	0.0	1.4
1.1		0.038	0.000	1.5	0.0	1.4
2.1		0.072	0.000	2.9	0.0	1.4
3.1		0.107	0.000	4.3	0.0	1.4
5.1	0.0555	0.175	0.003	6.9	0.0	1.3
8.1	0.274	0.278	0.023	10.2	0.1	1.3
13.1	0.585	0.449	0.096	14.1	0.3	1.1
18.1	0.854	0.620	0.203	16.7	0.4	0.9
28.1	1.08	0.963	0.473	19.6	0.7	0.7
38.1	1.22	1.305	0.778	21.1	0.8	0.6
58.1	1.37	1.990	1.463	21.1	1.0	0.4
73.1	1.45	2.504	2.007	19.9	1.1	0.3

FROM STRIPPING TEMPERATURE SERIES

			strip rate (assume linear	.)
Т	stri	p time	mg/mL/min	
	65	263	0.080	
	70	251	0.084	
	75	212	0.099	
	80	184	0.114	
	85	142	0.148	
	88	146	0.144	

25 g/L Fe Est	<u>imates</u>
Strip Time	Strip Rate
mins	mg/mL/min
316	0.067
301	0.070
254	0.083
221	0.095
170	0.123
175	0.120

STRIP TEMP = 85C

Strip Rate 0.123 mg Fe / mL / min

	•		-			electrolyte	and resin	required	
BV loaded	mg Fe/mL	Strip Time	BV Strip	BV / cycle	% Time Stripping	g/L to resin	g/L idle	g/L total	L/min
0.0	0.0	0.0	0.0	0.0	64.9	1.4	0.0	0.5	1446
0.2	0.3	2.1	0.3	0.5	64.9	1.4	0.0	0.5	1446
1.1	1.5	12.4	2.1	3.2	64.9	1.4	0.0	0.5	1446
2.1	2.9	23.5	3.9	6.0	64.9	1.4	0.0	0.5	1446
3.1	4.3	34.6	5.8	8.9	64.9	1.4	0.0	0.5	1446
5.1	6.9	55.9	9.3	14.4	64.6	1.3	0.0	0.5	1454
8.1	10.2	82.6	13.8	21.9	62.9	1.3	0.0	0.5	1492
13.1	14.1	114.5	19.1	32.2	59.3	1.1	0.0	0.4	1585
18.1	16.7	135.4	22.6	40.7	55.5	0.9	0.0	0.4	1693
28.1	19.6	158.9	26.5	54.6	48.5	0.7	0.0	0.4	1936
38.1	21.1	171.1	28.5	66.6	42.8	0.6	0.0	0.3	2194
58.1	21.1	171.1	28.5	86.6	32.9	0.4	0.0	0.2	2853
73.1	19.9	161.4	26.9	100.0	26.9	0.3	0.0	0.2	3492

стр	D	TER	ис	 or	າຕ	
ЭІК			VIF	o١	JC	
		-		 		

Strip Rate 0.095 mg Fe / mL / min

	•		-			electrolyte	and resin	required	
BV loaded	mg Fe/mL	Strip Time	BV Strip	BV / cycle	% Time Stripping	g/L loaded	g/L idle	g/L total	L/min
0.0	0.0	0.0	0.0	0.0	70.6	1.4	0.0	0.4	1723
0.2	0.3	2.7	0.4	0.6	70.6	1.4	0.0	0.4	1723
1.1	1.5	16.0	2.7	3.8	70.6	1.4	0.0	0.4	1723
2.1	2.9	30.4	5.1	7.2	70.6	1.4	0.0	0.4	1723
3.1	4.3	44.8	7.5	10.6	70.6	1.4	0.0	0.4	1723
5.1	6.9	72.4	12.1	17.2	70.3	1.3	0.0	0.4	1731
8.1	10.2	107.0	17.8	25.9	68.7	1.3	0.0	0.4	1770
13.1	14.1	148.2	24.7	37.8	65.3	1.1	0.0	0.4	1862
18.1	16.7	175.4	29.2	47.3	61.7	0.9	0.0	0.4	1970
28.1	19.6	205.8	34.3	62.4	55.0	0.7	0.0	0.3	2213
38.1	21.1	221.6	36.9	75.0	49.2	0.6	0.0	0.3	2471
58.1	21.1	221.6	36.9	95.0	38.9	0.4	0.0	0.2	3130
73.1	19.9	209.0	34.8	107.9	32.3	0.3	0.0	0.2	3769

