UNIVERSIDADE FEDERAL DE MINAS GERAIS
Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas

Tese de Doutorado

"Recuperação de Níquel e Cobalto a partir de Polpas de Lixiviação Ácida de Minério Laterítico pelo Emprego de Resinas Poliméricas de Troca Iônica"

Autora: Flávia Dutra Mendes
Orientador: Afonso Henriques Martins

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Flávia Dutra Mendes

RECUPERAÇÃO DE NÍQUEL E COBALTO A PARTIR DE POLPAS DE LIXIVIAÇÃO ÁCIDA DE MINÉRIO LATERÍTICO PELO EMPREGO DE RESINAS POLIMÉRICAS DE TROCA IÔNICA

Tese de Doutorado apresentada ao Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas da Universidade Federal de Minas Gerais

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Ao Victor, que neste período chegou nas nossas vidas,
deixando nossos sonhos ainda mais lindos
e nossos dias cada vez mais cheios de muita graça,
fantasia e incondicional amor.

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RESUMO

Essa tese de doutorado aborda a extração seletiva de níquel e cobalto contidos no efluente da lixiviação ácida sulfúrica sob pressão de minério laterítico de níquel, através da aplicação de resinas poliméricas de troca iônica. A metodologia proposta consistiu basicamente de seis etapas distintas. Primeiramente, foi avaliado um elenco de resinas poliméricas comerciais quelantes (Dowex M4195®, Amberlite IRC748®, Ionac SR-5® e Purolite S930®), selecionadas a partir de consulta à literatura. A resina Amberlite IRC 748® apresentou os melhores resultados para a adsorção seletiva e carregamento - base seca - de níquel (2,13 mmol Ni/g) e cobalto (0,13 mmol Co/g) a partir de soluções ácidas sulfúricas. Em seguida, foram estudados alguns parâmetros de processo que exercem influência na adsorção seletiva de níquel e cobalto empregando resinas quelantes, tais como, pH da solução aquosa, tipo de álcali para elevação do pH da polpa, temperatura, relação volume da solução/massa de resina e intensidade de agitação.

A próxima etapa consistiu da remoção seletiva de níquel e cobalto, de soluções ácidas contendo impurezas, utilizando-se uma coluna de adsorção com a resina Amberlite IRC748®. Os resultados experimentais mostraram que valores mais altos de pH, menores taxas de percolação e o aumento da concentração de níquel na solução melhoraram o desempenho e a seletividade da resina, e maiores capacidades de carregamento de níquel foram obtidas. Posteriormente, ensaios de resina em polpa, em batelada, foram realizados a fim de se avaliar o desempenho de adsorção de níquel pela resina Amberlite IRC748® em contato com polpa efluente de lixiviação ácida sob pressão. Os resultados mostraram recuperações de níquel e cobalto superiores a 99% após cinco estágios em contra corrente.

Para continuidade dos estudos, utilizou-se uma resina do tipo quelante, descrita neste texto por ResChe, com grupo funcional de ácido iminodiacético, similar à resina Amberlite IRC748®, para adsorção de níquel e cobalto da polpa de lixiviação em escala contínua. Três campanhas de 50 horas foram realizadas visando a recuperação de níquel e cobalto da polpa efluente de lixiviação ácida de um minério laterítico de níquel Brasileiro. Finalmente, foi realizado um estudo de caracterização da resina Amberlite IRC748®, através de espectroscopia Raman, para avaliação da forma de adsorção de níquel ao grupo funcional de ácido iminodiacético da resina.

ABSTRACT

This work aimed at the selective extraction of nickel and cobalt, from high pressure acid leach discharge pulp of a Brazilian nickel laterite ore, through the application of ion exchange technique with polymeric resins. The proposed methodology consisted basically of six different stages. Firstly, some chelating commercial polymeric resins were evaluated (Dowex M4195®, Amberlite IRC748®, Ionac SR-5® and Purolite S930®). The resin Amberlite IRC748® presented the best results of nickel (2,13 mmol Ni/g) and cobalt (0,13 mmol Co/g) sorption from acidic solutions. Second stage consisted of a study of some process parameters, that have influence on nickel and cobalt selective sorption through the application of chelating resins, such as solution pH, alkali addition for pulp pH increase, temperature, resin/solution ratio and agitation.

The next stage consisted of selective removal of nickel and cobalt from acidic impure solutions by applying column sorption with Amberlite IRC748®. The experimental results showed that lower flow rate values, higher pH and higher nickel concentration in the solution improved the performance of the ion exchanger, thus resulting in larger load nickel capacities. Later, resin-in-pulp batch tests were carried out in order to evaluate the nickel sorption performance of the chelating resin Amberlite IRC748® regarding its contact with high pressure acid leach discharge pulp. The results showed that it was achieved good nickel and cobalt recoveries from solution higher than 99% after five counter-current stages.

Fifth stage consisted of a resin-in-pulp evaluation for nickel and cobalt sorption in a continuous scale using a chelating resin, defined in this text as CheRes, containing an iminodiacetic acid group. Three campaigns of 50 hours each were accomplished to evaluate the technical viability of resin-in-pulp process concerning nickel and cobalt recovery from a Brazilian laterite ore. Finally, a characterization study of Amberlite IRC748® through Raman Spectroscopy was carried out for the evaluation of nickel species sorption onto the iminodiacetic acid functional group of the resin.

Capítulo 1 - Introdução

O *US Geological Survey* estima que as reservas de níquel identificadas no mundo, com teor médio de 1%, contabilizam um valor mínimo de 130 Mt de níquel. Desse total, 60% está contido em depósitos lateríticos e 40% em depósitos sulfetados. Em termos de produção industrial, entretanto, as proporções são contrárias, com 60% da produção oriunda de depósitos sulfetados. Diante dessa informação, nos últimos anos tem ocorrido um esforço crescente para se tirar proveito das lateritas sub-exploradas.

Baseando-se na taxa de crescimento histórica de 4% ao ano, o mercado global de níquel necessita de 40.000 - 50.000 toneladas de produção adicional a cada ano. As expansões das usinas existentes não seriam suficientes para suprir a demanda. Assim, o mercado requer a implantação de novos projetos, já que o ciclo da demanda do metal voltou a apresentar elevações, implicando num nível de inventário criticamente baixo e num repentino aumento de preços (Allan, 2004).

De acordo com Cook (2005), desde o final de 2001, o preço do níquel vem aumentando, atingindo um pico de US$17.770/t no início de 2004. Foi um ano de extrema instabilidade, com média histórica de US$13.823/t para o preço do níquel. Os especialistas esperam que os preços permaneçam altos e voláteis para todo o ano de 2005. O aumento dos preços (vide Figura 1.1) tem duas grandes causas: o lento crescimento da produção de níquel e o crescimento maciço do consumo chinês.

O cenário atual mostra que a combinação do lento crescimento da oferta e o rápido crescimento da demanda resultou em um declínio contínuo do estoque de níquel nos últimos anos, reduzindo a razão estoque-consumo para o seu nível histórico mais baixo. Além disso, os elevados preços do níquel e do cobalto têm levado a indústria do níquel a buscar alternativas de processos que possam reduzir os custos operacionais, para manter a rentabilidade do negócio em níveis de preços mais baixos para esses metais. Os fatores acima citados conciliados ao grande volume de depósitos lateríticos sub-explorados e à possibilidade de redução dos custos de extração e de obtenção de maiores rendimentos para estes depósitos têm motivado, não somente a maior utilização do minério de níquel de origem laterítica (maiores reservas), mas também a busca por tecnologias menos onerosas. As usinas que adotam o processo de lixiviação ácida sob pressão HPAL (High Pressure Acid Leaching), aplicado a minérios lateríticos, utilizam as opções tecnológicas de precipitação ou extração por solvente para a purificação das soluções. Entretanto, o processo HPAL conciliado a novas alternativas tecnológicas pode possibilitar a obtenção de níquel com grandes vantagens econômicas, em termos de custos de investimento e operacional. A tecnologia de troca iônica é uma opção na busca efetiva da redução de custos, onde as reais vantagens desse processo para minérios lateríticos podem afetar positivamente a competitividade da indústria do níquel (Andrade et al., 2000).

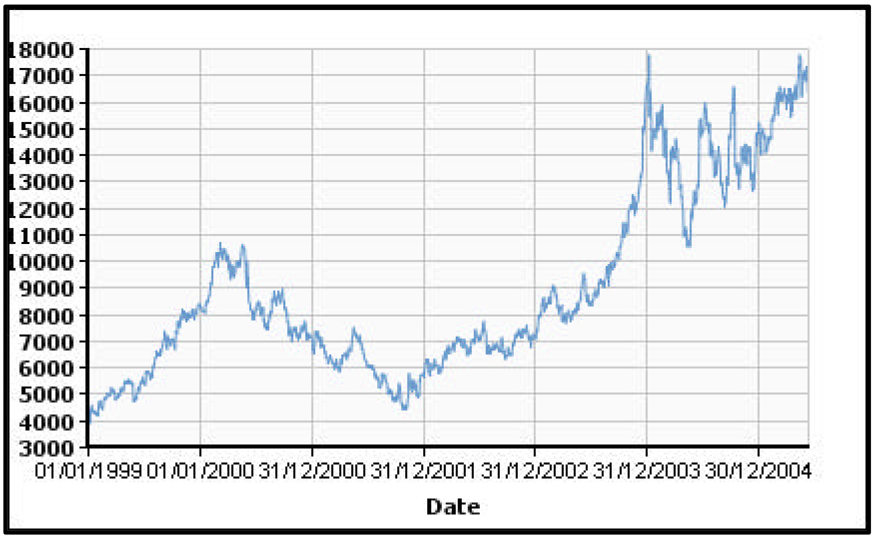

Figura 1.1 - Preço do níquel em US$/t (Fonte: London Metal Exchange)

As quatro usinas de beneficiamento de minério laterítico de níquel através de lixiviação sulfúrica sob pressão são Moa Bay, Cawse, Murrin Murrin e Bulong. A primeira localiza-se em Cuba e as demais na Austrália, sendo que a última encerrou suas atividades em 2003. Em todos os processos, adota-se uma etapa de decantação em contra-corrente para a lavagem de sólidos e separação sólido-líquido que envolve altos custos de capital e operacional. Além disso, esta etapa ocupa grandes áreas e consome quantidades significativas de água de lavagem. Visando melhorias e otimização do processo, uma opção, neste caso, seria o uso de um sistema de resina em polpa, empregado na recuperação de níquel e cobalto a partir da polpa lixiviada. Essa técnica ocasionaria a eliminação da etapa de decantação contra-corrente (Counter-Current Decantation - CCD), sem a necessidade do uso de espessadores. Além disso, resinas poliméricas de troca iônica são comercialmente disponíveis para a grande maioria dos processos de separação metálica. Aquelas do tipo quelante são exemplos de trocadores iônicos bastante eficientes na remoção seletiva de metais pesados, como níquel e cobalto, se comparado a outros trocadores. A sua aplicação pode fornecer uma purificação mais efetiva e simples comparada à purificação por precipitação ou extração por solventes, que são os métodos mais comumente usados para este propósito (Leinonen et al., 1994).

Estes resultados sugerem uma forte tendência à obtenção de um fluxograma robusto para tratamento de minérios lateríticos de níquel baseado na técnica de troca iônica com resinas poliméricas. Essa tecnologia apresenta o potencial de revolucionar todo o fluxograma de recuperação de níquel e cobalto para este tipo de minério, através da redução dos custos e maior eficiência do processo. O conceito principal envolve a substituição do circuito de CCD convencional pelo processo de resina em polpa. Este fato sugere que a polpa proveniente da lixiviação ácida sob pressão, após contactação com a resina e eluição dos elementos adsorvidos, deverá ser convertida em um licor rico com alta concentração de níquel e pureza, o qual poderá ser encaminhado ao estágio de eletrólise.

Assim, diante do potencial para a abertura de novos projetos para a produção de níquel a partir de minérios lateríticos com vantagens econômicas, a Companhia Vale do Rio Doce - CVRD iniciou, no ano de 2000, a avaliação da aplicação da tecnologia de lixiviação ácida sob pressão para vários depósitos de níquel laterítico, conciliada à aplicação de resina polimérica de troca iônica para recuperação de níquel. O objetivo principal foi avaliar, tecnicamente, uma resina capaz de recuperar, seletivamente, níquel e cobalto presentes no efluente da lixiviação sulfúrica ácida sob pressão de minério laterítico de níquel empregando a tecnologia de troca iônica. A obtenção de uma resina com estas características e a sua análise positiva quanto à seletividade e capacidade de carregamento para níquel e cobalto representa um grande estágio no desenvolvimento da técnica e posiciona a Companhia Vale do Rio Doce em nível diferenciado junto a comunidade de pesquisa tecnológica.

O estudo abordado nesta tese de Doutorado fez parte de um convênio entre a UFMG e a CVRD e toda a parte experimental foi realizada nos laboratórios de hidrometalurgia das instituições conveniadas. A primeira abordagem consistiu em avaliar várias resinas poliméricas, das quais aquela com maior grau de eficiência na extração de Ni/Co e seletividade em relação às impurezas foi posterior e detalhadamente estudada. (*Capítulo 4 - Adsorção seletiva de níquel e cobalto através da aplicação de resinas quelantes comerciais,* **Mendes,** F. D. and **Martins,** A. H.. **Selective sorption of nickel and cobalt from sulphate solutions using chelating resins.** *International Journal of Mineral Processing, Volume 74, Issues 1-4, 19 November 2004, Pages 359-371)*

Vários parâmetros do processo que exercem influência na recuperação de níquel e cobalto, tais como pH da solução aquosa, tipo de álcali para elevação do pH da polpa, temperatura de operação, relação volume de solução/massa de resina, agentes de eluição e intensidade de agitação, foram estudados e avaliadas as condições ótimas de operação para a obtenção da máxima extração de níquel e cobalto (*Capítulo 5 - Avaliação de parâmetros na adsorção seletiva de níquel e cobalto através de resinas poliméricas comerciais,* **Mendes**, F. D., **Martins**, A. H., **Costa**, R. S., **Selective sorption of nickel and cobalt from pressure acid leach discharge liquors using chelating resin**. *XXII International Mineral Processing Congress, XXII IMPC, 2003 - Cape Town – South Africa*).

Definidas a melhor opção de resina e as condições ótimas de operação, duas alternativas de processo foram abordadas:

- A primeira consistiu de um estudo da resina polimérica de troca iônica, Amberlite IRC 748®, aplicada à solução resultante da lixiviação sulfúrica sob pressão de minério laterítico. Para isso, fez-se uso de uma avaliação do processo de adsorção em colunas sob diversas condições (*Capítulo 6 - Recuperação seletiva de níquel e cobalto de solução HPAL usando coluna de resina de troca iônica,* **Mendes,** F.D. and **Martins,** A.H.. **Selective nickel and cobalt uptake from pressure sulfuric acid leach solutions**

using column resin sorption. *International Journal of Mineral Processing, Volume 77, Issue 1, September 2005, Pages 53-63*).

- Para a segunda abordagem, foram avaliadas:
    - a aplicação da resina Amberlite IRC 748® junto à polpa proveniente da lixiviação sulfúrica sob pressão em regime de batelada. *(Capítulo 7 - Recuperação seletiva de níquel e cobalto de polpa HPAL usando resina quelante de troca iônica.* **Mendes,** F.D. and **Martins,** A.H. **Recovery of nickel and cobalt from acid leach pulp by ion exchange using chelating resin** • *Minerals Engineering, Volume 18, Issue 9, August 2005, Pages 945-954);*

    - a aplicação da resina quelante CheRes, com grupo funcional ácido iminodiacético, junto à polpa proveniente da lixiviação sulfúrica sob pressão em regime contínuo. *(Capítulo 8 - Aplicação de resina de troca iônica em escala contínua para a recuperação de níquel e cobalto).* Neste estágio de desenvolvimento do trabalho, fez-se necessária a avaliação do processo de resina em polpa em escala contínua para a consolidação dos resultados. Para isso, foi contratada a empresa fabricante da resina quelante CheRes que dispunha de grande volume de resina e equipamentos compatíveis com a escala que se desejava trabalhar. As resinas CheRes e Amberlite IRC 748® apresentam em comum o grupo funcional ácido iminodiacético. Nesta etapa, foi possível avaliar a performance deste agente quelante, a base de ácido amino, na adsorção de níquel em polpa ácida, em regime contínuo.

Finalmente, a resina foi analisada através de espectroscopia Raman, após as etapas de adsorção e dessorção de níquel e cobalto, para se avaliar a influência da estrutura funcional da resina na adsorção seletiva dos íons Ni^{2+} através da formação de um composto do tipo quelato *(Capítulo 9 - Efeitos do carregamento de níquel na estrutura química da resina quelante Amberlite IRC 748 â)*

Capítulo 2 - Objetivos

Principal:

O objetivo principal desse trabalho experimental foi extrair, seletivamente, níquel e cobalto presentes no efluente da lixiviação ácida sulfúrica sob pressão de minério laterítico de níquel empregando resinas poliméricas de troca iônica.

Específicos:

- Seleção de uma resina polimérica com potencial de aplicação em um efluente de lixiviação ácida sulfúrica sob pressão para a extração seletiva de níquel e cobalto, a partir de um elenco de resinas quelantes de troca iônica comerciais disponíveis no mercado internacional.
- Avaliação do desempenho das resinas poliméricas selecionadas na etapa anterior - Amberlite IRC748® e Dowex M4195® - na adsorção de níquel da solução efluente de lixiviação ácida sulfúrica sob pressão e definição de valores ótimos dos principais parâmetros que influenciam na extração seletiva de níquel e cobalto.
- Estudo da recuperação de níquel e cobalto da solução efluente de lixiviação ácida sulfúrica sob pressão, empregando-se colunas de troca iônica com a resina Amberlite IRC748®. Este tipo de abordagem incluiu a avaliação da influência de vários parâmetros na eficiência de adsorção.
- Estudo da recuperação de níquel e cobalto da polpa efluente de lixiviação ácida sulfúrica sob pressão em escala contínua e em batelada, visando maximizar a recuperação seletiva de níquel e cobalto, através de resinas com grupo funcional de ácido iminodiacético - resinas CheRes e Amberlite IRC748®, respectivamente.
- Caracterização da resina polimérica de troca iônica Amberlite IRC748® através de Espectroscopia Raman, com o objetivo de se avaliar a adsorção das espécies Ni^{2+} no grupamento funcional (ácido iminodiacético) da resina.

Capítulo 3 - Revisão Bibliográfica

Unidades industriais que adotam o processo de lixiviação ácida sob pressão (HPAL) para a recuperação de Ni/Co laterítico

Há quarenta anos foi construída a primeira planta de lixiviação ácida sob pressão, *Moa Bay* – Cuba, para processamento de níquel laterítico. Posteriormente, três novas unidades industriais entraram em operação na Austrália: *Bulong, Cawse e Murrin Murrin*, sendo que a primeira, desde 2003, já não opera. Embora novos e modernos modelos de autoclaves e sistemas de regeneração de calor tenham sido adotados nos últimos anos, o conceito básico e atual de lixiviação sob pressão mantém-se inalterado ao longo de todos esses anos (Taylor e Jansen, 2000).

As principais diferenças entre as três unidades industriais australianas, bem como em relação a Moa Bay, se encontram na maneira em que o níquel e o cobalto são recuperados e refinados. A unidade de *Murrin Murrin* é a mais similar à unidade de *Moa Bay*. É caracterizada pela opção de precipitação de sulfetos, que acarreta numa estratégia prudente de operação em razão dos valores de investimento de capital e produção. *Bulong*, desenvolvida durante um longo período de tempo, adotou o processo direto de extração por solventes de forma a reduzir os custos de investimento. Neste caso, cobalto e níquel eram extraídos seqüencialmente da solução oriunda da etapa de lixiviação sob pressão. *Cawse*, por outro lado, optou pela precipitação de hidróxidos, seguida de re-lixiviação com amônia, a qual permitiu a aplicação posterior de uma etapa de extração por solventes do níquel (Taylor e Jansen, 2000; Dickson, 2000).

Usina Cawse

Cawse Nickel Refinery está localizada a 50 km a noroeste de Kalgoorlie, Austrália (Grassi et al., 2000). O processo de produção de *Cawse Nickel Refinery* (Doll, 2005), conforme apresentado na Figura 3.1, consiste do beneficiamento de uma fração de minério limonítico, com baixo teor de cobalto e manganês, juntamente com um minério de alto teor de cobalto, seletivamente lavrado, de forma a fornecer uma alimentação de alto teor para a lixiviação. Após 105 minutos de lixiviação ácida sob pressão a 250°C e 35% de sólidos, a polpa é neutralizada com calcário, onde a maioria dos íons férricos é precipitada, permanecendo ainda impurezas como manganês e íons ferrosos. Estes últimos são oxidados a íons férricos e removidos via precipitação com calcário em pH maior do que 5.0. Em seguida, a polpa é encaminhada à lavagem de sólidos e separação sólido-líquido, através de um circuito CCD de 6 estágios de espessadores em contra-corrente. A solução produzida encontra-se, então, adequada à precipitação de hidróxidos de Ni e Co através do uso de magnésia (MgO) e cal em duas etapas distintas.

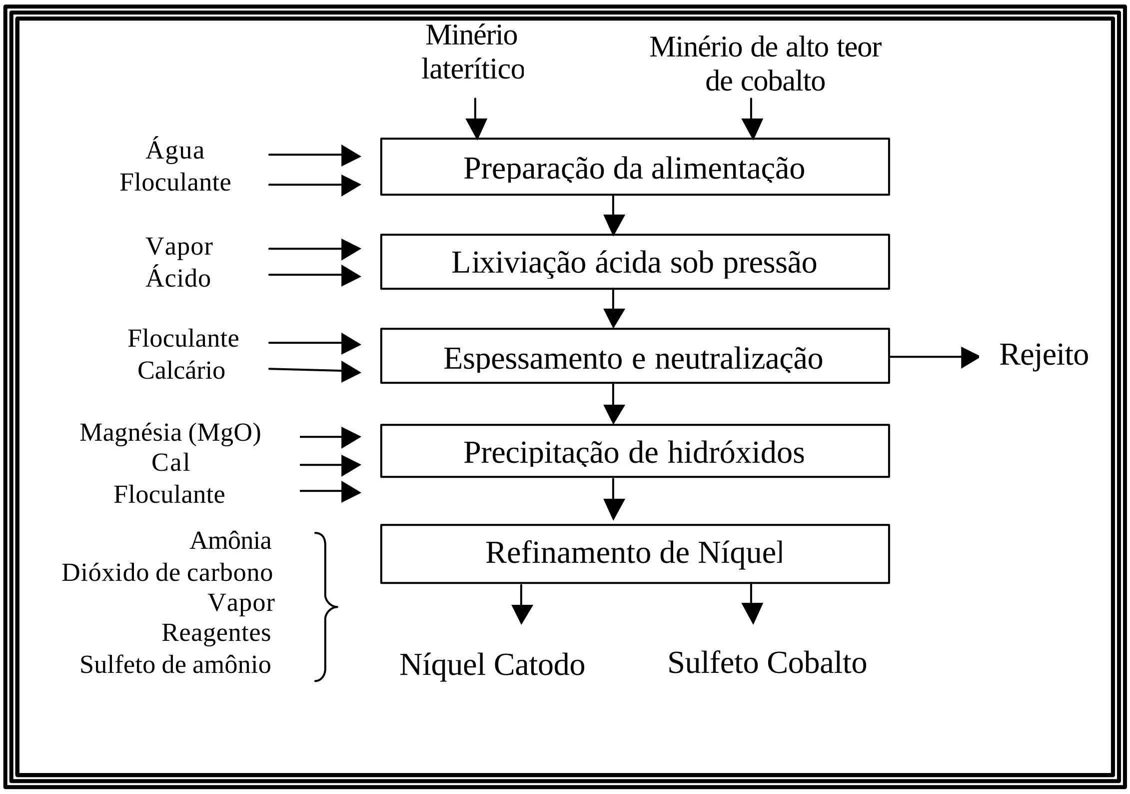

Figura 3.1 - Fluxograma de processo para *Cawse Nickel Refinery*

O hidróxido produzido é relixiviado com solução de carbonato de amônio, redissolvendo níquel e cobalto, com solubilização mínima de manganês, magnésio e ferro. A separação níquel-cobalto é alcançada através de extração por solventes, onde o extratante orgânico (LIX 84I) extrai o níquel e deixa o cobalto em solução. Níquel é produzido via eletrólise, enquanto cobalto é recuperado na forma de sulfeto precipitado com o uso de hidrosulfeto de sódio, para posterior refino.

Usina Bulong

Bulong Nickel and Cobalt Project está situada a 30 km ao leste de Kalgoorlie, na Austrália. *Bulong* foi projetada para processamento de 537 mil toneladas por ano de minério, resultando dessa forma, na produção de 9600 tpa de níquel e 940 tpa de cobalto (Griffin e Becker, 2000). Entretanto, desde 2003, a usina encontra-se fora de operação.

O processo de preparação do minério consistiu de um classificador, moinho de bolas e espessador. A polpa era alimentada na autoclave onde a adição de vapor, juntamente com o calor de reação resultante da injeção de ácido sulfúrico, elevavam a temperatura para 250^{o}C (pressão de 4000kPa). Níquel, cobalto e outros metais eram dissolvidos sob essas condições. Um circuito contínuo de decantação em contra-corrente separava a solução do resíduo de lixiviação, o qual, logo em seguida, era neutralizado com cal e calcário. A solução rica em metais dissolvidos era também parcialmente neutralizada para controle das concentrações de ferro e cromo, e posteriormente, encaminhada à extração por solventes de cobalto através do uso do extratante Cyanex 272.

O licor rico em cobalto era primeiramente encaminhado à etapa de remoção de impurezas: manganês, magnésio, zinco, cobre e chumbo. Magnésio era removido por precipitação de sulfetos (sulfetação com Na_2S). Zinco era removido por extração por solventes. Cobre era removido por troca iônica. O licor rico em cobalto após purificação era, finalmente, destinado à etapa de eletrólise, para produção de cobalto catodo. Enquanto isso, o rafinado da extração por solventes do cobalto, livre de cobalto e rico em níquel, era bombeado ao circuito de extração por solventes de níquel com o extratante Ácido Versático (ácido carboxílico) e, posteriormente, à eletrólise, onde o níquel era depositado nos catodos. O rafinado da etapa de extração por solventes do níquel era usado como água de lavagem no circuito CCD. A Figura 3.2 apresenta o fluxograma de processo para *Bulong Nickel and Cobalt Project* (Doll, 2005)

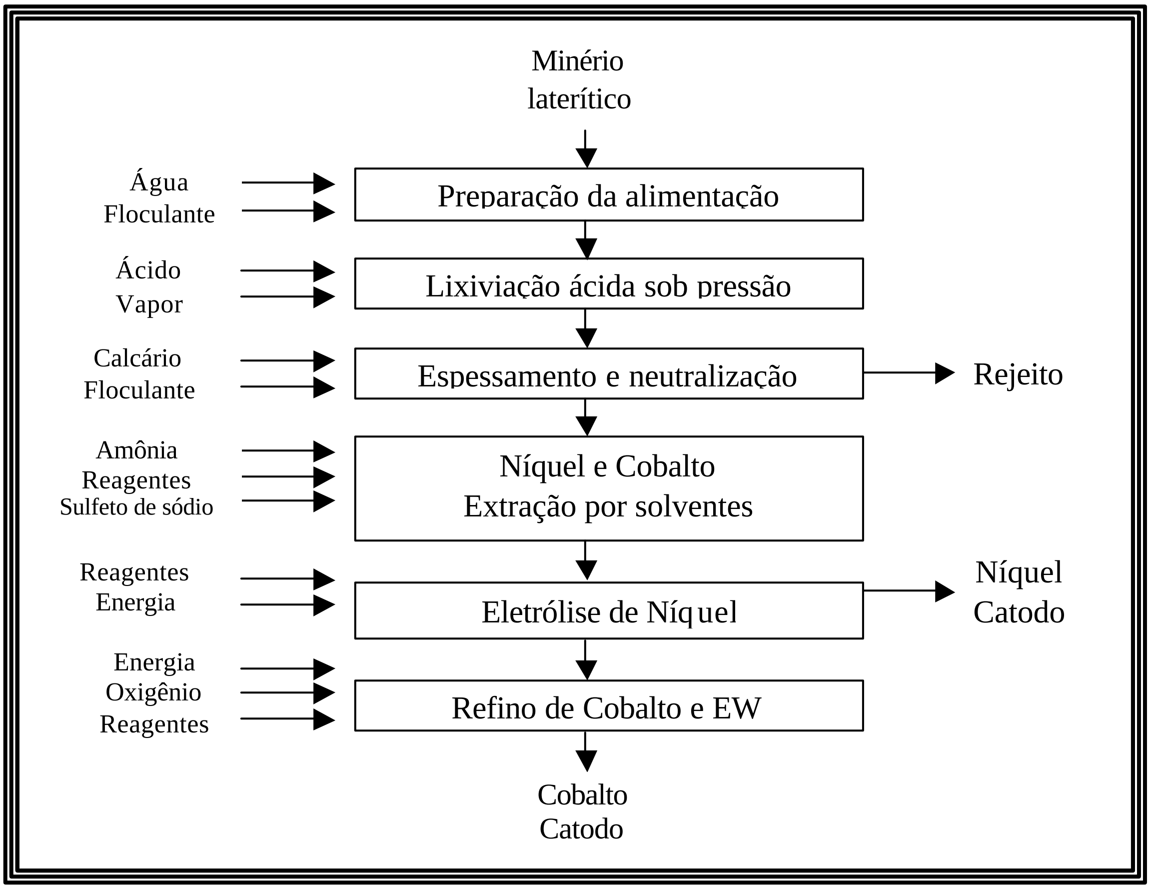

Figura 3.2 - Fluxograma de processo para *Bulong Nickel and Cobalt Project*.

<u>Usina Murrin Murrin</u>

De acordo com o trabalho de Mayze (1999), no processo adotado em *Murrin Murrin*, o minério é inicialmente beneficiado para a liberação dos minerais de níquel e para definição da granulometria apropriada para alimentação da autoclave. A polpa é armazenada em quatro tanques, um para cada autoclave, a qual opera a 255^{o}C para máxima dissolução de níquel e cobalto juntamente com extração mínima de ferro. A solução de níquel e cobalto, mais as impurezas (Fe^{2+}, Al, Cu, Zn, Mn, Mg) é separada dos sólidos através do processo de decantação em contra-corrente. O tamanho dos espessadores é função das características de sedimentação e da taxa de fluxo de sólidos, enquanto que o número de estágios é determinado pelo teor de sólidos no *underflow* do espessador. *Murrin Murrin* possui sete espessadores com uma densidade de sólidos de 55%.

Na neutralização da solução em pH próximo de 2,5, os íons férricos são precipitados. Em seguida, é produzido um precipitado intermediário de sulfeto de níquel através da reação com sulfeto de hidrogênio sob alta pressão e temperatura de 95°C. A etapa de precipitação é responsável pela remoção de impurezas. O produto contém aproximadamente 55% de níquel e é recuperado por filtração. O produto na forma de sulfetos é dissolvido numa etapa de lixiviação sob condições oxidantes, onde oxigênio puro reage com sulfetos em uma autoclave operando a 165°C e 1100 kPa. Finalmente, uma primeira etapa de extração por solventes com extratante Cyanex 272 recupera seletivamente o cobalto em relação ao níquel, enquanto que uma segunda etapa de extração por solventes produz uma solução pura de cobalto para sua recuperação direta na forma de briquete ou cobalto metálico por redução com hidrogênio. Níquel metálico é igualmente recuperado por redução com hidrogênio. A Figura 3.3 apresenta o fluxograma de processo da *Murrin Murrin Nickel Operation* (Doll, 2005)

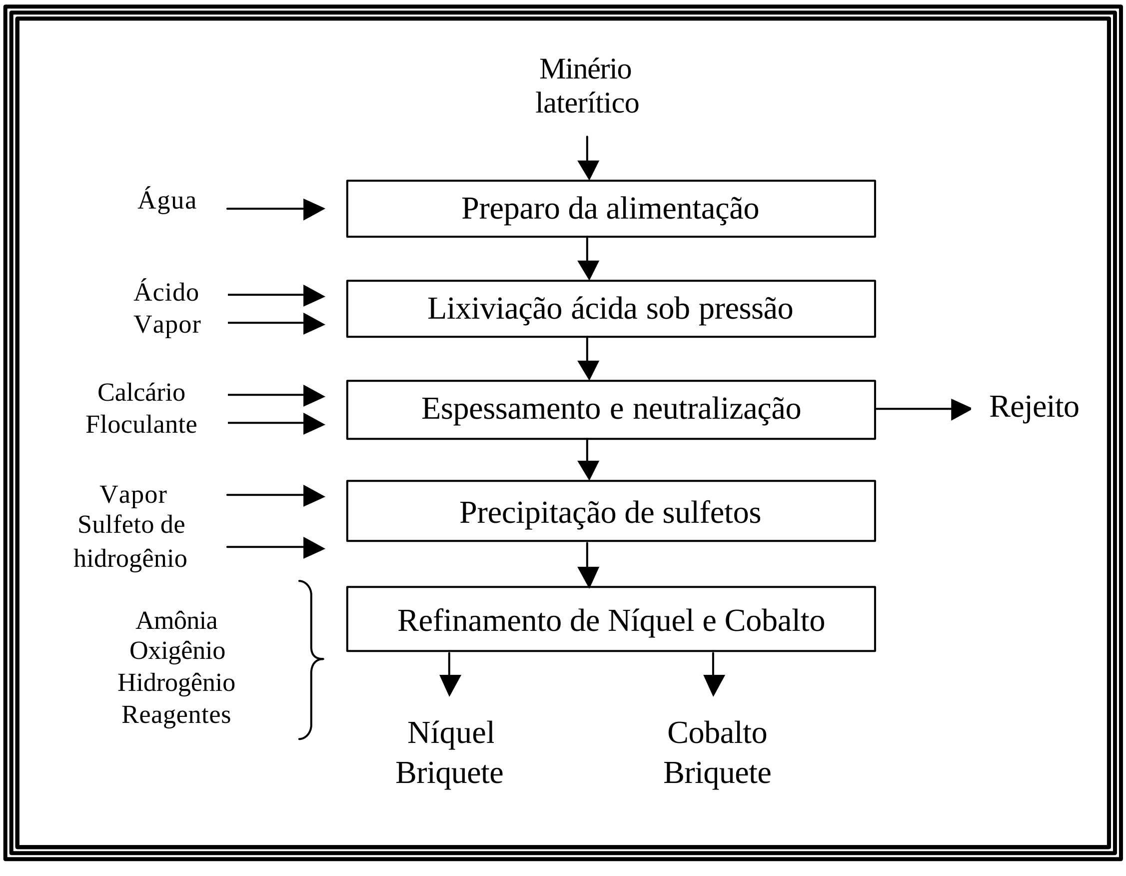

Figura 3.3 - Fluxograma de processo para *Murri Murrin Nickel Operation.*

Com base nas informações disponíveis e no campo de novos desenvolvimentos tecnológicos para as unidades industriais de lixiviação ácida sob pressão, há uma constante busca por melhorias de processo a fim de se obter reduções de custos de capital e operacionais, ao mesmo tempo em que se procura recuperações crescentes e minimização de riscos. Taylor e Jansen (2000) propuseram uma série de alternativas tecnológicas que podem ser estudadas e aperfeiçoadas para aplicações futuras. Uma delas aborda o objetivo central dessa tese de doutorado, que é a aplicação de resinas poliméricas de troca iônica para a recuperação de níquel e cobalto de polpas ácidas.

Aplicação de resina em polpa (resin-in-pulp-RIP)

As unidades industriais citadas anteriormente incluem um circuito multi-estagiado de decantadores em contra-corrente, responsáveis pela separação sólido-líquido e lavagem de sólidos para maximização das recuperações de níquel e cobalto a partir da polpa efluente de lixiviação. Para isso, é empregada uma série de espessadores resistentes à corrosão, que envolvem altos custos de capital e operacional, além de ocuparem grandes áreas e consumirem quantidades significativas de água de lavagem. Uma opção neste caso, em substituição à etapa onerosa de decantação em contra-corrente, é o uso de um sistema de resina em polpa, empregado na recuperação de níquel e cobalto a partir da polpa lixiviada, sem a necessidade do uso de espessadores. Em seguida, níquel e cobalto seriam individualmente recuperados, separados e purificados, via extração por solventes, por exemplo, a partir da solução eluente concentrada. A solução eluente poderia ser à base de cloreto ou sulfato. A recuperação final poderia ocorrer através de eletrólise ou redução por hidrogênio, entre outras, conforme apresentado na Figura 3.4.

A tecnologia RIP pode ser usada para aprimorar sistemas pré-existentes ou substituir tecnologias convencionais. Nos casos em que a engenharia de processo está sob consideração, essa tecnologia pode ser proposta em substituição à tecnologia CCD e com redução do impacto ambiental. Já em plantas em operação onde o processo de CCD é aplicado, a tecnologia de resina em polpa pode aprimorar a tecnologia pré-existente, aumentar a recuperação dos metais, melhorar a pureza metálica e reduzir o impacto ambiental. Esta alternativa em série com o circuito de separação sólido-líquido torna-se particularmente atrativa em casos onde os minérios lateríticos apresentam restrições (longo tempo de deposição) ao processamento em circuitos CCD, resultando em perdas metálicas nos resíduos (Zontov, 2001).

