

SELECTIVE AMMONIACAL ELUTION OF NICKEL AND COBALT FROM IMINODIACETATE CATION EXCHANGE RESIN

By

P. Littlejohn and J. Vaughan

School of Chemical Engineering – Metallurgy Program, The University of
Queensland, Australia

Presented by

Patrick Littlejohn

patrick.littlejohn@uqconnect.edu.au

CONTENTS

1. INTRODUCTION AND BACKGROUND
2. EXPERIMENTAL METHOD AND RESULTS
3. DISCUSSION
4. FUTURE WORK
5. CONCLUSION
6. REFERENCES

1. INTRODUCTION AND BACKGROUND

1.1 RESIN IN PULP

Over the last several years resin-in-pulp (RIP) processes have gained attention as a potential method to improve the efficiency of nickel operations^[1]. The RIP process involves contacting ion exchange resin with nickel laterite leach slurry at conditions where the valuable metals load onto the resin. The resin is subsequently separated from the slurry by screening. This is possible because the slurry particles are much finer than the large resin beads. There are two potential applications of RIP in the nickel industry. One is to use RIP to scavenge nickel and cobalt from tailings ponds or from counter-current decantation (CCD) underflow^{[2][3][4][5]}. The second more ambitious possibility is to use RIP to treat the whole leach slurry. This would enable a significant reduction or even elimination of the CCD circuit^[6]. There have been efforts by industry to advance nickel RIP. Resin manufacturers have been tailoring resin for the purpose and mining companies have invested in demonstrating the technology^{[7][8][9]}.

To date, the focus of the majority of resin elution work has been metal recovery via acid contact (usually H₂SO₄). It is difficult to effectively separate impurity metals from nickel and cobalt using an acid elution because strong acid is not a selective eluent. Nickel and cobalt are both readily soluble in ammonia solutions due to the high stability of their ammine complexes. The solubility of relevant impurities such as Al, Fe, Ca, Mn, and Mg are much lower. By contacting loaded resin with ammoniacal eluents this chemistry can be exploited in order to carry out a much more selective strip.

1.2 RESIN CHARACTERISTICS

For this study Lewatit MonoPlus TP207XL resin was used. This is a monosize variant of a micro/macroporous iminodiacetic resin with a dvb-styrene matrix. The Lewatit MonoPlus TP207XL variant is designed specifically for resin-in-pulp, with wet sodium form resin beads in the 700-800 micron diameter range. The selectivity of the resin is roughly in the following order but can vary depending on how the selectivity experiment is conducted, the pH, and ion concentration:

Cu, Fe(III) > Ni, Al(III) > Fe(II) > Co > Mn > Ca > Mg > Na

A sample of the loaded resin was analyzed using an SEM. The resin was prepared by thoroughly drying it at room temperature and then contacting it with liquid nitrogen. Some of the resin was fractured by striking it with a small hammer and some was left as intact spheres. The resin was then mounted on a stub via sticky carbon and lightly coated with platinum to avoid surface charging. The following micrographs were taken using a JEOL JSM6610 SEM. In Figure 1 the resin bead is fractured due to rapid cooling on contact with liquid nitrogen.

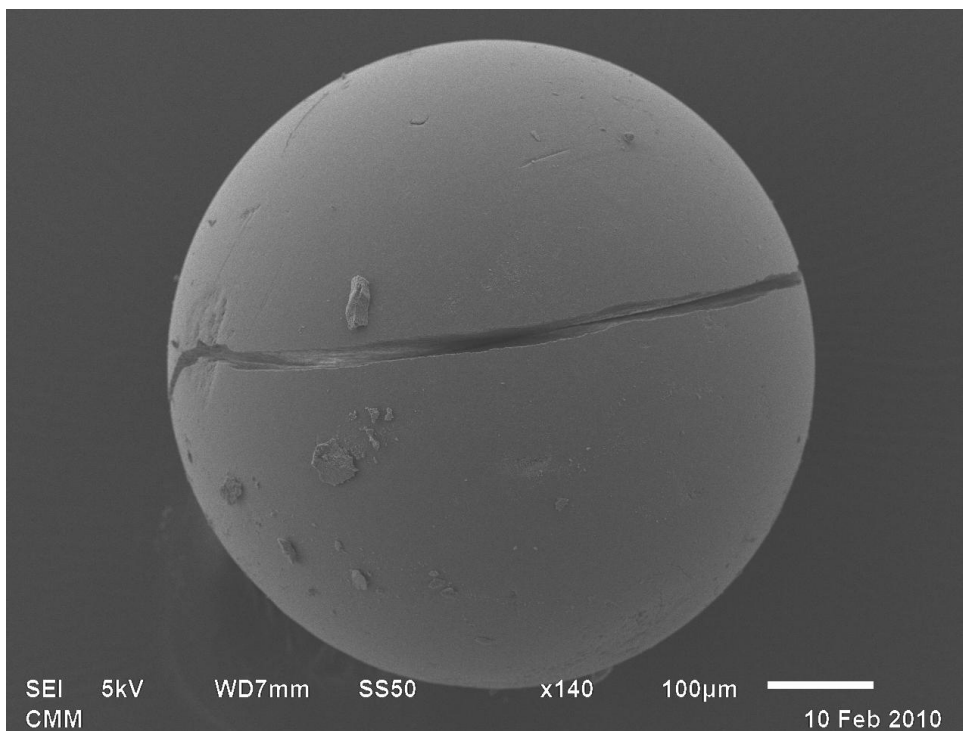


Figure 1 – Single Ni loaded Lewatit MonoPlus TP207XL bead, frozen with liquid N₂ and platinum coated