STRIP TEMP = 75C

Strip Rate 0.083 mg Fe / mL / min

	-					electrolyte	and resin	required	
BV loaded	mg Fe/mL	Strip Time	BV Strip	BV / cycle	% Time Stripping	g/L loaded	g/L idle	g/L total	L/min
0.0	0.0	0.0	0.0	0.0	73.4	1.4	0.0	0.4	1909
0.2	0.3	3.1	0.5	0.7	73.4	1.4	0.0	0.4	1909
1.1	1.5	18.5	3.1	4.2	73.4	1.4	0.0	0.4	1909
2.1	2.9	35.1	5.8	8.0	73.4	1.4	0.0	0.4	1909
3.1	4.3	51.7	8.6	11.7	73.4	1.4	0.0	0.4	1909
5.1	6.9	83.5	13.9	19.0	73.1	1.3	0.0	0.4	1917
8.1	10.2	123.3	20.6	28.7	71.7	1.3	0.0	0.4	1955
13.1	14.1	170.9	28.5	41.6	68.5	1.1	0.0	0.3	2048
18.1	16.7	202.1	33.7	51.8	65.0	0.9	0.0	0.3	2156
28.1	19.6	237.3	39.5	67.7	58.4	0.7	0.0	0.3	2399
38.1	21.1	255.4	42.6	80.7	52.8	0.6	0.0	0.3	2657
58.1	21.1	255.4	42.6	100.7	42.3	0.4	0.0	0.2	3316
73.1	19.9	240.9	40.2	113.3	35.4	0.3	0.0	0.2	3955

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			Ų						
						electrolyte	and resin	required	
BV loaded	mg Fe/mL	Strip Time	BV Strip	BV / cycle	% Time Stripping	g/L loaded	g/L idle	g/L total	L/min
0.0	0.0	0.0	0.0	0.0	76.6	1.4	0.0	0.3	2167
0.2	0.3	3.7	0.6	0.8	76.6	1.4	0.0	0.3	2167
1.1	1.5	21.9	3.6	4.8	76.6	1.4	0.0	0.3	2167
2.1	2.9	41.5	6.9	9.0	76.6	1.4	0.0	0.3	2167
3.1	4.3	61.2	10.2	13.3	76.6	1.4	0.0	0.3	2167
5.1	6.9	98.9	16.5	21.6	76.3	1.3	0.0	0.3	2175
8.1	10.2	146.0	24.3	32.5	75.0	1.3	0.0	0.3	2213
13.1	14.1	202.3	33.7	46.8	72.0	1.1	0.0	0.3	2306
18.1	16.7	239.3	39.9	58.0	68.8	0.9	0.0	0.3	2414
28.1	19.6	280.9	46.8	74.9	62.5	0.7	0.0	0.3	2657
38.1	21.1	302.4	50.4	88.5	56.9	0.6	0.0	0.2	2915
58.1	21.1	302.4	50.4	108.5	46.4	0.4	0.0	0.2	3574
73.1	19.9	285.2	47.5	120.7	39.4	0.3	0.0	0.2	4213