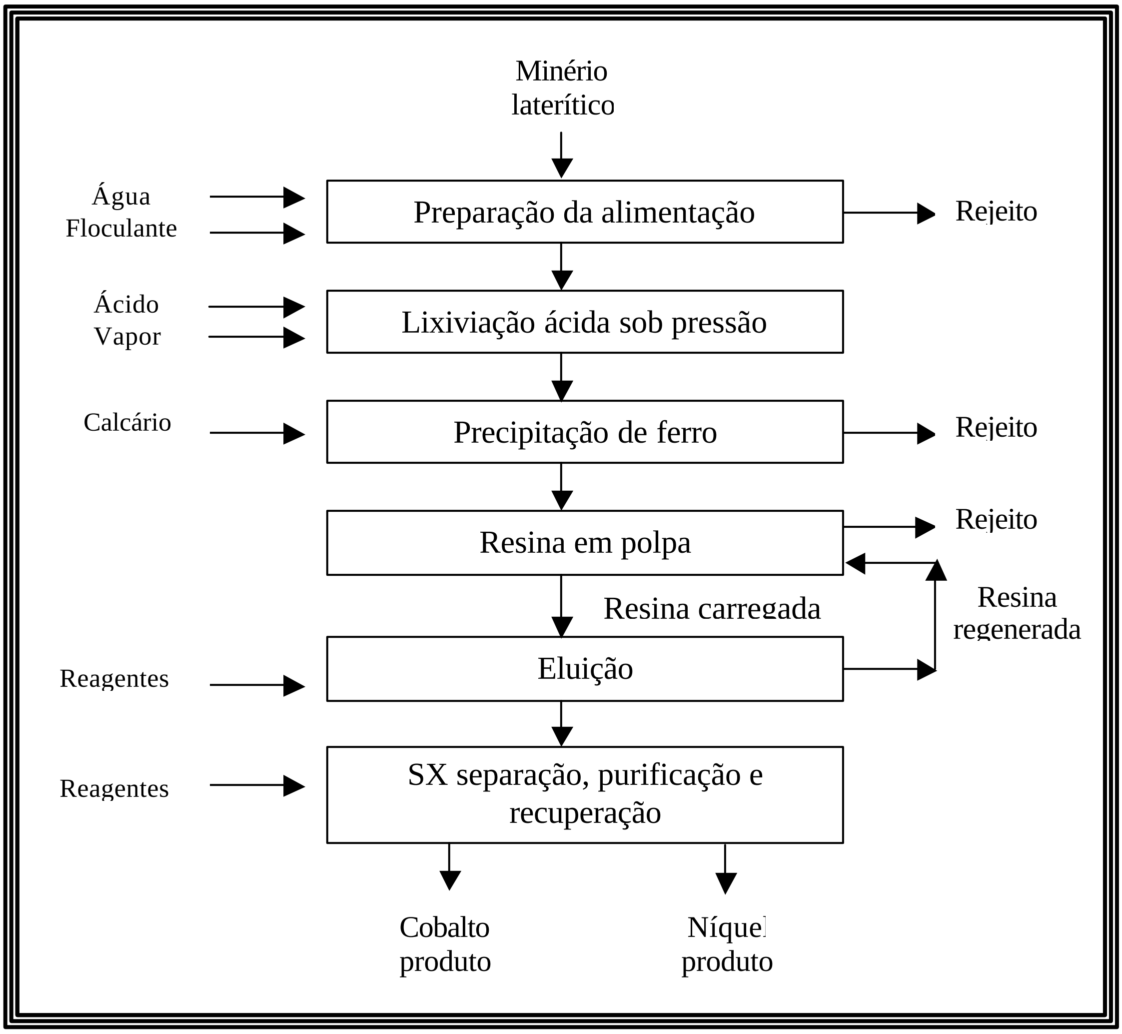

Figura 3.4 - Fluxograma de processo sugerido para resina em polpa-RIP (Taylor e Jansen, 2000)

O processo de resina em polpa envolve a contactação da resina polimérica de troca iônica diretamente com a polpa de lixiviação em fluxo contra-corrente. A resina é separada da polpa por peneiramento e os metais carregados na resina são recuperados por eluição (Lukey et al., 2000). Este tipo de sistema tem sido comumente usado na recuperação comercial de urânio, especialmente para polpas de baixo teor e de difícil sedimentação. O processo de carvão em polpa (carbon-in-pulp - CIP) apresenta uma concepção similar, onde o carvão faz o papel da resina. A principal característica da tecnologia de resina em polpa consiste do fenômeno “sorção-lixiviação”. Neste caso, o processo de troca iônica remove continuamente níquel e cobalto da fase líquida, permitindo uma lixiviação subseqüente. Dessa forma, uma quantidade adicional de níquel e cobalto é recuperada da porção sólida da polpa, a qual não é normalmente recuperada em outros processos (Zontov, 2001).

Troca iônica com resinas poliméricas

A troca iônica pode ser definida como uma troca reversível de íons de mesma carga entre um sólido e um eletrólito aquoso, de forma que não ocorra nenhuma mudança significativa na estrutura do sólido. Neste caso, o sólido é o material trocador de íons, que pode ser de natureza inorgânica (por exemplo, zeólitos) ou de natureza orgânica, que correspondem aos materiais baseados em resinas poliméricas sintéticas (The Dow Chemical Company, 1959; Dorfner, 1972).

A matriz de uma resina é formada por uma cadeia de hidrocarbonetos de alto peso molecular, insolúvel, irregular, macromolecular, tridimensional e elástica, resultado da copolimerização de estireno e divinilbenzeno. Nela, grupos funcionais positivos ou negativos estão firmemente ligados (íons fixos), os quais são compensados por íons de sinais opostos (íons contrários). Estes são livres para se mover dentro da matriz e podem ser estequiometricamente substituídos por outros íons de mesmo sinal. Em contraste, os chamados co-íons são todas aquelas espécies iônicas que podem estar presentes no trocador e que apresentam mesma carga que os íons fixos. A matriz possui, ainda, uma estrutura capaz de oferecer a máxima resistência à oxidação, redução, desgaste mecânico, além de serem insolúveis nos solventes comuns e apresentarem formas esféricas ou granuladas com propriedades hidráulicas apropriadas. A natureza dos grupos ionizáveis (íons contrários) fixados à matriz hidrocarbônica determina o comportamento químico de uma resina de troca iônica.

Os principais tipos de resinas comercialmente usadas são as resinas catiônicas que, dependendo do grau de acidez do grupo funcional, podem ser de ácidos fortes ou fracos, e as resinas aniônicas que dependendo do grau de basicidade podem ser de bases fortes ou fracas, além das resinas quelantes. Certos materiais, denominados anfotéricos, são capazes de realizar a troca de cátions e ânions (Grinstead, 1979).

As resinas catiônicas, caracterizadas por uma matriz negativa de grupos funcionais ácidos, como por exemplo, sulfônico (forte), carboxílico (fraco), fenólico e radicais contendo arsênio e fósforo, apresentam a capacidade de trocar cátions com os íons-contrários, como mostra a equação 3.1.

$$2\ NaX + CaCl_2(aq) \Leftrightarrow CaX_2 + 2\ NaCl\ (aq) \qquad (3.1)$$

Onde X é a matriz negativa de grupos funcionais ácidos. Resinas que apresentam ácido sulfônico como grupo funcional são ionizadas em pH>1 e podem remover íons em baixos valores de pH, entretanto são pouco seletivas. Já as resinas de ácido fraco, com grupos funcionais tais como fosfônico e carboxílico, são mais seletivas, mas apenas removem efetivamente cátions em valores de pH acima dos valores de pK_a (ex: pH > 4-6) (Duyvesteyn, 1997).

Já as resinas aniônicas formadas por uma matriz positiva de grupos funcionais básicos, como por exemplo, poliamina (fraca), amina quartenária (forte) e piridina, são capazes de trocar anions com os íons-contrários de acordo com a equação 3.2.

$$2XCl + Na_2SO_4(aq) \Leftrightarrow X_2SO_4 + 2\ NaCl\ (aq) \qquad (3.2)$$

Onde X é a matriz positiva de grupos funcionais básicos. Resinas de base fraca e forte somente podem extrair anions quando protonadas, o que significa que o pH da solução deve estar abaixo do pK_a do grupo funcional. Já que o pK_a de resinas de base forte excede o valor 13, elas podem remover anions efetivamente em ampla faixa de pH. Em contra partida, resinas de base fraca são efetivas somente em pH abaixo de 9 (Duyvesteyn, 1997).

No processo de troca iônica, onde cátions metálicos são removidos, utilizam-se resinas catiônicas contendo grupos funcionais tanto de ácidos fortes (sulfônico), como de ácidos fracos (carboxílico). Estas resinas, entretanto, não são especialmente seletivas para muitos cátions. Se uma solução contém agentes complexantes em quantidade considerável ou outros cátions, além de metais alcalinos e alcalino-terrosos, possivelmente essas resinas não vão remover todos os metais desejados. Para isso, as resinas quelantes foram desenvolvidas para recuperar seletivamente os metais de transição em solução, uma vez que elas formam complexos quelantes altamente estáveis ou quelatos heterocíclicos metálicos com estes cátions (Fortes, 2000). Os quelatos podem ser definidos como qualquer composto em que se forma um anel graças a um enlace coordenado entre dois ou mais sítios de uma molécula e um íon metálico. As resinas que apresentam propriedades quelantes são baseadas no mesmo tipo de matriz estireno-divinilbenzeno, como as resinas catiônicas e aniônicas. Entretanto, elas contêm grupos ativos que estão diretamente fixados à matriz estireno e fornecem alta afinidade para cátions polivalentes de metais pesados (Kunin e Myers, 1950; The Dow Chemical Company, 1959).

Normalmente os grupos funcionais responsáveis pela seletividade contêm átomos como nitrogênio, oxigênio, fósforo e enxofre. Exemplos de grupos funcionais quelantes incluem amidoxima, aminofosfonato, carbamatos, poliaminas, piridinas, iminodiacetato e picolilamina (Duyvesteyn, 1997). Como metais alcalinos e alcalinos terrosos não formam complexos com o grupamento funcional das resinas quelantes, estas não são muito efetivas para a extração desses metais (Lehto, 1999).

De acordo com Dorfner (1972), a atual importância das resinas sintéticas é justificada pela sua resistência mecânica e química, altas taxas de troca, capacidade de adsorção e possibilidade de variação de suas propriedades em razão da natureza sintética. As propriedades químicas, térmicas e mecânicas, além do comportamento de uma resina, dependem da estrutura de cadeias carbônicas, do tamanho das partículas, do grau de entrelaçamento ou *cross-linking* (variação de 2-12% divinilbenzeno) na matriz e da natureza e número de grupos iônicos fixos. O grau de cross-linking determina a largura de poros e, conseqüentemente, a habilidade de inchamento e mobilidade dos íons contrários da resina. Quanto menor o teor de divinilbenzeno na matriz da resina, maior é a sua expansão, mais macia e gelatinosa ela será, permitindo um melhor desempenho na adsorção de metais.

No equilíbrio da troca iônica, as concentrações dos íons contrários competindo entre si no trocador iônico e na solução não são as mesmas, ou seja, o trocador iônico prefere uma espécie à outra. Este fato mostra que a redistribuição dos íons contrários não é puramente estatística, mas a preferência por uma dada espécie pode ter algumas causas específicas que dependem da natureza dos íons contrários (Helfferich, 1962). As interações eletrostáticas (coulombianas) entre a matriz carregada e os íons contrários dependem do tamanho e, em particular, da valência dos íons contrários. Além das forças eletrostáticas, outras interações entre os íons e suas vizinhanças também são efetivas.

Os principais procedimentos para contactação em bancada de soluções com resinas são em reator aberto (ensaios em batelada) e em coluna (ensaios semi-contínuos), este último pode ser subdividido em categorias dependendo do tipo de leito: fixo ou móvel, e se a solução de alimentação e solução eluente fluem através da resina na mesma direção relativa ou em direção oposta.

Uma etapa igualmente importante é a eluição do íon retido na resina. A eluição é a dessorção provocada por um fluxo de líquido contactado à resina carregada, que causa a sua regeneração. É desejável que a afinidade de um íon por um trocador seja tal que este íon possa ser dessorvido. Caso contrário, pode ocorrer o envenenamento da resina devido ao seu uso prolongado nos ciclos de adsorção/eluição, reduzindo a sua capacidade de troca iônica.

As aplicações e usos do processo de troca iônica podem ser divididos em duas grandes áreas: tratamento de águas e processamento químico. Resinas catiônicas na forma sódica são amplamente utilizadas para o tratamento de águas. Processos de troca iônica são empregados também num grande número de indústrias, como por exemplo, bebidas, química, drogas, eletrogalvanização, colas, gelatina, leite e derivados do leite, hidrometalurgia, petróleo, açúcar e tratamento de efluentes. As aplicações em processos químicos podem ser classificadas de acordo com os seguintes tipos: conversão, purificação, concentração, cromatografia e catálise. Dentro da área de aplicações especiais, tem-se: exclusão de íons, separação não-iônica, separação analítica, separação envolvendo o uso de resinas de retardação de íons, separação de ácidos dos seus sais através do uso do método de equilíbrio polivalente-monovalente (Dorfner, 1972).

Troca iônica para recuperação de níquel e cobalto

De acordo com Villegas (2000), as técnicas hidrometalúrgicas são cada vez mais empregadas na recuperação de metais pesados em função de razões ecológicas, econômicas e estratégicas. Os métodos podem ser de natureza química como oxidação química e precipitação química, ou de natureza físico-química como adsorção em carvão ativado, trocador iônico e extração por solventes, além daqueles de natureza física, eletroquímica e biológica.

Níquel e cobalto apresentam propriedades químicas muito semelhantes, fato este que facilita as operações de recuperação mútua desses metais, seja através de precipitação na forma de sulfetos e hidróxidos ou extração por solventes em meio cloreto, amoniacal e sulfato (Zhou and Pesic, 1997). No campo de troca iônica, estudos vêm se intensificando com diversas abordagens e resultados bastante promissores. De acordo com Nagib et al. (1999), o uso da técnica de troca iônica deve oferecer algumas vantagens, como por exemplo, a ausência de perdas de reagentes por arraste, além de apresentar-se mais adequada para recuperação e remoção de pequenas concentrações de alguns íons metálicos em relação a um excesso de outros metais.

Já o emprego de resinas poliméricas de troca iônica para recuperação de metais como níquel e cobalto vêm sendo amplamente abordado na literatura. De acordo com Zontov (2001), os avanços recentes na tecnologia de resinas poliméricas de troca iônica têm proporcionado um aumento de sua aplicação em processos de extração hidrometalúrgica, principalmente na indústria do ouro e urânio. As vantagens dessa tecnologia para aplicações futuras incluem: alta seletividade para os metais de interesse, elevada capacidade de separação, regimes flexíveis de processo, configuração simples de processo, etapa de alta concentração e alto nível de automação. Estas características refletem num menor custo de capital e operacional, além de um menor impacto ambiental (menor consumo de água e oportunidade de reciclo de água usada). A seguir são apresentadas duas das principais resinas quelantes comerciais, mais freqüentemente citadas em textos técnicos, que objetivam a recuperação seletiva de níquel e cobalto em meio ácido.

Resinas Quelantes

As resinas poliméricas quelantes são exemplos de trocadores iônicos bastante eficientes na remoção seletiva de metais pesados, como níquel e cobalto, se comparado a outros trocadores. Essas resinas poliméricas de troca iônica são copolímeros com grupos funcionais covalentemente ligados, os quais contém um ou múltiplos átomos doadores (Base de Lewis) que podem formar ligações coordenadas com a maioria dos íons metálicos (Ácido de Lewis). Interações coulombicas e hidrofóbicas também estão presentes, entretanto a contribuição na alta seletividade de íons metálicos é relativamente pequena se comparada às interações ácido-base de Lewis. Para as resinas constituídas do grupo funcional de ácido iminodiacético, a presença de grupamentos de ácido fraco faz com que este trocador apresente alta afinidade pelos íons H^+. Assim, quanto menor o pH, menor a recuperação seletiva de íons metálicos em função da competição com os íons H^+. Estas resinas podem ser normalmente regeneradas com soluções ácidas (ácido sulfúrico ou clorídrico, por exemplo), com obtenção de alta eficiência.

Trocadores quelantes constituídos do grupo funcional bis-picolilamina com átomos doadores de nitrogênio exibem algumas propriedades pouco comuns em relação à recuperação de íons metálicos da fase aquosa. Conforme apresentado por Sengupta et al. (1991), especificamente para estes trocadores quelantes, (a) a recuperação do íon metálico aumenta com o aumento da concentração dos íons competidores Ca^{2+} e Na^{2+}; (b) a capacidade de remoção de metais permanece quase que inalterada em baixos valores de pH, tal como pH =1; (c) a regeneração ou dessorção dos íons metálicos com amônia é muito eficiente, enquanto a regeneração ácida é menos efetiva, (d) tanto os cátions metálicos quanto os anions podem ser removidos simultaneamente da fase aquosa e (e) em razão dos grupamentos funcionais de ácido fraco e base fraca, estes trocadores apresentam também afinidade aos íons hidrogênio. Assim quanto menor o pH, menor a recuperação seletiva de íons metálicos em função da competição com os íons H^+. Através do estudo de Sengupta et al. (1991), todas essas características foram explicadas e comprovadas através de um complexo estudo de mecanismos de adsorção.

Duas das principais resinas abordadas neste texto são as resinas Dowex M4195® e Amberlite IRC 748®. Ambas são resinas do tipo quelante com diferentes grupos funcionais e originadas de diferentes fabricantes.

Resina DOWEX M4195 â

A *Dow Chemical Company* tem reportado uma série de resinas quelantes, dentre elas, Dowex M4195®, que atua eficientemente na adsorção de cátions de metais de transição, com alta seletividade para cobre, níquel e cobalto na presença de altas concentrações de ferro em meio muito ácido (Jones and Pyper, 1979). Essa resina consiste de um copolímero macroporoso do tipo poliestireno/divinilbenzeno, no qual estão afixados derivados quelantes picolilamina de base fraca: bis-picolilamina (Rosato et al., 1984; Grinstead, 1984a; Grinstead, 1984b). A Tabela III.1 apresenta as principais características desta resina.

Tabela III.1 - Propriedades de resinas quelantes (Dow Chemical Company, 2000)

Produto	*Descrição*	*Matrix*	*Capacidade total de troca*	*Formas disponíveis*
DOWEX M4195®	Altamente efetiva para separações de Co, Ni e Cu	Macroporosa estireno- DVB	0,65 moles Cu/L 0,61 moles Ni/L	H^+

As características de seletividade dessas resinas quelantes sugerem a sua aplicação em alguns tipos de separação hidrometalúrgica onde resinas catiônicas e aniônicas nem sempre se apresentam eficientes, como mostrado por Diniz (1999). Embora primeiramente indicadas para o tratamento de licores de cobre, um estudo posterior envolvendo o cálculo dos seus coeficientes de adsorção revelou que estas resinas podem ser potencialmente eficazes na recuperação de sulfatos de metais de transição como níquel e cobalto, como mostra a Tabela III.2 (Rosato et al., 1984).

Tabela III.2 - Propriedades de resinas quelantes em função do pH

Resina	*Capacidade de carregamento de metal (mol/L)*	*Constante de adsorção (L/mol)*					
		pH 1,5		*pH 2,5*		*pH 4,5*	
		Ni	*Co*	*Ni*	*Co*	*Ni*	*Co*
DOWEX M4195®	0,50	85	11	265	67	323	143

No caso específico da resina M4195®, a estrutura geral é baseada no grupo quelante bispicolilamina, fracamente básico, o qual é covalentemente ligado ao copolímero polestireno-divinilbenzeno, como mostra a Figura 3.5.

Dowex M4195â – resina quelante
Fabricante: Dow Chemical
Granulometria (mesh): -20 +50
Teor de água (%): 51-52
PK$_a$ aparente em 0,10N Na_2SO_4: 3.5
Variação de volume, ácido → base (%): -24

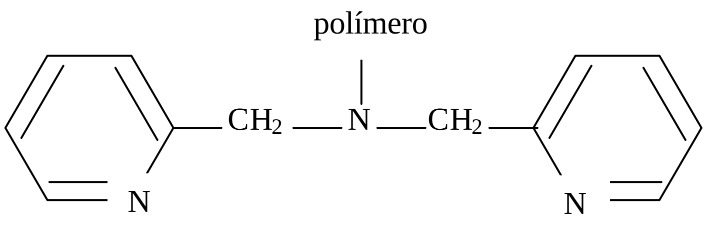

Figura 3.5 - Propriedades e estrutura da resina DOWEX M4195®

A resina Dowex M4195® apresenta um grande potencial de sucesso para o objetivo que essa tese apresenta. Trata-se da resina com o maior número de citações em literatura, embora nenhum registro foi encontrado acerca de recuperação de Ni/Co em processos de tratamento de minérios lateríticos de níquel.

O grupamento funcional da resina M4195® atua como um agente complexante mais eficiente para níquel, se comparada a outras resinas, em toda faixa de pH, entretanto a seletividade para cobalto é sensivelmente menor. O cobalto, que é rapidamente adsorvido nos instantes iniciais de carregamento, é logo dessorvido em razão da seletividade preferencial ao níquel. Entretanto, quanto maior o pH, mais fácil é a recuperação de Ni e Co simultaneamente. Na resina M4195, Cu e Ni são efetivamente adsorvidos mesmo em baixos valores de pH, na seguinte ordem de adsorção Cu>Ni>Co>Zn>Al. (Nagib et al., 1999). A Tabela III.3 apresenta as constantes de adsorção da resina M4195® para diversos metais em valores de pH=2.

Tabela III.3 - Constantes de adsorção para diversos metais na resina M4195®

Constante de adsorção (L/mol) para a resina DOWEX M4195® *(solução de sulfato, pH = 2)*										
Metal	Cu	Ni	Fe(III)	Cd	Zn	Co	Fe(II)	Ca	Mg	Al
Constante de adsorção	700	190	80	70	60	30	3	<2	<1	<1

Cátions metálicos são adsorvidos na razão 1:1, coordenados com os três átomos de nitrogênio da molécula de amina. A presença dos átomos de nitrogênio no grupo funcional propicia propriedades básicas à resina. O valor de pK_a foi estimado através de titulações da resina em 0,5N Na_2SO_4. Como este valor indica, a resina existe na sua forma protonada em soluções ácidas. O tratamento com soluções alcalinas vai convertê-la para a forma básica livre, o que pode causar o encolhimento da resina em 20-25%. A adsorção do metal na resina sob a forma básica livre é mais lenta se comparada à forma ácida e, conseqüentemente, essa última forma é recomendada para a maioria das aplicações (Jones e Grinstead, 1977).

Estudos anteriores realizados por diversos autores visaram a recuperação de níquel através da aplicação da resina Dowex M4195®: (1) Grinstead (1984b) mostrou que o efeito da concentração de sulfato, variando na faixa de 0,03M a 1,0M, causa uma diminuição na constante de adsorção num fator de 2 para os metais cobre, níquel e cobalto em pH=3 constante; (2) Grinstead (1984a) afirmou, também, que para a grande maioria dos metais, a constante de adsorção é fortemente dependente do pH, principalmente, em baixos valores de pH; (3) Grinstead (1984a) concluiu que se variando a concentração de íons metálicos, ocorrem variações no carregamento da resina; (4) Diniz (2000), após um estudo sobre a influência do pH e das concentrações dos metais em solução, concluiu que a adsorção de níquel e cobalto aumenta com o pH e depende diretamente do grau de protonação da resina; (5) Nagib et al. (1999) avaliaram os efeitos do tempo de contato na adsorção de Ni até se atingir o equilíbrio e os efeitos do pH na razão de distribuição. Eles ainda mostraram que o níquel é efetivamente adsorvido pela resina até mesmo em baixos valores de pH.

Estudos de eluição da resina Dowex M4195® também já foram abordados na literatura, como por exemplo, Jones e Grinstead (1977), que concluiu que a eluição seletiva de metais da resina pode ser feita em duas etapas distintas: com H_2SO_4 para recuperação seletiva de Co e Ni e NH_4OH para remoção de Cu, ou em duas etapas com mesmo reagente em concentrações diferentes.

Resina AMBERLITE IRC 748 â

A resina Amberlite IRC 748® é do tipo quelante com alta seletividade para cátions de metais pesados se comparados a metais alcalinos. A seletividade é alcançada pelo grupo funcional de ácido iminodiacético quimicamente ligado a uma matriz macroreticular. De acordo com o fabricante Rohm & Haas (2001), em função da alta seletividade por metais pesados e excelente performance cinética, esta resina pode remover metais da solução mesmo na presença de alta concentração de sais de cálcio e sódio. Além disso, a estrutura macroreticular é altamente resistente ao choque osmótico e apresenta excelente estabilidade física. As principais propriedades da resina Amberlite IRC 748® são apresentadas na Tabela III.4. A Figura 3.6 apresenta a estrutura do grupo funcional de ácido iminodiacético e algumas propriedades físicas.

Tabela III.4 - Propriedades da resina Amberlite IRC 748®

Matriz	Macroporosa estireno divinilbenzeno
Grupo funcional	Ácido iminodiácetico
Forma iônica	Na^+
Capacidade total de troca	≥ 1,35 eq/L (forma Na^+)
Densidade(base seca)	460 g/L
Tamanho médio *Partículas finas* *Partículas grossas*	0,5 – 0,65 mm < 0,30 mm: 1,0% Max > 1,100 mm: 5,0% max
Expansão reversível	$H^+ \rightarrow Na^+$: 30%
Temperatura máxima de operação	90ºC
pH	1,5 – 14

Em geral, a seletividade na adsorção segue a seguinte ordem: $Na^+ << Ca^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Cd^{2+} < Zn^{2+} < Ni^{2+} < Pb^{2+} < Cu^{2+} < Hg^{2+} < Fe^{3+}$. A afinidade por íons H^+ em pH 4 está situada entre Pb^{2+} e Cu^{2+}. Conseqüentemente, para metais com seletividade inferior ao Cu^{2+}, a resina deve ser utilizada na forma Na^+, por exemplo. Em pH 2, a resina se apresenta na forma H^+ em função da acidez do meio e, neste caso, remove preferencialmente Fe^{3+}, Cu^{2+} e Hg^{2+}. A Tabela III.5 apresenta a ordem de seletividade da resina em diferentes valores de pH.

Tabela III.5 - Seletividade da resina Amberlite IRC 748® em função do pH

pH = 2		*pH = 4*		*pH = 9*	
Metal	*K (M/Ca)*	*Metal*	*K (M/Ca)*	*Metal*	*K (M/Ca)*
Fe^{3+}	325000	Hg^{2+}	2800	Ni^{2+}	30
Cu^{2+}	130000	Cu^{2+}	2300	Cd^{2+}	14
Hg^{2+}	> 43000	Pb^{2+}	1200	Cu^{2+}	10
		Ni^{2+}	57	Zn^{2+}	3
		Zn^{2+}	17	Ca^{2+}	1,0
		Cd^{2+}	15		
		Co^{2+}	6,7		
		Fe^{2+}	4,0		
		Mn^{2+}	1,2		
		Ca^{2+}	1,0		

Amberlite IRC 748 â – resina quelante
Fabricante: Rohm & Haas
Granulometria (mm): 0,5-0,65 mm
Capacidade troca: > 1,35 eq/L
Capacidade de retenção de água (%): 60-65 (forma Na^+)
Variação de volume, ácido → base (%): -30

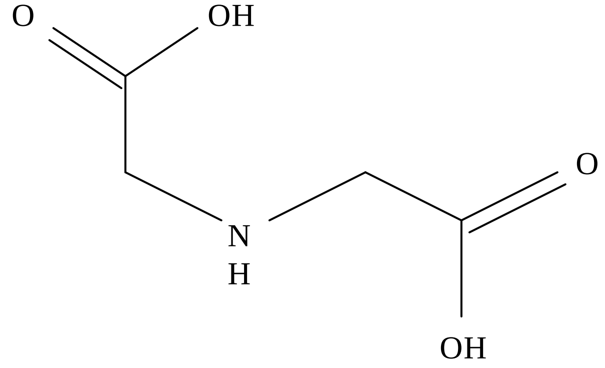

Figura 3.6 - Propriedades e estrutura da resina Amberlite IRC 748®

É possível encontrar na literatura referências à resina Amberlite IRC 748® no que diz respeito a estudos de adsorção de níquel em meio ácido. Como exemplo, Leinonen *et al.* (1994) testaram uma grande variedade de resinas orgânicas quelantes e inorgânicas para a remoção de níquel e zinco de efluentes residuais. Foram executados vários experimentos avaliando-se a dependência da separação em função do pH da solução. Para isso, foram preparadas soluções puras de sais de níquel e zinco a fim de se excluir a interferência de qualquer outro parâmetro além do pH. Três principais resinas quelantes se destacaram nos ensaios em batelada na recuperação de níquel, fornecendo recuperações superiores a 99%, como mostrado a seguir na Tabela III.6.

Tabela III.6 - Características das principais resinas utilizadas por Leinonen *et al.* (1994)

Resina	*Grupo funcional*	*Fabricante*	*pH*	*Separação*
Amberlite IRC 748®	Ácido Iminodiacético	Rohm & Haas	6,17	99,88%
Duolite ES 467®	Aminofosfonato	Rohm & Haas	7,30	99,86%
AG 50W-X8®	Ácido sulfônico	Bio-Rad	1,98	99,80%

Capítulo 4 - Adsorção seletiva de níquel e cobalto através da aplicação de resinas quelantes comerciais

Mendes, F. D. and **Martins,** A. H.. **Selective sorption of nickel and cobalt from sulphate solutions using chelating resins.** *International Journal of Mineral Processing, Volume 74, Issues 1-4, 19 November 2004, Pages 359-371*

Este capítulo apresenta os resultados experimentais obtidos para os estudos de avaliação de quatro resinas poliméricas quelantes comerciais e disponíveis no mercado (Amberlite IRC748®, Ionac SR-5®, Purolite S930® e Dowex M4195®) na recuperação seletiva de níquel e cobalto em soluções aquosas ácidas. O principal objetivo foi selecionar a(s) resina(s) polimérica(s) de troca iônica com grupo quelante e comercialmente disponíveis, capaz(es) de extrair seletivamente níquel e cobalto. Os seguintes parâmetros foram adotados para a seleção da resina: seletividade, capacidade de carregamento da resina polimérica e recuperação dos metais de interesse.

SELECTIVE SORPTION OF NICKEL AND COBALT FROM SULPHATE SOLUTIONS USING CHELATING RESINS

F.D. Mendes (*) and A.H. Martins

Researcher, Companhia Vale do Rio Doce and Assistant Professor,
Department of Materials and Metallurgical Engineering – UFMG, respectively

Abstract

Four chelating ion exchange polymeric resins were tested to remove Ni and Co from synthetic solutions simulating pressure acid leach liquor. The goal of this work was to select a commercial resin capable of extracting nickel and cobalt with high selectivity. The resins behavior regarding nickel and cobalt sorption and desorption was described and some parameters discussed. Nickel and cobalt sorption was studied according to some experimental parameters, such as time, initial metals concentration, Ni/Co concentration ratio and pH of the aqueous solution.

The nickel and cobalt sorption results evaluated in a preliminary basis were very promising. The four commercially available ion exchange polymeric resins, Dowex M4195®, Amberlite IRC748®, Ionac SR-5® and Purolite S930®, presented very peculiar features concerning selectivity and each of them seemed to be efficient on nickel and cobalt sorption under certain experimental conditions. Dowex M4195® showed the best results for nickel and cobalt selective sorption from acid liquors, since nickel and cobalt were equally recovered, in all pH range, with small influence of other elements. Even in lower pH, such as pH = 1, Dowex M4195® had the best performance for nickel and cobalt sorption. Amberlite IRC 748® also presented very promising results and further testwork would appear to be worthwhile.

Keywords: nickel, cobalt, resin, ion exchange

(*) Corresponding author.
E-mail: flavia.mendes@cvrd.com.br
Phone: + 55-31-36914467

Introduction

The first pressure acid leaching (PAL) plant for nickel laterites processing, Moa Bay – Cuba, was constructed forty years ago, and two PAL plants are in operation in Western Australia, now, Cawse and Murrin Murrin. The main difference among all four PAL plants for laterite ore, Moa Bay, Bulong, Cawse and Murrin Murrin, lies in how the nickel and cobalt are recovered and refined. Murrin Murrin adopted a mixed sulphide precipitation. Bulong selected a direct solvent extraction approach, in which nickel and cobalt are extracted sequentially from the pressure leach solution. Finally, Cawse chose mixed hydroxide precipitation followed by ammonia releach (Taylor and Jansen, 2000).

All these four plants include multi-stage counter-current decantation (CCD) circuits to wash nickel and cobalt values out of the leach pulp. These circuits involve significant capital and operating costs, occupy large footprint area, and require a significant quantity of wash water. An alternative to recovery nickel and cobalt values from the leach pulp without thickening is to use a resin-in-pulp (RIP) system. Ion exchange polymeric resins have found increasing application over the last decade. This is highlighted through the drive towards resin-in-leach technology at the expense of the carbon-in-pulp process in the gold mining sector (Coetzee and Rejaldien, 2001). Moreover, ion exchange resins for almost any separation process are available commercially. In addition, their application is able to provide a more effective and straightforward purification compared to purification by precipitation or solvent extraction, which are the most commonly used method at present for these purpose (Leinonen et al., 1994; Kononova et al., 2000; Kholmogorov et al., 1997). Besides, ion exchange process is more suitable for the purpose of recovering or removing small amounts of some metal ions from a large excess of other metals (Nagib et al., 1999). Ion exchange process using polymeric resins is also free from the loss of reagents through entrainment, costly filtration and poor selectivity for nickel over other metals ions, inherent drawbacks of solvent extraction processes.

The pressure acid leach process discharges a hot acidic pulp, which contains dissolved metals, including high levels of iron, aluminum, manganese, magnesium, besides nickel, cobalt and copper. Some advantages pointed out by Zontov (2001) influence the decision of ion exchange technology application to hydrometallurgical extraction processes. They are: (1) lower environmental burden – less water consumption and water recycling opportunity; (2) economic constraints – lower operating and capital costs of equipment and (3) the quality of manufactured metal products – high selectivity for target metals and high separation capabilities.

According to Zontov (2001), resin-in-pulp technology can be applied to (1) existing operations where CCD processes are used to augment current systems, recover wasted metal values, upgrade metal purity and reduce environmental burden or (2) process design under consideration for replacing CCD conventional technology and reducing environmental burden. Based on this new approach, four years ago, The Center for Mineral Development from Vale do Rio Doce Mining Co. (Brazil) started evaluating the application of HPAL technology to Níquel do Vermelho Deposit ore located at Carajás Mineral Province - Brazil. The combination of good metallurgical behavior for pressure acid leaching (PAL) process route with reasonable mineable grades and existing infrastructure justified the evaluation of the economic viability of the project. (Ribeiro et al., 2001).

The metallurgical studies continued with optimization of leach parameters and one step in the development included the evaluation of the application of resin for recovery of nickel and cobalt. The goal was to determine whether resin-in-pulp might provide higher recoveries of nickel and cobalt than a more conventional CCD circuit. Some preliminary results are shown here and the primary purpose of this study was to find a commercial resin capable of extracting nickel and cobalt in simulating solutions with a reasonable degree of selectivity, so that the resin loading is not affected by another element. This paper presents experimental results on four commercial polymeric resins for selectivity, loading capacity, metal recovery and desorption.

Nickel and cobalt sorption was studied according to some experimental parameters, such as pH, initial metals concentration, initial Ni/Co concentration ratio and time. The pH influence was evaluated during the kinetics sorption studies, which is the most important variable governing metal ion sorption. In its simplest form, the sorption of a metal ion by the resin can be expressed as shown in equations 4.1 and 4.2:

$$M^{+m} + \overline{R.nH^{+}} \rightarrow \overline{MR^{+m}} + nH^{+} \tag{4.1}$$

$$K' = \frac{(\overline{MR^{+m}})(H^{+})^{n}}{(\overline{R.nH^{+}})(M^{+m})} \tag{4.2}$$

where R represents the resin structure, and barred species are in the resin phase. This is not a complete expression of the sorption process, since if $m \neq n$, then some sulfate species must transfer into or out of the resin to maintain electrical neutrality. In such a situation, K' will not be a constant, but will depend upon the sulfate concentrations in both the resin and solution phases (Grinstead, 1979).

The selective behavior of many resins in electrolyte solutions, equilibrium prediction and mass transfer kinetics, where the chemistry of the solutes is similar, can become complex due to the interference of other metal ions. One of the methods used to investigate ionic sorption is the sorption isotherm for a given specie. The Langmuir-type equation is one of the most widely used equations for modeling sorption from solutions at the solid/liquid interface.

Although equilibrium is of fundamental importance to characterize a polymeric resin, the rate at which equilibrium is achieved is equally important from a practical point of view. The sorption and desorption kinetics and the selective loading characteristics of some chelating ion exchange commercial resins are governed not only by the target metal concentrations, but also by the competing metal concentrations. Chelating resins have shown better performance with respect to transition metal ions compared to ordinary organic ion exchangers (Lehto et al., 1996). Since chelating resins form strong complexing chelates with transition metals, they can strip complexes present in the solution that are weaker than those in the resin (Koivula et al., 2000). In the same way, since alkali and alkaline earth metals do not form complexes, these metals are not loaded (Lehto et al., 1999).

Methods and Materials

Polymeric Resins Tested

Four polymeric resins containing different chelating groups for transition metal ions (see Table IV.1) were first tested by a batch ion exchange method to find the most promising exchanger for nickel and cobalt sorption, selectivity, and elution characteristics. Resins Amberlite IRC748®, Ionac SR-5® and Purolite S930® present typical chelating functional groups (iminodiacetic acid), while resin Dowex M4195® forms complexes with transition metals through their free electron pair-bearing nitrogen atom (bis-picolylamine group) (Koivula et al., 2000; Sengupta et al., 1991).

Table IV.1 - The four commercially available ion exchange polymeric resins used for the selective sorption of Ni and Co

Resin	*Manufacturer*	*Functional group*	*Matrix*
Dowex M4195®	Dow Chemical	Bis-picolylamine	Macroporous styrene divinylbenzene
Amberlite IRC748®	Rohm and Haas	Iminodiacetic acid	Macroporous styrene divinylbenzene
Ionac SR-5®	Sybron	Iminodiacetic acid	Macroporous styrene divinylbenzene
S 930®	Purolite	Iminodiacetic acid	Macroporous styrene divinylbenzene

The ion exchange experiments used polymeric resins under sodium and hydrogen-forms. The resins were conditioned by washing with acid or basic solutions and rinsed with distilled water. The conditioning followed the recommendations provided by the manufacturers and it was carried out to remove all the impurities from the resin and to obtain a free base form. It was performed in a beaker agitated by an impeller, at a speed of approximately 200 rpm. Each resin was contacted with a specific concentration solution during a certain time. After that, the resins were dried at the room temperature.

Influence of Variables on Nickel and Cobalt Sorption

The selective behavior of the resins must be investigated under various operating conditions. Each system design must be calculated from laboratory and pilot tests. In order to evaluate the nickel and cobalt sorption performance for chelating resins, parameters such as time, pH and metals initial concentration were studied.

All ion exchange chelating resins were tested in batch mode experiments for their capability to remove Ni and Co from sulphate solutions. Because large amounts of solution were required in this phase of the test program, synthetic solutions were used. Metal ions were analyzed by flame atomic sorption spectrophotometry for zinc and Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES- Spectro - model Modula) for all other metals.

The effects of pH and initial Ni/Co concentration ratio on nickel and cobalt uptake were investigated. Prior to determining the isotherms, the kinetic of the sorption was studied to ensure that equilibrium was reached. Approximately 1.0 g tapped-settled resin was added to 50 mL of solution and stirred at about 200 rpm and at 25^oC in a controlled environment incubator shaker - New Brunswick Scientific-USA. The resin to solution ratio, temperature and agitation speed were constant for all the experiments.

Nickel and cobalt uptake from simulating HPAL solution

Nickel and cobalt recoveries in the presence of other metals were evaluated. It is known that HPAL pulp contains iron, aluminum, zinc, copper, manganese, magnesium, besides nickel and cobalt. Synthetic solutions simulating HPAL solution were used. Batchwise experiments were carried out by taking 50 ml of aqueous solution at varying pH values, together with 1.0 g absorbent into a 250 ml flask shaken, in a speed of 200 rpm at 25^oC for 24 hours.

The main goal of this work was to evaluate the selectivity of each resin for these elements. At this first approach, a solution with all these metals dissolved, except iron, was used. Due to resins high selectivity for iron, this metal was omitted from the solution. All resins were tested for their capability to remove Ni, Co, Al, Mg, Mn, Cu and Zn from a solution containing about 1.0 g/L of each metal ion. After filtration, metal concentration and pH in the aqueous solution were measured using a pHmeter coupled with a glass electrode.

The second part of the experimental work consisted of studying the metals recovery in different values of pH from sulphate solutions, simulating HPAL solution, with high impurities concentration, including aluminum, magnesium, manganese, iron and nickel. The aqueous solutions used in batchwise experiments were prepared by individually dissolving reagent grade metal sulfate in dilute sulfuric acid solution.

Metals desorption

Metal ions can be eluted with sulfuric acid, hydrochloric acid or ammonium hydroxide solutions. An effective eluant for copper from Dowex M4195® would be 1 M NH_4OH solutions and for nickel and cobalt would be 1 M NH_4OH or 1 M H_2SO_4 solutions; thus these two solutions plus 1.6 M HCl were selected for the desorption studies (Jones and Grinstead, 1977). Resin Dowex M4195® and Amberlite IRC748® were eluted with 1.0 M H_2SO_4, 1 M NH_4OH and 1.6 M HCl; and finally, Ionac SR-5® with 1 M H_2SO_4 . Each resin sample was placed in 50 mL of the solution and they were contacted for 1 hour. After determining the equilibrium metals concentration in sulfuric acid solution, the amount of metal that desorbed from the resin was calculated by mass balance.