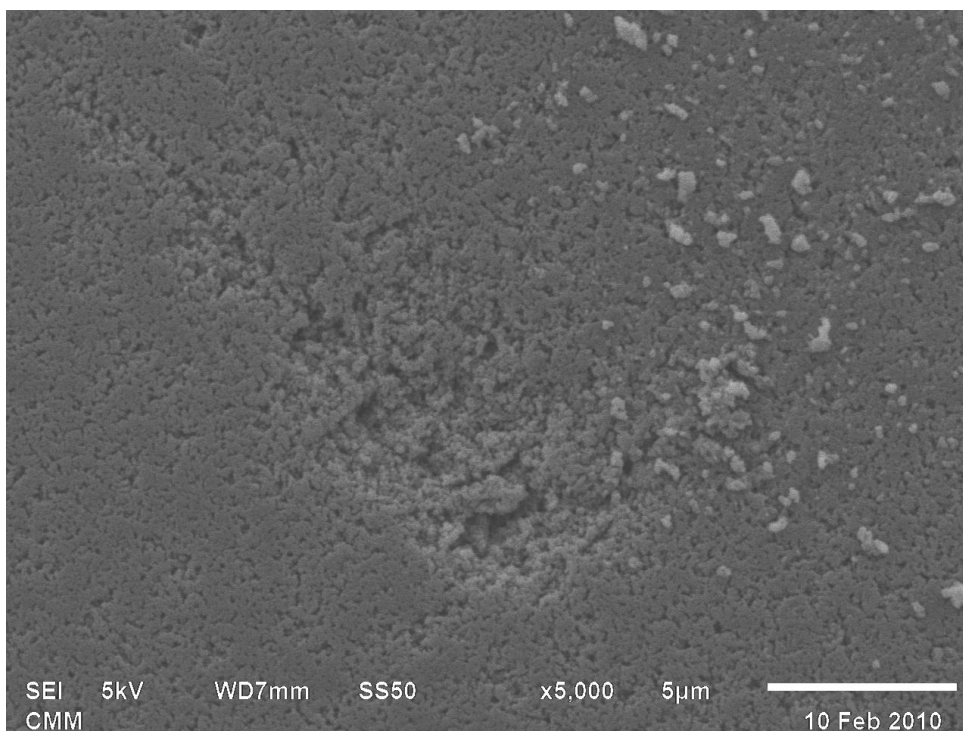


Figure 2 - Porous surface of a Ni loaded Lewatit MonoPlus TP207XL bead, frozen with liquid N₂ and platinum coated

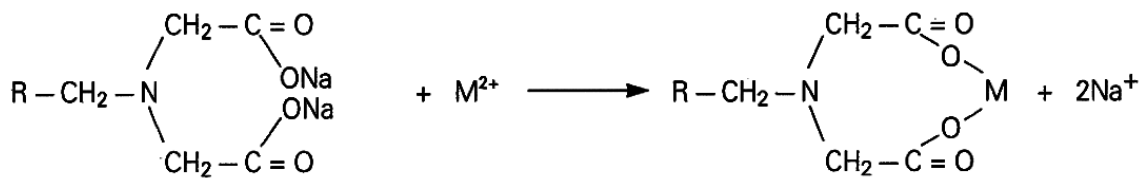
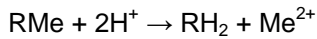
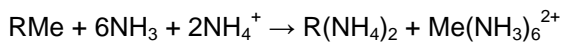


Figure 3 – Chelating cation exchange reaction for the iminodiacetic functional group, exchanging a bivalent metal cation for two sodium ions

The chemistry of acid elution in ion exchange shown in Figure 3 can be simplified as follows, where R is the iminodiacetic functional group ($-\text{N}(\text{CH}_2)_2(\text{COO})_2^{2-}$) and Me^{2+} is the metal ion.



Similarly, in elution using ammonium, where NH_4^+ acts as the counterion and NH_3 complexes the metal. The metal is shown here forming a hexamine complex:



Additionally, the counterion can be a different metal ion. For example at the back end of a loading train where the slurry is nearly void of nickel the resin will initially load magnesium and calcium. As the resin progresses up the loading train and the concentration of nickel increases, the magnesium and calcium will gradually be crowded off by the cobalt and nickel. The extent to which metals are crowded off are primarily due to the resin selectivity and solution concentrations. Also in an operation where throughput is being maximized the loading kinetics will also have some influence.

2. EXPERIMENTAL METHOD AND RESULTS

2.1 RESIN

Ion exchange resins typically change volume as they absorb water. The volume also change as a function of the loaded ions, with metals such as nickel or magnesium being larger than protons. In addition, the volume of resin in a column will depend on how tightly packed the spheres are. In this work resin volume will always refer to tapped wet settled resin volume (twsr). This was done by placing the wet resin in a graduated cylinder and tapping the cylinder until there was no noticeable change in total resin volume. The form of the resin loading will be explicitly stated as protonated (H⁺ form), metal form (referring to the RIP resin loaded predominantly with nickel) or nickel form (referring to the synthetically loaded pure nickel resin).

One batch of nickel loaded resin was prepared during the course of this work. 1 L of sodium form Lewatit MonoPlus TP207XL resin was contacted with 2 L of 150 g/L H₂SO₄ solution to change it to the proton form. The resin was lightly agitated in a reactor for 24 hours at room temperature and was then separated and thoroughly rinsed. The protonated resin was then contacted with 2 L of solution containing 32.5 g/L nickel for 24 hours. This insured that even after the nickel loaded to max capacity the resin would be in contact with a 10 g/L Ni solution. The pH of this solution was adjusted with NaOH as protons were exchanged for Ni(II) ions. The final pH of the Ni load solution was 5.5. The loaded resin was roughly 5% larger by volume than the protonated resin. The loaded resin contained 50.3 g Ni/L (Ni Form), equivalent to 51.8 g/L (H Form).

In addition, one industrially loaded resin was used. This was Lewatit MonoPlus TP207XL loaded in a resin-in-pulp by contacting with a neutralized nickel laterite leach slurry (Donated by BHP Billiton SSM). As it was loaded in a real leach slurry, the resin also loaded cobalt and other impurities listed in Table 1. All resin assays were conducted by stripping 5 mL of resin with 100 mL of 100 g/L HCl for 24 hours at 50°C. All solutions were analyzed by atomic adsorption spectrometry (AAS) and/or inductively coupled plasma mass spectroscopy (ICP-MS).

Table 1 - Resin Assays

g/L _{twsr} (H form)	Ni	Co	Mn	Ca	Mg	Cr	Cu	Fe	Al
RIP Resin	41.58	0.69	1.06	1.11	3.48	0.01	0.01	0.06	0.05
Synthetic Resin	51.84	-	-	-	-	-	-	-	-

2.2 EQUILIBRIUM ISOTHERMS

As part of the initial scoping of this problem, two ammonia eluent solutions were tested. Each eluent was designed to be similar to the ammoniacal leach liquors in the Yabulu and the Kwinana nickel refineries, respectively. Table 2 shows the composition of each eluent. The resin used was the industrially loaded RIP resin as shown in Table 1.

Table 2 – Isotherm eluent composition

	Yabulu	Kwinana
Anion	Carbonate	Sulphate
NH₃ g/L	65.9	38.3
NH₄ g/L	30.3	60.4
pH	9.5	9.0

For each point, 2 to 80 mL of metal loaded resin was contacted with 100 mL of eluent for 24 hours at 30C in temperature controlled rotating flask shaker. The eluate was collected and a sample of resin also stripped with HCl to complete the mass balance. The solution (and any precipitate, if present) was separated from the resin. If precipitate was present a sample was dried and weighed, dissolved in 100 g/L HCl and analyzed using AAS. Hydrochloric was used as an analytical eluent to ensure that gypsum was not formed which is a possibility if sulfuric acid is used.