STRIP TEMP = 65C

STRIP TEMP = 70C

Strip Rate

Strip Rate

0.067 mg Fe / mL / min

0.070 mg Fe / mL / min

	-		-			electrolyte	and resin	required	
BV loaded	mg Fe/mL	Strip Time	BV Strip	BV / cycle	% Time Stripping	g/L loaded	g/L idle	g/L total	L/min
0.0	0.0	0.0	0.0	0.0	77.4	1.4	0.0	0.3	2246
0.2	0.3	3.8	0.6	0.8	77.4	1.4	0.0	0.3	2246
1.1	1.5	22.9	3.8	4.9	77.4	1.4	0.0	0.3	2246
2.1	2.9	43.5	7.3	9.4	77.4	1.4	0.0	0.3	2246
3.1	4.3	64.1	10.7	13.8	77.4	1.4	0.0	0.3	2246
5.1	6.9	103.6	17.3	22.4	77.2	1.3	0.0	0.3	2254
8.1	10.2	153.0	25.5	33.6	75.9	1.3	0.0	0.3	2293
13.1	14.1	212.0	35.3	48.4	72.9	1.1	0.0	0.3	2385
18.1	16.7	250.8	41.8	59.9	69.8	0.9	0.0	0.3	2493
28.1	19.6	294.4	49.1	77.2	63.6	0.7	0.0	0.3	2736
38.1	21.1	316.9	52.8	90.9	58.1	0.6	0.0	0.2	2995
58.1	21.1	316.9	52.8	110.9	47.6	0.4	0.0	0.2	3653
73.1	19.9	298.9	49.8	122.9	40.5	0.3	0.0	0.2	4293

The following calculations were performed in sizing the columns for the two ion exchange system. See Appendix X for an explanation of the individual calculations performed.

FULL DESIGN CALCULATION RESULTS:

ION EXCHANGE -SIZING COLUMNS

1000 kg/day iron bled to First Stage

From Purolite Column Load Curve Test Data:

1.37 g/L Ferric in Feed 21 mg Fe/mL resin fully loaded

	BV		loaded soln fe			
	Passed	g/L Fe	g/L	Electrolyte a	ld resin required	
		_	-	g/L to resin	L/min	Bed Size m3
	0.0		0.0	1.4	507	3.0
	0.2		0.0	1.4	507	3.0
	1.1		0.0	1.4	507	3.0
	2.1		0.0	1. 4	507	3.0
	3.1		0.0	1.4	507	3.0
	5.1	0.0555	0.0	1.3	515	3.1
	8.1	0.274	0.1	1.3	553	3.3
	13.1	0.585	0.3	1.1	646	3.9
Design	18.1	0.854	0.4	0.9	754	4.5
Operation	28.1	1.08	0.7	0.7	997	6.0
-	38.1	1.22	0.8	0.6	1255	7.5
	58.1	1.37	1.0	0.4	1914	11.5
	73.1	1.45	1.1	0.3	2553	15.3

		Time taken to	strip at 10)BV/hr	······
mg/mL loaded	65	70	75	80	85
0.0	4.E-04	4.E-04	3.E-04	3.E-04	2.E-04
0.3	4	4	3	3	2
1.5	23	22	18	16	12
2.9	44	42	35	30	23
4.3	64	61	52	45	35
6.9	104	99	84	72	56
10.2	153	146	123	107	83
14.1	212	202	171	148	114
16.7	251	239	202	175	135
19.6	294	281	237	206	159
21.1	317	302	255	222	171
21.1	317	302	255	222	171
19.9	299	285	241	209	161
		BV to stri	p at 10BV/	hr	
mg/mL loaded	65	70	75	80	85
0.0	0.0	0.0	0.0	0.0	0.0
0.3	0.6	0.6	0.5	0.4	0.3
1.5	3.8	3.6	3.1	2.7	2.1
2.9	7.3	6.9	5.8	5.1	3.9
4.3	10.7	10.2	8.6	7.5	5.8
6.9	17.3	16.5	13.9	12.1	9.3
10.2	25.5	24.3	20.6	17.8	13.8
14.1	35.3	33.7	28.5	24.7	19.1
16.7	41.8	39.9	33.7	29.2	22.6
19.6	49.1	46.8	39.5	34.3	26.5
21.1	52.8	50.4	42.6	36.9	28.5
01 1	52.8	50 4	42.6	36.9	28.5
21.1	52.0	00.1	12.0	00.0	20.0