Results and discussion

Kinetics of metals sorption

The relation between contact time and amount of sorption of Ni and Co in mmol/g dry adsorbent was measured for the purpose of examining the time necessary to attain equilibrium in different pH and [Ni]/[Co] concentration ratio. To determine metal ion removal and to evaluate the kinetics of sorption, samples were taken from the bulk solution at time intervals ranging from 1 to 24 hours and the metal ion concentrations were determined as described in metal ion analysis. The nickel concentration to cobalt concentration ratio was varied and the experiments were performed in the following [Ni]/[Co] ratios: 10/1 (10g/L Ni / 1 g/L Co); 5/1 (5g/L Ni / 1 g/L Co); and 1/1 (1g/L Ni / 1g/L Co). A typical HPAL solution presents [Ni]/[Co] ratio = 10/1, thus other two ratios were selected to be evaluated comparatively, including [Ni]/[Co] ratio = 1/1, where both metals are equally distributed in the solution. It was found that in most cases, after about 4.0 h the Ni sorption reaches equilibrium under the experimental conditions studied.

Figure 4.1 shows nickel sorption for three different resins: Dowex M4195®, Amberlite IRC 748® and SR-5® during 24 hours. The static exchange capacity (amount of the ions sorbed in mmol/g of the resin) was calculated from chemical analysis data. The minimum time to reach equilibrium in the batch experiments with different initial nickel concentration was 4.0 hours, although nickel exchange reaction was fast enough to be carried out in a great extent before one hour of contact.

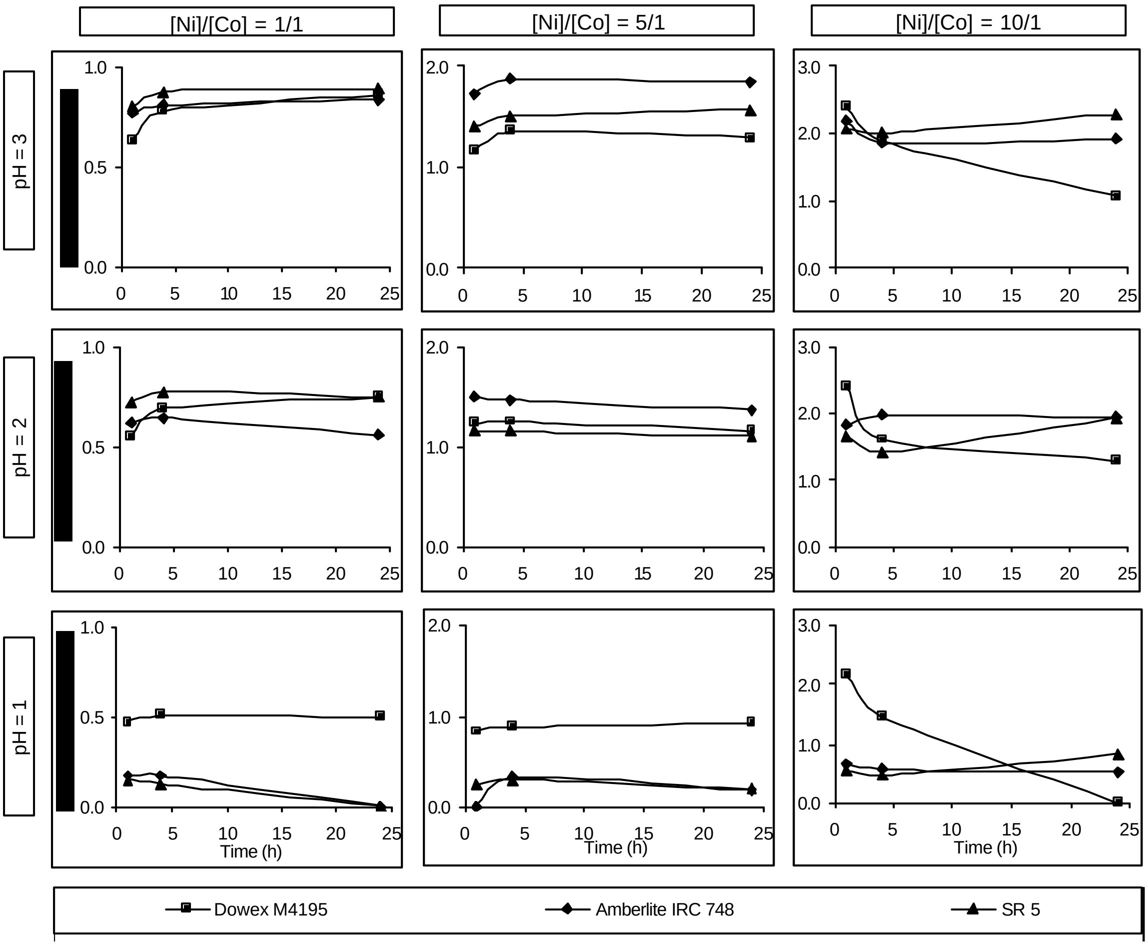

Figure 4.1 - Kinetics of nickel sorption on resin for three different resins

Increasing pH of the solution and the initial nickel concentration from [Ni]/[Co] = 1/1 to [Ni]/[Co] = 10/1 had a marked positive effect on the nickel uptake by the resin. Increasing the nickel content of the feed at a constant cobalt concentration resulted in increased resin selectivity (higher Ni/Co ratios on the loaded resin) and a reduction in the amount of feed solution that could be processed before complete nickel loading was achieved. The effect of [Ni]/[Co] ratio in the feed on resin selectivity is in agreement with the results reported by Rosato et al. (1984), who found that lower loaded resin Co/Ni ratios are obtained as nickel concentration of the feed increases. In figure 4.1 it can also be observed a particular behavior for [Ni]/[Co] = 10/1, where nickel sorption on resin Dowex M4195® decreased with contact time for all pH values.

Figure 4.2 shows cobalt sorption on resin for three resins: Dowex M4195®, Amberlite IRC 748® and SR-5®. Increasing the pH of the solution had a significant effect on cobalt sorption. On the other hand, the cobalt sorption tended to decrease during the time showing that the cobalt initially adsorbed by the resin seemed to be displaced by nickel ions due to their apparent higher affinity for the resin. Even greater nickel loading and lower cobalt loading would have resulted if more nickel concentrated solution (higher Ni/Co ratio) had been processed; and if the sorption process had been continued until the resin was nearly saturated with nickel, practically no cobalt would have remained in the resin.

The best results of cobalt sorption on the three studied resins were obtained in short times, approximately 1.0 hour of contact time. One other striking feature observed is that while initial nickel concentration in solution was increasing (higher Ni/Co ratios), the cobalt sorption decreased markedly. This behavior was less pronounced in resin Dowex M4195®, which presented the best performance for cobalt uptake in [Ni]/[Co] = 10/1 for all the studied pH range.

Influence of pH behavior

The equilibrium pH values in the preliminary tests varied in a wide range. Nickel and cobalt uptake were evaluated in acidic solution with pH varying in the range of 0 to 3.

Sulfuric acid and lime were used to adjust the initial solution to lower and higher pH values, respectively. A typical HPAL pulp contains approximately 40 g/L H_2SO_4, which generates a pulp of pH = 0.3. The goal was to verify the metals uptake at extremely low pH, as well as at higher ones, during 60 minutes of contact time.

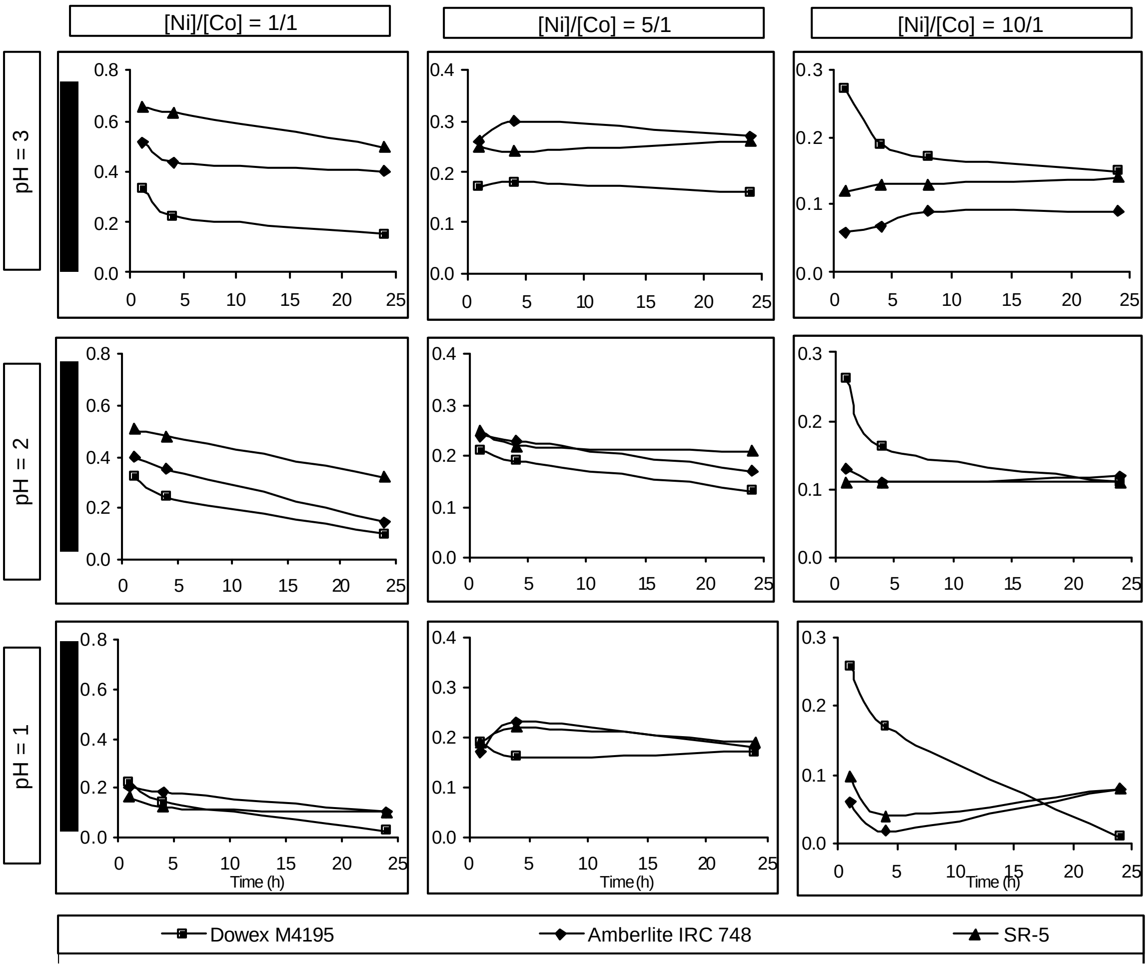

Figure 4.2 - Kinetics of cobalt sorption on resin for three different resins

Solution pH had a strong effect on nickel recovery. Increasing pH from 1 up to 2 and then to 3 was able to provide an increase on nickel sorption, as shown in Figure 4.3. This was due to the different chelating groups for transition metal ions. In general, most chelating exchangers are weakly acidic in nature. The iminodiacetate and aminophosphonate functional groups are affected by pH due to the presence of acidic groups, which can dissociate depending on pH. At lower pH values, only a small fraction of the functional groups will likely be dissociated and since cations cannot be removed by neutral acids, the nickel capacity of resins is reduced. The pH increase from 0 to 3 leads to the exchange capacity rise in the Ni^{2+} and Co^{2+} form for all ion exchangers investigated because the concentration of coordination – active (non protonated) functional groups decreases with the solutions' acidity increase (Kononova et al., 2000).

Figure 4.3 also shows the effect of solution pH on cobalt sorption. pH appeared to have a effect also on cobalt removal after 60 minutes, since at pH = 3.0, cobalt sorption on resins was slightly higher. From this figure, it is apparent that Ni is effectively adsorbed on the resin Dowex M4195® even at very low pH, as pH = 1.0. It also can be observed that for Ni/Co concentration ratio = 10/1, Dowex M4195® shows a marked selectivity for cobalt while for all other resins, the excess of nickel in solution inhibits the cobalt sorption. Resin Dowex M4195® also presents better performance for nickel uptake in all studied pH conditions for Ni/Co = 10/1.

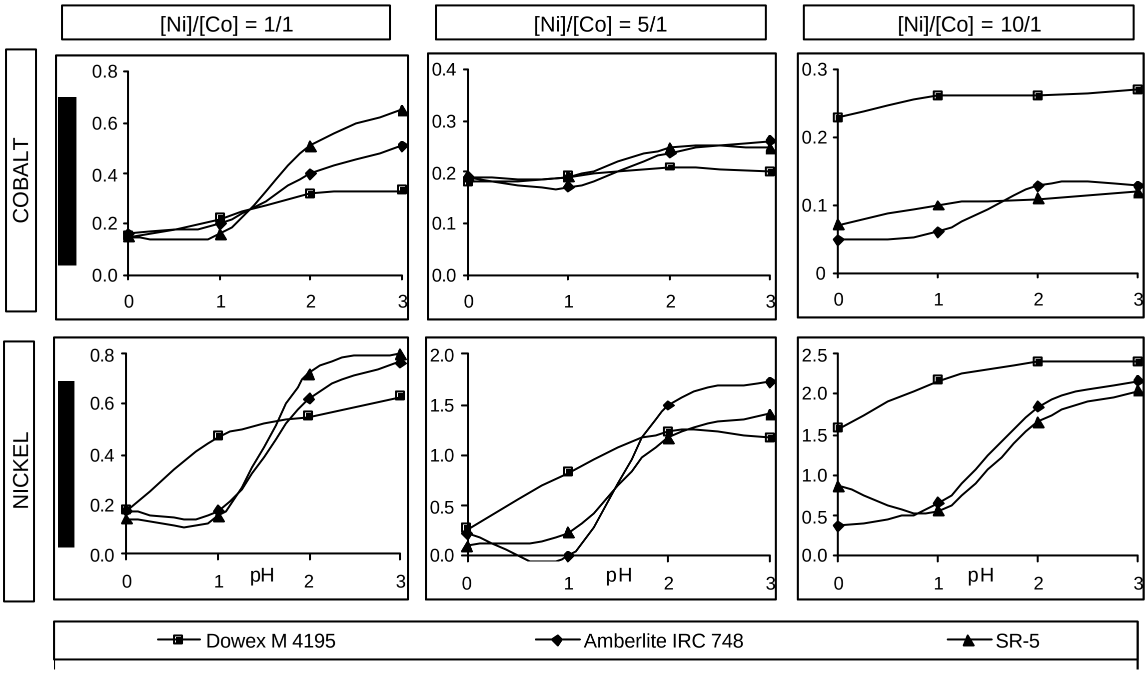

Figure 4.3 - Effect of pH on nickel and cobalt sorption (1 hour contact time)

Nickel sorption isotherm

To generate the sorption isotherm, approximately 1.0 g of vacuum-dried resin was contacted with varying volumes of solution of the same initial metal concentration to ensure a constant ionic strength for each sorption experiment. For each experimental point of the sorption isotherm, the resin was contacted with the solution (pH = 3), in a shaker operating at 200 rpm and at 25ºC, for 4 hours to ensure that equilibrium has been reached. After determining the metal concentration in solution, the amount of metal adsorbed onto the resin was calculated by difference and the sorption isotherm was plotted. Sorption isotherms were generated for three different resins: Dowex M4195®, Amberlite IRC 748® and Ionac SR-5®. The lines in the figure 4.4 were determined by a non-linear regression fit of the Langmuir isotherm according to the equation 4.3. It was used Origin software that was able to plot Langmuir isotherm fitted to equation 4.3 and simultaneously provide the parameters P_1, P_2 e n_s and their respective errors and correlation coefficient for three resins, as shown in table IV.2.

$$q_e = \frac{P_1 C_e}{1 + P_2 C_e} \tag{4.3}$$

where $P_1 = n_s \frac{k}{a_1}$ and $P_2 = \frac{k}{a_1}$, $\mathbf{n_s}$ is the number of moles of sorption sites per gram, $\mathbf{a_1}$ is the solvent activity in solution and **k** is the equilibrium constant.

For comparison, the linearized form of the Langmuir equation to identify the parameters is obtained according to equation 4.4.

$$\frac{C_e}{q} = \frac{1}{P_1} + \frac{C_e}{n_s} = \frac{1}{P_1} + \frac{C_e P_2}{P_1} \tag{4.4}$$

hence a plot of C_e/q against C_e yields P_1 from the intercept, and P_2 from the gradient.

The linear curve equation obtained for each resin is shown in equations 4.5, 4.6 e 4.7 and the parameters obtained by linearization method are very similar to those obtained by software Origin .

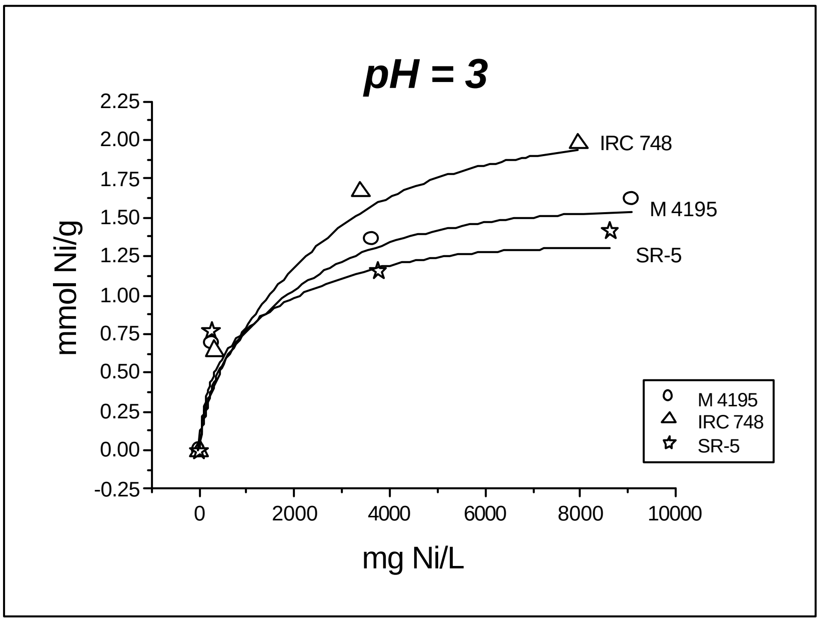

Figure 4.4 - Nickel sorption isotherms for three resins (4 hours contact time)

Table IV.2 - Parameters and errors obtained in Langmuir non linear curve fitting carried out for three resins loaded at pH = 3.

pH = 3			
	Dowex M4195 â	*Amberlite IRC 748 â*	*Ionac SR-5 â*
P_1	0.00409 ± 0.00095	0.00261 ± 0.0003	0.00689 ± 0.00243
P_2	0.00254 ± 0.00066	0.00122 ± 0.00017	0.00515 ± 0.00199
R^2	0.99055	0.99799	0.97974
n^s	1.61	2.13	1.35

Notation:

P_1 and P_2: Langmuir parameters
n^s : number of moles of sorption sites per gram of resin
R^2: correlation coefficient

Amberlite IRC 748®: $C_e/q = 0.4714\ C_e + 288.34$ (4.5)
$P_1 = 0.003468$ $P_2 = 0.001635$ $n_s = 2.12$

Dowex M4195®: $C_e/q = 0.6203\ C_e + 236.64$ (4.6)
$P_1 = 0.004226$ $P_2 = 0.002621$ $n_s = 1.61$

Ionac SR-5®: $C_e/q = 0.7422\ C_e + 152.61$ (4.7)
$P_1 = 0.006553$ $P_2 = 0.004863$ $n_s = 1.35$

The nickel loading results were fitted to a Langmuir isotherm. Figure 4.4 shows the relation between the concentration of Ni at time of 4.0 hours in the aqueous solution and the amount of sorption of Ni on different resins. It can be seen that the plots tend to approach a constant value with increasing nickel concentration, from which the maximum loading capacity on the chelating resins was evaluated. Table IV.2 shows the parameters and errors obtained in Langmuir non-linear curve fitting carried out for the three resins. The maximum exchange capacity was also determined for each resin in pH=3.

Nickel and cobalt uptake from simulating HPAL solution

The effect of impurities on resin loading was studied for the metals sulfate system. Four resins were tested in different pH values and all metal concentration (except iron) in solution was 1.0 g/L.

Figure 4.5 shows the selectivity of each resin for many metals. Iron was not included in solution. Clearly, all resins have an extremely high selectivity for copper and the second most extracted metal from the solution is nickel in the absence of iron. For all resins, pH had again a great influence on nickel recovery. The higher the pH of the solution, the better nickel recoveries were obtained for all resins. The best results of nickel uptake were obtained by Dowex M4195® in all pH values. Even in low pH such as pH = 1, Dowex M4195® has the best performance both for copper, which was totally recovered and for nickel, which was 25% recovered.

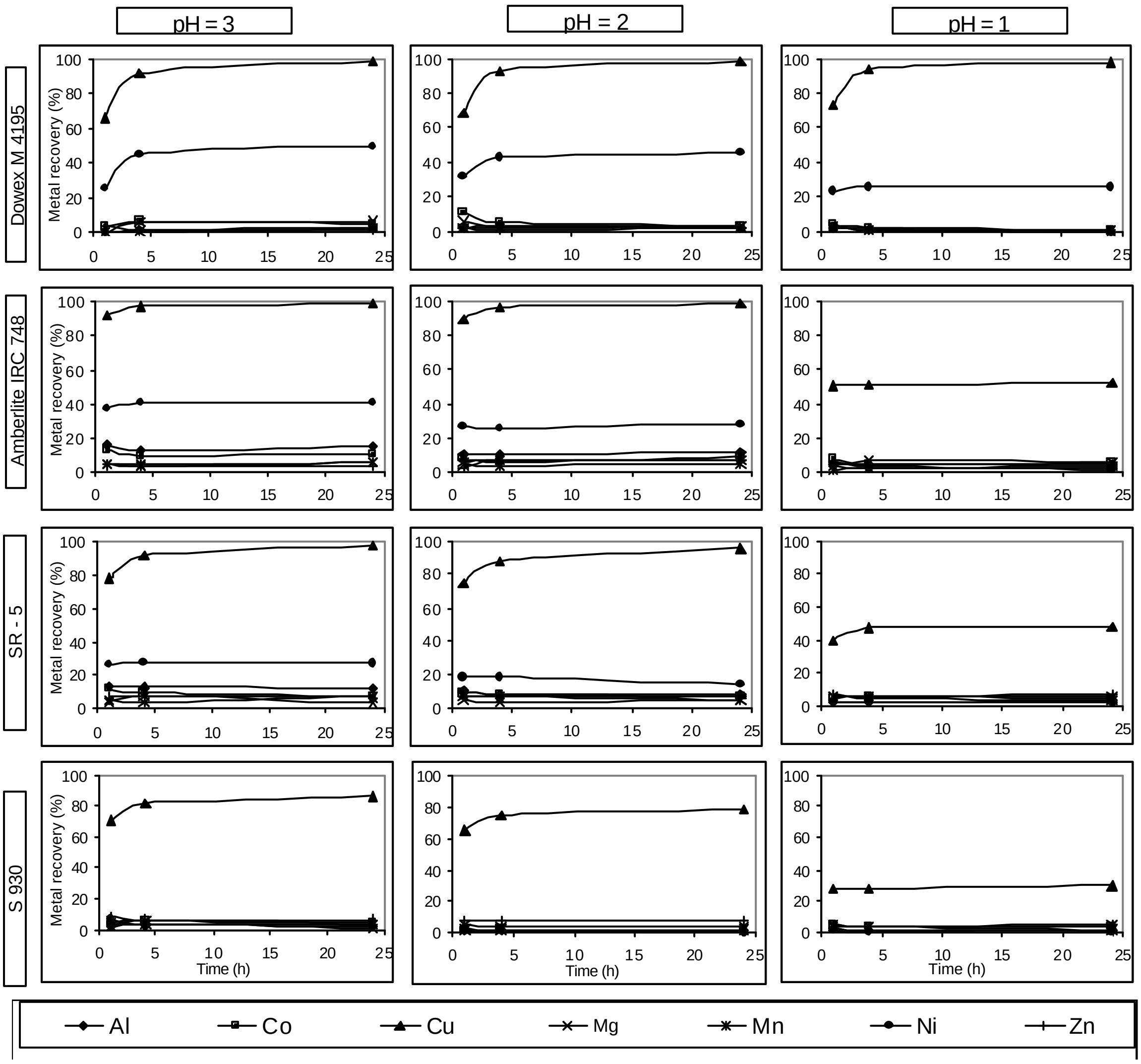

Figure 4.5 - Selectivity of resins for many metals

Other resins extracted less than 5.0% of nickel in pH = 1.0. Resin Amberlite IRC 748® presented the second best results followed by resins Ionac SR-5® and Purolite S 930®. Figure 4.5 also shows that while all other resins extracted small quantities of Al, Mg, Mn and Zn, these metals were less extracted by Dowex M4195®, avoiding the resin contamination.

After this first approach concerning the resin selectivity and behavior at different pH values, a solution simulating a typical HPAL solution was prepared and the metals uptake were evaluated. At pH 0.3, the concentration of iron (ferrous/ferric) in solution was high and would interfere with the sorption kinetics and loading capacity of the resin. Most studied chelating resins are firstly selective for iron. Previous works done by Zontov (2001) and Taylor and Jansen (2001) suggested that a more complete solution purification from iron could be reached by iron precipitation in the form of hydroxide, prior to RIP stage to avoid the resin loading with other metals besides nickel and cobalt.

In order to eliminate interference by soluble iron, the pH of the pulp was adjusted up to pH 4. Selective precipitation of the impurities was attempted using lime as an alkali reagent, as can be observed in Table IV.3. Virtually complete removal of Fe(III) iron and large removal of Fe(II) iron were achieved. Partial precipitation of nickel and cobalt occurred during neutralization. There was no special requirement for a ferrous oxidation stage at the same time as solution neutralization. Figures 4.6, 4.7, 4.8 and 4.9 show Al, Co, Cu, Fe, Fe(II), Mg, Mn, Ni, Zn recoveries at different pH values of 1 to 4 for four resins: Dowex M4195®, Amberlite IRC 748®, Ionac SR-5® and Purolite S-930®, respectively.

Table IV.3 - Solution metals concentration in all studied pH values after addition of lime

Metals concentration (g/L)									
pH	Al	Co	Cu	Fe	Fe(II)	Mg	Mn	Ni	Zn
1	6.90	0.50	0.13	3.24	1.02	8.96	1,78	6.50	0.18
2	6.44	0.38	0.08	2.93	0.90	8.30	1.64	7.15	0.09
3	6.31	0.38	0.08	0.71	0.69	8.38	1.65	7.04	0.09
4	0.67	0.26	0.03	0.44	0.42	7.61	1.29	5.02	0.07

Figure 4.6 shows the performance of Dowex M4195® on metals sorption. At low pH, this resin rejected iron better than any other resin tested and exhibited an increase of several fold in the copper/iron (III) selectivity. The presence of Fe, Al, Mg, Mn in high concentrations at low pH (pH=1 and pH=2) causes the sorption of these metals on the resin, although in a small extent, provoking the resin contamination. Nickel is approximately 25% adsorbed in the range of pH from 1 to 4 and pH does not seem to have a significant influence on nickel uptake. The pH increase avoided the impurity loading on resin. The best results for cobalt uptake were 10% recovery obtained at pH = 4 and for the studied pH range. The selectivity of Dowex M4195® is as follows: Cu>Ni>Co.

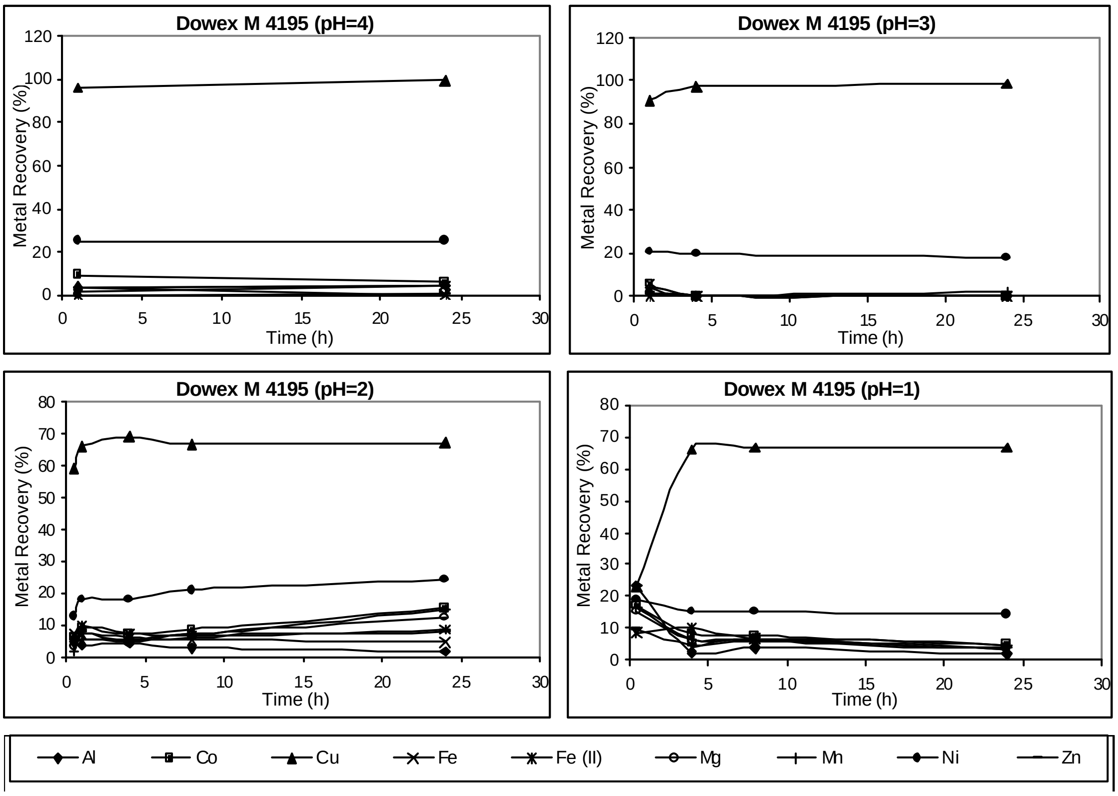

Figure 4.6 - Performance of Dowex M4195® on metals sorption for different pH values

Figure 4.7 shows the metals sorption on resin Amberlite IRC 748® in pH values varying from 1 to 4. Although good results for percent nickel recovery were obtained from the low pH processing solution, such as pH=1 or pH=2, the loaded resin contained considerable amounts of iron and copper ions. The other metals are less than 10% recovered. As pH increases to values such as, 3 or 4, copper is 100% recovered and nickel and cobalt sorption increase up to values such as 15% and 9%, respectively, at pH = 3, and 30% and 15%, respectively, at pH =4.

Figure 4.8 presents the metals sorption on resin Ionac SR-5® in different pH values. At pH = 1 and pH = 2, the resin shows a high selectivity mainly for iron followed by copper ions. The other metals are less than 10% recovered. When pH is increased the copper ions tend to be 100% recovered and at pH = 3, iron is still rather adsorbed by the resin than nickel. At pH = 4, the resin is selective for copper, nickel and cobalt, without the influence of iron, where Ni and Co are 24% and 15% recovered, respectively.

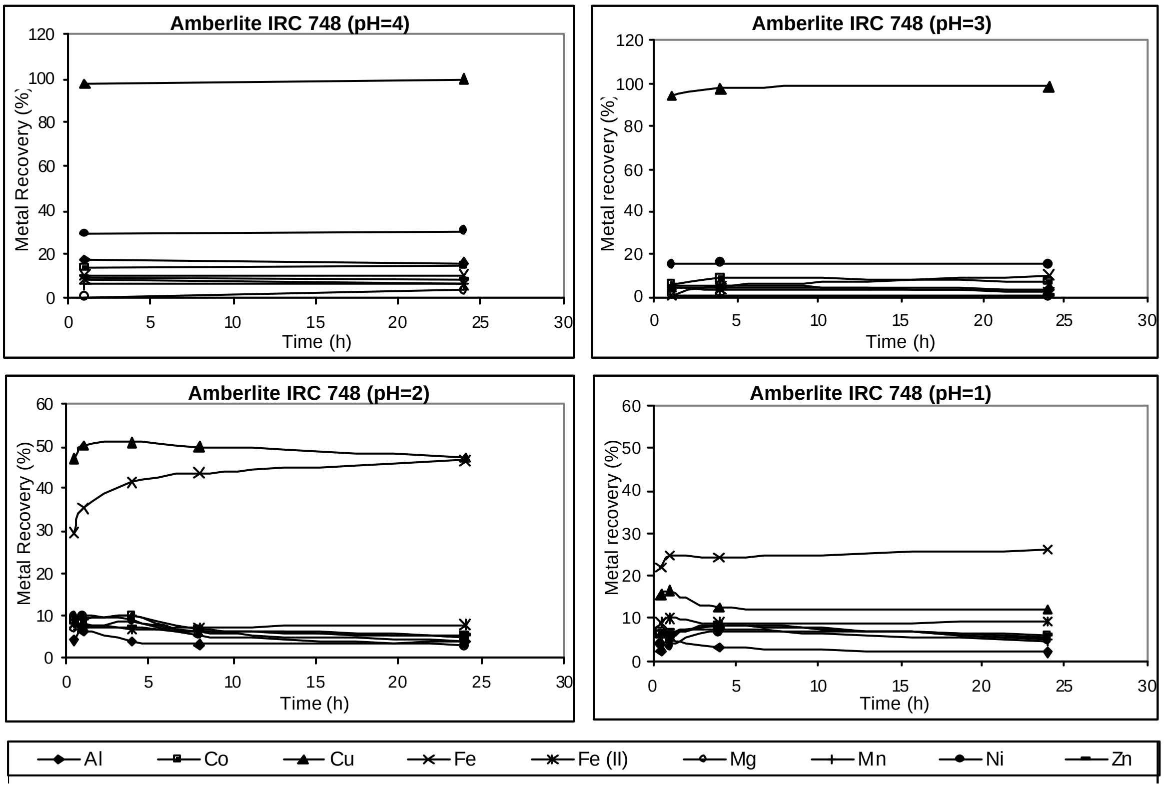

Figure 4.7 - Metals sorption on resin Amberlite IRC 748® in pH varying from 1 to 4

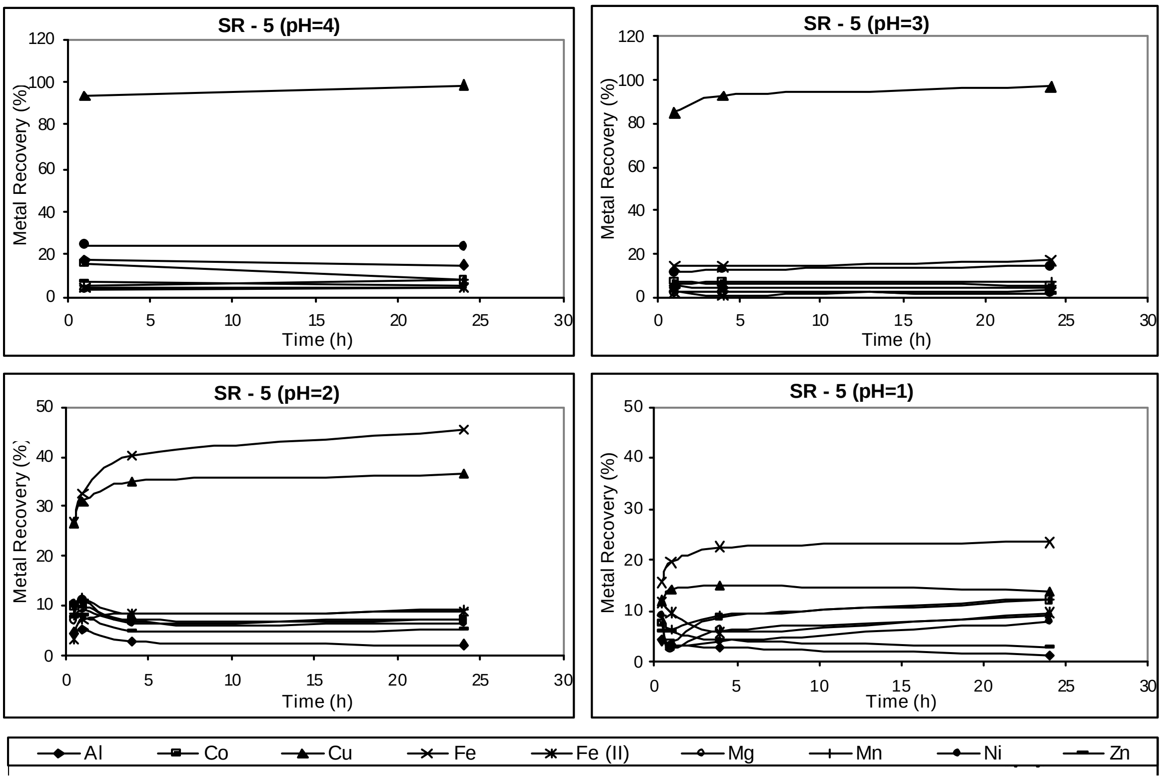

Figure 4.8 - Metals sorption on resin Ionac SR-5® in different pH values

Finally, Figure 4.9 shows resin S 930® performance on metals uptake. Even in high pH, such as pH= 3 or 4, and even with decreased impurities concentration in solution, the resin is not selective for nickel or cobalt. But on the other hand, copper ions are 96-98% recovered by this resin in high pH values.

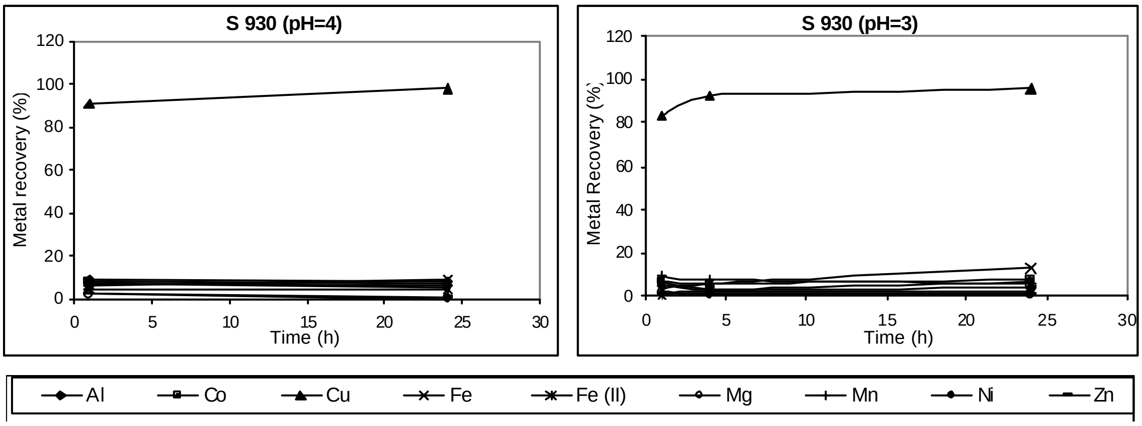

Figure 4.9 - Resin S 930® performance on metals uptake

Metals desorption

The resins Dowex M4195®, Amberlite IRC 748® and Ionac SR-5®, loaded in pH = 4, were eluted during 1.0 hour with different solutions concentration, as shown in Table IV.4. For resin Dowex M4195®, 1 M H_2SO_4 solution removed some loaded metals such as nickel, cobalt, iron, zinc, less quantities of copper and very low quantities of Al, Mn and Mg. However, 1.6 M HCl removed more nickel and less cobalt and iron compared to H_2SO_4. On the other hand, copper was more than 80% eluted using 1 M NH_4OH from resin Dowex M4195® loaded at pH = 4, while this reagent was not efficient in eluting other metals. This requirement was an advantage since it provided a mean of producing acidic eluates with less concentration of copper. The elution results obtained for resin Amberlite IRC 748® with sulfuric and hydrochloric acid solutions were very similar. Both solutions were able to elute almost all of these metals, except manganese which was less than 40% eluted. Nevertheless, NH_4OH was not able to elute any metal from the resin Amberlite IRC 748®. The same behavior could be observed for resin Ionac SR-5®. Sulfuric acid solutions eluted most of the loaded metals, but less quantities of Mn and Mg.