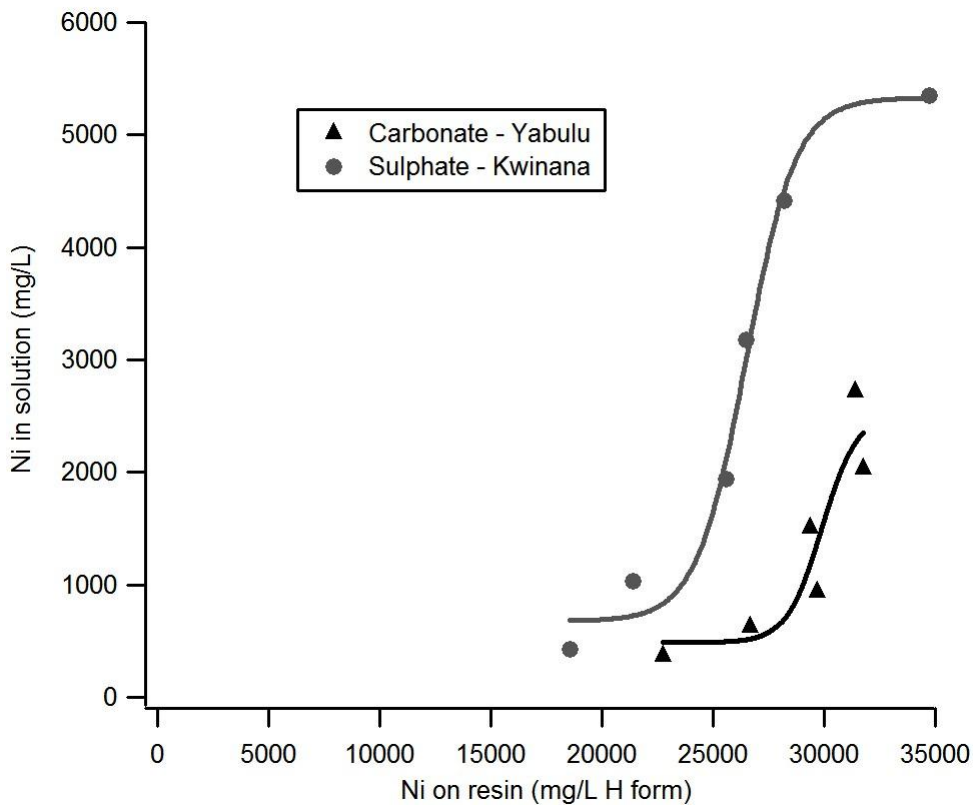


Figure 4 - Ammoniacal elution isotherms for the sulphate (Kwinana) and carbonate (Yabulu) systems

During the course of producing these isotherms, precipitates formed in each of the carbonate flasks once the amount of resin exceeded 2 mL, making the solution cloudy and opaque. AAS analysis of dissolved precipitate showed the metals were predominantly Mg and Ca with a small fraction of a Mn. When the dried precipitates were contacted with acid there was significant production of bubbles, indicating that they were at least in part carbonate rather than hydroxide precipitates.

It was clear from these tests that precipitation was much more significant in the carbonate system than the sulphate system. Although some of this difference in behaviour could be due to the higher pH of the carbonate system versus the sulphate system, the intrinsic solubility of carbonate salts in aqueous solutions is much lower, as shown in Table 3.

Table 3 – Solubility products of carbonate and sulphate salts in water at 25°C^[10]

Compound	K_{sp} (in H ₂ O, 25C)
CaCO ₃	0.9×10^{-8}
CaSO ₄	4.9×10^{-5}
MnCO ₃	9.0×10^{-11}
MnSO ₄	6.8
MgCO ₃	2.6×10^{-5}
MgSO ₄	4.5

As the solubility of the carbonates are lower than the sulphates by several orders of magnitude, it is unsurprising that precipitates are forming. It is unclear if the recovery of nickel in carbonate eluents is being limited by precipitation or if there are other factors. When the carbonate isotherm was rerun using pure Ni loaded synthetic resin rather than impure RIP resin the recovery did not improve, indicating that if precipitation is the cause of the problem, it is occurring even with nickel alone and is not specifically due to Ca and Mg.

The solutions from these isotherms were also analyzed for the presence of other impurity elements in order to see the recovery of undesirable metals in the ammonia system. The following two figures (Figure 5 and Figure 6) show the relative amounts of metal stripped using 100 g/L HCl and the two ammonia eluents. Nickel extraction in the tests shown was 47% for the sulphate eluent and 28% for

the carbonate eluent. Cobalt extraction was 19% and 48% for the sulphate and carbonate eluents, respectively.