The ferric loading rate was defined as: mg Fe / mL Resin / BV loaded soln. These results were plotted against BV loaded and mg Fe / mL Resin. Calculation results and graphs appear below:

ION EXCHANGE -SIZING COLUMNS

1000 kg/day iron bled to First Stage

From Purolite Column Load Curve Test Data:

1.37 21 g/L Ferric in Feed mg Fe/mL resin fully loaded

LOADING CALCULATIONS

-					
		g/L Fe		g/L Fe to	Fe Loading Rate
BV Passed	Avg BV	Sample	mg Fe/mL	Resin	mg Fe / mL / BV
0.0	0.0	0	0.0	1.37	1.37
0.2	0.1	0	0.3	1.37	1.37
1.1	0.6	0	1.5	1.37	1.37
2.1	1.6	0	2.9	1.37	1.37
3.1	2.6	0	4.3	1.37	1.31
5.1	4.1	0.0555	6.9	1.35	1.10
8.1	6.6	0.274	10.2	1.25	0.79
13.1	10.6	0.585	14.1	1.08	0.52
18.1	15.6	0.854	16.7	0.92	0.29
28,1	23.1	1.08	19.6	0.70	0.15
38.1	33.1	1.22	21.1	0.55	0.00
58.1	48.1	1.37	21.1	0.36	-0.08
73.1	65.6	1.45	19.9	0.27	0.27





Note how the plot of loading rate is linear with the amount of ferric loaded onto the resin. The maximum loading of 1.37 mg Fe / mL / BV occurs when there is no ferric breakthough into the loaded solution, and is equal to the initial concentration of ferric in the feed solution. This loading rate likely also depends on the concentration of ferric in the feed solution, however, this information is not available since no loading curves were generated at other ferric concentrations in this work.

The loading rate of the lead-lag column system were then calculated iteratively for each length of loading cycle (i.e. one set of iterative calculations if the columns are switched after 6 BV, another set for if the columns switched after 10 BV, etc.). For each iteration, the following values are calculated for each BV^* for both the lead and the lag columns:

- o mg Fe / mL resin before this BV of solution passes through
- Calculated rate of resin load rate. This is set to zero if the resin is fully loaded (20 mg Fe / mL resin), otherwise it is the value predicted by the linear fit: 1.6043 0.0764 * (mg Fe / mL resin before)
- Actual resin load rate. This is equal to the concentration of iron in the feed solution or the calculated resin load rate; whichever is less.
- o mg Fe / mL resin after this BV of solution passes through. (before + rate)
- Concentration of iron in the loaded solution exiting the column. This equals the concentration of iron in the feed – rate of iron loaded. Note that the concentration of iron in the loaded solution from the lead column became the concentration of iron in the feed to the lag column.

^{*} This is essentially a finite difference model, with a $\Delta BV = 1$. If calculations were performed at different numbers of BV, various terms would need to be multiplied by the ΔBV value.

Based on the concentration of the iron in the loaded solution exiting the lag column, the g/L from solution to resin, the required volume of electrolyte flow, and the required volume of resin bed were calculated, as previously described in Appendix X.

The required stripping rate was then calculated based on the amount of iron loaded onto the lead column and the number of BVs between switching columns.