Table IV.4 - Elution results for the resins loaded at pH 4

Metal Elution (%) for resin loaded at pH = 4								
	Al	*Co*	*Cu*	*Fe*	*Mg*	*Mn*	*Ni*	*Zn*
Dowex M4195® (1 M H_2SO_4)	8.8	64.3	49.7	88.7	10	6.7	78.2	100
Dowex M4195® (1 M NH_4OH)	9.2	5.3	82.1	54.7	44.7	0.5	46.2	100
Dowex M4195® (1.6 M HCl)	na	29.81	na	10.1	na	na	96.4	na
Amberlite IRC 748 ® (1M H_2SO_4)	80.7	100	100	100	66.5	39.4	100	98.9
Amberlite IRC 748 ® (1.6 M HCl)	85.9	61.4	100	100	21.1	35.9	96	100
Amberlite IRC 748® (1 M NH_4OH)	na	0.1	na	0.01	na	na	0.1	na
Ionac SR-5® (1 M H_2SO_4)	65.2	88.4	100	69	23.8	48.1	100	100

Notation:
na: not available

The group bis-picolylamine (Dowex M4195) provides the option of selective elution according to the solution contacted to the resin. Nickel, cobalt or copper may be preferentially removed as long as a specific reagent is applied. The optimization of solution concentration should result in selective elution. On the other hand, the group iminodiacetic does not offer metals elution selectivity, where are almost totally eluted with hydrochloric acid or sulphuric acid. However, the latter provided the best results for nickel and cobalt removal.

Conclusions

All resins presented high selectivity for copper. Nickel is the second most extracted metal from the solution if some parameters are optimized such as pH, time, metals initial concentration and Ni/Co concentration ratio.

Increasing pH of the solution and the initial nickel concentration from [Ni]/[Co] = 1/1 to [Ni]/[Co] = 10/1 has a marked positive effect on nickel uptake. On the other hand, increasing the initial nickel concentration in solution (higher Ni/Co ratios), results in a decrease of the cobalt sorption. Cobalt sorption tended to decrease during the time and pH of the solution has a positive effect on cobalt sorption.

Even at low pH such as pH = 1.0, Dowex M4195® has the best performance both for nickel, which was 25% recovered and for cobalt. Other resins extracted less than 5% of nickel at pH = 1. At low pH, this resin rejects iron better than any other resin tested and exhibits a high copper/iron (III) selectivity. Dowex M4195® seems to be the best choice for nickel and cobalt selective sorption from PAL discharge liquor in all studied pH range, with small influence of other elements. Resin Amberlite IRC 748® presented very promising results, which justifies further evaluation in future studies. At pH = 4, this resin is selective for copper, nickel and cobalt, with small influence of iron, which was previously precipitated from solution. Nickel and cobalt recoveries were 30% and 15%, respectively.

Although Amberlite IRC 748®, Ionac SR-5 and Purolite S- 930 have the same functional group iminodiacetic acid, some fairly substantive differences concerning the ion exchange capacity were observed. The chemical stability and ion exchange behavior of the resin depend chiefly on the hydrocarbon chains structure, particle size, degree of crosslinking of the matrix (2-12% divinylbenzene) and the number of the fixed ionic groups.

For resin Dowex M4195®, 1 M sulphuric acid solution removed some loaded metals such as nickel, cobalt, iron, zinc, less quantities of copper and very low quantities of Al, Mn and Mg. On the other hand, copper was more than 80% eluted using 1 M ammonium hydroxide. For the other two studied resins, sulfuric acid and chloride acid solutions eluted most of the loaded metals, without any particular selectivity.

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Capítulo 5 - Avaliação de parâmetros na adsorção seletiva de níquel e cobalto através de resinas poliméricas comerciais

Mendes, F. D. ; **Martins**, A. H. ; **Costa**, R. S. . **Selective sorption of nickel and cobalt from pressure acid leach discharge liquors using chelating resins**. In: *XXII International Mineral Processing Congress, 2003, Cape Town. XXII IMPC, 2003*.

Este capítulo apresenta os resultados experimentais da recuperação de níquel e cobalto de soluções ácidas alcançados pelo emprego das resinas quelantes Amberlite IRC 748® e Dowex M4195®. Conforme apresentado no capítulo anterior, essas resinas apresentaram os melhores resultados de carregamento de níquel, sem a influência predominante de outros metais, principalmente em valores de pH superiores a 3 e após a precipitação de ferro da solução (Mendes et al., 2002). A avaliação do desempenho das resinas foi efetuada sob o ponto de vista da influência de alguns parâmetros, tais como a composição química da solução e o pH, que estão intimamente ligados à eficiência de adsorção. Também foram estudadas as resistências térmica e mecânica das resinas, a capacidade de carregamento para os metais de interesse para diferentes tempos de contato resina/solução aquosa, velocidades de agitação e relações massa de resina/volume de solução. O co-carregamento de outros metais e as cinéticas de adsorção e eluição também foram alvo de avaliação.

SELECTIVE SORPTION OF NICKEL AND COBALT FROM ACID LIQUORS USING CHELATING RESINS

Flávia D. Mendes and Renato S. Costa
Mineral Development Centre
Companhia Vale do Rio Doce
Rodovia BR 262 – km 296 – PO Box 09 - Santa Luzia – Minas Gerais - CEP: 33010-970 - Brazil
flavia.mendes@cvrd.com.br, renato.costa@cvrd.com.br

Afonso H. Martins
Universidade Federal de Minas Gerais
Rua Espírito Santo 35 sala 206
Centro, Belo Horizonte, Minas Gerais, CEP 30160-030, BRAZIL
ahmartin@demet.ufmg.br

Abstract

This paper presents some important aspects regarding the ion exchange treatment of a Ni and Co sulphate acidic liquor using chelating resins. Chelating resins possessing iminodiacetic or bis-picolylamine functional groups were compared in terms of nickel and cobalt recovery. The experimental resin with bispicolylamine functionalities (Dowex M4195) was evaluated with respect to Ni and Co uptake, and compared with Rohm & Haas commercial chelating iminodiacetate acid resin. The Rohm & Haas chelating resin, Amberlite IRC 748, with its weakly acidic groups, did not work in acidic solution but exhibited good results at pH 4 and above. The resin that efficiently removed metals from high acidic solutions was the bis-picolylamine resin. Maximum nickel uptake values ranged between 85 g and 112 g Ni per Kg of resin.

The experimental part dealt with the working conditions, resin characteristics and the influence upon the resin maximum exchange capacity of the following factors: nickel concentration, temperature, pH and resin-to-solution ratio. Based on the experimental data obtained, it has been proposed a innovative technological treatment.

Keywords: nickel, cobalt, sorption, ion exchange, chelating resin.

Introduction

Nickeliferous laterite ores constitute most of the world’s known nickel and cobalt resources and will likely be the world’s largest potential source of new nickel and cobalt in the future. Pressure acid leaching in horizontal agitated autoclaves is common to all new hydrometallurgical laterite treatment processes. Nickel and cobalt are recovered by the employment of a selective acid leach followed by a variety of techniques such as precipitation, solvent extraction, electrowinning that are being used for the upgrading, recovery and separation of the nickel and cobalt from clear leach liquor generated from the leaching of high-grade ores (Mayze, 2001). Ion exchange may be an attractive technology for the recovery of nickel and cobalt from these leachates. The potential benefits of increasing the plant throughput by resin-in-pulp are becoming increasingly evident (Outola et al., 2001). Because only limited ore upgrading is possible, large volumes of relatively dilute leach solution are produced, contained about 5 g Ni/L and 0.5 g Co/L, as well as significant quantities of Fe, Mg and Mn. Nickel and cobalt report to an impure solution, and must be recovered in purified forms.

Ion exchange (IX) processes are employed for the separation of metals, recovery of metals and removal of impurities from solution, slurries, and waste. It can also be more cost-effective and successfully applied to (1) the primary recovery of base metals from low-grade leached pulp (without any solid-liquid separation); (2) repulped precipitation residues to recover soluble base metal losses, such as filter cakes; (3) repulped leach residues and (4) counter-current decantation (CCD) or thickener underflows. Solid liquid separation of leach or precipitation residues, that are difficult to filter or settle, often result in significant losses of valuable metal and revenue (Zontov, 2001). When low-grade ores are processed, costs of filtration and settling become significant. With resin-in-pulp process, solid-liquid requirements may be reduced or possibly eliminated and higher recoveries can generally be achieved (Kotze et al., 2001). Furthermore, when these residues are discharged, they can pose environmental problems that contribute to operational expenditure if the residues have to be stabilised. In addition, it may be possible to significantly reduce wash water requirements associated with conventional solid-liquid separation steps. Ion exchange can recover soluble or entrained losses of the valuables metals from these residue slurries, improving the overall metal recoveries on the plant. A further advantage of ion exchange is that losses of co-precipitated (during iron removal) or adsorbed metal can generally also be recovered.

The use of selective ion exchange to recover metals from sulphuric acid liquors has been studied for a long time (Rosato et al., 1984). Companhia Vale do Rio Doce (CVRD) has been actively involved in hydrometallurgical applications of ion exchange (IX) and has researched in selecting the optimum resin for nickel and cobalt selective removal and the design of a suitable IX circuit. When an ion exchange operation is contemplated for a specific application, it is followed a screening process which generally involves consideration of the solution composition and pH, speciation of the metals in the liquor to be treated and other possible techniques that can be applied to achieve the desired specifications or recoveries. Once a decision has been made to use IX for a specific application, relevant testwork should be done to select the most cost-effective resin and design the IX circuit to achieve the desired criteria.

The first phase of project focused on the selective removal of nickel and cobalt from solution employing chelating synthetic resins. It has been found that these metals could selectively be recovered. Commercially available resins are considered for most applications and a testwork program should be developed to evaluate their potential, as well as feed pH and position of the ion exchange operation in the overall process flowsheet. Depending on the metal and the ionic form of the metal, the most likely resin types are selected for screening tests. Based on the results of the screening tests, preliminary economic evaluations are done in order to choose the most cost-effective product for further work. Elution tests are also conducted to determine the optimum elution, regeneration and washing strategies. Some criteria were taken into account for resin selection: feed composition, pH, and solution speciation; loading capacity of the resin for the metal of interest; co-loading of other metals or impurities; ease of elution (stripping); regeneration requirements; anticipated resin losses.

The commercial resins Dowex M4195®, Amberlite IRC748®, Ionac SR-5® and Purolite S930® are part of the group of ion exchange polimeric resins suitable for nickel and cobalt recovery from acid aqueous solutions. In previous works, the chelating resins

Dowex M4195® and Amberlite IRC 748® presented the best results, without the predominant influence of other metals, mainly in values of pH higher than 3 and after the precipitation of iron from the solution (Mendes et al, 2002). The chelating resins are examples of quite efficient ion exchangers in the selective removal of heavy metals, as nickel and cobalt, if compared to other ones. For the case of the resin Amberlite IRC 748®, constituted of iminodiacetic acid functional group, the presence of weak acid groups makes this resin selective for hydrogen ions. The lower the pH, the smaller the selective recovery of metallic ions due to the competition with the H^+ ions. These resins can usually be regenerated with acid solutions (sulphuric acid or hydrochloric), with high efficiency. On the other hand, chelating resins as Dowex M4195®, constituted by bis-picolylamine functional group with nitrogen atoms donors, exhibits some peculiar properties concerning the recovery of metallic ions from aqueous phase (Nagib et al., 1999). The metal load capacity is unaffected in low pH values, such as pH=1, for instance. Cations and anions can be removed simultaneously from solution. Finally, the regeneration or desorption of ions with ammonia is very efficient, while the acid regeneration is less effective (Sengupta et al., 1991).

The resins Dowex M4195® and Amberlite IRC 748® proved to be the best material for both nickel and cobalt recovery. This paper outlines chelating resins evaluation for nickel and cobalt removal. The influence of various parameters and their selectivity for nickel and cobalt over the other metals have been established. pH study for metals ions, effect of metal ion concentration on exchange capacity were also investigated. It was observed that time, temperature, resin/solution ratio and contact speed had influence on nickel and cobalt uptake.

Experimental

Two experimental resin were utilised. Dowex M4195 with bispicolylamine functionalities was manufactured by Dow Chemical and Amberlite IRC 748 is a Rohm & Haas commercial chelating iminodiacetate acid resin. A nickel and cobalt leach solution was applied.

Elimination of metal impurities by precipitation

The concentration of iron (ferrous/ferric), aluminium, and magnesium in solution was high and would interfere on the sorption kinetics and loading capacity of the resin. In order to eliminate interference by soluble metals, the pH of the pulp was adjusted up to pH 3.5 and Eh 500mV, resulting in metals hydroxide being precipitated. At this condition, as show in Table V.1, the purification is carried out in a way that the concentration of iron, aluminium, zinc, copper are reduced with a minimum precipitation of nickel and cobalt in the solution. Selective precipitation of the impurities was attempted using lime as an alkali reagent. The separation tests of metal impurities from solution were carried out using a 1000-mL beaker in one stage operation. Air was injected for 2 hours to oxidise iron and precipitate the impurities. The purified solution and precipitate were separated by filtration. The content of each metal in the filtrate was measured.

Table V.1 - Metals concentration in solution according to pH

pH	**Metals (mg/l)**				
	Al	*Co*	*Cu*	*Fe*	*Fe(II)*
0.5	7165	486	70	3284	882
3.5	914	453	3	22	17

pH	**Metals (mg/l)**				
	Mg	*Mn*	*Ni*	*Zn*	
0.5	8980	1879	8581	7	
3.5	8904	1826	7697	2	

Mechanical resistance

A study of the mechanical resistance of the resins to the abrasion was also made. The method is based on a particle size study made before and after the contact between the resin and water, in agitation of 1000 rpm, during different times (20, 40, 60 min and 24 hours). The sample is screened in 0.425 mm and the retained mass is submitted to the tests. The resin screening in 0.425 mm after the tests, allowed the evaluation of the generation of fine particles and, consequently, of the physical degradation of the resin.

Influence of parameters

The variables dependence experiments were carried out at constant standard conditions in order to exclude the interference of all other parameters besides the one of interest. Four variable were studied: time, temperature, contact speed, resin-to-solution ratio. These conditions were defined in previous work carried out to evaluate the variables influence on nickel and cobalt uptake. A solution containing 8.58 g/L Ni and 0.49 g/L Co, and adjusted to pH = 3.5 by the addition of lime, was preliminarily prepared as a treating solution. Batch-mode experiments were done by shaking resin in this treating solution, according to the parameters described in Table V.2 and using a controlled environment incubator shaker - New Brunswick Scientific-USA. The influence of four variables on the nickel and cobalt recovery was evaluated. Coupled Plasma (ICP/AES-Spectro - model Modula) was used to determine chemical analysis for all metals in solution. Any required sample dilutions used acidified distilled water (1mL of sulphuric acid, minimum assay: 96%, density: 1.84g/mL in 1000 ml of distilled water) to preclude/avoid precipitation of any metal.

Table V.2 - Standard conditions for variables evaluation

Test	**Variables**				
	pH	*Time (min)*	*Contact speed (rpm)*	*Temperature (C)*	*Resin-to-solution ratio (g/mL)*
Temperature dependence	3.5	60	200	25; 40; 50; 60; 75	1/50
Resin-to-solution ratio dependence	3.5	60	200	25	0.25/50; 0.5/50; 1/50; 2/50; 3/50; 4/50
Time dependence	3.5	5; 10; 20; 60; 180; 300	200	25	1/50
Contact speed dependence	3.5	60	100; 200; 250; 300; 350	25	1/50

Isotherms

Prior to determining the isotherms, the kinetic of the sorption was studied to ensure that equilibrium was reached. The extraction isotherms presented the equilibrium concentrations of nickel and cobalt in solution and adsorbed on the resin. Nickel concentration was varied in the range of 0.5 to 50 g/L Ni in solution and 1.0 g tapped-settled resin was added to 50 mL of solution and stirred at about 200 rpm for 1 hour at 25^{o}C.

Multiple sorption

Multiple sorption experiment was performed to determine whether the sorption of metals deviated from the sorption isotherm. The resin was equilibrated in a four-stage procedure. First, 1g of fresh resin was contacted with 50 mL aliquots of treating solution under 25C and 200 rpm for 15 and 45 minutes to saturate the resin. The solid and liquid phases were separated by filtration. And then, the obtained aqueous phase was again contacted with 1g of fresh resin. This procedure was repeated twice. The final solution was finally taken to determine the concentrations of cobalt and nickel.

Elution: reagents and concentration

Nickel and cobalt sorbed on the chelating resin could be quantitatively eluted stepwise by a series of suitable solutions. Once the conditions were determined that would ensure equilibrium, further desorption studies were undertaken, including desorption into different solutions. Two different reagents were tested in three concentrations as shown in Table V.3.

Table V.3 - Reagents and concentrations tested in elution tests

Reagent	*Concentration*		
Sulphuric acid	0.5 N	2.0 N	10.0 N
Hydrochloric acid	2 %	6 %	18 %

The kinetics of metals desorption were studied by contacting load resin with sulphuric acid and hydrochloric acid in a shaker. Approximately 1g of resin was added to 50 mL acid solution and stirred at about 200 rpm for 1 hour. After each desorption, the amount of metal adsorbed on the resin was determined by mass balance, using the concentration of metal in the solution and the amount presented on the resin surface.

Results

Parameters: temperature, time, contact speed, resin-to-solution ratio

The effect of four variables on nickel, cobalt and iron uptake was studied under batch conditions for resins Dowex M4195 e Amberlite IRC 748. The relationship between the nickel and cobalt sorption on resins and the variable under study is shown in figure 5.1 and 5.2.

Figure 5.1 illustrates that the nickel sorbing is affected significantly by the resin to solution ratio and a maximum load was achieved in 3g resins/50 ml solution. The resin load did not improve with the increase of temperature thereupon. The effect of contact speed on the sorption of nickel demonstrated that both resins have opposite behaviour compared to each other with small change on the load results obtained. It is also shown time dependency of nickel sorption. According to the kinetics results, a period of 45 minutes was sufficient to get maximum nickel load capacity. However, when contact time was longer than 45 minutes, the sorbing of nickel remained stable showing that equilibrium was reached. Based on these experimental results, the final optimum conditions for the nickel sorption procedure were determined to be: 25^{o}C, 200 rpm and 45 minutes of contact. Under these conditions 100 mg/g of nickel could be recovered by the resin.

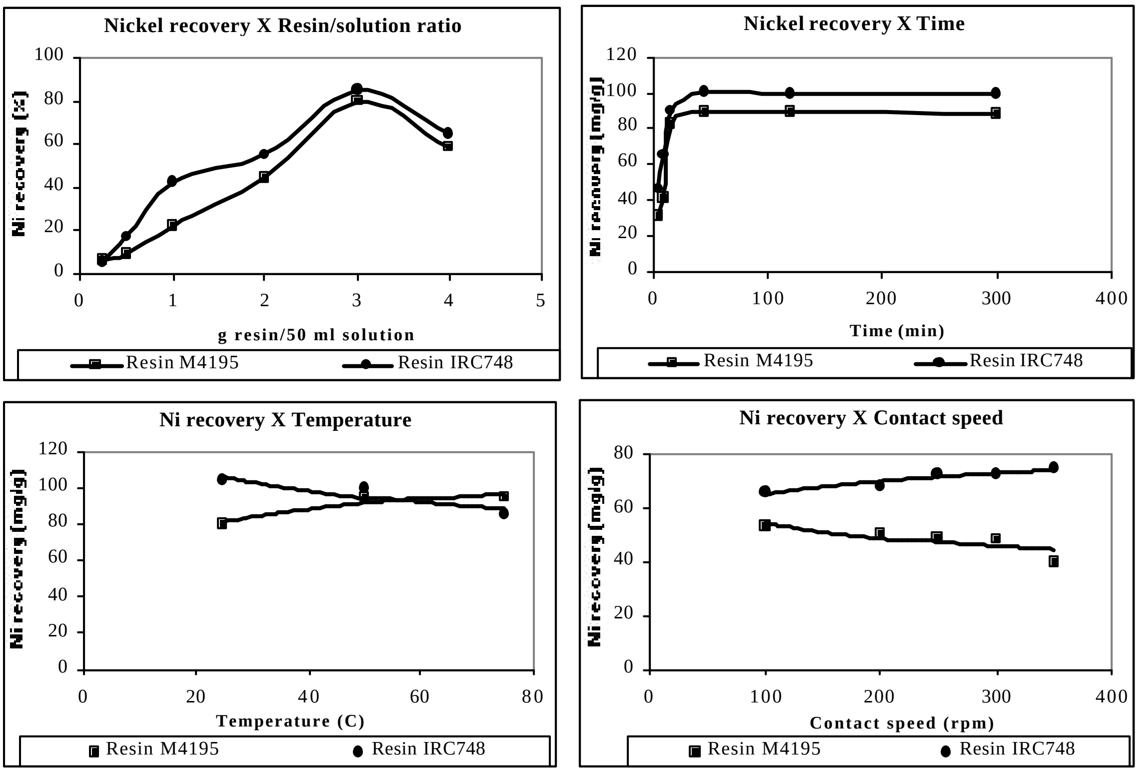

Figure 5.1 - Variables influence on nickel uptake

Figure 5.2 shows that the sorption of cobalt decreased with the increase of temperature, although this behaviour has not been observed for nickel uptake. On the other hand, the cobalt sorption did not change when contact speed increased. Cobalt sorption did rise steadily with the increase of time within the first experimental 15 minutes and then it started to decrease significantly. This phenomenon can be attributed to the competitive sorbing on the ionic exchange sites between nickel and cobalt. As the resins are more selective for nickel, the adsorbed cobalt was returned to solution. The effects of all variables under study on this procedure are shown in figure 5.2. Overall, high R/S ratio and high temperature gave high cobalt sorption efficiency. However, the use of an excessively large time is evidently undesirable from the point of view of high productivity and convenience.

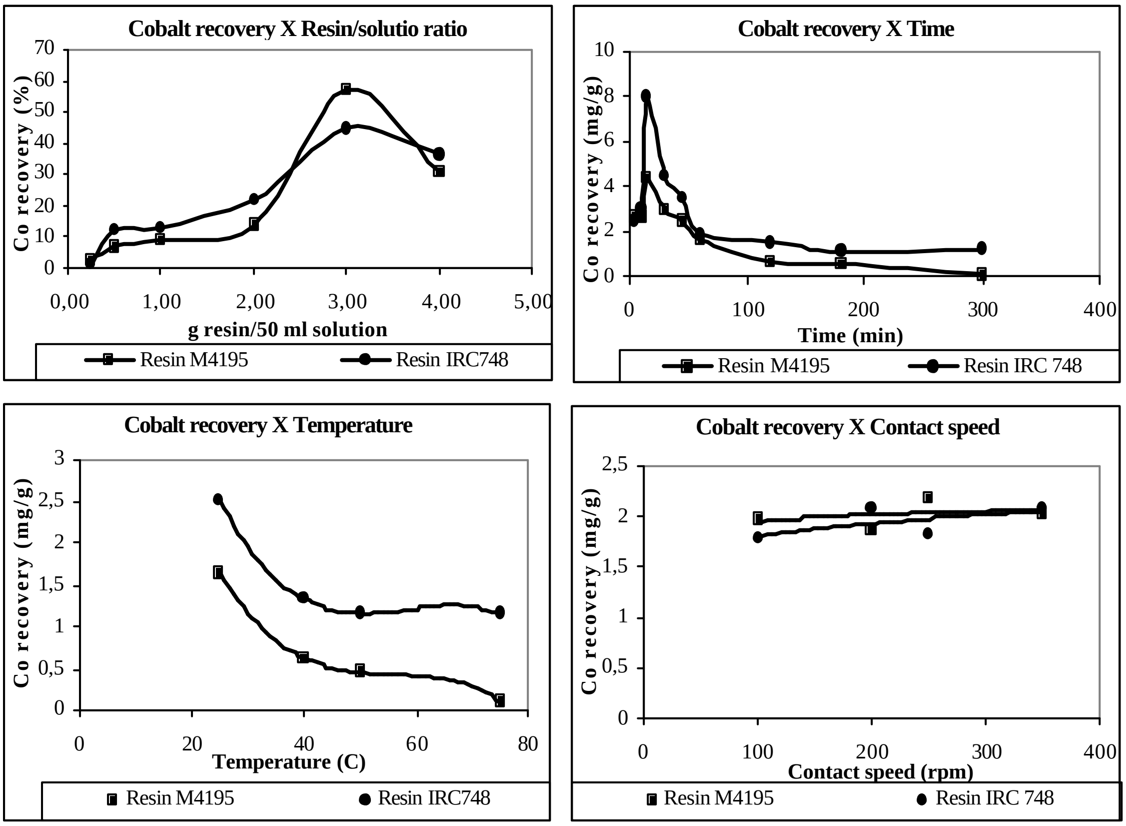

Figure 5.2 - Variables influence on cobalt uptake

Mechanical resistance

The resistance experiments showed that resin Dowex M4195® presented a larger loss of physical surface due to the largest generation of fine, according to Figure 5.3. The influence of contact time, in this case, seemed to have a small influence. For resin Amberlite IRC 748® this effect was comparatively much less pronounced, with a small but increasing degradation of the surface of the resin as the contact time increased.

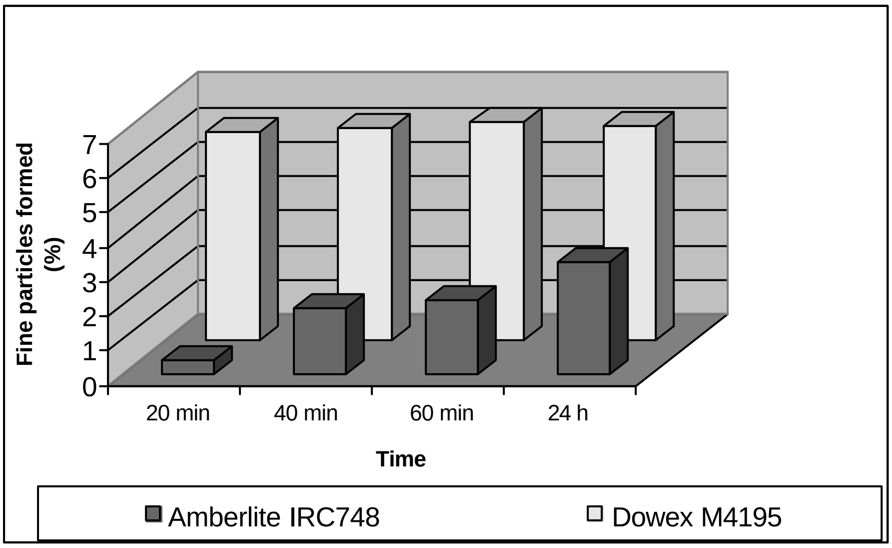

Figure 5.3 - Formation of fine particles during resistance tests

Isotherms

The isotherms of Figure 5.4 show equilibrium concentrations among nickel in the solution and nickel and cobalt adsorbed on the resin. Sensitivity of the resin towards the level of nickel in solution was observed to enhance the sorption performance of the resin.

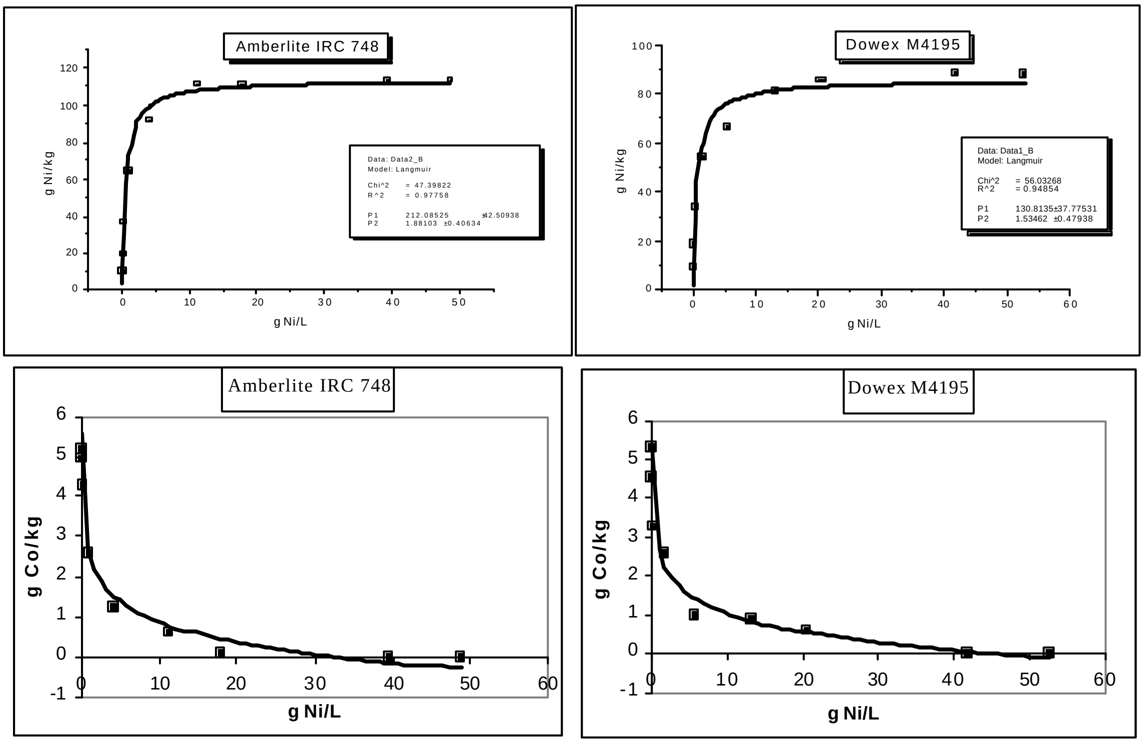

Figure 5.4 - Nickel and cobalt isotherms

It is observed that for the two resins, the concentration of adsorbed nickel increases as equilibrium nickel concentration rises. Due to the conditions adopted in the experimental procedure, the maximum load capacity was 85 g Ni/kg for resin Dowex M4195®, while for the resin Amberlite IRC748®, this value was sensibly higher, around 112 g Ni/kg. An inverse behaviour was identified for the sorption of cobalt in the resin. As the nickel concentration in the solution was increased, it occurred a decrease of cobalt recovery by the resins. That fact can be justified for the higher selectivity for nickel ions rather than cobalt ions, mainly if nickel is present in high concentration in the solution, resulting in a minimised cobalt recovery. A maximum load of 5.3 gCo/kg was achieved in conditions of low nickel concentration for resin Amberlite IRC748®.

Multiple sorption

Based on the batch experimental results, it is observed in the Figure 5.5 that the best results of nickel and cobalt recovery along four stages were reached by the resin Amberlite IRC748® independently of time. It is interesting to notice that, while the largest nickel recoveries occurred in 45 minutes, contrarily, the best sorption of cobalt occurred in shorter time, about 15 minutes. This fact was verified for both resins. The best nickel load was 488 g Ni/kg after four consecutive stages obtained by the resin Amberlite IRC748® during 45 minutes. The best recovery of cobalt was 14 g Co/kg verified for the same resin after 15 minutes.

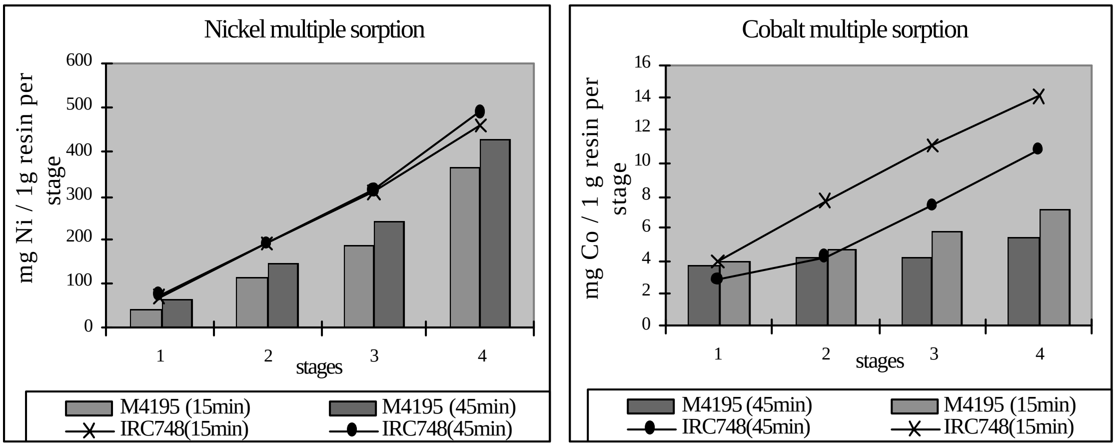

Figure 5.5 - Nickel and cobalt multiple sorption

The last part of the experimental work was the study of elution of the loaded resins. Solutions of sulphuric acid and hydrochloric acid were used in three different concentrations. Figure 5.6 displays that the sulphuric acid was the best reagent for nickel and cobalt desorption in both resins. Better results, however, were obtained by the resin Amberlite IRC748®. Nickel could be eluted by 0,5N sulphuric acid solution, while other impurities were retained. Opposed effect was observed with the hydrochloric acid as eluate agent, since nickel and cobalt were more easily eluted from the resin Dowex M4195® with the use of this reagent. It can also be observed that the smaller the concentration of the reagent, the larger the amount of metal eluted from the resins. Besides, a significant decrease in metal elution was verified with the application of very concentrated solutions. The elution rate increased with a decrease in acid concentration.

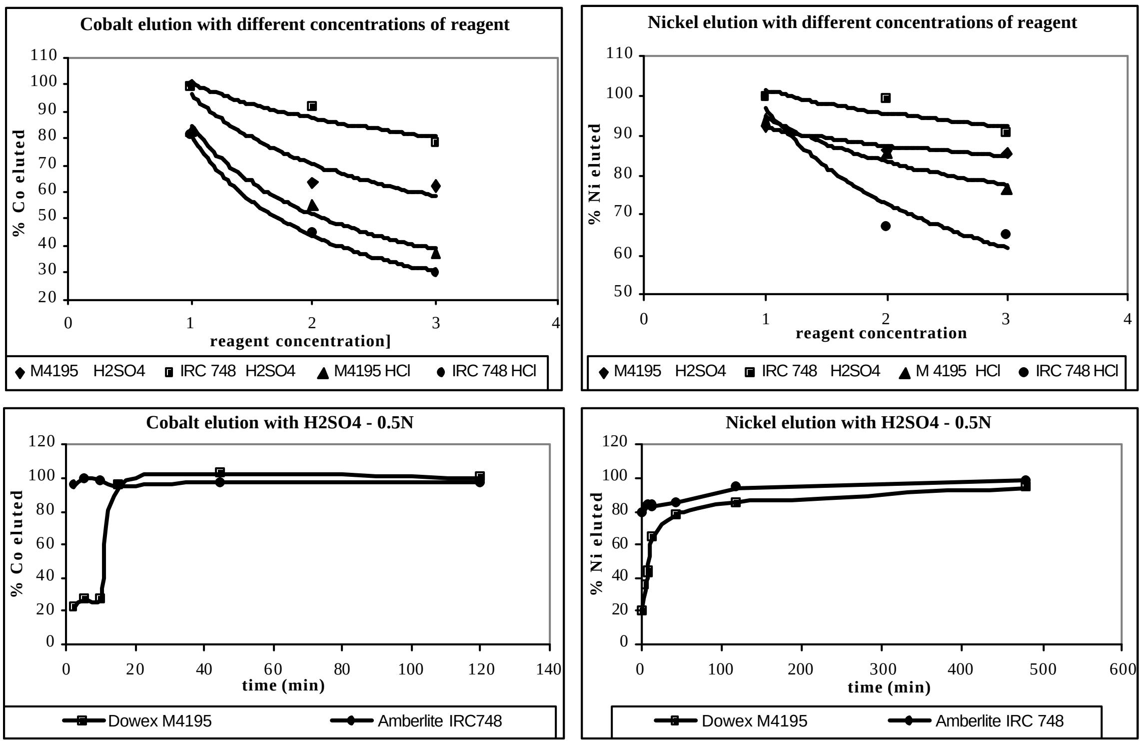

Figure 5.6 - Nickel and cobalt elution

According to the best condition of elution for resins Dowex M4195® and Amberlite IRC748®: sulphuric acid in the concentration of 0.5 N, kinetics data of nickel and cobalt elution were achieved for the two resins. Figure 5.6 also shows that for the resin

Amberlite IRC748®, the process of nickel and cobalt elution was quite fast with removal of high amounts of loaded metals in the first minutes. The behaviour of the resin Dowex M4195® was slower, with a curve sharply rising in the initial minutes, showing to be essential a minimum time for the equilibrium to be reached.

Conclusions

The resin Dowex M4195® was considered a selective resin for nickel and cobalt sorption from acid solutions. Due to the great similarity of the studied resins regarding nickel and cobalt selectivity, the results showed that the resin Amberlite IRC748® presented a high potential of application in the recovery of those metals since some conditions are followed, as solution pH higher than 3.5 and elimination of ferric ions from solution. The resin Amberlite IRC748® provided the best nickel load results, besides presenting appropriate mechanical resistance and acceptable thermal stability, without modification of your physical structure when submitted to temperature as high as 80°C. The application of the resin Amberlite IRC 748® for nickel and cobalt recovery from laterite ore leach solutions depends on a previous treatment of the solution, as for instance the elimination of some impurities and operation in pH values above 3. The elution of both resins was efficient with the use of sulphuric acid 0.5N, showing that it is a quite fast process with removal of great part of nickel and cobalt in short times.

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Capítulo 6 - Recuperação seletiva de níquel e cobalto de solução HPAL usando coluna de resina de troca iônica

Mendes, F.D. and **Martins,** A.H.. **Selective nickel and cobalt uptake from pressure sulfuric acid leach solutions using column resin sorption.** *International Journal of Mineral Processing, Volume 77, Issue 1, September 2005, Pages 53-63*

Este capítulo apresenta os resultados experimentais da recuperação de níquel alcançados nos ensaios de adsorção em coluna realizados com a resina Amberlite IRC 748®. Devido aos resultados positivos de adsorção seletiva de níquel após a otimização de parâmetros (vide capítulos anteriores), essa resina foi escolhida para ser utilizada no prosseguimento desse trabalho. O desempenho dessa resina frente à adsorção de níquel em colunas de vidro foi avaliado diante da variação de parâmetros tais como pH, taxa de alimentação e concentração de níquel na solução.