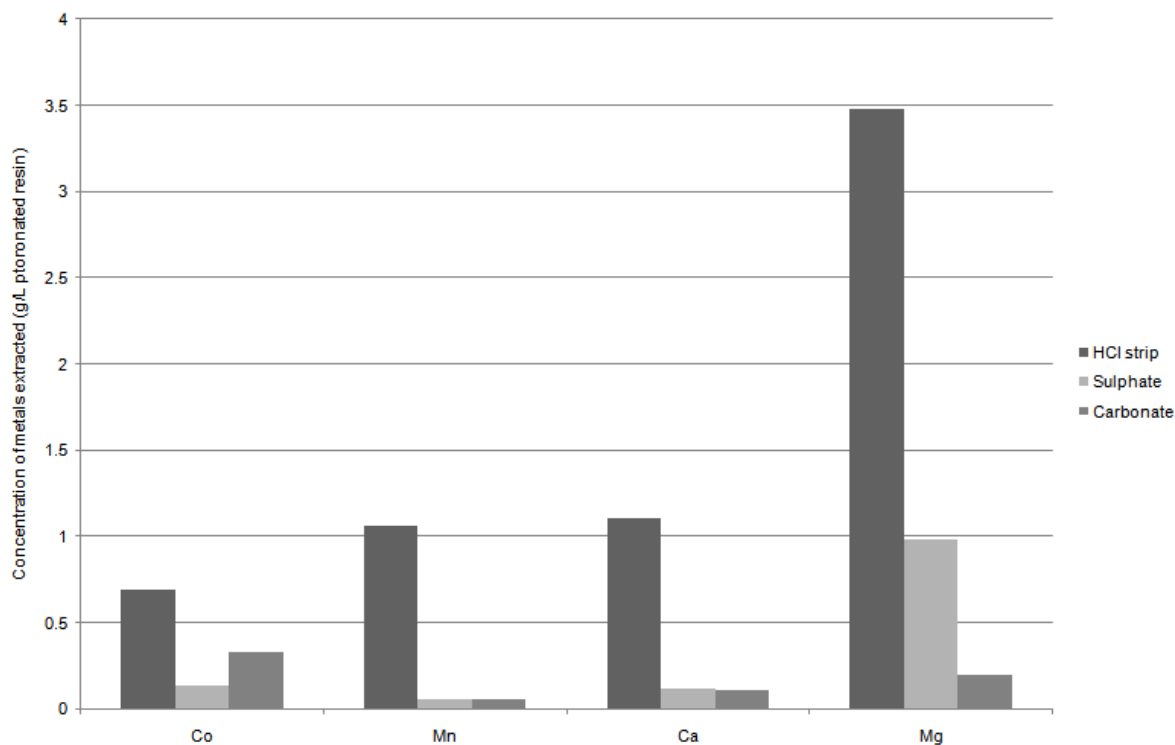


Figure 5 - Extraction of minor constituents in HCl vs $\text{NH}_3\text{-SO}_4$ and $\text{NH}_3\text{-CO}_3$ – Co, Mn, Ca, Mg

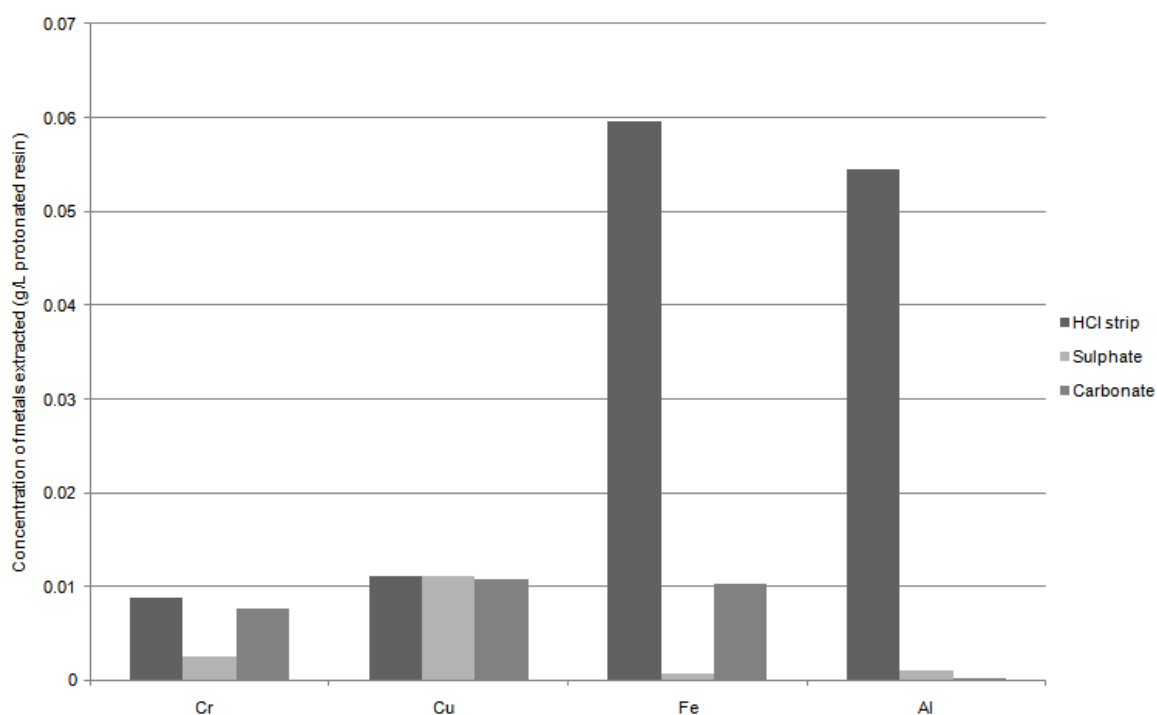


Figure 6 - Extraction of minor constituents in HCl vs $\text{NH}_3\text{-SO}_4$ and $\text{NH}_3\text{-CO}_3$ – Cr, Cu, Fe, Al

It can be seen in these figures that Al, Mn and Ca extraction are all very limited in ammonia based eluents. Copper is easily extracted in ammonia because of the stability of copper-ammonia complexes. Chromium and iron are extracted more in ammonia-carbonate than ammonia-sulphate, but the extraction of both are still quite limited compared to the HCl system. Magnesium is extracted more in the ammonia-sulphate system than the carbonate but a significant portion still remains on the resin compared to the acid system.

2.3 ELUENT COMPOSITION

In order to determine the optimal eluent composition in terms of ammonia and ammonium, nine equilibrium tests were run. In each experiment, 5 mL of metal loaded synthetic resin was contacted with 100 mL of eluent for 24 hours at 25°C. After the resin was separated from the solution and stripped using 100 mL of 100 g/L HCl and both solutions were analyzed using AAS. As can be seen in Figure 7, it was found that increasing the concentration of both NH_3 and NH_4^+ led to a significant improvement in recovery. The strip efficiency was not obviously limited by NH_3 over NH_4^+ or vice versa. Both are needed to drive the strip reaction – NH_4^+ to act as a counterion, and NH_3 to complex the nickel and cobalt in solution. The maximum nickel extraction of 88% occurred through use of an eluent with an added divalent metal salt as detailed in the next section (MgSO_4).