To check the various model calculations, the iron loaded onto the resin and the concentration of iron in the loaded solution exiting each column was calculated for an extended load for two columns, both of which had no iron loaded initially. These results were compared to the experimental data and showed good correlation, as shown in the following two graphs:





These graphs show a good correlation of the lead column calculations with experimental data, indicating that the finite difference model calculations are valid. NOTE THAT THE CALCULATIONS FOR THE LAG COLUMN DO NOT TAKE INTO ACCOUNT THE CHANGE IN LOAD RATE DUE TO THE FACT THAT THE FEED SOLUTION IS LESS THAN 1.37 g / L IRON AS NO MODEL IS CURRENTLY AVAILABLE TO ACCOUNT FOR THIS.

		max load ra	ate = Conc	entration of	Iron in Feed	d 1.3 7	g/L Fe in Electrolyte		Eqbm Resi	n load	0.0	mg Fe / m	L Resin
		mg Fe / ml	_ / BV =	1.6043	-	0.0764	* mg Fe / mL Resin		Change ev	ery	10	BV	
		Fully Loade	ed Resin =	21	mg Fe / m	L			Recirc Flor	ate	10	BV / hr	
		At Steady S	State?		> if > 0	not at stead	ly-state						
ITERATION	N	LEAD COLUMN				LAG COLUMN							
Difference	BV	g/L Fe Fee	mg Fe/mL	Calc Rate	Actual Rat	amg Fe/mL	g/L Fe out	g/L Fe Fe	e mg Fe/mL	Calc Rate	Actual Rate	mg Fe/mL	g/L Fe out
1	1	1.37	0.00	1.60	1.37	1.37	0.00	0.00	0.00	1.60	0.00	0.00	0.00
	2	1.37	1.37	1.50	1.37	2.74	0.00	0.00	0.00	1.60	0.00	0.00	0.00
	3	1.37	2.74	1.39	1.37	4.11	0.00	0.00	0.00	1.60	0.00	0.00	0.00
	4	1.37	4.11	1.29	1.29	5.40	0.08	0.08	0.00	1.60	0.08	0.08	0.00
	5	1.37	5.40	1.19	1.19	6.59	0.18	0.18	0.08	1.60	0.18	0.26	0.00
	6	1.37	6.59	1.10	1.10	7.69	0.27	0.27	0.26	1.58	0.27	0.53	0.00
2	1	1.37	0.53	1.56	1.37	1.90	0.00	0.00	0.00	1.60	0.00	0.00	0.00
0.527	2	1.37	1.90	1.46	1.37	3.27	0.00	0.00	0.00	1.60	0.00	0.00	0.00
	3	1.37	3.27	1.35	1.35	4.62	0.02	0.02	0.00	1.60	0.02	0.02	0.00
	4	1.37	4.62	1.25	1.25	5.87	0.12	0.12	0.02	1.60	0.12	0.13	0.00
	5	1.37	5.87	1.16	1.16	7.03	0.21	0.21	0.13	1.59	0.21	0.35	0.00
	6	1.37	7.03	1.07	1.07	8.10	0.30	0.30	0.35	1.58	0.30	0.65	0.00
3	1	1.37	0.65	1.55	1.37	2.02	0.00	0.00	0.00	1.60	0.00	0.00	0.00
0.124	2	1.37	2.02	1.45	1.37	3.39	0.00	0.00	0.00	1.60	0.00	0.00	0.00
1	3	1.37	3.39	1.35	1.35	4.74	0.02	0.02	0.00	1.60	0.02	0.02	0.00
	4	1.37	4.74	1.24	1.24	5.98	0.13	0.13	0.02	1.60	0.13	0.15	0.00
	5	1.37	5.98	1.15	1.15	7.13	0.22	0.22	0.15	1.59	0.22	0.37	0.00
•	6	1.37	7.13	1.06	1.06	8.19	0.31	0.31	0.37	1.58	0.31	0.69	0.00
8	1	1.37	0.70	1.55	1.37	2.07	0.00	0.00	0.00	1.60	0.00	0.00	0.00
0.000	2	1.37	2.07	1.45	1.37	3.44	0.00	0.00	0.00	1.60	0.00	0.00	0.00
	3	1.37	3.44	1.34	1.34	4.78	0.03	0.03	0.00	1.60	0.03	0.03	0.00
	4	1.37	4.78	1.24	1.24	6.02	0.13	0.13	0.03	1.60	0.13	0.16	0.00
	5	1.37	6.02	1.14	1.14	7.16	0.23	0.23	0.16	1.59	0.23	0.38	0.00
	6	1.37	7.16	1.06	1.06	8.22	0.31	0.31	0.38	1.57	0.31	0.70	0.00