SELECTIVE NICKEL AND COBALT UPTAKE FROM PRESSURE SULFURIC ACID LEACH SOLUTIONS USING COLUMN RESIN SORPTION

F.D. Mendes ([a,*]) and A. H. Martins ([b])
([a]) Research Engineer, Companhia Vale do Rio Doce-Brazil
([b])Adjunct Professor, Department of Metallurgical and Materials Engineering at Federal University of Minas Gerais–UFMG/Brazil

Abstract

Selective removal of Ni and Co, from a high pressure acid leach (HPAL) solution of a Brazilian laterite nickel ore that contains relatively high concentration of impurities, was carried out with an ion exchange chelating resin possessing iminodiacetic acid group (Amberlite IRC 748®). The resin was tested in column experiments. The experimental results showed that higher pH values improved the ion exchanger performance and higher nickel load capacities were achieved. Besides, increasing nickel concentration in solution, nickel uptake and selectivity were substantially improved. The breakthrough experimental curves also showed that many metals were immediately brokenthrough just after the initiation of the feed, while the breakthrough of Ni began later. These results suggested that it is feasible to purify HPAL solution recovering nickel selectively using the chelating resin Amberlite IRC748® if some specific conditions related to pH, flow rate and nickel concentration are applied. Removal of metals from the resin was successfully performed with HCl and H_2SO_4 solutions. Nickel was eluted concentrated more than 20 times its initial concentration in the feed solution, while only a trace amount of impurities was eluted.

Keywords: nickel, cobalt, resin, ion exchange

* Corresponding author: Tel.:+55-31-36914467
E-mail address: flavia.mendes@cvrd.com.br

Introduction

High pressure acid leaching (HPAL) of laterites is one of the alternatives to recover nickel and cobalt from equatorial lateritic ores, with high selectivity due to occurrence of simultaneous iron and aluminum dissolution, followed by their precipitation. Laterite leach solutions consist of a large number of metal sulfates, including Al, Mg, Ni, Mn, Zn, Fe, Co, Cu, obtained from the usage of excess sulfuric acid at high temperature and pressure. The metals concentration in the leach solution depends on the ore composition, the feed acidity, the temperature, the solid liquid ratio and the leaching time.

The downstream Ni/Co recovery process is different in each of the existing nickel laterite processing plants. At present, HPAL solutions are purified by solvent extraction or ordinary precipitation method, in which alkalis are added to aqueous solutions to precipitate metal hydroxides. One other option is the ion exchange (IX) technology application, which is considered to be a straightforward technique, which may offer an effective performance and provide a cost effective solution to downstream process. Some advantages pointed out by Zontov (2001) include: (1) lower environmental burden – less water consumption and water recycling opportunity; (2) economic constraints – lower operating and capital costs of equipment and (3) the quality of manufactured metal products – high selectivity for target metals and high separation capabilities. Besides, an IX-based process combined with counter current decantation (CCD) may provide savings in operational costs when compared with other process options.

Ion exchange processes, where cations are removed from solution, usually utilize ordinary ion exchange polymeric resins, containing either strongly acidic sulphonic or weakly acidic carboxylic functionalities. Chelating resins have been developed to selectively take up transition metals from solutions, since they form strongly complexing chelates with them. Since alkali and alkaline earth metals do not form complexes, in general, these resins do not favor their removal. Most chelating resins are produced by main resin manufacturers and are used and studied for processing metallurgical process and waste effluents treatment. The most typical chelating resins, iminodiacetate and aminophosphonate resins, are weakly acidic and thus do not work as cation exchangers in acidic solutions.

The goal of these laboratory trails was to assess the suitability of the chelating iminodiacetic acid resin - Amberlite IRC 748® (Rohm and Haas Química Company-USA) - for nickel and cobalt recovery from HPAL discharge, to establish performance data and to optimize some operating conditions. The resin was evaluated with respect to Ni and Co uptake when changes in pH, metals concentration in the feed solution and flow rate through the column bed occur. Column tests with the resin Amberlite IRC 748® were carried out to determine its total metal loading and to evaluate its feasibility for practical use. The selective sorption of nickel from HPAL solution is a challenging work, because it has competing metal ions in addition to nickel and it is worthwhile to determine how the presence of these ions would affect the nickel uptake capacity of the resin.

Experimental Procedure

Material

Breakthrough tests were carried out using a packed column of borosilicate glass with 40 cm height, an internal diameter of 4.5 cm and a sintered glass bottom. When filling the column with resin, a short backwash with deionised water was done to ensure proper packing of the bed. Amberlite IRC 748® was chosen to be used in these laboratory tests. The leach solution used in the experiments was obtained from a high pressure acid leaching of a Brazilian laterite. Solutions were passed through the column downflow in different flow rates, metal concentrations and pH values. Effluent solution samples were collected along the experiments and their metals concentration results were used to build breakthrough curves. After the experiment, the resins were washed with deionised water and eluted with sulfuric acid and hydrochloric acid solutions in different concentrations.

Pretreatment of resins

The resin was pretreated in column. All the ion exchange experiments were done with sodium-converted resins. Resin was eluted with acid solution to remove metal species, rinsed with deionized water, eluted with four bed volumes of NaOH 5% solution and rinsed with distilled water until the pH value of the eluent reached 7.0-8.5. Rinsing was stopped at this pH range to avoid resin hydrolysis, i.e. formation of H^+/Na^+ mixed form resin in large extent.

Sorption Experiments

The actual selectivity and loading capacity values observed for chelating resins depend on pH solution, flow rate, metal concentration and the presence of other metal complexing ligands. This makes absolute selectivities very difficult to determine. Because of this, laboratory testing is essential when a resin is required to remove one or more types of metal ions selectively. In general for Amberlite IRC 748®, the selectivity follows the following order: $Na^+ << Ca^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Cd^{2+} < Zn^{2+} < Ni^{2+} < Pb^{2+} < Cu^{2+} < Hg^{2+} < Fe^{3+}$. In column tests, samples of the effluents were collected to determine the metals ion concentration after their sorption on resin (C_f) and this value was compared to metals feed concentration (C_i). The results are presented as breakthrough and elution curves for a number of metals. Two parameters were chosen to determine the resin performance: the percent nickel and cobalt sorption and load capacity. They were shown comparatively to indicate the optimum conditions to obtain the best results. Their calculation were based on the difference between the metal mass in the feed solution (metal concentration in a known volume of feed solution) and metal mass in the effluent solution (metal concentration in a known volume of effluent solution) along the bed volumes that passed through the column and were collected in the effluent. The final nickel and cobalt load capacity was confirmed by determining metals concentration in pregnant solution at elution stage. This analysis provided the quantification of metals mass adsorbed in a know mass of resin. Some parameters dependence on metal uptake was also studied:

- ***Effect of pH***: the initial pH of HPAL solution was between 0.5 and 0.7. This high acidity is not desirable for nickel and cobalt uptake using chelating resins (Grinstead, 1984). In general, most chelating exchangers are weakly acidic in nature. The iminodiacetate and aminophosphonate functional groups are affected by pH, due to the presence of acidic groups, which can dissociate depending on pH. At lower pH values, only a small fraction of the functional groups will likely be dissociated and since cations can not be removed by neutral acids, the nickel loading capacity of the resins is reduced (Kononova et al., 2000). Consequently, the effect of higher pH solutions on nickel sorption was examined. Tests were carried out with pH solutions at 2, 3 and 4. The pH of the solution leaving the column should be high at the beginning of the experiment, because of the sodium ions, with a basic nature, introduced into the solution from the resin. The pH then should decrease gradually, until reaching the pH of the feed solution. During the pH adjustment to higher values, it was verified the precipitation of some metal hydroxides, mainly at pH = 4, when 95% of iron, 87% of aluminum, 96% of copper, 10% of nickel, and 7% of cobalt were precipitated from feed solution. After solid-liquid separation, this residue was not of interest and was disposed. The only goal was to have solutions with different pH and different concentrations of elements, mainly different ratios of [Ni]/[Fe].

- ***Effect of metals concentration in the feed solution:*** The effect of high nickel feed concentration on resin loading was examined at room temperature. Solutions of different nickel concentration were pumped through the 22 cm resin bed at different flow rates, as shown in table VI.1. Iron concentration was controlled by precipitation to range between 0.5-1.0 g/L, while nickel concentration varied between low values (1.5- 1.8 g/L) and high values (7.3-8.4 g/L) according to the test. The goal was to evaluate the resin selectivity in two different conditions: when nickel and iron concentrations are low (tests 1, 2 and 5) and when nickel concentration is much higher than iron concentration (tests 3 and 4). According to table VI.1, the solutions presented a higher concentration of Fe^{3+} if compared to Fe^{2+}, due to the ferric sulfate formed in HPAL. As shown before, the selectivity of Amberlite IRC 748® for Fe^{3+} is much higher than for Fe^{2+}.

Table VI.1 - Metals concentration in feed solution (g/L)

Concentration (g/L)											
Test	*pH*	*Flow rate (BV/h)*	*Al*	*Co*	*Cu*	*Fe^{2+}*	*Fe^{3+}*	*Mg*	*Mn*	*Ni*	*[Ni]/[Fe] ratio*
1	2	11.0	0.3	0.08	0.01	0.7	0.2	2.6	0.2	1.5	1.7
2	3	11.0	0.3	0.08	0.01	0.5	0.1	2.4	0.3	1.6	2.7
3	3	1.7	2.3	0.45	0.07	0.6	0.2	7.1	1.6	7.3	9.1
4	4	1.7	0.02	0.43	0.04	2.0	0.5	14.4	1.8	8.4	3.4
5	4	11.0	0.2	0.09	0.01	0.3	0.1	2.7	0.3	1.8	4.5

- ***Effect of flow rate on resin loading:*** The effect of flow rate on the resin loading characteristics was investigated at room temperature with 22 cm deep resin bed at 1.7 BV/h e 11 BV/h. The experiments run continuously until the nickel concentration in the effluent (Ni_f) was the same as that in the feed solution (Ni_0), represented by the ratio $Ni_f/Ni_0 = 1$.

Elution experiments

From an economic point of view, it is crucial to obtain as high a metal concentration in the regenerant as possible. This can be achieved by utilizing concentrated acid solutions and employing an appropriate arrangement of ion exchange unit operation. Preliminary results for elution tests were obtained with H_2SO_4 (7.5%w/w, 10%w/w) and HCl (6%w/w, 10%w/w, 15%w/w) solutions passing through fully loaded Amberlite IRC 748® resin at 2.3 BV/h flow rate and at room temperature.

Results

Five tests were carried out with HPAL solutions obtained with a Brazilian Laterite ore. Parameters such as Ni concentration, flow rate and pH were varied. Different nickel concentrations were adopted and for samples dilutions, it was used acidified distilled water. The feed solution rate was controlled using a peristaltic pump. Sulfuric acid and lime were used to adjust the initial pH solution to lower and higher values, respectively.

- **TEST 1**: Initial comparative metals loading data for resin Amberlite IRC 748® was obtained by processing approximately 70 bed volumes (BV) of HPAL solution (1.5 g/L Ni) at pH 2.0 through 0.36 L resin bed at 4 L/h (11 BV/h) during 6 hours and room temperature. Figure 6.1 shows the breakthrough curves obtained in test 1 for many metals, such as Ni, Co, Fe, Cu, Mn, Mg and Al.

At the beginning of the experiment, the ascending curve of Ni, Co, Al, Mn e Mg means that they were rapidly adsorbed on resin and then displaced to solution, since the ratio $C_f/C_0 > 1$ was obtained. After desorption, the metals in the feed solution started to be slowly adsorbed again according to their selectivity in the free available sites on resin. Finally, metals concentration in the outlet solution tended to be constant, approximately the same as in the feed solution concentration, meaning that the sorption reached equilibrium with no more sorption or desorption occurrence.

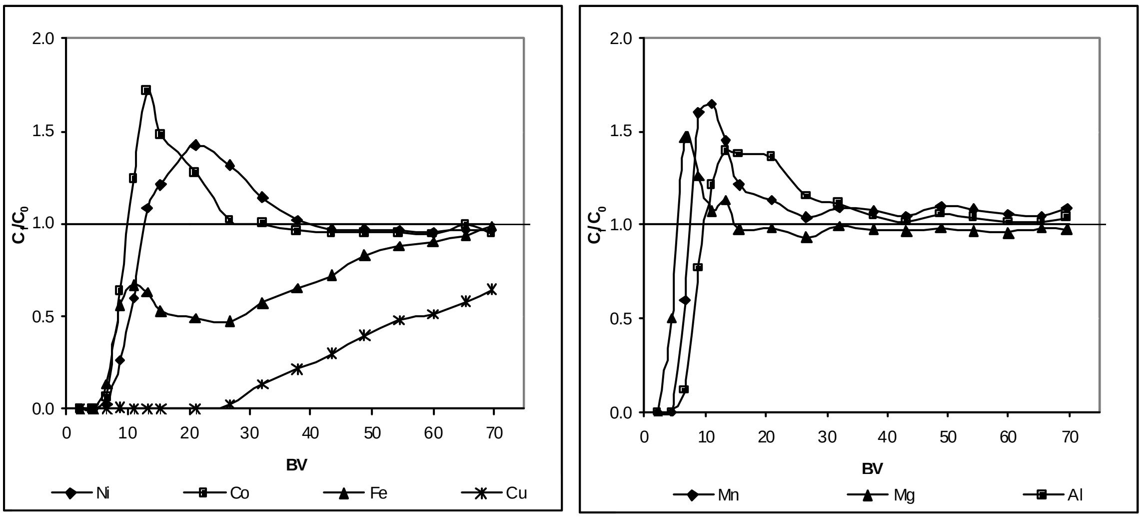

Figure 6.1 - Breakthrough curves – Test 1 (Ni concentration: 1.5 g/L - pH = 2 - 11 BV/h)

At pH 2.0 when Ni concentration in solution was low, the resin was more selective for Cu and Fe, and both metals presented the ratio $C_f/C_0 < 1$, indicating no saturation occurrence. As long as the displacement of Ni, Co, Al, Mn e Mg occurs, Fe and mainly Cu were preferably adsorbed on the free sites of the resin due to their affinity to resin under these conditions. According to figure 6.1, Fe and Cu were not displaced to solution after being continuously adsorbed during the whole experiment. At the end of the experiment, their sorption on resin was still proceeding, as shown by the Cu ascending curve. At pH 2.0 (high concentration of H^+ ions), the resin presented the lowest metals load capacity, since the resin has a preferable affinity to H^+ ions. The experimental conditions, mainly the low pH, adopted in this test were not favorable to high and selective nickel and cobalt sorption on resin.

TEST 2: Figure 6.2 shows the breakthrough profile for elements such as Ni, Co, Fe, Cu, Mg, Mn e Al. The column was packed with resin Amberlite IRC 748® and the feed solution containing 1.6 g/L Ni and pH = 3 passed through it at a flow rate of 11BV/h during 6 hours. The main observed characteristic was that Ni was adsorbed until Ni outlet concentration becomes similar to Ni feed concentration ($C_f/C_0 = 1$) with a very small Ni displacement to the solution. The higher Ni sorption and selectivity, compared with test 1, were due to the increase of pH from 2 to 3. These conditions also favoured complete Cu sorption on resin, since no copper was observed in outlet solution and no breakthrough occurrence. During the experiment, iron outlet concentration remained lower than iron feed concentration, showing that iron saturation on resin has not occurred as well, being continuously adsorbed with no displacement.

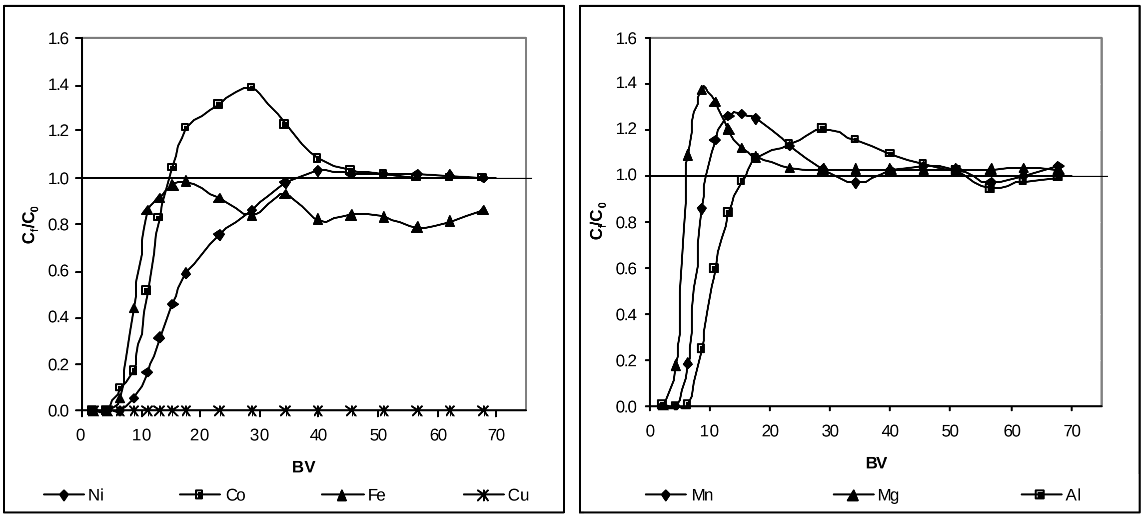

Figure 6.2 - Breakthrough curves – Test 2 (Ni concentration: 1.6 g/L - pH = 3 – 11 BV/h)

According to Figure 6.2, it is clear that the resin adsorbed copper and iron rather than nickel. After 35 BV, Ni outlet concentration reached its feed concentration and its load capacity remained constant until the end of the experiment. The solution pH increase is an important parameter to be considerate in load capacity evaluation. The lower it is, the higher H^+ ions concentration and the lower metals load capacity are verified, mainly nickel, since the resin has a preferable affinity to H^+ ions.

The breakthrough of Mg, Mn and Al began just after the initiation of the feed. The resin presented low selectivity for Mg, which was adsorbed and rapidly displaced to solution. Co and Al displacement also occurred. Co was adsorbed until 13 BV. From this point until 40 BV - when Co ions were displaced from the resin - iron was notably re-adsorbed on the resin until the end of the experiment with no iron saturation. From 40 BV on, cobalt loading was very low and constant.

Figure 6.3 shows the elution profile of the loaded column with 15% w/w HCl solution at flow rate of 2BV/h – 0.8 L/h during 4 hours. As seen from this figure, Ni is eluted at a concentration as great as 12 times its initial concentration in the feed. However, due to the high iron concentration on the resin, it was rapid and completely eluted in a high concentration, increasing its concentration 26 times compared to the feed solution and resulting in a solution with 17g/L Fe.

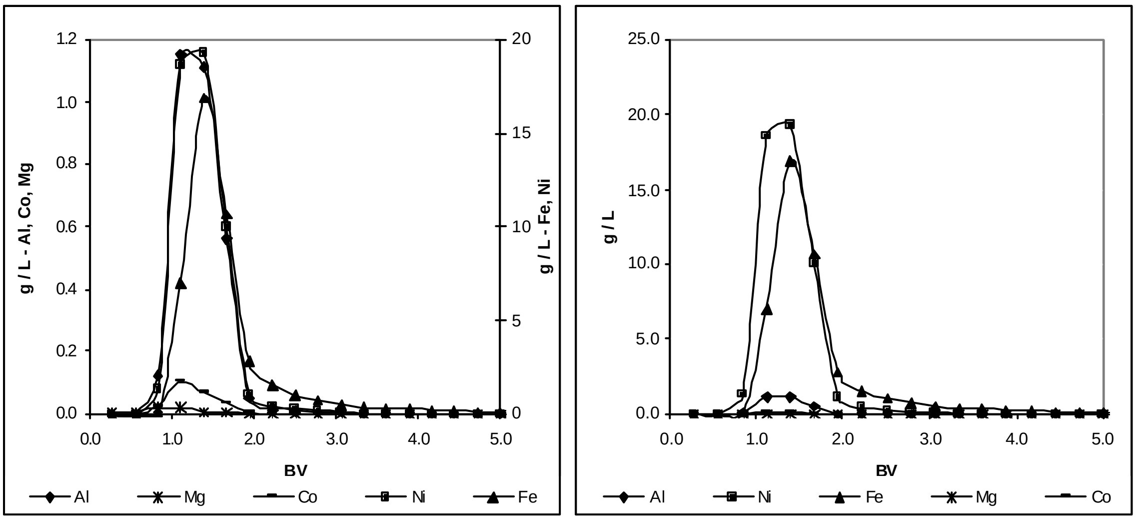

Figure 6.3 - Elution curve – Test 2 (HCl 15% w/w - 2 BV/h)

Although pH feed solution = 3 has provided good nickel sorption, the low nickel concentration in feed solution, very similar to iron's, caused a competition among them for the free sites of resin. High iron sorption was observed on resin as well as high iron concentration in eluted solution.

- **TEST 3**: Loading data for resin Amberlite IRC 748® was obtained by processing approximately 14 bed volumes (BV) of HPAL solution (7.3 g/L Ni) at pH 3.0 through 0.36 L resin bed at 0.6 L/h (1.7 BV/h) flow rate during 6 hours and room temperature. Compared to test 2, although the pH condition has remained the same (pH 3.0), the influence of a higher nickel concentration (7.3 g/L Ni) and low iron concentration (0.8 g/L) has a significant effect on nickel selectivity. Figure 6.4 presents the breakthrough curves for Ni, Co, Cu, Fe, Al, Mn and Mg obtained from the column bed packed with Amberlite IRC 748®. At these conditions, iron ions do not compete with nickel ions in a large extent. An opposite behavior has been seen in the previous tests. Here, iron and cobalt, which were rapidly adsorbed during the initial loading stages, were subsequently displaced by nickel throughout the test. The same displacement to solution was observed for Mg, Mn and Al.

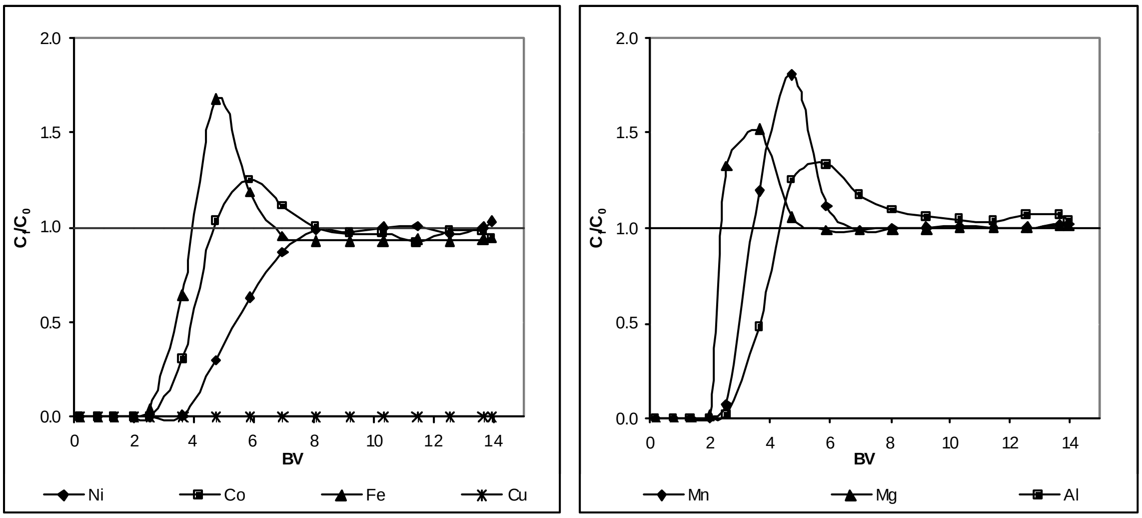

Figure 6.4 - Breakthrough curves – Test 3 (Ni concentration: 7.3 g/L - pH = 3 – 1.7 BV/h)

Nickel sorption markedly increased while the first 8 BV of solution was passed through the column. Ni was completely adsorbed until 3 BV and between 3 BV and 8 BV the sorption was verified in a less intensity. At 8 BV, Ni sorption stopped, the equilibrium has been reached and a constant Ni outlet concentration (the same as the initial Ni concentration) was observed with no displacement until the end of the experiment. The results obtained were markedly better than those obtained in the previous test, showing that the simultaneous increase of pH and increase of Ni concentration have a positive effect on resin selectivity and Ni sorption.

Figure 6.4 also shows that, due to the high selectivity for copper ions, it was complete adsorbed on resin and it was not detected in effluent during the whole experiment. Metals such as Fe, Co, Mg, Mn and Al were firstly brokenthrough, followed by Ni that began at 3.6 BV. At this point, complete nickel removal from feed solution was obtained with no nickel in the outlet solution and no cobalt displacement from the resin, which just started to happen from 4 BV on. After 8 BV of feed solution passing through the resin, Co sorption slowly started to increase.

Mg concentration in outlet solution presented a sharp increase at the beginning of the experiment, after passing 2 BV of solution through the resin, showing that under the applied conditions the resin is not selective for Mg, causing some Mg displacement from resin to solution from this point on. The same behavior was observed for Fe, Mn and Al, which were entirely adsorbed on resin until 3 BV and subsequently desorbed and returned to solution, since the outlet concentration started to be higher than the feed concentration.

Comparing the three first tests, a solution with higher Ni concentration in feed solution (7.3 g/L) and lower iron concentration (0.8 g/L) and higher pH, enhanced nickel sorption and selectivity, with no displacement to solution. Higher Co sorption and resin loading capacity were also observed. The increase of Ni/Fe concentration ratio is an important parameter to be considerate in load capacity evaluation. The higher it is, the less iron ions will compete with Ni, increasing Ni sorption.

Figure 6.5 shows elution curve obtained with 10% w/w H_2SO_4 solution at a flow rate of 2 BV/h (0.8L/h) during 4 hours. The elution data showed that the resin Amberlite IRC 748® can be effectively eluted with this reagent. Nickel elution was completed within 3.5 BV of acid solution. Iron elution followed nickel elution somewhat, and it was complete after this same point. As seen from Figure 6.5, nickel was eluted at a concentration as great as 3 times its concentration in the feed solution although considerable concentration of impurities, mainly Al and Mg, was detected. The goal of testing different reagents and concentrations in elution stage is to observe their capacity. Comparing the three first tests, it can be seen that nickel was quickly desorbed in all of them, but test 3 presented a higher nickel concentration in solution and impurities were detected in a less intensity.

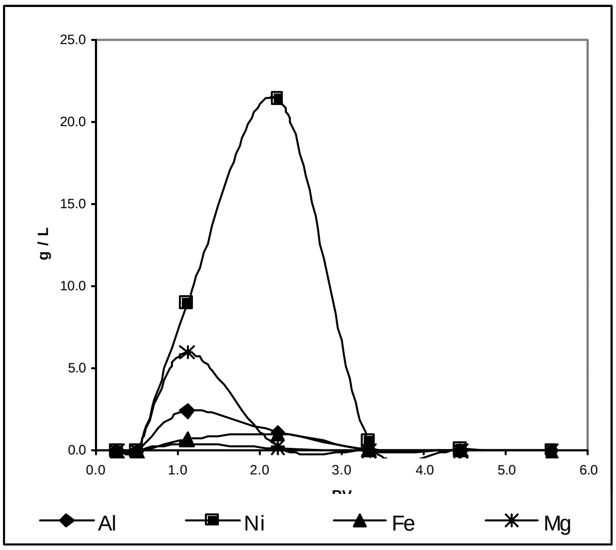

Figure 6.5 - Elution curve – Test 3 (H_2SO_4 10% w/w - 2 BV/h)

- **TEST 4**: Figure 6.6 presents the breakthrough profiles of Ni, Cu, Fe, Mn, Mg, Al and Co at 1.7 BV/h (0.6 L/h) flow rate, 8.4 g/L Ni and pH = 4 of the feed solution. These experimental conditions illustrate the best performance of the resin Amberlite IRC 748®. It can be seen that the resin presented a very high selectivity for copper, which was continuously adsorbed during the experiment and no breakthrough was observed. A large amount of Mn, Mg and Al was brokenthrough just after the beginning of the experiment (before 3.5 BV), while the breakthrough of Ni, Co and Fe began after 4 bed volumes. It can be observed that Mg presented an instable sorption behavior with successive sorption and desorption phenomena on Amberlite IRC 748® under this conditions. Co and Fe brokethrough at 4.4 BV, while the breakthrough of Ni began at 5.6 BV, suggesting that it is possible to purify the solution free from Ni contamination by stopping the feed before 5.6 BV. The Ni sorption stopped at around 8 BV and no Ni displacement was observed until the end of the experiment. On the other hand, after the sorption of Al, Mn, Co and Fe on resin, they were displaced to solution due to higher selectivity for Ni species that were in a very high concentration in feed solution. The resin has a higher selectivity for Ni and Co rather than for Fe and Mg.

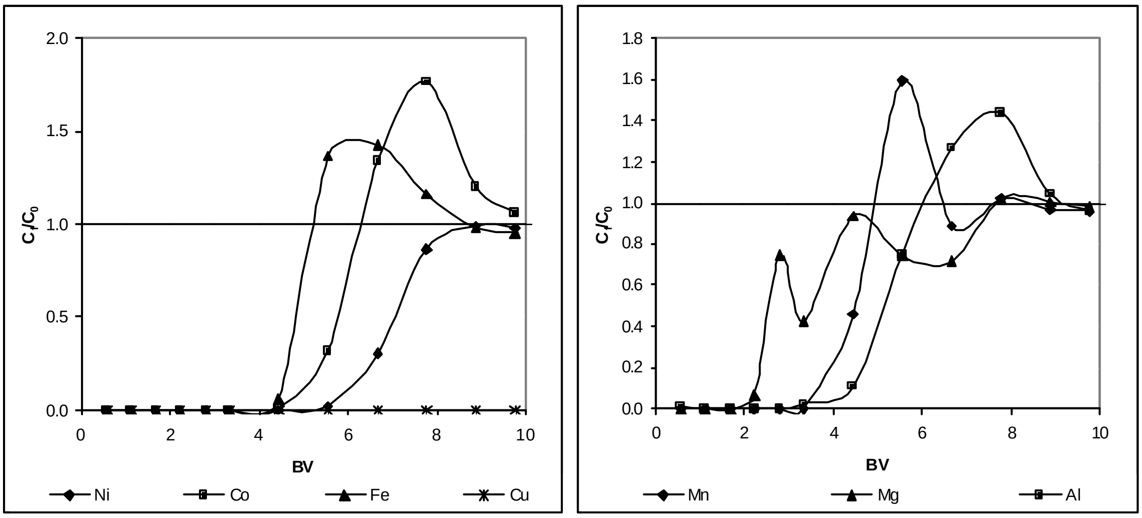

Figure 6.6 - Breakthrough curves – Test 4 (Ni concentration: 8.4 g/L - pH = 4 – 1.7 BV/h)

According to Figure 6.7 that shows Ni and Co sorption and resin loading capacity, the maximum nickel load (112.4 mg/g) was obtained after 8 BV which represented 66.5% of Ni sorption, comparing nickel masses in feed and effluent solution. The Ni sorption remained constant after this point and no desorption was observed until the end of the experiment. Compared to test 3, both tests applied a very high nickel feed solution, but test 4 feed solution presented a higher pH. Increasing the pH and the nickel concentration of the feed, compared to the other metals, resulted in a higher resin selectivity for Ni (lower Co/Ni and Fe/Ni ratios on the loaded resin), while iron and cobalt ions sorption on resin is reversible, returning to solution after being adsorbed by the resin. Nickel ions were not displaced to solution. It allows performing a satisfactory nickel and iron separation. Besides the better breakthrough profiles, load capacity was sensibly higher at pH 4. Maximum cobalt loading of 4.6 mg/g occurred at approximately 5.5 BV, which means that 53% Co was recovery from solution at this point. From this point on, part of Co adsorbed was returned to solution, resulting in a decrease in Co load on resin.

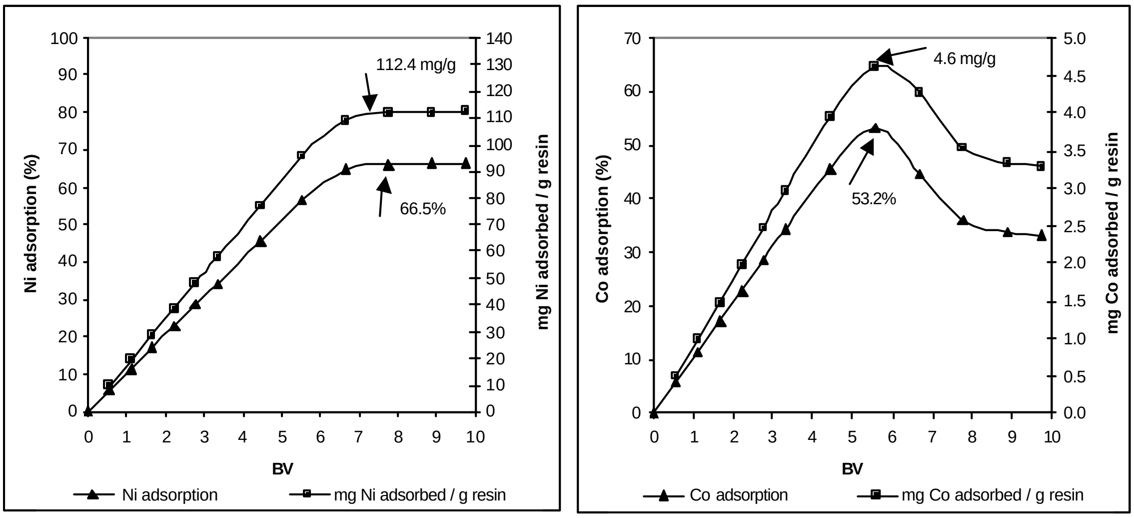

Figure 6.7 - Ni and Co sorption and resin loading capacity – Test 4 (Ni concentration: 8.4 g/L - pH = 4 – 1.7 BV/h)

Figure 6.8 presents elution data obtained with H_2SO_4 7.5% w/w at 2 BV/h flow rate. The elution profiles showed that all nickel was stripped with 3.0 BV of sulfuric acid, while all cobalt was eluted with 2.5 BV. The maximum eluted nickel concentration occurred at 2.0 BV, after that for cobalt. The Mg and Fe elution initiated before the Ni and Co elution and after 2 BV their elution had already been completed. In this case, although Co, Fe, Al and Mg have been completely eluted, only a trace concentration of them was detected (less than 1.6 g/L of impurities), while nickel was eluted concentrated as great as 4 times its concentration in the feed solution, suggesting the successful separation of Ni from a large excess of impurities using the resin Amberlite IRC 748®. Nickel concentration in eluted solution was 32 g/L.

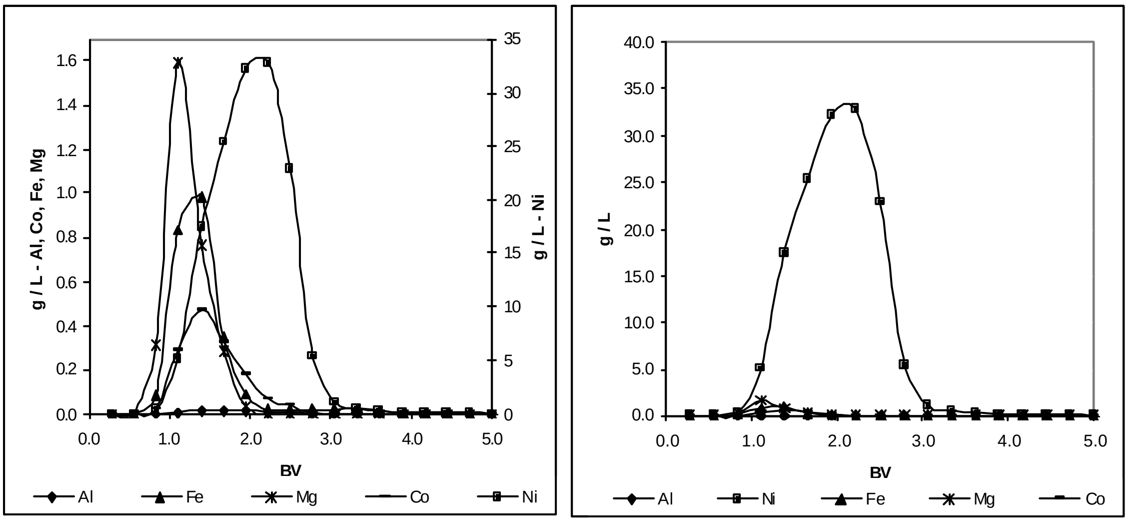

Figure 6.8 - Elution curve – Test 4 (H_2SO_4 7.5% w/w - 2 BV/h)

- **TEST 5**: Test 5 corresponds to loading data for resin Amberlite IRC 748®, obtained by processing approximately 70 bed volumes (BV) of HPAL solution (1.8 g/L Ni) at pH 4.0 through 0.36 L resin bed at 11 BV/h during 6 hours and room temperature. The breakthrough curves in Figure 6.9 show that both cobalt and iron were rapidly adsorbed on the resin due to low nickel concentration in the feed solution, and as expected, copper and nickel were selectively adsorbed but copper rather than nickel has a higher affinity to resin in pH 4. The iron and cobalt breakthrough curves rose rapidly to a greater value than the feed concentration indicating that nickel displaced iron, manganese, magnesium and cobalt from the resin. Mg was rapidly adsorbed by the resin but it was immediately returned to solution due to the resin low selectivity for Mg. No nickel was displaced from resin to solution during the experiment. Analyzing the conditions applied in test 5, it can be concluded that the high pH has a strong influence on nickel selectivity and nickel loading capacity on resin. It was the first time that iron was displaced to solution after being adsorbed (compare tests 1, 2 and 5 low iron and nickel concentration solution) in a way that nickel rather than iron is increasingly adsorbed by the resin, even working with a feed solution that has low Ni and Fe concentration competing among them.

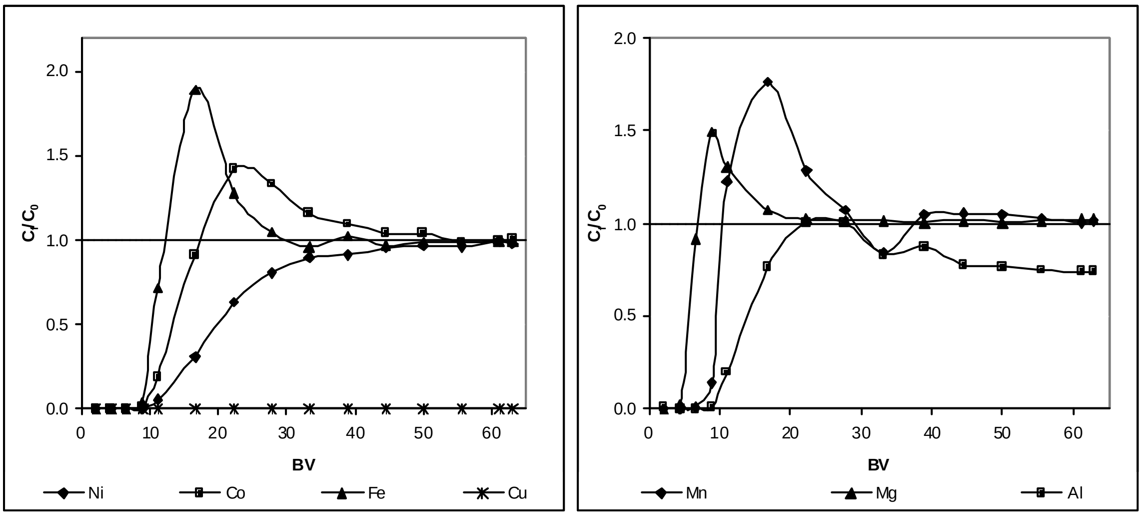

Figure 6.9 - Breakthrough curves – Test 5 (Ni concentration: 1.8 g/L - pH = 4 – 11 BV/h)

Figure 6.10 illustrates the crescent Ni sorption during the experiment. The maximum nickel loading was 73.5 mg/g which represents 31.4% recovery. Compared to the previous test - the same pH but a high Ni concentration - here Ni sorption was markedly lower, due to the competition with iron. On the other hand, compared to test 2 – low Ni feed concentration but lower pH - here Ni sorption was markedly higher due to the pH influence on resin selectivity. The maximum cobalt loading was obtained at 15 BV which was 2.1 mg/g (17.6% recovery). After being adsorbed by the resin, Co started to be returned to solution at 15 BV.