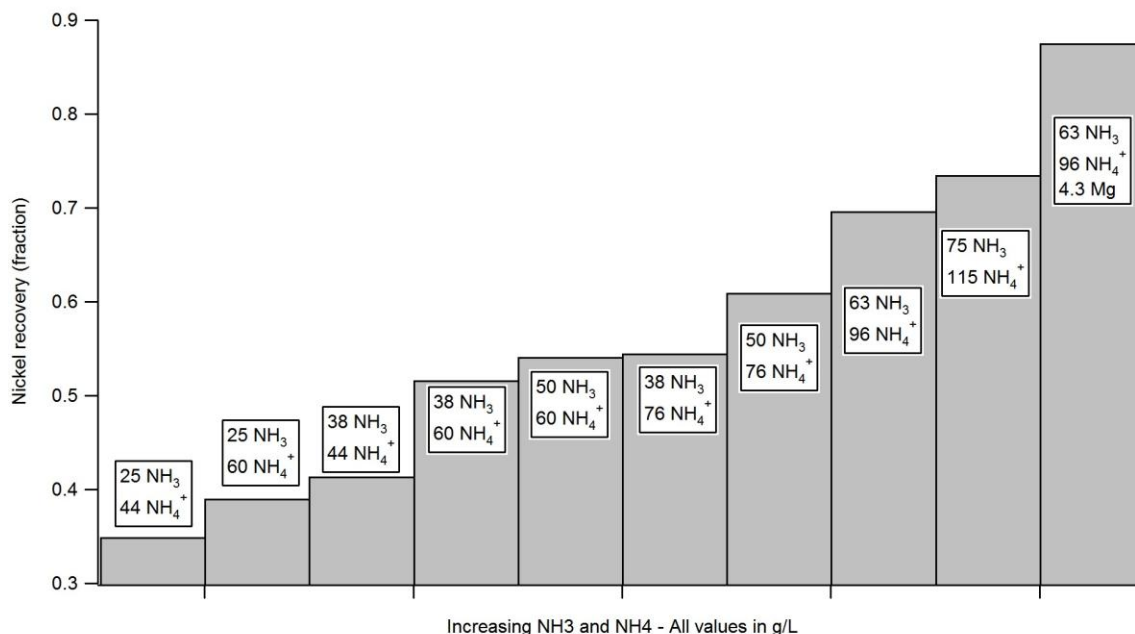


Figure 7 - Effect of ammonia/ammonium concentration in the sulphate system. 5 mL loaded resin, 100 mL eluent, 25C, 24 h residence time.

To investigate the effect of the presence of other counterions than NH_4^+ , several tests were conducted with small amounts of additional sulphate salts. The results are shown in Figure 8. The three salts utilized for this purpose in this work were $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, anhydrous CaSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. All 3 salts were found to have a positive effect on nickel recovery, in particular Mn and Mg. However, Ca and Mn tended to precipitate. A significant portion of the CaSO_4 did not dissolve to begin with, while the MnSO_4 initially dissolved but then reprecipitated. Mg was equally effective as Mn but did not reprecipitate. By increasing the Mg concentration to the solubility limit, the Ni recovery was further improved.

Nickel and cobalt extraction were greatly increased from the isotherm results presented in Section 2.2 through the optimization of eluent composition. In the baseline mock Kwinana solution (38.3 g/L NH_3 and 60.4 g/L NH_4^+ , as shown in Figure 4) the equilibrium extraction from 5 mL of loaded resin in 100 mL of eluent was 47% and 19% for Ni and Co, respectively. With optimized ammonia-ammonium levels (63 g/L NH_3 and 96 g/L NH_4^+) extraction improved to 70% and 42% for Ni and Co respectively. With the addition of 4.3 g/L Mg as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ to the same eluent, extraction of Ni and Co improved to 88% and 80%, respectively.

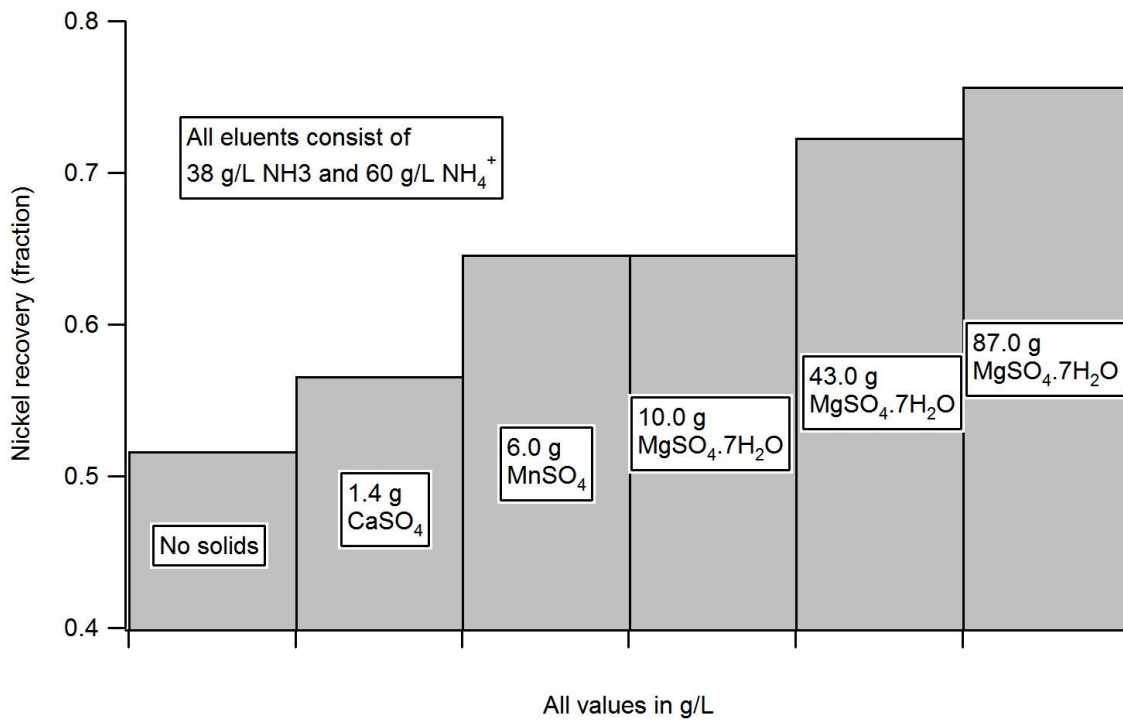


Figure 8 - Effect of additional salts in the sulphate system, 5 mL loaded resin, 100 mL eluent, 25C, 24 h residence time.

2.4 KINETICS

In order to compare the kinetics of ammonia elution versus acid elution, two shake flask tests were run simultaneously. 5 mL of RIP loaded resin was contacted with 100 mL of each eluent. The acidic stream was 10 g/L HCl and the ammoniacal stream was 63 g/L NH₃, 96 g/L NH₄⁺ as (NH₄)₂SO₄, and 4.3 g/L Mg as MgSO₄. This composition of eluent was chosen so that each would have approximately the same equilibrium nickel recovery. Small samples (250 µL) of solution were withdrawn at intervals for analysis. For the acidic eluent only Ni concentration was determined (because there was no Mg in the system) while for the ammoniacal eluent both Ni and Mg were tracked.