The results of a set of iterative calculations for the case where the columns are switched every 6 BV is shown below:

REQ'D STRIPPING RATE

BV	g/L to Resin	_/min	m3 resin	mg
1	1.37	507	3.0	
2	1.37	507	3.0	
3	1.37	507	3.0	
4	1.37	507	3.0	
5	1.37	507	3.0	
6	1.37	507	3.0	
1	1.37	507	3.0	
2	1.37	507	3.0	
3	1.37	507	3.0	
4	1.37	507	3.0	
5	1.37	507	3.0	
6	1.37	507	3.0	
1	1.37	507	3.0	
2	1.37	507	3.0	
3	1.37	507	3.0	
4	1.37	507	3.0	
5	1.37	507	3.0	
6	1.37	507	3.0	
1	1.37	507	3.0	
2	1.37	507	3.0	
3	1.37	507	3.0	
4	1.37	507	3.0	
5	1.37	507	3.0	
6	1.37	507	3.0	

Fe / mL /BV 1.37 1.37 1.37 1.35 1.32 1.28	mg Fe / mL / n 0.228 0.228 0.228 0.225 0.220 0.214	nin
1.35	0.225	
1.36	0.227	

1.37 0.228

The final iteration results, highlighted as white numbers on a black background, from each set of different column switching times were put together to generate the design graphs. The results are summarized below:

Switch every # BVs	Lead Column Load	Lag Column Load	L / min Electrolyte Reqd	m3 Resin per Column	Required Strip Rate mg/mL/min	g/L Fe leaving lag
1	1.4	0.0	507	3.0	0.228	0.0
2	2.7	0.0	507	3.0	0.228	0.0
3	4.1	0.0	507	3.0	0.228	0.0
6	8.2	0.7	507	3.0	0.228	0.0
10	13.7	4.8	507	3.0	0.228	0.0
13	17.4	10.9	612	3.7	0.223	0.2
15	18.6	13.1	817	4.9	0.207	0.5
18	19.6	15.2	1170	7.0	0.182	0.8
20	20.0	16.2	1453	8.7	0.167	0.9
25	20.6	17.9	2386	14.3	0.137	1.1

BED VOLUMES PER LOADING CYCLE

FROM STRIPPING TEMPERATURE SERIES

		25 g/L Fe Estimates			
	strip rate	Strip Time	Strip Rate		
strip time	mg/mL/min	mins	mg/mL/min		
263	0.080	316	0.067		
251	0.084	301	0.070		
212	0.099	254	0.083		
184	0.114	221	0.095		
142	0.148	170	0.123		
146	0.144	175	0.120		
	strip time 263 251 212 184 142 146	strip ratestrip timemg/mL/min2630.0802510.0842120.0991840.1141420.1481460.144	strip rate 25 g/L Fe E: strip time mg/mL/min mins 263 0.080 316 251 0.084 301 212 0.099 254 184 0.114 221 142 0.148 170 146 0.144 175		

65C	70C	75C	80C	85C
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123
0.067	0.070	0.083	0.095	0.123

3 COLUMN SYSTEM - POSSIBLE STRIP RATES

4 COLUMN SYSTEM - POSSIBLE STRIP RATES

65C	70C	75C	80C	85C
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246
0.133	0.139	0.165	0.190	0.246

Note that this table also includes the possible strip rates for a three and four column system, based on the stripping estimates for a 25 g/L Fe solution (see Appendix X). In a three column system, one column is used for stripping, whereas in a four column system, two columns would be used for stripping. Therefore, the possible stripping rate of iron from resin in a four column system is double that for the three column system.

APPENDIX XIII: PROCESS FLOWSHEETS FOR EACH PORTION OF IX CYCLE

Process Flowsheet for Iron Ion Exchange at CRED - LOADING STEP