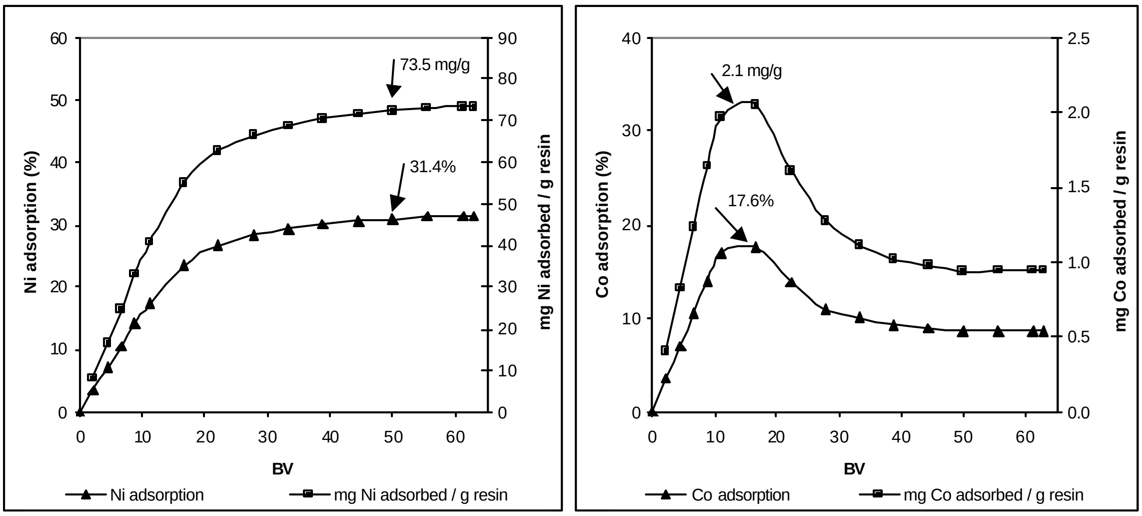

Figure 6.10 - Ni and Co sorption and resin loading capacity – Test 5 (Ni concentration: 1.8 g/L - pH = 4 – 11 BV/h)

The resin was eluted with 10% w/w HCl at 2 BV/h during 4 hours. According to Figure 6.11, approximately 100% of the cobalt was stripped after 2.2 BV, while nickel could be stripped with 3 BV. Mg, Co and Al were eluted much faster than Ni and Fe. Ni was eluted at a concentration as great as 25 times its concentration in the feed solution while only low concentration of other metals was detected. The conditions applied in test 5 provided the best results of elution: very fast procedure, high nickel concentration (45g/L) and low concentration of impurities.

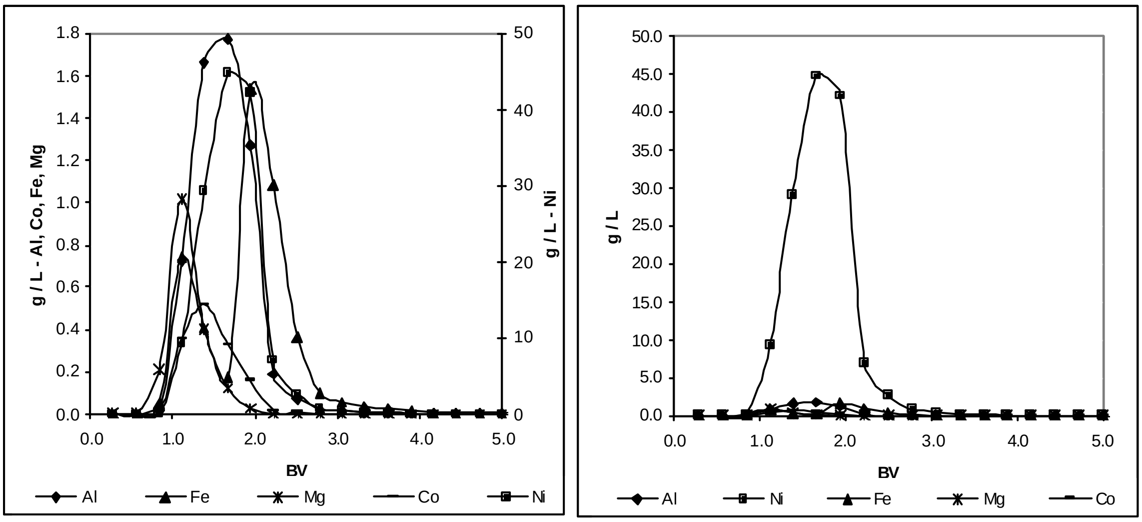

Figure 6.11 - Elution curve – Test 5 (HCl 10% w/w - 2 BV/h)

Conclusions

The results obtained allowed us to conclude that the ion exchange IRC 748® resin was suitable for nickel recovery from sulfuric acid solutions after hydrometallurgical high pressure leaching of nickel laterite ores. The selectivity for transition metals is achieved by the iminodiacetic acid functionality chemically bound to a macroreticular resin matrix.

From HPAL solution, Ni in a large excess of impurities can be separated successfully by iminodiacetic resin to produce a Ni concentrated solution free from Al, Fe and Mg. The experimental results also confirmed that the apparent selectivity of the resin for metals separation depends upon nickel concentration, the presence of other species, mainly iron, and pH. It was determined that the largest separation coefficients of nickel were obtained in sulfate solutions at pH >3. At pH = 4, the resin is preferentially selective for Ni compared to Fe, even if they have low concentration in solution. The resin presented the highest selectivity for copper ions in all runs. It was found that at pH ≥ 4, the order of the selectivity for the Amberlite IRC 748® resin among metal ions is as follows: Cu (II) >> Ni (II) >> Co (II) > Fe(III) >Al (III) > Mn (II) > Mg (II). According to test 4, the increase of feed solution pH and the decrease of feed flowrate considerably enhanced the performance of Amberlite IRC 748® as was expected.

From breakthrough experiments, it was found that for most of them the breakthrough of Fe, Al, Co occurred before Ni breakthrough, whereas their displacement is observed in most of the cases. It may be seen that their concentration rises well above the initial feed solution value. This indicates their desorption and nickel sorption in the upper layers of the Amberlite IRC 748® column.

Comparing solutions with the same pH, the presence of low nickel concentration in solution is expected to reduce the resin selectivity for Ni, because of the competition between nickel and other metals in solution. Comparing solutions with the same metals concentration, the higher the pH, the better nickel sorption is achieved, due to low concentration of H^+ ions which the resin has a preferable affinity for.

Regeneration of this resin with inorganic acid was very efficient and adequately regeneration could be reached. Ni can be eluted with HCl and H_2SO_4 and the concentration of Ni, after elution with HCl 10% w/w, was concentrated more than 25 times of the feed solution, while only a small concentration of impurities was detected.

Acknowledgments

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Capítulo 7 - Recuperação seletiva de níquel e cobalto de polpa HPAL usando resina quelante de troca iônica

Mendes, F.D. and **Martins,** A.H. **Recovery of nickel and cobalt from acid leach pulp by ion exchange using chelating resin** • *Minerals Engineering, Volume 18, Issue 9, August 2005, Pages 945-954*

Este capítulo apresenta os resultados obtidos nos ensaios de resina em polpa realizados em regime de batelada. Inicialmente, foi estudada a influência de alguns parâmetros, tais como pH, tempo, razão resina/polpa, temperatura, na recuperação de níquel contido em polpa efluente de lixiviação ácida. Uma segunda abordagem consistiu da avaliação do número de estágios de contacto resina/polpa necessários para a máxima recuperação do níquel contido na fase aquosa da polpa e para a obtenção da capacidade máxima de carregamento da resina.

RECOVERY OF NICKEL AND COBALT FROM ACID LEACH PULP BY ION EXCHANGE USING CHELATING RESIN

F. D. Mendes(1) & A H. Martins (2)

(1)Research Engineer, Companhia Vale do Rio Doce, Brazil

(2)Adjunct Professor, Department of Materials and Metallurgical Engineering – Federal University of Minas Gerais (UFMG), Brazil.

Abstract

Sorption processes, especially sorption from pulps, are of considerable interest in nickel hydrometallurgy. The use of polymeric resins in pulp process allows elimination of expensive and extensive operations of filtration or countercurrent decantation from the flowsheet. The preliminary comparison of capital and operating costs indicates that resin-in-pulp process can compete successfully with liquid-liquid extraction and precipitation processes and may be considered as a feasible alternative when designing nickel hydrometallurgical plants. Based on this approach, resin-in-pulp batch tests were carried out to evaluate the nickel sorption characteristics. An iminodiacetic acid polymeric resin was selected for nickel sorption from sulfate acidic solutions. The results showed that the resin was able to provide nickel and cobalt extractions from solution greater than 99% after five counter-current stages. It was also observed that nickel and cobalt could be extracted from solids in the pulp due to *sorption leach* phenomena. The resin process continuously removed nickel and cobalt from the solution allowing the potential for further solids leaching. A maximum load resin capacity of 100g Ni/kg was obtained in these tests.

Keywords: hydrometallurgy, ion exchange

Introduction

All nickel laterite processing plants include multi-stage counter-current decantation (CCD) circuits to wash nickel and cobalt values out of the leach pulp, followed by precipitation and/or solvent extraction for metal recovery. When a low-grade ore is treated in a hydrometallurgical process and a solid-liquid separation is required, the level of production relative to the volumes of pulp being leached and filtered is high and therefore, the operating cost of this step is probably significant. One solution to this economic problem is to recover the dissolved metal from the pulp after leaching by using a solid reagent that makes the solid-liquid separation step unnecessary. Loss of valuable product occurs during a solid-liquid separation step of a conventional process because of the unfeasibility to wash the solids and recover dissolved species.

An alternative to recovery nickel and cobalt values from the leach pulp is to use a resin-in-pulp (RIP) system. According to Zontov (2001), resin-in-pulp technology can be applied to (1) existing operations with CCD processes or (2) process design under consideration for replacing CCD conventional technology. A resin-in-pulp process can be designed so that the adsorbent recovers significant amounts of the dissolved product before it is screened from the pulp, avoiding losses of valuable product that occurs during a solid-liquid separation step. Ion exchange polymeric resins have found increasing application over the last decade and are available commercially for almost any separation process. In addition, their application is able to provide a more effective and straightforward purification compared to purification by precipitation or solvent extraction, which are the most commonly used techniques at present for these purpose (Leinonen et al., 1994; Kononova et al., 2000; Kholmogorov et al., 1997). Ion exchange process using polymeric resins is also free from the loss of reagents through entrainment, costly solid-liquid separation and poor selectivity for nickel over other metals ions, inherent drawbacks of solvent extraction processes.

If resin-in-pulp process is used in the recovery of nickel from an acid leach the following benefits are expected:

a) The acid leach might produce a pulp which is difficult to clarify or solids that, when separated, are difficult to wash. RIP could cope with this situation.
b) Neutralization of acid introduced by the resin during sorption is conveniently done in the contactors. Cheap reagents such as lime or limestone could be used and the relatively insoluble reagent and gypsum formed during neutralization merely become part of the pulp.
c) The use of resin that is non-selective over iron will require the prior removal of iron by oxidation and precipitation before nickel is recovered. The insoluble ferric hydroxide precipitate also becomes part of the pulp.

Based on this new approach, The Center for Mineral Development from Vale do Rio Doce Mining Co. (Brazil) started evaluating the application of resin-in-pulp to nickel laterite ores. The pressure acid leach process discharges a hot acidic pulp, which contains dissolved metals, including high levels of iron, aluminum, manganese, magnesium, besides nickel, cobalt and copper. The resin-in-pulp process option presents the advantage of sorption-leach phenomena (Zontov, 2001). In this case an additional concentration of nickel and cobalt is recovered from solid phase, which is not commonly recovered in other process options. This paper reviews the developments and results that have been obtained in recent studies done at CVRD using the resin-in-pulp (RIP) technology in the extraction of nickel and cobalt.

Experimental Procedure

Material

The resin selected for the sorption of nickel/cobalt from high pressure acid leach (HPAL) pulp of a Brazilian laterite was Amberlite IRC 748® from Rohm & Haas (USA), a chelate-based resin with iminodiacetic acid group. The resin has been chosen based on its high selectivity for nickel and cobalt in the presence of competing ions. Pulps were contacted with resin in a beaker agitated by an impeller, at different speed, time, temperature and resin/pulp ratio.

Pretreatment of resins

The ion exchange experiments used polymeric resins under sodium and hydrogen-forms. The resins were conditioned by washing with acid or basic solutions and rinsed with distilled water. The conditioning followed the recommendations provided by the manufacturers and it was carried out to remove all the impurities from the resin and to obtain a free base form.

Method

In the first stage, resin-in-pulp batch tests were carried out to evaluate the sorption characteristics. The use of RIP technique involved a previous oxidation of iron (II) to iron (III) after leaching, followed by addition of limestone to precipitate iron. After pulp pre-treatment for iron removal, some parameters were studied in bench sorption tests and had their values varied in order to identify their influence on percent of nickel recovery. After defining the best conditions for maximizing nickel sorption, additional RIP experiments were carried out.

Sorption Experiments

The actual selectivity and loading capacity values observed for chelating resins depend on pH solution, time, stirring speed, temperature and resin to pulp ratio. Fixing the pH, these parameters were varied in order to determine their effect on the loading of nickel in the resin. Samples of the effluents were collected to determine their metal ion concentration in solution after their sorption on resin. The best conditions for nickel recovery from HPAL pulp were adopted in further experimental RIP evaluation.

- ***pH:*** the initial pH of HPAL leach solution was between 0.5 and 0.7. This high acidity is not desirable for nickel and cobalt uptake using chelating resins (Grinstead, 1984). In general, most chelating exchangers are weakly acidic in nature. The iminodiacetate and aminophosphonate functional groups are affected by pH due to the presence of acidic groups, which can dissociate depending on pH. At lower pH values, only a small fraction of the functional groups will likely be dissociated and since cations cannot be removed by neutral acids, the nickel loading capacity of the resins is reduced (Kononova et al., 2000). Consequently, the effect of higher pH on nickel sorption was examined. Tests were carried out with pH pulps at 2, 3 and 4.

- ***Effect of time:*** The effect of different residence times on the resin loading was examined at room temperature and 200 rpm of stirring speed. Tests were carried out during 20, 45 and 120 minutes.

- ***Effect of speed:*** The effect of stirring speed on the resin loading characteristics was investigated at room temperature during 45 minutes. Stirring speed of 100 rpm, 200 rpm and 400 rpm were evaluated.

- ***Effect of temperature:*** The effect of temperature on the resin loading characteristics was evaluated. Temperatures of 25 and 40°C were studied during 45 minutes and 200 rpm of stirring speed.

- ***Effect of resin to pulp ratio:*** The effect of resin to pulp ratio on the resin loading characteristics was investigated at room temperature, during 45 minutes and 200 rpm. Resin to pulp ration of 3% and 6% were studied.

Results

Parameters evaluation

Fixing solution pH, batch tests were carried out in order to study the influence of time, speed, temperature and resin to pulp ratio on resin loading. Besides nickel extraction from solution, nickel extraction from solids was evaluated as well, observing the advantage of sorption-leach phenomena. This means that nickel and cobalt are continuously removed from the liquid phase allowing the potential for further nickel leaching from solids and consecutively recover from solution. Tables VII.1, VII.2 and

VII.3 show the results of nickel extraction from solution and solids for tests carried out at pH = 2, 3 and 4.

Table VII.1 - The influence of parameters on nickel extraction - pH = 2

pH = 2						
Parameters	*Time (min)*	*Speed (rpm)*	*Temperature (C)*	*Resin to pulp ratio (%)*	*Ni extraction from solution (%)*	*Ni extraction from solids (%)*
Time influence	20	200	25	6	19.8	25.9
	45	**200**	**25**	**6**	**22.0**	**25.9**
	120	200	25	6	3.8	27.8
Speed influence	45	100	25	6	23.8	25.9
	45	200	25	6	22.0	25.9
	45	**400**	**25**	**6**	**29.5**	**25.9**
Temperature influence	**45**	**200**	**25**	**6**	**22.0**	**25.9**
	45	200	40	6	9.2	25.9
Resin to pulp ratio influence	45	200	25	3	5.1	25.9
	45	**200**	**25**	**6**	**22.0**	**25.9**

Table VII.2 - The influence of parameters on nickel extraction - pH = 3

pH = 3						
Parameters	*Time (min)*	*Speed (rpm)*	*Temperature (C)*	*Resin to pulp ratio (%)*	*Ni extraction from solution (%)*	*Ni extraction from solids (%)*
Time influence	20	200	25	6	73.9	12.0
	45	200	25	6	75.9	12.0
	120	**200**	**25**	**6**	**79.6**	**12.0**
Speed influence	45	100	25	6	74.7	12.0
	45	**200**	**25**	**6**	**75.9**	**12.0**
	45	400	25	6	69.9	12.0
Temperature influence	**45**	**200**	**25**	**6**	**75.9**	**12.0**
	45	200	40	6	72.5	12.0
Resin to pulp ratio influence	45	200	25	3	31.0	12.0
	45	**200**	**25**	**6**	**75.9**	**12.0**

Table VII.3 - The influence of parameters on nickel extraction - pH = 4

pH = 4						
Parameters	*Time (min)*	*Speed (rpm)*	*Temperature (C)*	*Resin to pulp ratio (%)*	*Ni extraction from solution (%)*	*Ni extraction from solids (%)*
Time influence	20	200	25	6	53.1	28.0
	45	**200**	**25**	**6**	**62.3**	**28.0**
	120	200	25	6	62.1	28.0
Speed influence	45	100	25	6	62.3	28.0
	45	**200**	**25**	**6**	**63.0**	**28.0**
	45	400	25	6	62.8	28.0
Temperature influence	45	200	25	6	60.9	28.0
	45	**200**	**40**	**6**	**62.3**	**28.0**
Resin to pulp ratio influence	45	200	25	3	22.3	26.0
	45	**200**	**25**	**6**	**62.3**	**28.0**

Maximum nickel loading was obtained with pH 4. At pH = 3, nickel recovery from solution was slightly higher, however low nickel recovery from solids was detected. At pH 4, the overall nickel extraction was higher, showing that nickel in solid phase was leached and subsequently recovered by the resin as expected. The capacity of IRC 748® dropped as pH was reduced progressively. The best conditions for maximizing nickel extraction are 40^{o}C, 200 rpm, 6% resin to pulp ratio and 45 minutes.

Resin sorption from HPAL pulp - part 1

A typical process scheme for the sorption of nickel and cobalt from HPAL pulp involves the three process steps according to Zontov (2001). This procedure involves fresh resin that is contacted with the same HPAL pulp in five stages.

STEP 01

HPAL pulp was discharged from the autoclave at pH = 0.3 and free acid = 40 g/L. A typical analysis of the pulp is shown in table VII.4.

Table VII.4 - Chemical analysis of HPAL pulp

Element	*Element in liquid phase (mg/L)*	*Element*	*Element in liquid phase (mg/L)*
Ni	5750	Al	207
Co	236.5	Mg	9920
Fe	3740	Cu	29.5
Mn	690	Zn	274

STEP 02

At pH 0.3, the concentration of ferrous/ferric ions in solution is high and has large influence on loading capacity of the resin. A reasonable option to deal with this interference was to adjust the pH of the pulp to pH 4, forming a precipitate of iron hydroxide. This procedure was able to eliminate large part of soluble iron in HPAL pulp. Table VII.5 shows the result of the analysis of the liquid and solid phase of neutralized pulp. As expected, iron was 95% precipitated. The nickel concentration in solution has been reduced from 5750 mg/L to 5175 mg/L. The nickel has been lost from the solution through co-precipitation with the iron hydroxide. During the resin-pulp contact, part of the precipitated nickel may be leached again and after returning to solution, it may be adsorbed by the resin.

Table VII.5 - Chemical analysis of the liquid and solid phase of neutralized pulp

Element	*Element in liquid phase (mg/L)*	*% Precipitated from solution*	*Element in solid phase (mg/kg)*
Ni	5175	10	3700
Co	220	7	200
Fe	187.4	95	421000
Mn	670	3	800
Al	27.0	87	9200
Mg	9825	1	2400
Cu	1.2	96	100
Zn	94.7	66	1900

STEP 03

The present testwork was carried out in 5-stage counter current RIP using a HPAL pulp with ferric hydroxide precipitate at pH = 4. The pH in each contactor was maintained at a value of 4 by addition of limestone. An amount of 30g fresh Amberlite IRC 748® resin under sodium form was added to the 500mL pulp at 60°C, stirred at 200 rpm and reacted for 45 minutes while monitoring pH and adjusting it if necessary. The resin and pulp components were then separated and the loaded resin was stored for later desorption. A sample of the pulp was taken and solid and liquid phases analyzed for many metals concentration determination. The same pulp was then combined again with 30g of fresh resin and the procedure was repeated until completing five stages. At each stage the solid and liquid phases of the pulp were analyzed and the loaded resins were combined for elution. Table VII.6 presents nickel concentration after each stage and its recovery from solution and solids. Figures 7.1 and 7.2 illustrate nickel concentration and nickel extraction from liquid and solid phases, respectively.

Table VII.6 - Results of nickel recovery from liquid and solid phase after 5 stages of RIP test

Stage	*Nickel in liquid phase (mg/L)*	*Recovery (%)*	*Cumulative recovery (%)*	*Nickel in solid phase (mg/kg)*	*Recovery (%)*	*Cumulative recovery (%)*
initial	3742			4000		
1	358	90.4	90.4	3500	12.5	12.5
2	82	77.1	97.8	3400	2.9	15.0
3	26	67.8	99.3	3300	2.9	17.5
4	16	37.9	99.6	3200	3.0	20.0
5	7	60.5	99.8	3200	0	20.0

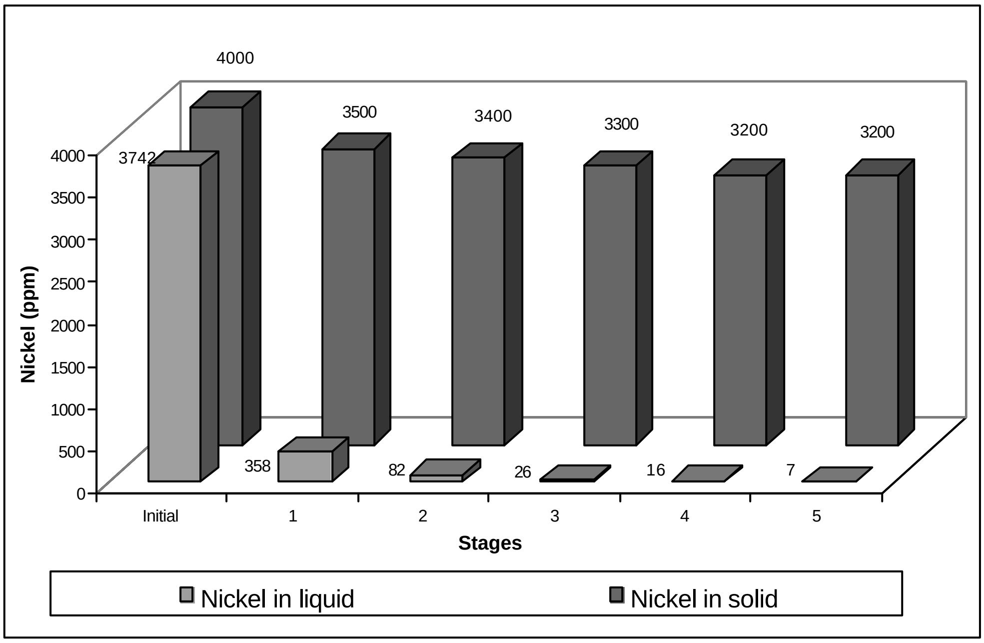


Figure 7.1 - Nickel concentration in solid and liquid phases

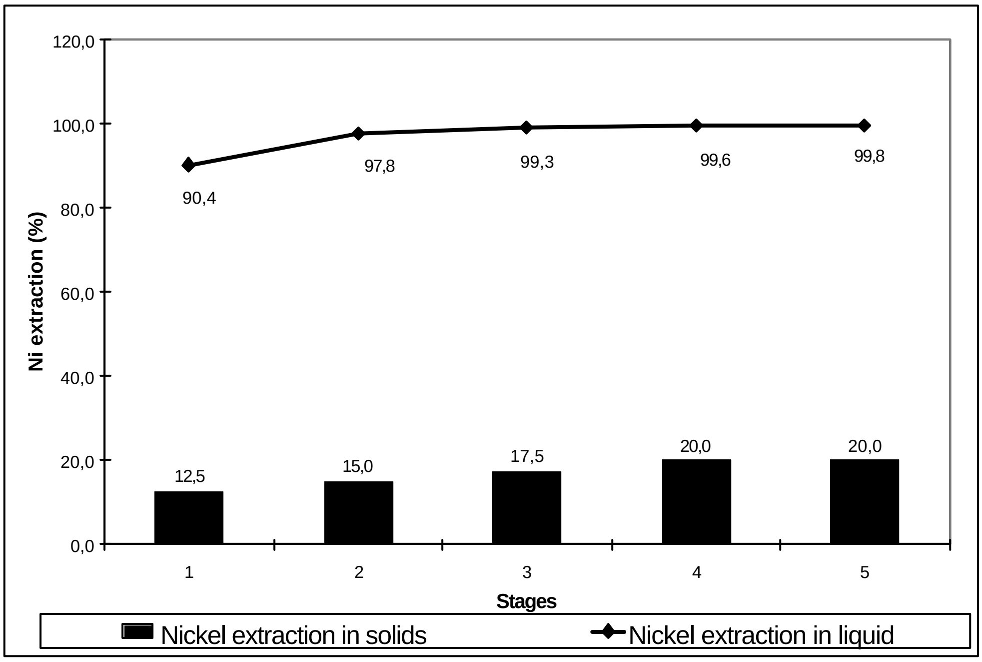


Figure 7.2 - Nickel extraction from liquid and solid phases

After three stages, nickel has already been more than 99% recovered from solution. Nickel was 20% recovered from solids as well. It means that nickel in solid phase was leached during RIP test and subsequently recovered by the resin. Most of nickel (90%) was recovered from solution in first stage, simultaneously 12.5% was recovered from solid phase. This fact indicated that part of nickel precipitated in neutralization stage could be recovered at this stage. Table VII.7 shows the results obtained for cobalt recovery that was very similar to nickel behavior, even being present in a lower concentration compared to nickel. Figures 7.3 and 7.4 illustrate cobalt concentration and cobalt extraction from liquid and solid phases, respectively.

Table VII.7 - Results of cobalt recovery from liquid and solid phases after 5 stages of RIP test

Stage	*Cobalt in liquid phase (mg/L)*	*Recovery (%)*	*Cumulative recovery (%)*	*Cobalt in solid phase (mg/kg)*	*Recovery (%)*	*Cumulative recovery (%)*
initial	161			200		
1	39	75.9	75.9	190	5.0	5.0
2	2	95.3	98.9	180	5.3	10.0
3	2	0.0	98.9	170	5.6	15.0
4	1	75.0	99.7	160	5.9	20.0

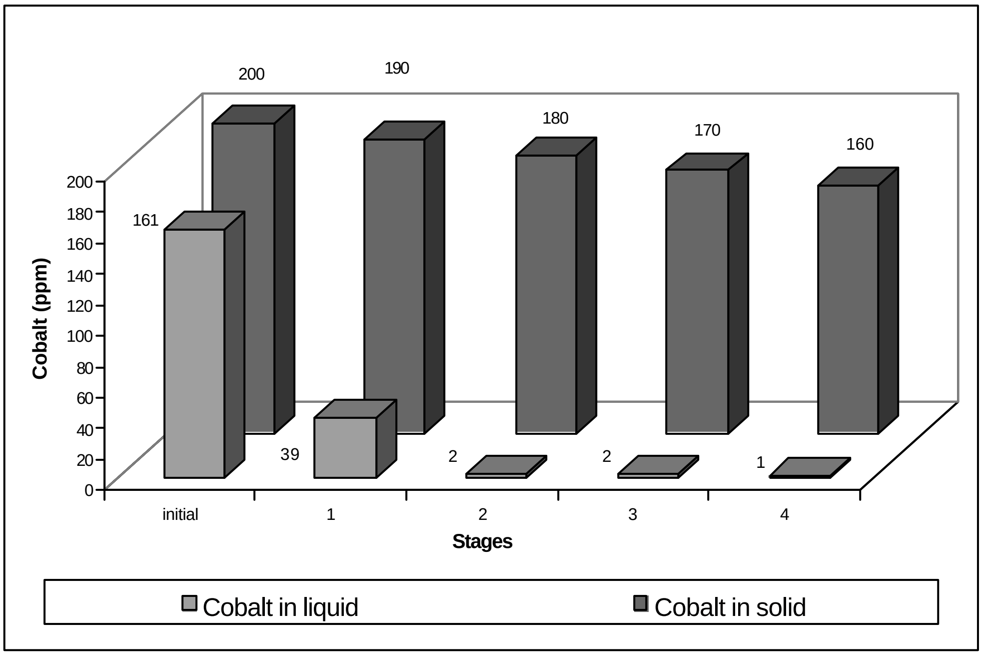


Figure 7.3 - Cobalt concentration in solid and liquid phases

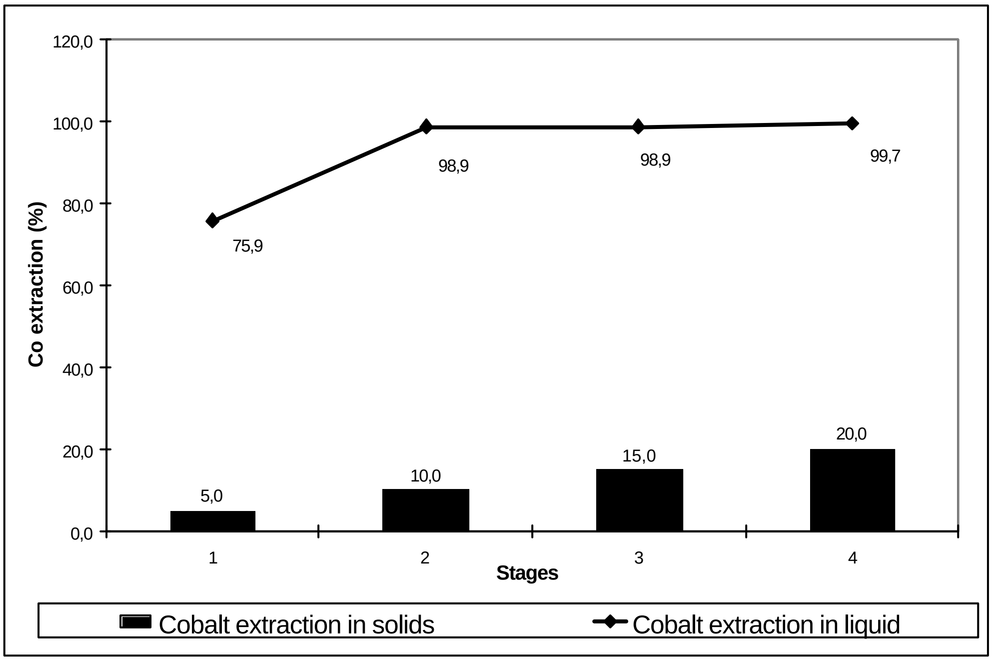


Figure 7.4 - Cobalt extraction from liquid and solid phases

The results indicated the ability of the resin Amberlite IRC 748® to capture the soluble metal values in the pulp and additionally extract nickel and cobalt from the solid fraction of the pulp through leach-sorption phenomena. Table VII.8 shows typical recovery values obtained by the resin-in-pulp tests described before. In the five-stage set-up used in this work the recovery of nickel and cobalt was greater than 99 percent.

Table VII.8 - Total recovery of nickel and cobalt from liquid and solid phases

Source	*Total Recovery (%)*
Nickel from liquid phase	99.8
Nickel from solid phase	20.0
Cobalt from liquid phase	99.7
Cobalt from solid phase	20.0

Resin sorption from HPAL pulp - part 2

The same neutralized HPAL pulp was adopted in resin sorption tests – part 2. The concept was contrary to the previous one (part 1), because this procedure involved a fresh pulp for each stage that was contacted with the same resin in eight stages.

Fresh resin Amberlite IRC 748® in sodium form was added to a fresh pulp, stirred and reacted for appropriate time while pH was monitored and adjusted if necessary. The resin (100g) was contacted with 500 mL of fresh pulp at 60^{o}C, 45 minutes, 200 rpm, pH=4. The resin and pulp were then separated and the loaded resin was contacted again with 500mL of fresh pulp. A sample of the pulp was taken and solid and liquid phases analyzed for determination of metals concentration. This procedure was repeated until the final solution had nickel concentration equal or higher than the initial one. After eight stages, the loaded resin was eluted. The results for nickel recovery are shown in Table VII.9 and illustrated in figures 7.5 to 7.8.

Table VII.9 - Nickel recovery from solid and liquid phases

Stage	*Nickel in liquid phase (mg/L)*		*Recovery (%)*	*Nickel in solid phase (mg/kg)*		*Recovery (%)*
	Initial	Final		Initial	Final	
1	5175	53	99.0	3700	3200	13.5
2	5175	74	98.6	3700	3200	13.5
3	5175	305	94.1	3700	3300	10.8
4	5175	809	84.4	3700	3400	8.1
5	5175	2945	43.1	3700	3500	5.4
6	5175	3379	34.7	3700	3700	0
7	5175	4279	17.3	3700	3700	0
8	5175	6055	-17.0*	3700	3700	0

*: The negative value of nickel recovery means that load nickel was desorbed and returned to solution

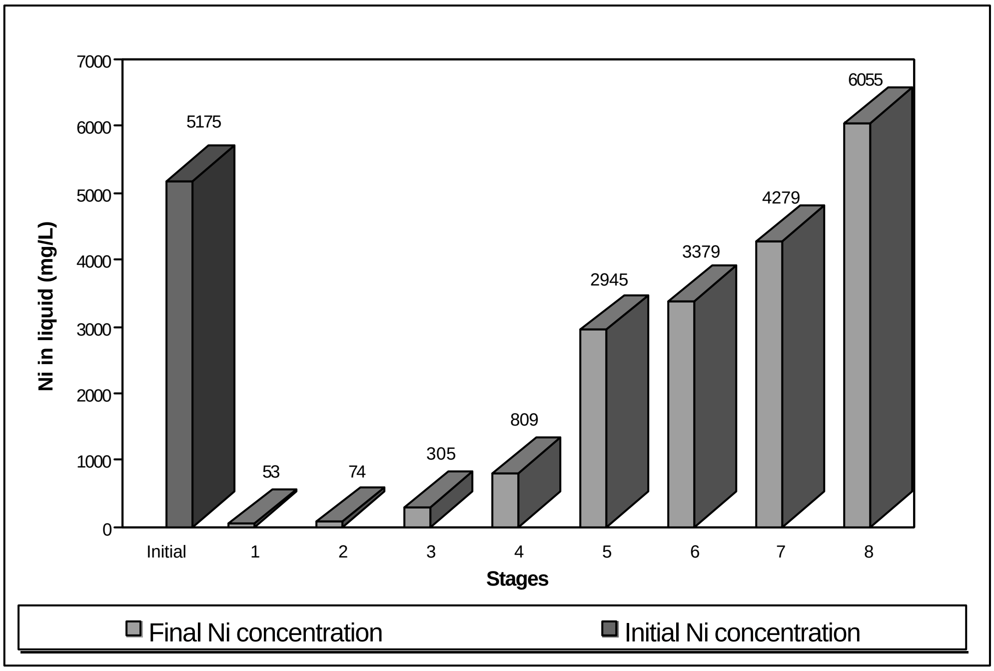
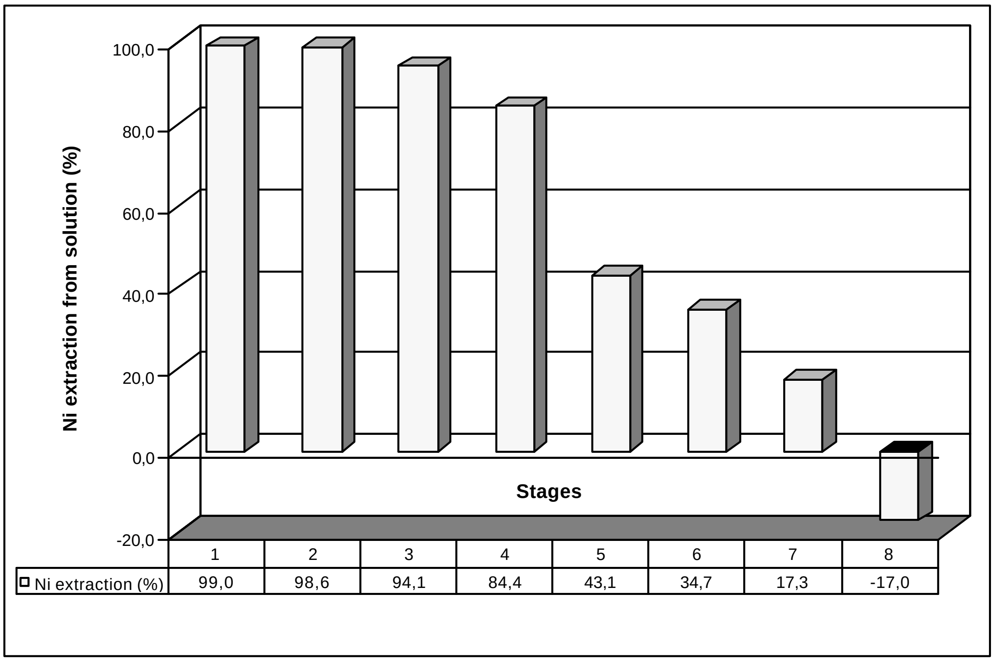


Figure 7.5 - Initial and final nickel concentration in liquid phase



	1	2	3	4	5	6	7	8
□ Ni extraction (%)	99,0	98,6	94,1	84,4	43,1	34,7	17,3	-17,0

Figure 7.6 - Ni extraction from liquid phase

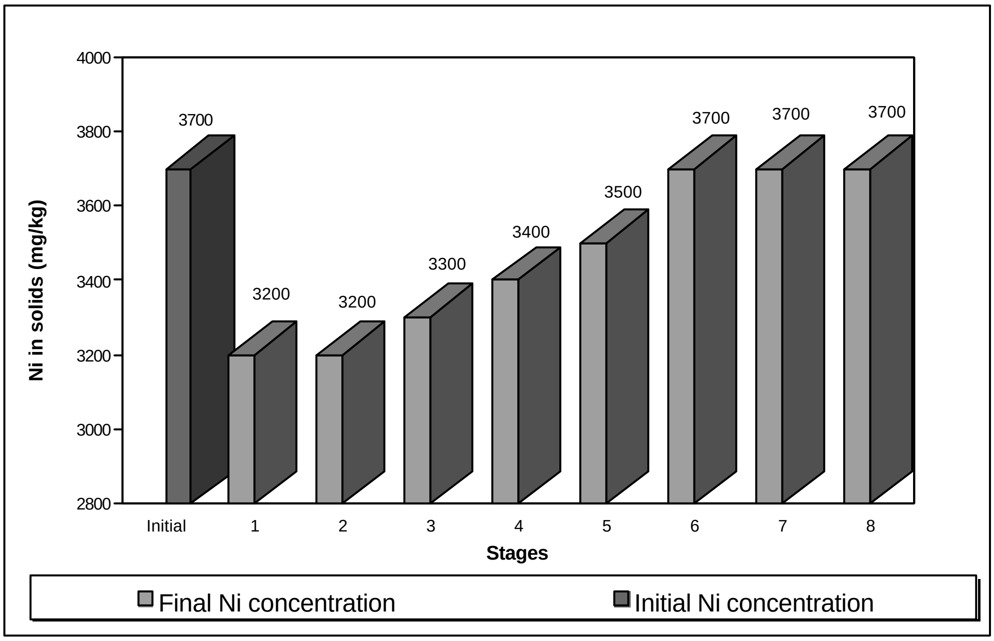


Figure 7.7 - Initial and final nickel concentration in solid phase

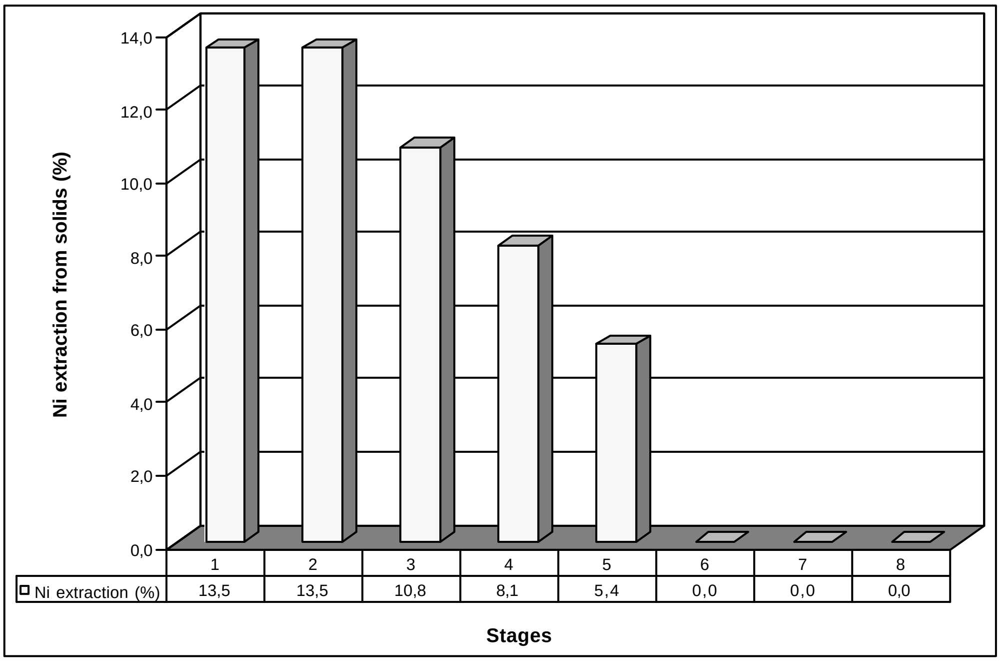


Figure 7.8 - Ni extraction from solid phase

The results again clearly indicated the rapid extraction of nickel from the liquid phase in the first stages of sorption on the resin Amberlite IRC 748® when there were available sites on the resin for nickel sorption. Nickel extraction was higher than 98% in the first two stages. As long as the resin has become loaded, the nickel recovery has decreased as well. In stage number 8, the saturated resin was not able to adsorb nickel anymore and was verified some nickel desorption which returned to the aqueous solution. A similar behavior was verified for nickel extraction from solid phase with a maximum nickel sorption of 13.5% in just one stage. After the sixth stage no more nickel was extracted from solids phase.