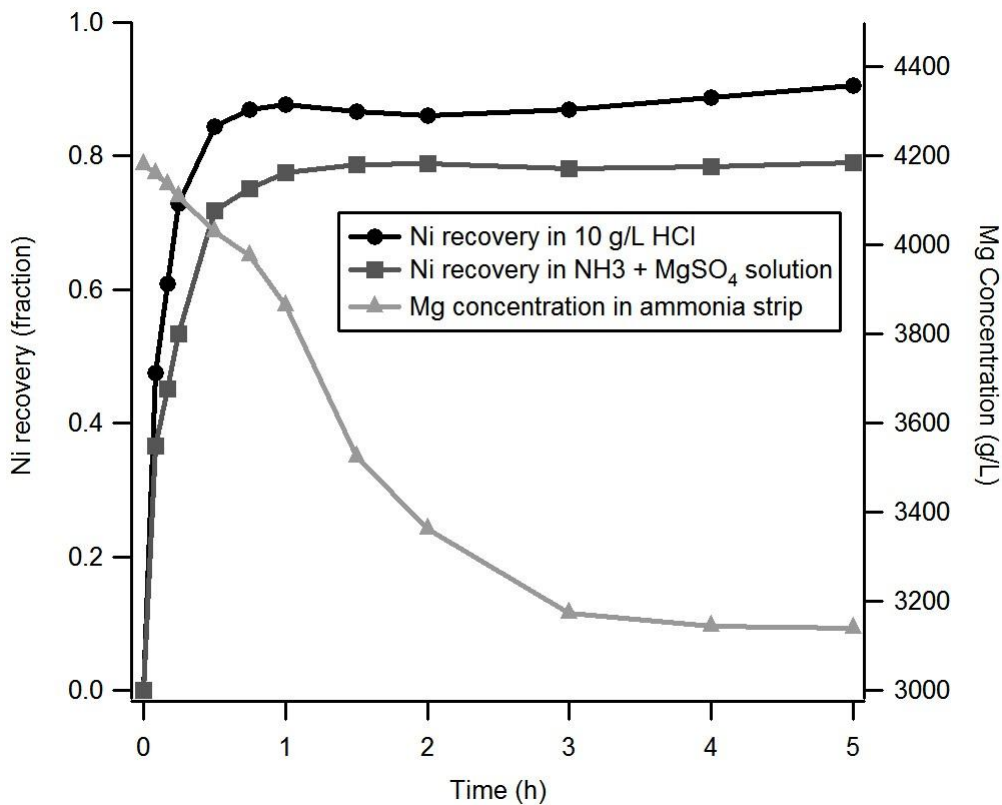
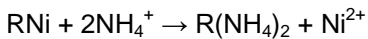


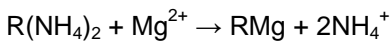
Figure 9 - Kinetics of ammonia-ammonium-magnesium-sulphate elution vs HCl elution

In both cases, the peak concentration of nickel was reached in under 2 hours. The acidic strip was notably faster, hitting 90% of the peak value in 30 minutes while the equivalent point took 60 minutes in the ammoniacal system.

It is worth noting that the magnesium curve in Figure 9 continues to decrease even after the peak nickel concentration has been reached. The only two counterions in this test are NH_4^+ and Mg^{2+} . The rapid increase in nickel recovery followed by the gradual decrease in magnesium concentration implies two reactions. First, the rapid exchange of nickel for ammonium:



Followed by the slower exchange of ammonium for magnesium:



It is unsurprising that ammonium is readily displaced for magnesium because the selectivity of the resin for univalent ions is considerably lower than bivalent ions.

2.5 COLUMN TESTING

Once preliminary scoping work was done, one column test was run to see a full strip profile. 200 mL of synthetic nickel loaded Lewatit MonoPlus TP207XL was set in a column and a solution of 63 g/L NH_3 , 96 g/L NH_4^+ as $(\text{NH}_4)_2\text{SO}_4$, and 4.3 g/L Mg as MgSO_4 was prepared. The column and eluent reservoir were sealed to avoid ammonia losses through evaporation. The eluent flowrate of 0.5 Bed Volumes (BV) / hour using a peristaltic pump, with the rate controlled by adjusting the spigot at the bottom of the column. Eluate samples were collected for analysis every 0.25 BV. Once the eluate turned clear the column was rinsed with 30 BV of de-ionized water and the resin was collected. A composite sample of the resin was stripped using HCl to confirm the extent of elution and magnesium loading.

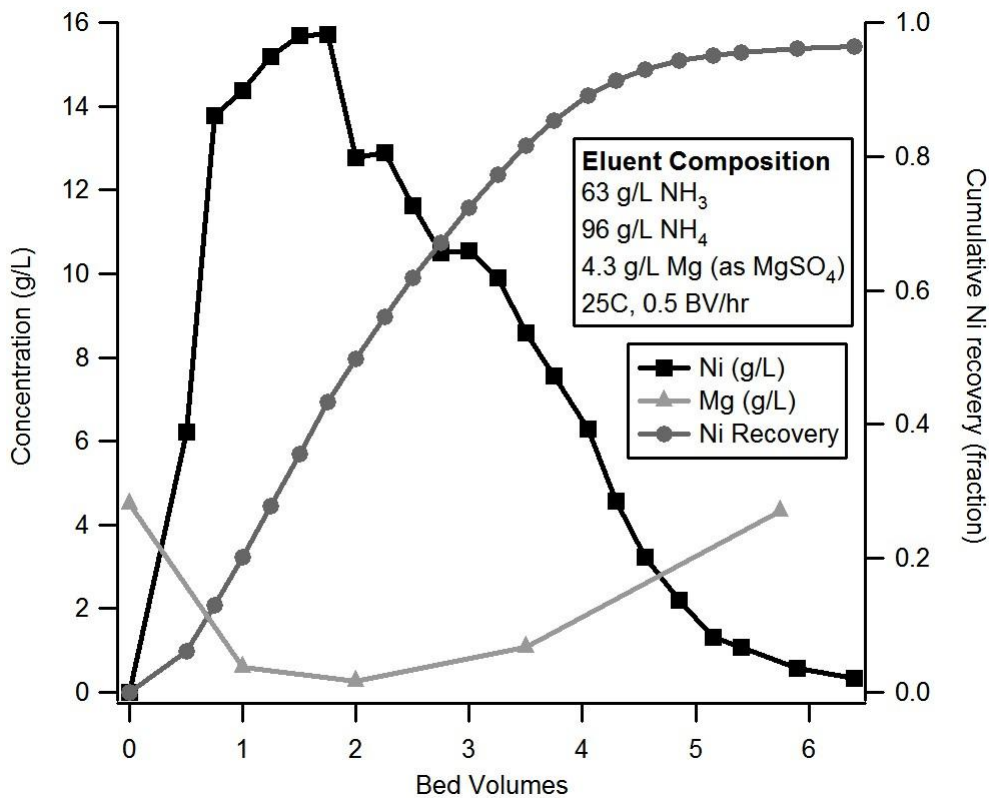


Figure 10 - Column test results. 200 mL Ni loaded Lewatit MonoPlus TP207XL, 1BV = 200 mL, 0.5 BV/hr, 25C

The results of the column test were quite positive. The peak concentration of the eluate was just shy of 16 g/L nickel, with 3 bed volumes containing greater than 10 g/L nickel. Roughly 97% of the nickel in the column was recovered after 6 BVs. The magnesium curve in the eluate is approximately the inverse of the nickel curve, as magnesium is replacing ammonium on the resin which in turn replaces nickel. By the end of the experiment when very little nickel was in the eluate, the concentration of magnesium was 95% of its concentration in the starting eluent.