Table VII.10 shows the results of cobalt recovery from solid and liquid phase. The extraction of cobalt from the liquid phase is also very apparent, mainly in the first two stages where cobalt extractions higher than 97% were achieved. From the sixth stage on, after resin saturation, cobalt desorption was detected since its concentration in final solution has increased compared to the initial solution. Small amount of cobalt (5%) was recovered from solid phase. No more cobalt extraction was verified after third stage. Figures 7.9 to 7.12 illustrate all the results obtained for cobalt recovery from solid and liquid phase.

Table VII.10 - Cobalt recovery from solid and liquid phases

Stage	*Cobalt in liquid phase (mg/L)*		*Recovery (%)*	*Cobalt in solid phase (mg/kg)*		*Recovery (%)*
	Initial	Final		Initial	Final	
1	220	3	98.5	200	190	5.0
2	220	7	97.0	200	190	5.0
3	220	61	72.4	200	200	0.0
4	220	126	42.8	200	200	0.0
5	220	213	3.1	200	200	0.0
6	220	224	-1.9*	200	200	0.0
7	220	295	-34.0*	200	200	0.0
8	220	297	-34.9*	200	200	0.0

*: The negative value of cobalt recovery means that load cobalt was desorbed and returned to solution

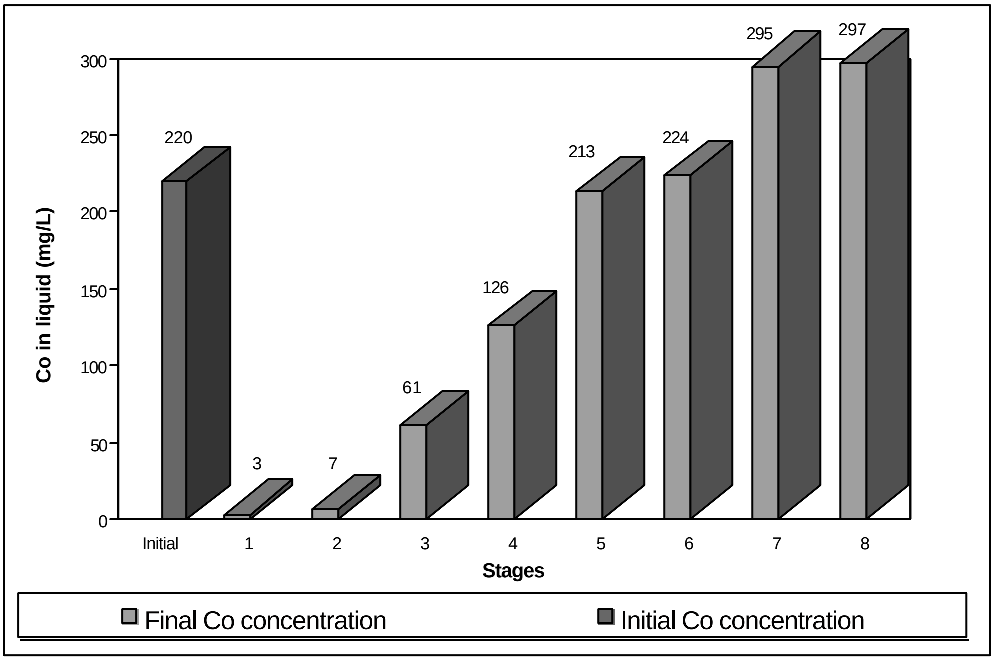
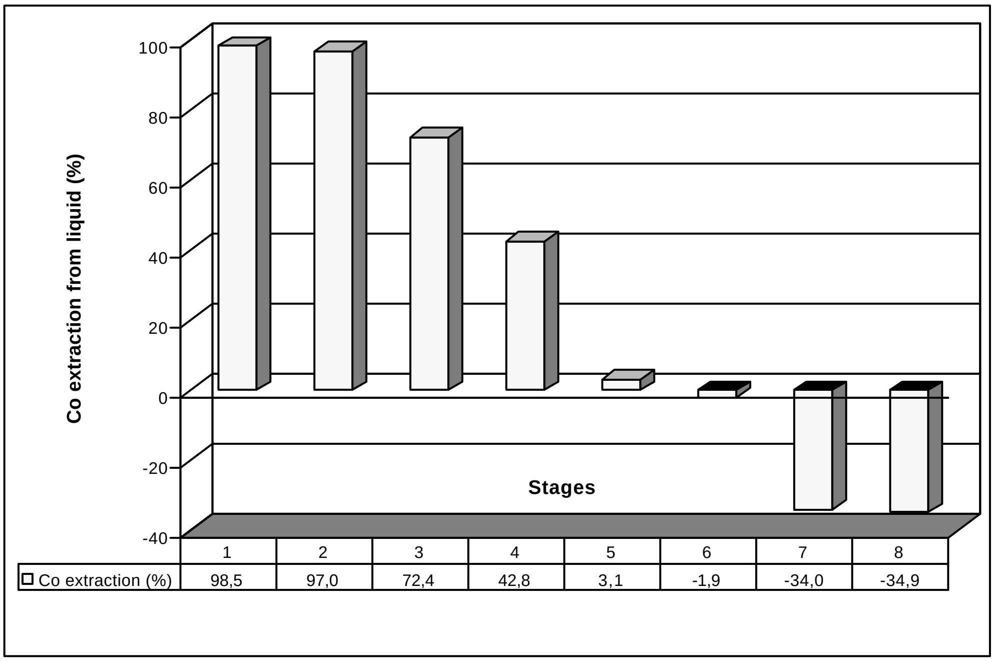


Figure 7.9 - Initial and final cobalt concentration in liquid phase



	1	2	3	4	5	6	7	8
☐ Co extraction (%)	98,5	97,0	72,4	42,8	3,1	-1,9	-34,0	-34,9

Figure 7.10 - Co extraction from liquid phase

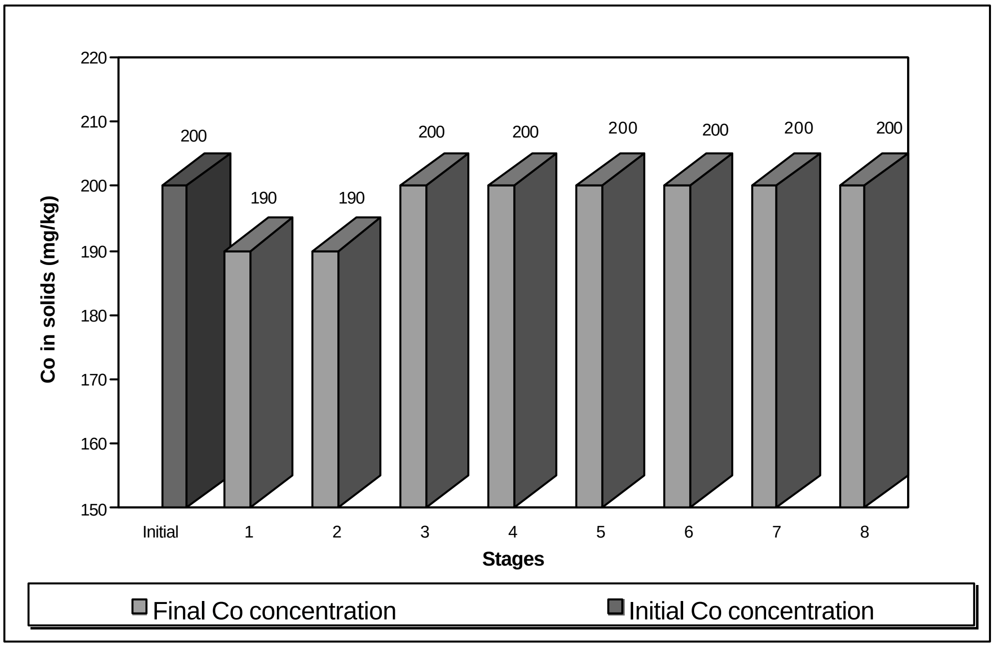


Figure 7.11 - Initial and final cobalt concentration in solid phase

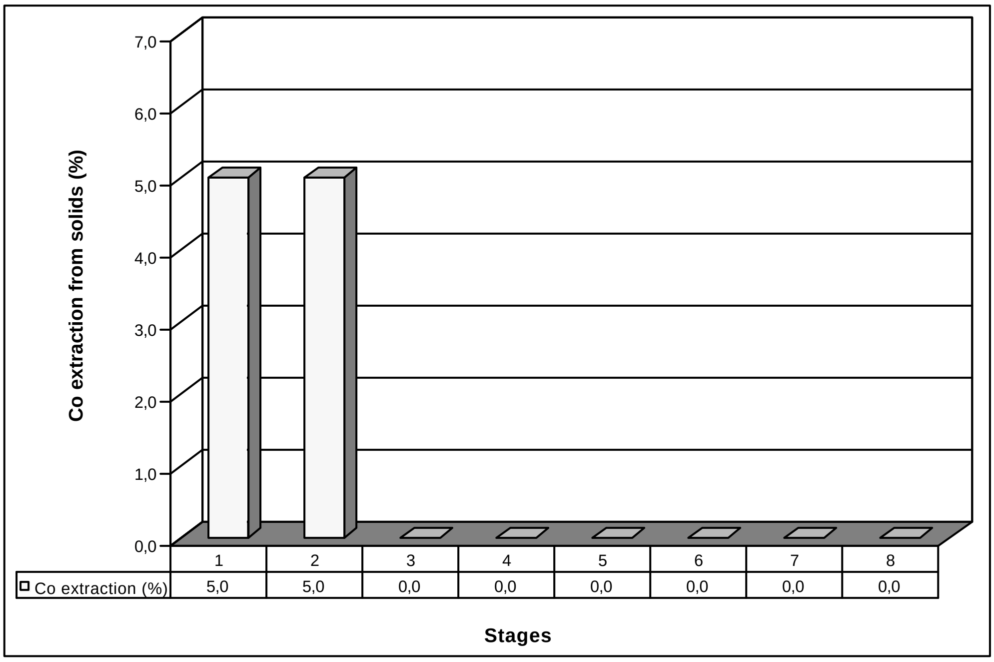


Figure 7.12 - Co extraction from solid phase

Resin elution

The loaded resin obtained in resin sorption tests – part 2 was washed with distilled water and desorbed with one liter of acid solution (sulfuric acid 7% v/v) to provide a pregnant solution. The pregnant solution obtained from this step was analyzed for determination of metal concentration and the results are shown in Table VII.11.

Table VII.11 - Chemical analysis of pregnant solution from the elution stage

Element	*mg/L*	*Element*	*mg/L*
Al	11.49	Mg	283.90
Ca	147.40	Mn	105.80
Co	203.40	Na	267.80
Cr	1.53	Ni	9761.00
Cu	8.85	Si	3.08
Fe	138.90	Zn	171.00

The concentration of nickel and cobalt in the pregnant solution is dependent on the initial concentrations of nickel and cobalt in the feed solution. Nickel concentration of 10 g/L was obtained in the pregnant solution, while very low concentration of impurities was detected. According to the results, the maximum nickel load capacity in the polymeric resin Amberlite IRC 748® was 97.6mg Ni/g along eight stages.

Stripping of the resin produced liquor with the different constituents. Utilization of resin loading capacity was high for nickel, due to its high affinity to resin and for that reason, nickel was upgraded in purity. The recovery of non-valuable metals (sodium, magnesium and iron) was low, for example, a low level of iron, 0.14 g/L was detected. It will be of interest, generally, to recover the cobalt and this can be done by solvent extraction using Cyanex 272® reagent. Co-extraction of the non-valuable metals during this step yields an acceptably pure nickel electrolyte.

Mechanical resistance study

A study of the mechanical resistance of the resins to the abrasion was also made. The life of the resin or the number of cycles that can be satisfactorily operated before renewing the resin bed is an important criterion of choice between various types of resins. The method to determine the mechanical resistance of the polymeric resin is based on a particle size study made before and after the contact between the resin and pulp with 30% solids, in agitation of 500 rpm, during 60 minutes. Then, the resin is separated from the pulp, screened in 0.35 mm and the retained mass is dried, weighted and submitted to a new test. This procedure was repeated ten times. The resin screening in 0.35 mm and weighting after each test allowed the evaluation of the generation of fine particles and, consequently, of the physical degradation of the resin.

The resin coarse fraction must not be too large because of its brittleness; osmotic shock breaks the coarse fraction first. Moreover, if it happens, the exchange capacity may be slightly lower. The smaller fraction has a good capacity but causes the pressure drop inside the resin bed to increase. In addition, fine resin particles are difficult to backwash without resin loss.

During successive cycles, around 10% of the resin particles are damaged and the granular distribution changes. Table VII.12 shows the retained resin mass in 0,35 mm and the progressive change in resin screen analysis after each test. Figure 7.13 shows the results of retained mass and fine particles generated in ten successive cycles.

Table VII.12 - Results of retained mass and fine particles produced in ten successive cycles

Stage	*Retained mass (g)*	*Fine particles (%)*
	30.26	
1	29.85	1.35
2	29.55	2.35
3	29.35	3.01
4	28.93	4.4
5	28.67	5.25
6	28.31	6.44
7	28.08	7.2
8	27.88	7.87
9	27.56	8.92
10	27.16	10.24

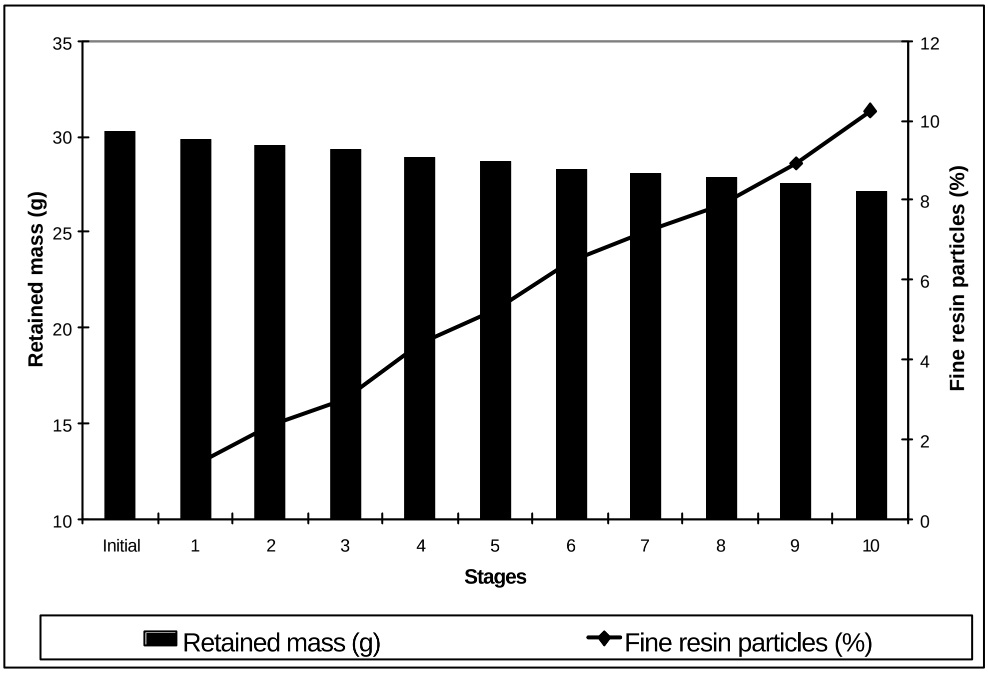


Figure 7.13 - Results of retained mass and fine particles generated in ten successive cycles

Comparison between new and degrading resin

After the mechanical tests, the degrading resin was added to a HPAL pulp, stirred and reacted for 45 minutes while pH equals to 4 was monitored and adjusted if necessary. The resin (10g) was contacted with 200 mL of fresh pulp at 60°C and 200 rpm. The resin and pulp components were then separated. A sample of the pulp was taken and solid and liquid phases analyzed for determination of metals concentration. For comparison, a new resin, which was not submitted to mechanical tests, was added to the same HPAL pulp sample and the same procedure was repeated. Tables VII.13 and VII.14 and Figures 7.14 and 7.15 show the sorption results obtained for both resins.

Table VII.13 - Metals sorption from solution obtained for new and degrading resins

	Initial concentration in solution (mg/L)				
	Al	*Co*	*Fe*	*Mg*	*Ni*
	260	211	476	12325	5116
	Final concentration in solution (mg/L)				
	Al	*Co*	*Fe*	*Mg*	*Ni*
Degrading resin test	1	52	13	12037	516
Extraction (%)	**99.7**	**75.4**	**97.4**	**2.3**	**89.9**
New resin test	5	80	14	12291	869
Extraction (%)	**98.2**	**62.3**	**97.0**	**0.3**	**83.0**

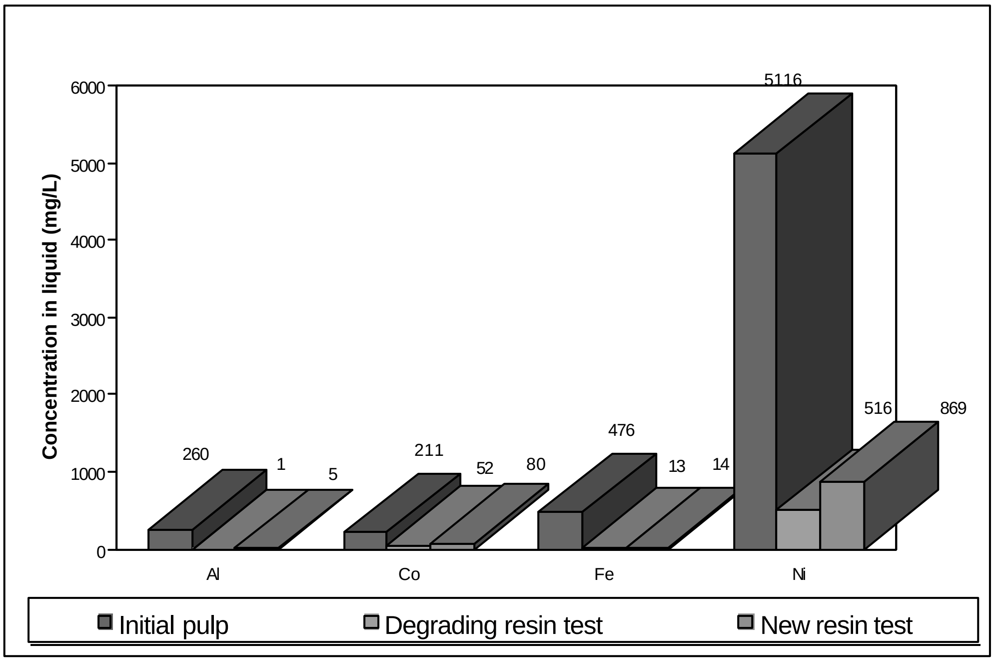


Figure 7.14 - Metals concentration in liquid before and after resin tests

Results in Table VII.13 shows that nickel extraction from solution for both resins was very similar. It was not observed a decrease in the loading capacity for the resin submitted to ten cycles of mechanical test on a bench scale. Contrarily, the sorption test carried out with this resin presented the best results of nickel recovery, showing that the formed fine resin particles improved the resin capacity. Table VII.14 presents nickel extraction from solids. Compared to nickel extraction from solution, in this case an opposite behavior could be observed, since the best results were obtained for the new resin.

Table VII.14 - Metals sorption from solids obtained for new and degrading resins

	Initial concentration in solids (%)				
	Al	*Co*	*Fe*	*Mg*	*Ni*
	8700	200	398000	6300	5200
	Final concentration in solids (%)				
	Al	*Co*	*Fe*	*Mg*	*Ni*
Degrading resin test	8600	200	386000	5200	3400
Extraction (%)	**1.1**	**0**	**3.0**	**17.5**	**34.6**
New resin test	8700	200	397000	3700	3200
Extraction (%)	**0**	**0**	**0.3**	**41.3**	**38.5**

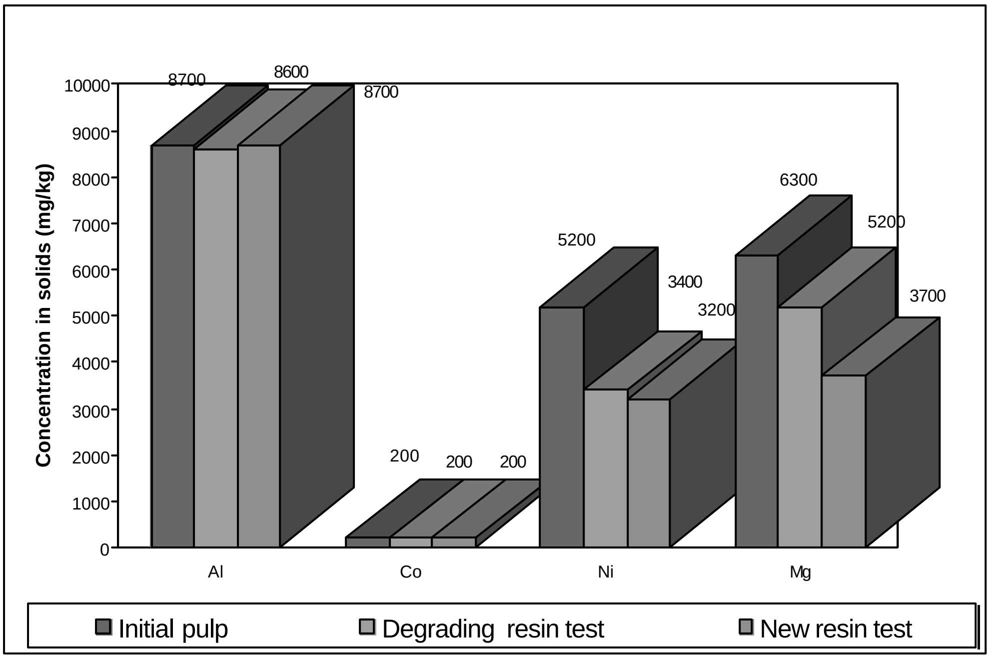


Figure 7.15 - Metals concentration in solids before and after resin tests

Conclusions

The polymeric resin Amberlite IRC 748® appeared to be more selective for nickel over other metals. The increase in pH value is able to provide a better nickel recovery from pulp. Other parameters such as temperature, stirring speed, time and resin to pulp ratio have some influence on nickel sorption and the best values for maximizing nickel recovery could be defined. The resin has a strong affinity for iron and copper, which should be removed from the solution by the addition of lime or limestone prior to RIP process.

Five stages were enough to obtain 99.8% nickel recovery. After three stages, nickel extraction was higher than 99%, showing that Amberlite IRC 748® is efficient and selective in nickel recovery from HPAL pulps. The resin saturation was reached after eight stages with a maximum loading capacity of 97.6 mgNi/g resin.

Mechanical resistance study showed that the working capacity is not impaired by the presence of a large number of fines in the resin bed, even if we have more than 10% broken beads.

The resin-in-pulp technology allows increased nickel recovery and elimination of expensive and low-effective equipment from the implementation of the process (thickeners and filters). Since pH functionality for nickel and cobalt was similar, these metals would probably co-extract and cobalt could then be separated from nickel in the eluate by known solvent extraction technology.

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Capítulo 8 - Aplicação de resina de troca iônica quelante em escala contínua para a recuperação de níquel e cobalto

Diante dos resultados positivos obtidos ao se avaliar o processo de resina em polpa em regime de batelada (vide Capítulo 7), fez-se necessário estudar a capacidade de carregamento, recuperação e seletividade, em regime contínuo, de uma resina quelante na adsorção de níquel e cobalto em polpa de lixiviação ácida. Este capítulo apresenta os resultados obtidos em três campanhas de 50 horas para avaliação da recuperação de níquel e cobalto, em regime contínuo de contacto, de uma polpa de lixiviação ácida por pressão de um minério laterítico de níquel com uma resina quelante não-comercial de grupo funcional de ácido iminodiacético, denominada neste trabalho como CheRes.

Para o estudo do processo de resina em polpa, em regime contínuo do tipo contra-corrente, tornou-se imprescindível avaliar um maior volume de resina polimérica quelante em equipamentos de maior porte, especificamente dimensionados para esta técnica. Já que não dispunha desta infra-estrutura, a CVRD contratou este serviço técnico especializado, o qual foi executado por uma empresa fabricante da resina quelante não-comercial CheRes, com grupamento funcional a base de ácido amino (ácido iminodiacético), que é similar ao grupamento funcional orgânico da resina Amberlite IRC 748®. Embora inviabilizada a realização deste tipo de abordagem com a resina Amberlite IRC 748®, objeto de estudo ao longo de toda esta tese, a aplicação da resina CheRes representou o grupo funcional em questão, tornando-se referência para esta aplicação específica. Assim, foi possível avaliar o desempenho da resina quelante de grupamento ácido iminodiacético frente à adsorção de níquel em mini-planta de resina em polpa. Todo o estudo realizado nesta etapa do trabalho são apresentados no Anexo I, por se tratar de uma abordagem específica da resina CheRes na estratégia da rota de estudo deste trabalho.

Capítulo 9 - Efeitos do Carregamento de Níquel na Estrutura Química da Resina Quelante Amberlite IRC748Ò

Este estudo teve o objetivo de investigar a influência do grupo funcional ácido iminodiacético e da matriz estireno divinilbenzeno da resina Amberlite IRC 748® na adsorção de níquel. A resina foi contatada à polpa e solução efluentes de lixiviação sob pressão de lateritas de níquel a fim de se produzir amostras de resina carregada, as quais foram analisadas em equipamento de espectroscopia RAMAN e comparadas com o espectro obtido na análise da resina nova, tal qual foi recebida do fabricante. A resina eluída teve também seu espectro comparado com o espectro da resina nova, a fim de se avaliar se a resina após carregada, eluída e regenerada preservava as mesmas características exibidas pela resina nova, sem modificação estrutural relevante.

THE DEPENDENCE OF SORBED NICKEL IONS ON ION EXCHANGE RESIN TYPE

F. D. Mendes(1) **& A H. Martins**(2)

(1)Research Engineer, Companhia Vale do Rio Doce, Brazil

(2)Adjunct Professor, Department of Materials and Metallurgical Engineering – Federal University of Minas Gerais (UFMG), Brazil.

Abstract

The present study investigates the influence of the functional group structure and the resin matrix on the nickel sorption onto chelating resin Amberlite IRC 748®. Batch sorption experiments were carried out using high pressure acid leaching (HPAL) discharge pulp and HPAL discharge clarified solution to generate loaded resin samples. Despite the presence of many elements dissolved in solution, it has been found, previously, that Amberlite IRC 748® resin, which has a polystyrene-divinylbenzene matrix, loads predominantly Ni ions due to its high selectivity and high nickel concentration in HPAL solution. Raman spectroscopy informed that the spectra for loaded resins contacted with HPAL pulp and HPAL clarified solution were very similar, except for the fact that Raman intensity was higher for loaded resin contacted with HPAL pulp. Comparing them with the fresh resin spectrum, it was possible to understand the changes in resin structure forming a chelating compound. The eluted resin spectrum also showed that the resin after being loaded, eluted and regenerated preserved the structural characteristics of a fresh resin.

Keywords: nickel, ion exchange resin, Raman spectroscopy

Introduction

The processing of nickel laterites is at present a major focus of attention in the nickel industry. The high capital and operational costs for hydrometallurgical routes applied to these laterites are challenging the research community to identify and develop new methods and/or technologies for the cost–effective processing of these types of ores.

The use of ion exchange polymeric resins for nickel extraction from laterites processing is currently under investigation and some alternatives are being studied. Ion exchange technology with polymeric resins can be used for selective nickel recovery from high pressure acid leach discharge pulp as well as from clarified solutions (Mayze, 1999). In this process, ion exchange polymeric resins are used to extract and concentrate nickel ions that have been leached from the ore. Mendes and Martins (2004) have studied previously the sorption of nickel onto chelating resins from acidic solutions containing high concentrations of nickel and some impurities such as, iron, aluminum, magnesium and manganese.

The chelating resin with polystyrene-dyvinilbenzene matrix and iminodiacetic acid functional group - Amberlite IRC 748® - was identified as the most suitable resin for this purpose. Some sorption tests, adopting optimized parameters defined previously, were carried out with HPAL pulp (45 minutes, 200 rpm, 40^{o}C, resin/pulp = 6%) and HPAL clarified solution in column (1.7 BV/h, 8.4 g/L, pH = 4, [Ni]/[Fe] = 3.4) followed by elution tests (HCl 10% w/w, 2BV/h) to generate samples of loaded and eluted resins for further analysis. In the present work, Raman spectroscopy was used to evaluate the way nickel ions (Ni^{2+}) have been sorbed onto this ion exchange resin.

The Raman Effect and Normal Raman Scattering.

Photons interact with molecules to induce transitions between energy states. In the discussion of Raman spectroscopy, a photon is scattered by the molecular system. Most photons are elastically scattered, a process which is called Rayleigh scattering. In Rayleigh scattering, the emitted photon has the same wavelength as the absorbing photon. Raman Spectroscopy is based on the Raman effect, which is the inelastic scattering of photons by molecules. The Raman effect comprises a very small fraction, about 1 in 10^7 of the incident photons. In Raman scattering, the energies of the incident and scattered photons are different. A simplified energy diagram that illustrates these concepts is given in Figure 9.1.

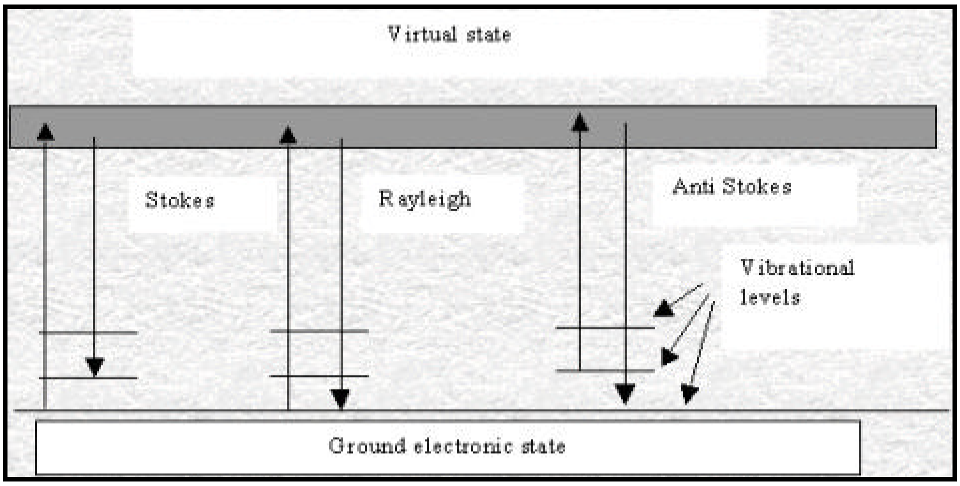


Figure 9.1 - Energy diagram showing incident and scattered photons (Anderson, 2000)

The energy of the scattered radiation is less than the incident radiation for the Stokes line and the energy of the scattered radiation is more than the incident radiation for the anti-Stokes line. The energy increase or decrease from the excitation is related to the vibrational energy spacing in the ground electronic state of the molecule and therefore the wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule. A schematic Raman spectrum showing Rayleigh, Stokes and anti-Stokes lines may appear as shown in Figure 9.2.

In the example spectrum, the Stokes and anti-Stokes lines are equally displaced from the Rayleigh line. This occurs because in either case one vibrational quantum of energy is gained or lost. Also, the anti-Stokes line is much less intense than the Stokes line. This occurs because only molecules that are vibrationally excited prior to irradiation can give rise to the anti-Stokes line. Hence, in Raman spectroscopy, only the more intense Stokes line is normally measured.

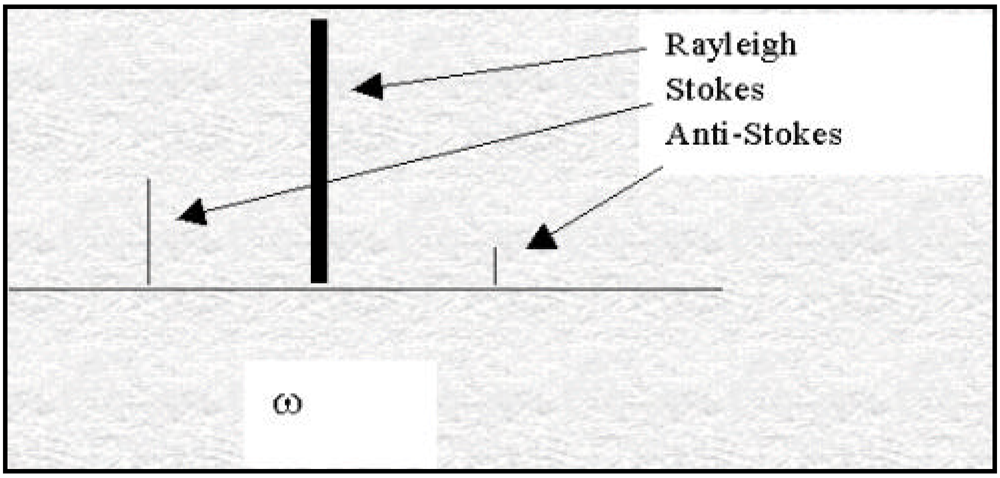


Figure 9.2 - Schematic Raman spectrum (Anderson, 2000)

Infrared (IR) and Raman spectroscopy both measure the vibrational energies of molecules but these methods rely only different selection rules. For a vibrational motion to be IR active, the dipole moment of the molecule must change. The asymmetric stretch is IR active due to a change in dipole moment, according to Figure 9.3.

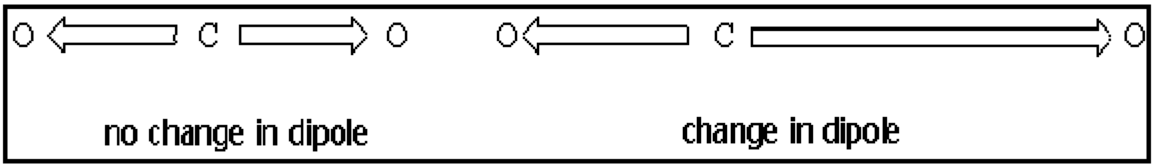


Figure 9.3 - Change in dipole moment according to symmetric and asymmetric stretch (Anderson, 2000)

For a transition to be Raman active there must be a change in polarization state of the molecule, as shown in Figure 9.4. For example, the symmetric stretch in carbon dioxide is Raman active because the polarizability of the molecule changes, comparing ellipsoid at the equilibrium bond length to the ellipsoid for the extended and compressed symmetric motions. For a vibration to be Raman active, the polarizability of the molecule must change with the vibrational motion. Thus, Raman spectroscopy complements IR spectroscopy.

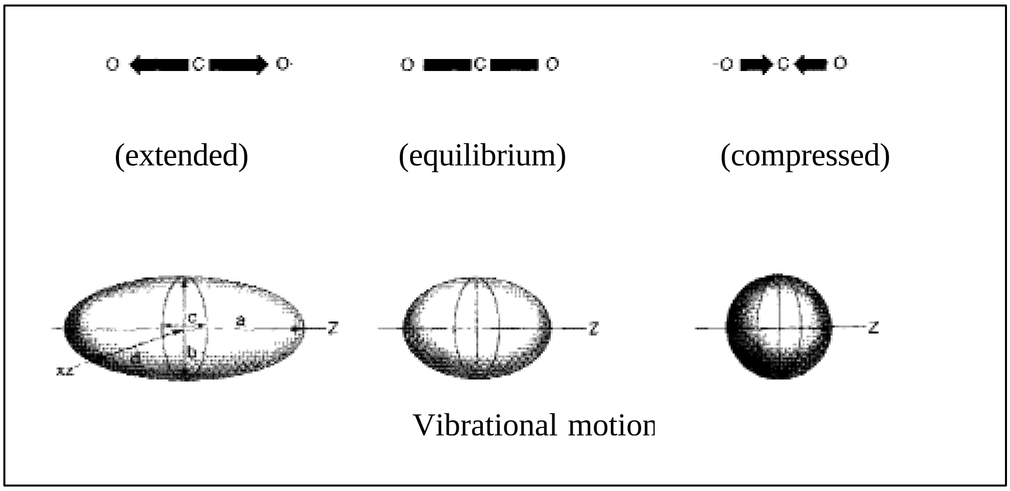


Figure 9.4 - Change in polarizability of the molecule (Anderson, 2000)

Experimentally, it is only observed the Stokes shift in a Raman spectrum. The Stokes lines will be at smaller wavenumbers (or higher wavelengths) than the exciting light. Since the Raman scattering is not very efficient, it is necessary a high power excitation source such as a laser. Also, as the interest is in the energy (wavenumber) difference between the excitation and the Stokes lines, the excitation source should be monochromatic (Anderson, 2000).