Stripping a composite sample of the eluted resin from the column confirmed the high nickel recovery and also showed that there was no ammonium left on the resin. In terms of charge equivalence, approximately 100% of the nickel was replaced by magnesium. This synthetic loaded resin contained only nickel with no cobalt, so no information on cobalt column stripping behaviour was obtained from this test.

The curve of an ammoniacal strip column can be compared that of an acidic strip column in Figure 11 and Figure 12. The peak of the H₂SO₄ curve is both more concentrated and narrower than the ammoniacal eluent, but the two are comparable.

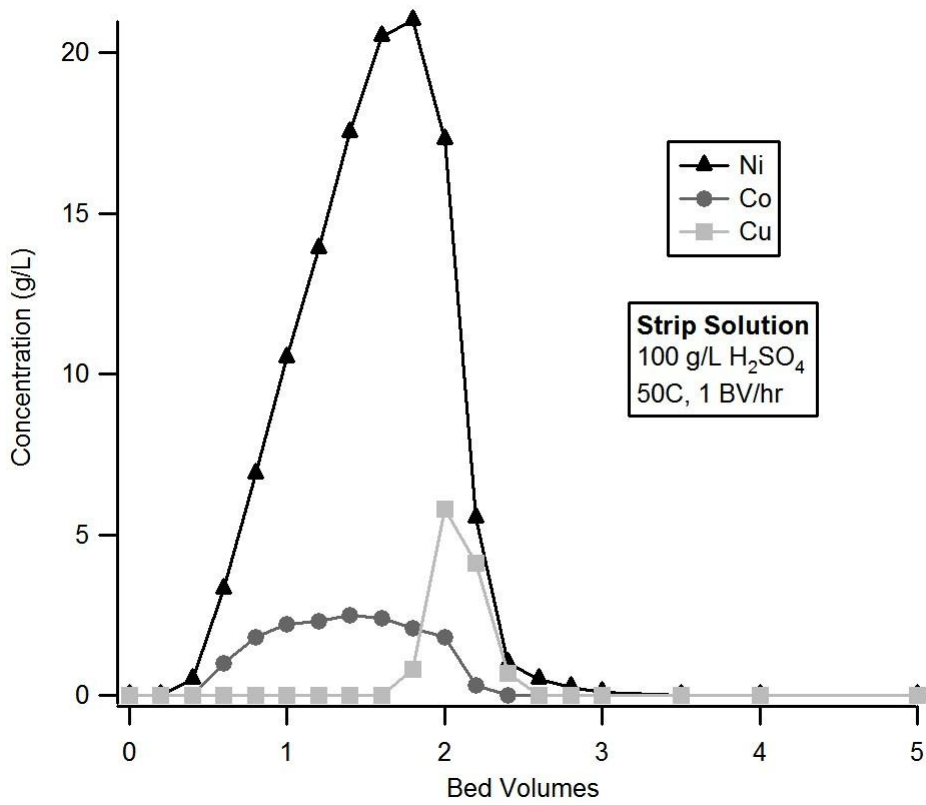


Figure 11 - Elution of a loaded iminodiacetate resin column using 100 g/L H₂SO₄ at 50C, 1 BV/hr^[3]

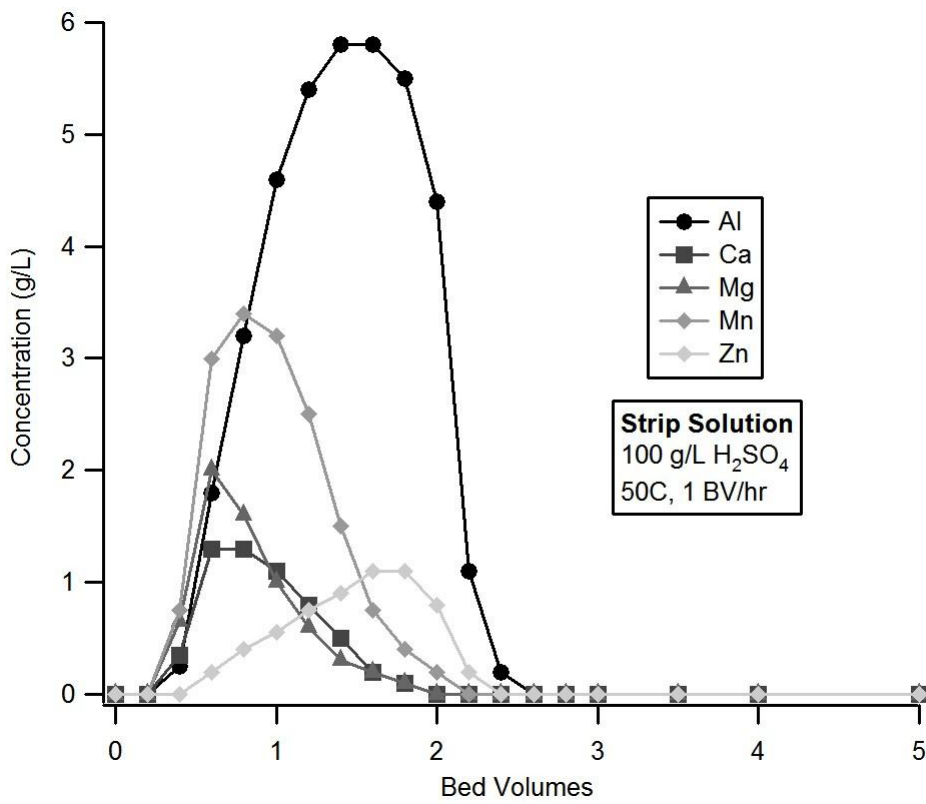


Figure 12 - Elution of a loaded iminodiacetate resin column using 100 g/L H₂SO₄ at 50C, 1BV/hr^[3]

3. DISCUSSION

High nickel and cobalt extraction was achieved in both batch and column tests using an eluent mixture of ammonia, ammonium sulphate and magnesium sulphate. Magnesium was very effective as an additional counterion as the resin is more selective for bivalent cations (Mg^{2+} , Ca^{2+} , Mn^{2+}) than univalent cations (NH_4^+ , H^+ , Na^+). In the sulphate system where magnesium has a high solubility this was particularly effective.

In the carbonate system, the recovery was not improved through the addition of solid $MgCO_3$ because of the very low solubility of $MgCO_3$. Without dissolved magnesium in the solution there is no driving force for the exchange of nickel or ammonium for magnesium. The results from the equivalent eluent in the ammonia-ammonium carbonate system was less impressive, both with synthetic loaded resin and impure RIP resin. However, the carbonate system was not explored as fully as the more agreeable sulphate system.

The selectivity of the strip reaction was very high compared to HCl eluents. Where HCl gives a virtually quantitative strip of the resin including all impurity metals, the ammoniacal strip recovery of Fe, Al, Mn, Ca, Mg, and Cr is one to two orders of magnitude less based on batch equilibrium tests. The behaviour of impurities in a column test of RIP resin remains to be seen.

The kinetics of ammoniacal stripping are slower than HCl elution but still comparable. This is unsurprising since the mobility of the proton is higher than the NH_4^+ counterion and the NH_3 complexation ion.

Column testing showed that while the peak of an ammoniacal stripping curve is fatter than that of acid, the peak concentration still exceeds 10 g/L Ni for 3 BVs. Through the use of counter current stripping of multiple columns, the production of a high tenor nickel stream while maintaining high total recovery seems reasonable.

Additionally, the use of magnesium as a counterion has positive implications for the design of an actual ammonia strip/resin-in-pulp process, because this would prevent NH_4^+ from being fed back into the resin loading cell. Instead, unwanted Mg^{2+} would return to the load cell with the resin. In an acid stripping process, barren resin would be protonated and thus would represent both a loss of acid as well as a adjustment to the pH of the loading cell as protons were exchanged for new metal.

4. FUTURE WORK

Increasing the concentration of magnesium in the eluent may improve kinetics and/or ultimate recovery of nickel. This could be accomplished by stripping at a higher temperature and increasing the concentration of magnesium. It is worth noting that stripping at higher temperature without increasing the concentration of magnesium may have the opposite effect because increasing stability of magnesium in solution will lower the driving force of the exchange reaction. It is possible that by lowering the pH of the solution more Mg could be dissolved, but this will alter the ratio of NH_3 - NH_4^+ as well.

The problems of precipitation in the carbonate system must be thoroughly analyzed in order to see if the precipitation reaction is what is causing relatively low Ni recovery. Analyzing individual beads using SEM and microprobe techniques will hopefully illuminate this problem. If other intrinsic chemical factors are at work adjusting the composition of the strip solution may improve recovery.

Additionally, we will investigate the ammonia stripping behaviour of other nickel loaded resins, including different resin bead sizes of Lewatit MonoPlus TP207XL as well as other resins with alternative functionality such as Dow 4195 and Lewatit MonoPlus TP 220.

Throughout this work the focus has been on nickel rather than nickel and cobalt as the synthetic resin was solely loaded with nickel. Batch results show that cobalt has similar stripping behaviour in this system as nickel, but fully exploring both elements will be a priority in the future.

5. CONCLUSIONS

In this work the ammoniacal elution of nickel and cobalt loaded Lewatit MonoPlus TP207XL iminodiacetic ion exchange resin was investigated in the carbonate and sulphate systems. Through the course of this scoping study it was shown that high nickel and cobalt recovery can be achieved through the ammoniacal elution of synthetic nickel resin as well as impure RIP resin. The sulphate system in particular was amenable to this process. High concentrations of ammonium and ammonia are needed to drive the ion exchange reaction and the complexation reaction, respectively. The addition of bivalent metal salts, in particular magnesium, had a strong positive effect on nickel and cobalt recovery, with 88% and 80% recovery respectively in batch shake flask tests using optimized eluent. Selectivity of nickel and cobalt over undesirable metals such as Fe, Al, Ca, Mn, Mg and Cr was high. Cu was extracted in the ammonia liquor because of its stability as an ammonia complex. In a column test, synthetic nickel loaded resin was stripped to 97% recovery in 6 BVs, achieving a peak concentration of 16 g/L Ni. During this column strip, all of the nickel was ultimately replaced by magnesium.

Although there is much left to do, this work suggests that the use of ammoniacal eluents for nickel resin-in-pulp applications is technically feasible and offers some potential advantages to acidic stripping. Important results were achieved in several key areas, such as selectivity, recovery, column strip behaviour, and kinetics.

The author of this work would like to acknowledge and thank Lanxess for providing samples of Lewatit MonoPlus TP207XL resin and BHP Biliton for providing a sample of RIP loaded resin.

6. REFERENCES

1. Taylor and Jansen 2000. "Future Trends in PAL Plant Design for Ni/Co Laterites," Proceedings of ALTA 2000.
2. Wyethe et al, 2002. "Cobalt, Nickel and Copper Recovery with Resin-in-Pulp," Proceedings of ALTA 2002.
3. Wassink et al. 2006. "Towards a Resin-in-Pulp Process for Recovery of Nickel and Cobalt from Laterite Leach Tailings: an Iminodiacetic Acid Ion Exchange Resin as a Prospective Resin," Proceedings of the International Water Conference 2006.
4. Adams, M. 2006. "Towards a Virtual Metallurgical Plant – CCD vs RIP Case Study," Proceedings of ALTA 2007.
5. Zainol and Nicol, 2009. "Comparative Study of Chelating Ion Exchange Resins for the Recovery of Nickel and Cobalt from Laterite Leach Tailings," Hydrometallurgy 96 (2009).
6. Zontov, 2001. "Potential Benefits of Resin-in-Pulp for PAL Plants," Proceedings of ALTA 2001.
7. Halle and Rossoni, 2005. "A New (Monodisperse) Chelating Resin Designed for Mining Application: Lewatit Monoplus TP 207," Proceedings of ALTA 2005.
8. Van Hege et al, 2006. "Recovery of Base Metals Using MetRIX," Proceedings of ALTA 2006.
9. Zainol and Nicol, 2009. "Ion-exchange equilibria of Ni(II), Co(II), Mn(II) and Mg(II) with iminodiacetic acid chelating resin Amberlite IRC 748," Hydrometallurgy 99 (2009).
10. Speight, J. "Lange's Handbook of Chemistry 16th Edition", McGraw-Hill 2005.