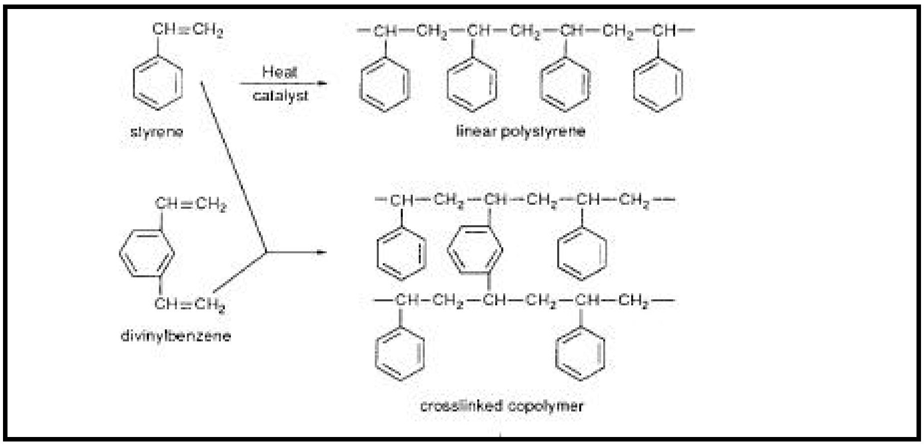
Experimental

In this experiment it was collected Raman spectra of fresh, loaded and eluted resin samples. Raman spectra were collected using Jobin Yvon Horiba labRam 800 spectrometer system. A linearly polarized HeNe laser (λ = 632.8 nm, 20mW output) was used as the excitation source of the Raman spectra. Optimum Raman spectra of each resin were obtained by using a 50X objective to focus the laser source on one resin bead. Computerized spectrometer control and data acquisition were used for this experiment. Data could be saved to a data file that was easily imported into a spreadsheet program for further analysis. The data file consisted of a column of wavelengths and a column of signal intensities. Amberlite IRC 748® was loaded by contacting the resin with HPAL discharge pulp (45 minutes, 200 rpm, 40^{o}C, resin/pulp = 6%) and HPAL clarified solution in a column sorption (1.7 BV/h, 8.4 g/L Ni, pH = 4,

[Ni]/[Fe] = 3.4). These loaded resins as well as fresh resin and eluted resin (HCl 10%, 2BV/h) were analyzed in Raman Spectroscopy.

Results

Results obtained from the literature are fundamental to assign the peaks to the particular vibrations in the molecule. A comparison between Raman spectra and literature values of the frequencies for the transitions of the molecules was carried out followed by a discussion of the similarities and differences in the data. Modern ion exchange polymeric resins are almost completely based on polymerization. The resin Amberlite IRC 748® has an inert matrix that can be generated from styrene (monomer organic electrolyte) and divinylbenzene (crosslinking agent). After the matrix has been synthesized, functional groups are added (Holl, 2003). Functionalisation with iminodiacetic acid leads to this chelating resin produced by Rohm & Haas (USA). Figure 9.5 shows the structure of styrene-divinylbenzene (matrix) and iminodiacetic acid (functional group).



Functional Group	Structure	Selective for
Iminodiacetic acid	 $-CH_2-N(CH_2-COOH)_2$	heavy metals

Figure 9.5 - Structure of styrene-divinylbenzene and iminodiacetic acid functional group of the resin Amberlite IRC 748®.

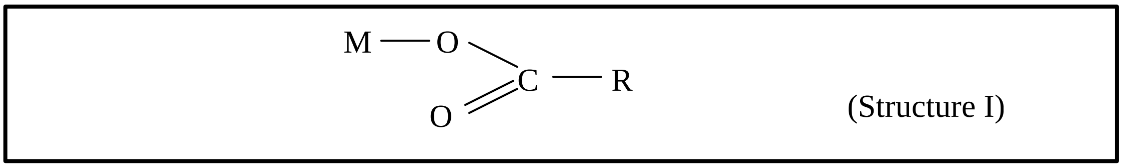
Table IX-1 presents the assignments of Raman peaks observed in fresh Amberlite IRC 748® resin regarding the approximate normal modes and observed frequencies of the vibrations of styrene-DVB structure. These values were found in the literature (Nakamoto, 1997) and had their values confirmed by the analyses of fresh resin spectrum. The modes are defined as follows:

ν (stretching) ρr (rocking) σ (scissoring)
δ(bending in plane) ρt (twisting)
ρw (wagging) π (bending out of plane)

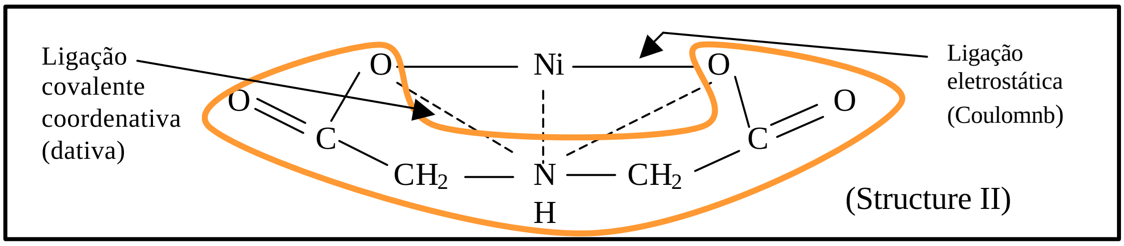
Table IX-1 - Raman frequencies of styrene-divinylbenzene

Band assignment	*Frequency, cm^{-1}*	*Band assignment*	*Frequency, cm^{-1}*
ν (CC benzene)	1610	ν (CH benzene)	3056
ν (CC benzene)	1001	ν (CH benzene)	3008
π (CC benzene)	852	δ (CH benzene)	1188
δ (CC benzene)	622	CH	2852
CH_2	1453		

Table IX-2 shows the frequencies and band assignments for iminociacetic acid (functional group). In the case of chelating resin Amberlite IRC 748®, carboxylate ion coordinates to a metal by forming unidentate complexes (structure I). Iminodiacetic acid coordinates to a metal by a trans-planar structure and the noncoordinating C=O groups are hydrogen-bonded to the neighboring molecule, or weakly bonded to the metal of the neighboring complex (structure II).



(Structure I)



(Structure II)

Table IX.2 - Raman frequencies of iminociacetic acid functional group

Band assignment	*Frequency, cm^{-1}*	*Band assignment*	*Frequency, cm^{-1}*
ν (NH)	2928	ν_a (CCN)	1202
ν (CC)	815	ν_s (CCN)	943
ν_s (COO)	1375	ρw (CH$_2$)	1328
ν_a (COO)	1643	δ (CH$_2$)	1453
ρw (COO)	641	ν (C=O)	1576
δ (COO)	736	ρw (NH)	1033
ν (CH)	2852	ρt (NH)	1079
ν (C-O)	1408	-	-

According to Nakamoto (1997), COO^- of amino acid complexes is affected by coordination as well as by intermolecular interactions. In any one physical state, the same frequency order is found for a series of metals, regardless of the nature of the ligand. When resin Amberlite IRC 748® is contacted with a neutralized HPAL pulp or HPAL solution, dissolved nickel is detected in a very high concentration compared to other elements. Due to this fact and considering the high selectivity for nickel, this metal is preferred sorbed onto resin. Nickel loading prevails over other metals on resin and Raman spectrum of loaded resin concerns nickel sorption rather than any other metal. After metal sorption onto resin, while the antisymmetric frequencies of COO^- increase, the symmetric frequencies decrease and the separation between them increases in the following order of metals:

Ni(II) < Zn (II) < Cu (II) < Co (II) < Pd (II) ~ Pt (II) < Cr (II)

Although there are several exceptions to this order, these results indicate that the effect of coordination is still the major factor in determining the frequency order in a given physical state. The above frequency order indicates the increasing order of the metal - oxygen interaction since the COO^- group becomes more asymmetrical as the metal-oxygen interaction becomes stronger. It is seen that the C=O stretching, N-H rocking, and M-N and M-O stretching bands, where M = metal, are metal sensitive and are shifted progressively to higher frequencies as the metal is changed in the order Ni (II) < Cu (II) < Pd (II) < Pt (II).

The determination of coordination numbers of the metals in metal chelate compounds of α-amino acids is based on the simple rule that the unionized and uncoordinated COO^- stretching band occurs at different wavenumber if compared to the ionized and coordinated COO^- stretching band. The latter frequency depends on the nature of the metal. Macroporous polystyrene based resins with iminodiacetic acid groups have a high affinity for heavy metals cations over alkali or alkali earth metals. The apparent selectivity for a given metal depends upon concentration, the presence of other species, and pH. This means that the affinity of the resin for a given metal can be increased or decreased by adjusting the pH value, for example. Having all these parameters well controlled, it is feasible to sorb nickel on resin preferably. Based on this fact, Table IX-3 illustrates the main differences between the fresh resin spectrum and the loaded resin spectrum, showing the changes occurred in the resin structure when nickel is selectively sorbed onto the resin. Figures 9.6 to 9.8 show the Raman spectra of fresh resin and loaded resin contacted with HPAL pulp and HPAL solution.

Table IX-3 - Main changes in resin structure after nickel sorption

Compound	*Un-ionized COOH*	*Coordinated COOM*	*Free COO-*	*C-O*	*C-N-C*	*C-N*	*N-H*	*O-H*	*Ni-O*	*Ni-N*	*N-O*
Fresh resin	1688	-	$1643\nu_a$ $1375\nu_s$	1408	$1202\nu_a$ $943\nu_s$	1220	1079	330	-	-	-
Loaded resin	-	$1704\nu_a$ $1356\nu_s$	-	1445	$1208\nu_a$ $943\nu_s$	1208	1091	-	335	415	976

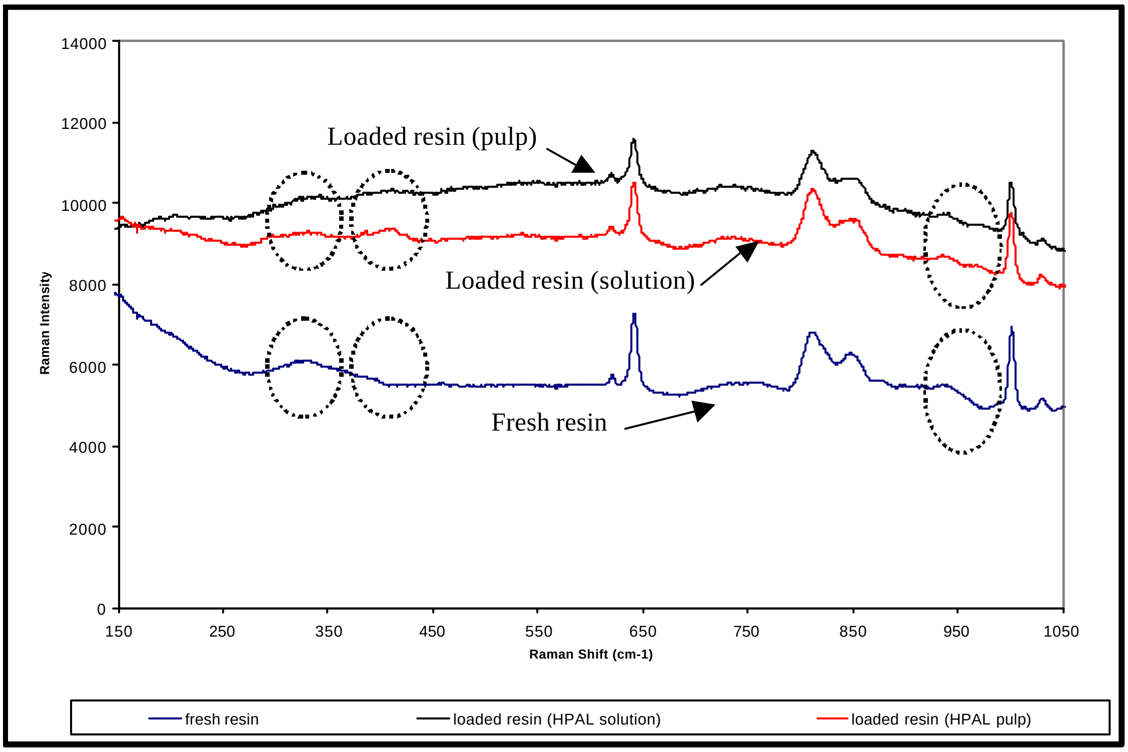


Figure 9.6 - Raman spectra of loaded and fresh resin – 150-1050 cm^{-1} range

The differences between loaded resin (HPAL solution) and loaded resin (HPAL pulp) spectra are minimum. The Raman intensity for the bands of the resin contacted with pulp is higher due to the presence of impurities, mainly any very fine ore particle fixed to resin surface during resin-in-pulp process. However, the differences between fresh and loaded resin are notable, informing nickel ions sorption on resin forming a chelating composite as shown in structure II. The loaded resin analyses showed that Amberlite IRC 748® coordinates to nickel via the oxygen atom as well as nitrogen atom, since ν(Ni-O) and ν(Ni-N) vibrations are observed. Figure 9.6 shows the main differences between fresh and loaded resin in the Raman frequency range of 150-1050 cm^{-1}. The Ni-O, Ni-N vibration exhibited peaks at 335 cm^{-1} and 415 cm^{-1}. Loaded resin also presented a peak at 976 cm^{-1} regarding the coordination N-O formed after nickel sorption.

Figure 9.7 shows the Raman spectra of fresh and loaded resin for 1000-1800 cm^{-1} range. The change in Raman shift for NH coordination at 1079 cm^{-1} confirms the sorption of nickel by the resin and the nickel coordination to resin via nitrogen atom.

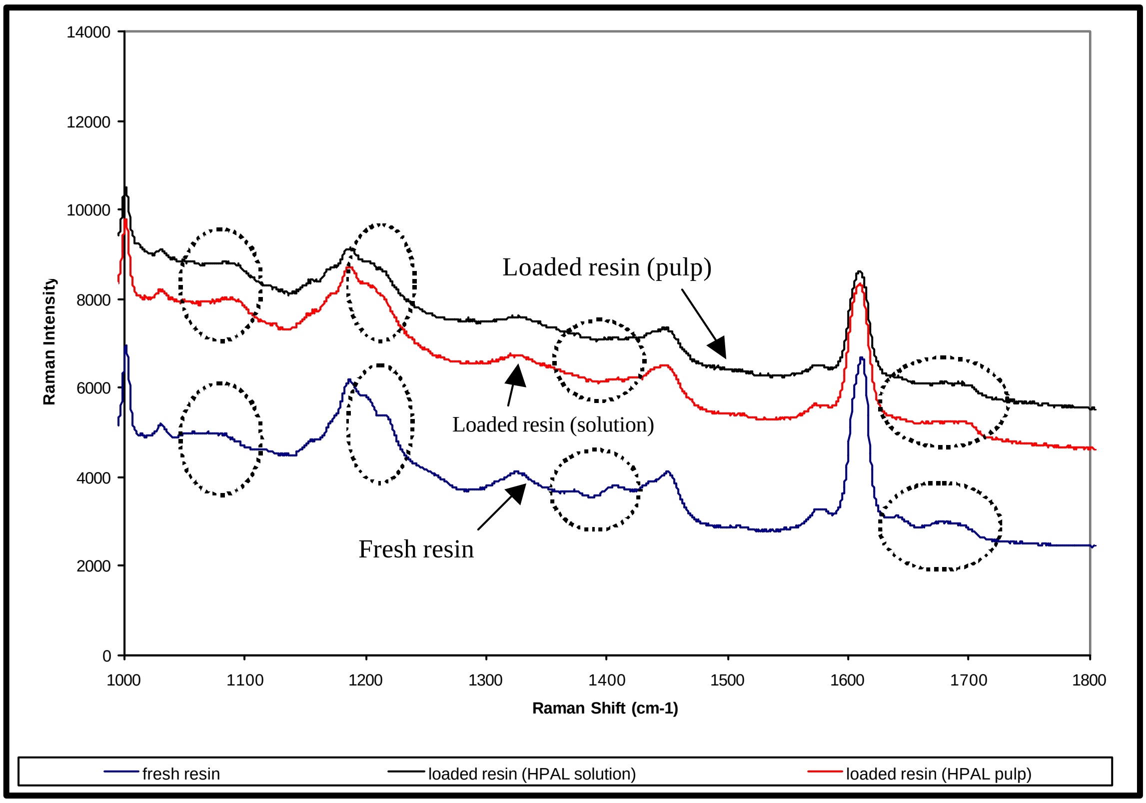


Figure 9.7 - Raman spectra of loaded and fresh resin – 1000-1800 cm^{-1} range

Figure 9.7 also illustrated that for loaded resins, the vibrations C-N-C overlaps with the vibration C-N at 1208 cm^{-1}. It is important to observe that for the fresh resin the Raman spectrum exhibited the peak of antisymmetric COO$^-$ stretching frequency at 1375 cm^{-1} and CO stretching frequency at 1408 cm^{-1}. After nickel sorption, it can be seen that the weak antisymmetric vibrational stretch assigned previously to the free COO$^-$ is not observed in the Raman spectrum of the loaded resin. This result suggests that free COO$^-$ coordinated to nickel generating a new band at 1356 cm^{-1}. CO stretching frequency was displaced to 1445 cm^{-1} band as a result of nickel coordination to oxygen atom of carboxylate complex. The unionized and uncoordinated COOH stretching band occurred at 1688 cm^{-1} in the fresh resin spectrum, while the symmetric vibrational stretching of free COO$^-$ occurred at 1643 cm^{-1}. The loaded resins spectra show that these bands are no more observed and they are replaced by the peak at 1704 cm^{-1} which is assigned to the coordinated COO band (COONi), confirming the chelating complex formation. Figure 9.8 presents the Raman spectra of fresh and loaded resin for 2700-

3300 cm^{-1} range. At this Raman shift interval no significant difference in the bands frequencies was observed.

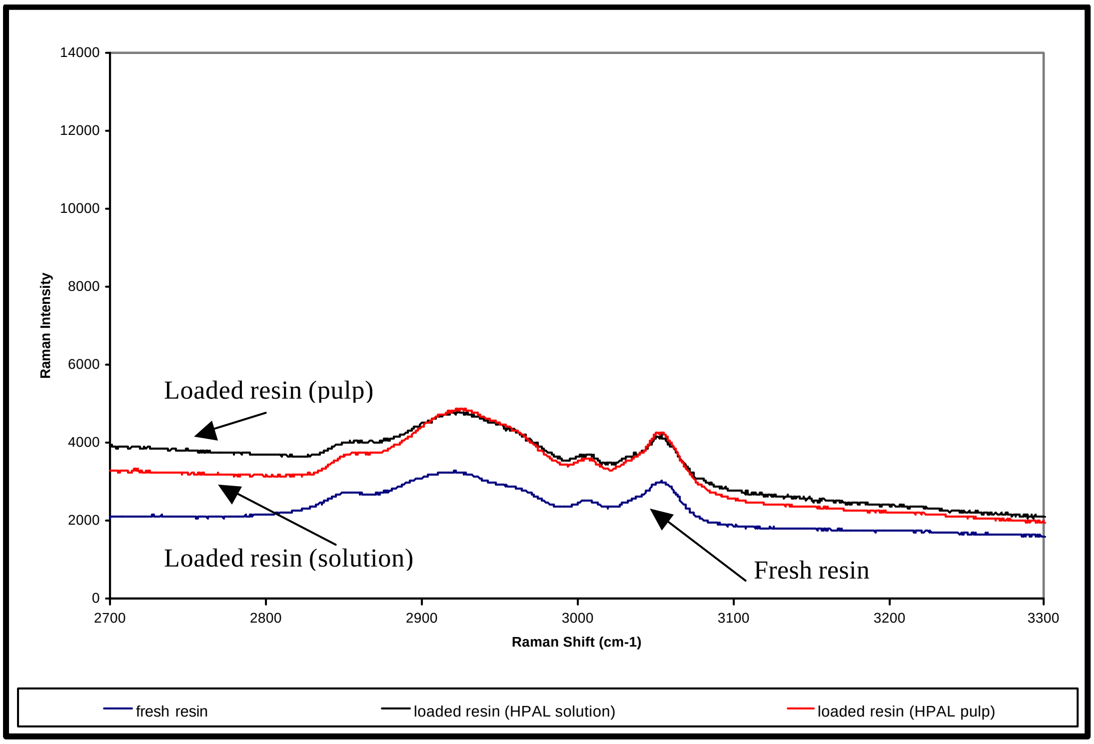


Figure 9.8 - Raman spectra of loaded and fresh resin – 2700-3300 cm^{-1} range

Figures 9.9 and 9.10 present the Raman spectra for fresh and eluted resins. Minimum differences between them were detected, indicating that the resin elution preserved the initial chemical structure characteristics of the fresh resin. No band concerning metal coordination was observed showing that the elution process was efficient and the regeneration process was able to prepare the resin for other sorption cycles without any loss in the resin structure. It is worthwhile to emphasize the difference in Raman intensity for the modes observed to eluted resin. This fact was expected since this resin had a chemical treatment after its use in sorption and elution tests. After elution, resin was rinsed with deionized water, eluted with four bed volumes of NaOH 5% solution and rinsed with distilled water until the pH value of the eluent reached a value between the range of 7.0-8.5. Rinsing was stopped at this pH range to avoid resin hydrolysis, i.e. formation of H^+/Na^+ mixed form resin in large extent.

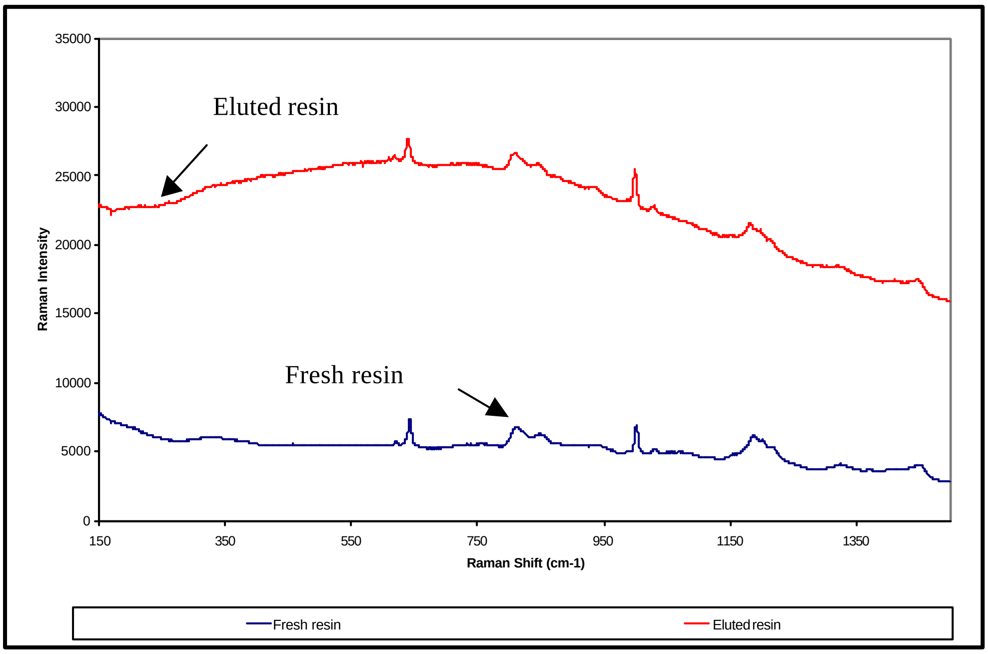


Figure 9.9 - Raman spectra of eluted and fresh resin – 150-1500 cm^{-1} range

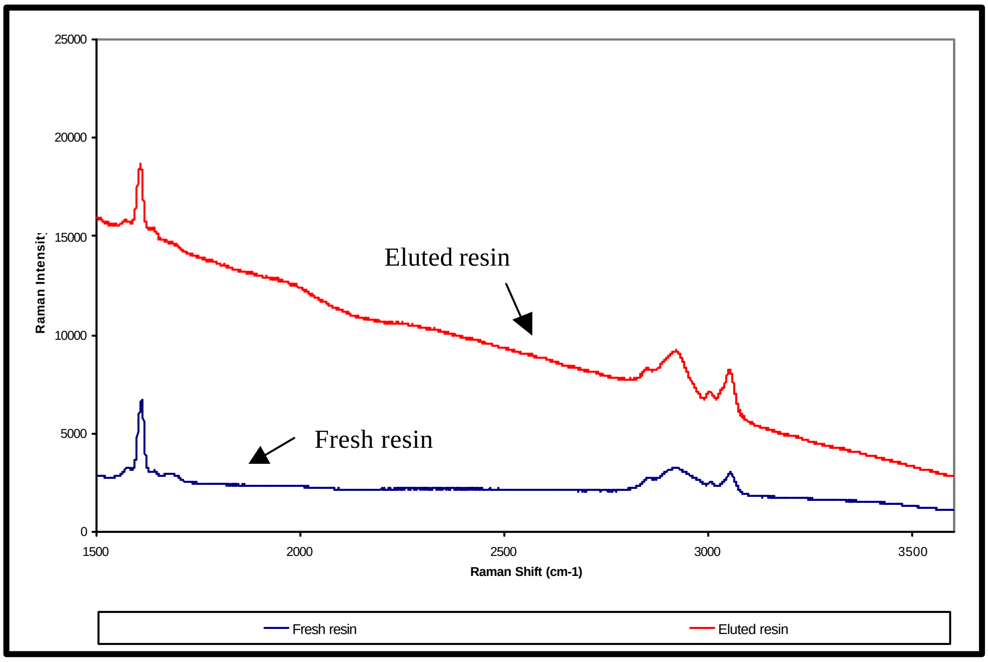


Figure 9.10 - Raman spectra of eluted and fresh resin – 150-1500 cm^{-1} range

Conclusions

Raman spectroscopy has been used to determine the changes in the resin structure after selective nickel sorption. The analyses of loaded resin showed that Amberlite IRC 748® coordinates to nickel via the oxygen atom, as well as nitrogen atom, since ν(Ni-O) and ν(Ni-N) vibrations were observed. Loaded resin also presented a peak regarding the coordination N-O formed after nickel sorption. The appearance of these bands as well as the knowledge of how carboxylate ions in iminodiacetic acid group coordinate to a metal guided the understanding of nickel sorption on resin. It is expected that this resin coordinates to metal by forming a chelating compound which is very stable and commonly observed for selective heavy metals sorption.

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Capítulo 10 – Conclusões

As informações obtidas ao longo deste trabalho mostraram que resinas quelantes com grupo funcional iminodiacético apresentaram resposta positiva em relação à recuperação seletiva de níquel e cobalto em meio sulfúrico, através da técnica de resina em polpa. Os objetivos propostos para esta tese foram alcançados através da realização de ensaios práticos que abrangeram uma avaliação voltada para a seletividade, capacidade de carregamento e recuperação de níquel em soluções e polpas, através de ensaios em batelada e contínuos. A consolidação e a análise de todos os resultados técnicos obtidos permitiram concluir que a aplicação de resinas de troca iônica para recuperação de níquel, em fluxogramas de processamento de minérios lateríticos de níquel, pode ser uma alternativa promissora, conforme mostrado pelos dados a seguir:

As resinas quelantes Dowex M4195® e Amberlite IRC 748® apresentaram os melhores resultados de capacidade de carregamento - base seca (85-112gNi/kg ou 39-51gNi/L), sem a influência predominante de outros metais, principalmente, em valores de pH superiores a 3 e após a precipitação de ferro da solução. A resina Dowex M4195® apresentou ainda uma vantagem em relação a todas as outras resinas avaliadas, uma vez que níquel e cobalto foram adsorvidos até mesmo em baixos valores de pH com pouca influência de outros elementos, principalmente o ferro. Trocadores quelantes como a resina Dowex M4195®, constituída do grupo funcional bis-picolilamina com átomos doadores de nitrogênio, exibem essa propriedade diferenciada se comparada às demais resinas avaliadas. Entretanto, trata-se de uma resina com elevado custo o que impacta substancialmente no balanço econômico de avaliação da técnica de resina em polpa. A resina Amberlite IRC 748® apresentou resultados bastante promissores, desde que sejam seguidas condições otimizadas levantadas nesta tese, que apontam valores específicos de pH, concentrações do metal de interesse e íons competidores na solução. Em valores de pH acima de 3 e em condições em que a concentração de níquel em solução é maior do que a concentração das impurezas, esta resina foi mais seletiva para cobre, níquel e cobalto, com pequena influência de adsorção de ferro, além da resistência mecânica superior e melhor estabilidade térmica. Já a recuperação de cobalto, é crescente com o aumento do pH e diminui com o aumento do tempo e da razão [Ni]/[Co]. Para o caso da resina Amberlite IRC 748®, constituída do grupo funcional de ácido iminodiacético, a presença de grupamentos de ácido fraco faz com que este trocador apresente alta afinidade aos íons hidrogênio. Assim, quanto menor o pH, menor a recuperação seletiva de níquel em função da competição com os íons H^+.

Os resultados experimentais em colunas de adsorção com a resina quelante Amberlite IRC 748® mostraram que o emprego de valores mais altos de pH melhora o desempenho do trocador de íons e maiores capacidades de carregamento de níquel são obtidas. Além disso, o aumento da concentração de níquel em relação à concentração de impurezas na solução acarretou um aumento substancial na seletividade e na capacidade de carregamento - base seca - de níquel (112 gNi/kg) e de cobalto (5 gCo/kg). As curvas de *breakthrough* indicam que vários metais foram rapidamente detectados no efluente da coluna logo no início do ensaios, enquanto que para o níquel, este fato foi observado posteriormente, confirmando a seletividade da resina em relação a este metal. A adsorção de Co ocorre nos cinco primeiros BV, a partir daí ocorre a sua dessorção. A adsorção de Ni ocorre nos sete primeiros BV, a partir daí a adsorção é paralisada e permanece constante. Estes resultados sugerem que é perfeitamente viável a adsorção seletiva de níquel a partir da solução HPAL, através do uso da resina quelante Amberlite IRC 748®, desde que algumas condições específicas de pH, taxa de alimentação e concentração de níquel sejam aplicadas. Para valores de pH acima de 4, a resina Amberlite IRC 748® foi preferencialmente seletiva para níquel se comparada ao ferro, mesmo se ambos apresentarem a mesma concentração na solução.

A remoção de metais da resina foi efetuada com sucesso utilizando os reagentes HCl e H_2SO_4. O melhor resultado da etapa de eluição foi obtido com o uso de HCl 10% w/w numa taxa de 2 BV/h. Neste caso, a solução resultante apresentou concentração de níquel de 45 g/L, ou seja, mais que 20 vezes superior a sua concentração inicial na solução de alimentação da coluna, enquanto apenas baixa concentração de impurezas foi detectada (< 1,5 g/L).

Os resultados da avaliação de resina em polpa em regime de batelada comprovaram que a resina Amberlite IRC 748® apresentou recuperações de níquel e cobalto da solução maiores que 99% após cinco estágios em contra corrente. A resina removeu continuamente níquel e cobalto da solução permitindo, durante o processo de troca iônica, a lixiviação de parte do níquel contido nos sólidos e sua posterior adsorção na resina - fenômeno sorção-lixiviação. Para que isso possa ocorrer de forma eficiente, o níquel precipitado durante o ajuste de pH deve ser redissolvido e recuperado pela resina. Uma proporção de cerca de 20% do níquel na fase sólida foi redissolvido para ser então completamente adsorvido pela resina. O cobalto foi adsorvido nos cinco primeiros estágios, e em seguida dessorvido, já o níquel foi continuamente adsorvido até o sétimo estágio. Um carregamento máximo de 98 g Ni/kg resina - base seca - foi obtido nesse estudo.

Três campanhas de 50 horas foram realizadas para se avaliar a viabilidade de aplicação do processo de resina quelante, com grupamento funcional orgânico iminodiacético (resina CheRes), em polpa proveniente da lixiviação ácida sulfúrica sob pressão de um minério laterítico Brasileiro sob estudo pela CVRD, para a recuperação de níquel e cobalto. Os resultados alcançados após dez estágios de contato mostraram: (1) efetiva recuperação de níquel e cobalto das fases líquida e sólida, onde foram obtidas soluções após a adsorção com 10 e 5mg/L de Ni e Co, respectivamente. Sete estágios de contatação foram suficientes para obtenção de 99,9% de recuperação de níquel da solução, além de 15-20% de recuperação do níquel contido na fase sólida. Para a recuperação de cobalto foi verificado que, entre os estágios 2 e 5, há uma dessorção do cobalto previamente adsorvido. Somente a partir do estágio 5, esse metal volta a ser adsorvido, atingindo 99% de recuperação no estágio número 10. Daí a necessidade de 10 estágios de contactação; (2) alto carregamento de níquel, da ordem de 40-45 g/L de resina, com baixos níveis de impurezas; (3) rápida e completa eluição de níquel e cobalto com H_2SO_4 e HCl; (4) solução eluída com ácido sulfúrico ou ácido clorídrico, obtendo-se alta concentração de níquel, com cerca de 46 g/L de Ni, podendo-se atingir 60g/L e assim realizar a sua recuperação direta com produto de elevada pureza; (5) baixo nível de impurezas, tanto na resina carregada quanto na solução eluída.

Finalmente, o estudo de caracterização da resina Amberlite IRC 748® utilizando espectroscopia RAMAN mostrou que a resina carregada adsorveu as espécies de níquel via ligação com átomos de oxigênio e de nitrogênio através da formação de um composto do tipo quelato altamente estável para metais de transição. Átomos de N, O, P, S doadores de elétrons (base de Lewis) formam ligações covalentes coordenativa (dativa) com íons metálicos (ácido de lewis) e interações eletrostáticas (Coulomb) ocorrem entre íons fixos e móveis. O espectro da resina eluída, quando comparado com o espectro da resina nova, tal qual foi recebida do fabricante, indicou que a resina após ser carregada, eluída e regenerada preservou as mesmas características químicas exibidas pela resina nova, sem degradação química relevante.

Os resultados, acima descritos, confirmaram o potencial de aplicabilidade da técnica de resina em polpa no fluxograma de minérios lateríticos de níquel, dados os resultados alcançados ao longo de 10 estágios de contactação em pH = 4,0, utilizando resina com grupo ácido iminodiacético. Uma vez otimizados os parâmetros que exercem influência na adsorção do Ni, é observada a reprodutibilidade dos resultados à medida que se foi aprimorando a escala, complexidade e representatividade do processo: ensaios em coluna, resina em polpa batelada, resina em polpa contínuo.

- Para a polpa descendente foram observados:

- 99,9% de extração de Ni da fase líquida em 7 estágios;
- 99,9% de extração de Co da fase líquida em 10 estágios, com adsorção somente nos reatores 5-10;
- 15-20% de extração de Ni e Co da fase sólida após 10 estágios;
- Eluição com HCl 15%;
- Solução eluída com alta concentração de Ni (46g/L) e baixa concentração de impurezas.

- Para a resina ascendente foram observados:

- Em 10 estágios ocorreu a saturação da resina com carregamento de 40-45g/L de Ni;
- Nos 5 primeiros estágios (reatores 10-5) ocorreu a saturação da resina em 4g/L de Co, a partir daí Co é dessorvido nos reatores 5-1;
- Formação de um composto quelato altamente estável para metais de transição.

Capítulo 11 - Sugestões para trabalhos futuros

Do ponto de vista de processo, uma série de riscos tecnológicos ainda necessitam ser avaliados antes de uma futura aplicação industrial de resinas de troca iônica para recuperação de níquel e cobalto em polpa efluente de lixiviação ácida de minérios lateríticos de níquel. Alguns pontos devem ser levantados:

- Perdas de níquel e cobalto na fração sólida durante o pré-tratamento do material para precipitação de ferro e outras impurezas. Para avaliação desse item, sugere-se efetuar um estudo criterioso dessa técnica de precipitação utilizando diferentes reagentes básicos e controle rigoroso de pH e Eh para minimização da co-precipitação de níquel nessas condições.
- Otimização da etapa de eluição que foi apenas avaliada de forma preliminar, expondo qualitativamente os reagentes com potencial para a rápida e seletiva dessorção de níquel. Para avaliação desse item, está em andamento atualmente um estudo detalhado do processo de eluição, visando a possibilidade de se obter um licor rico com concentração de níquel na faixa de 60 g/L. (Atualmente tema de dissertação de mestrado do CPGEM - UFMG)
- Definição da resistência mecânica (abrasão mecânica e choque osmótico) da resina Amberlite IRC 748® para avaliação do potencial econômico do processo RIP.

Do ponto de vista de caracterização de resina, a abordagem de espectroscopia Raman foi realizada de forma bastante preliminar. Para obtenção de informações mais abrangentes e para um maior conhecimento da influência da estrutura da resina no mecanismo de adsorção de metais, sugere-se a programação de um estudo mais amplo. Análises de espectroscopia Raman de soluções efluentes de lixiviação sob pressão em diferentes condições de concentração de níquel e impurezas, e de soluções sintéticas contendo isoladamente metais dissolvidos poderiam ser realizadas. A comparação com resinas carregadas com um único metal forneceria informações valiosas quanto ao comportamento de cada metal isoladamente frente à adsorção no grupamento funcional orgânico da resina.

Capítulo 12 - Publicações oriundas desta tese

1. **Mendes**, F. D. ; **Martins**, A. H. ; **Costa**, R. S. . **Selective sorption of nickel and cobalt from pressure acid leach discharge liquors using chelating resins**. In: *XXII International Mineral Processing Congress, 2003, Cape Town. XXII IMPC, 2003.*

2. **Mendes,** F. D. and **Martins,** A. H**. Selective sorption of nickel and cobalt from sulphate solutions using chelating resins.** *International Journal of Mineral Processing, Volume 74, Issues 1-4, 19 November 2004, Pages 359-371*

3. **Mendes,** F.D. and **Martins,** A.H. **Recovery of nickel and cobalt from acid leach pulp by ion exchange using chelating resin.** *Minerals Engineering, Volume 18, Issue 9, August 2005, Pages 945-954*

4. **Mendes,** F.D. and **Martins,** A.H.**. Selective nickel and cobalt uptake from pressure sulfuric acid leach solutions using column resin sorption.** *International Journal of Mineral Processing, Volume 77, Issue 1, September 2005, Pages 53-63*

5. **Mendes**, F. D. ; **Martins**, A. H. ; **Costa**, R. S. . **Adsorção seletiva de níquel e cobalto através da aplicação de resinas quelantes comerciais**. In: *10 Seminário de Metais Não Ferrosos, 2002, São Paulo, 19 a 21 de Março.* Anais do 10 Seminário de Metais Não Ferrosos. São Paulo: Associação Brasileira de Metalurgia e Materiais, 2002. p. 21-32.

6. **Mendes**, F. D. ; **Martins**, A. H. ; **Furtado** TLC . **Aplicação dos diagramas Eh x pH à extração de Níquel e Cobalto do Licor de Lixiviação do Minério Laterítico Níquel do Vermelho (PA)**. In: *57º Congresso Anual-Internacional da Associação Brasileira de Metalurgia e Materiais, 2002, São Paulo.* 57º Congresso Anual-Internacional da Associação Brasileira de Metalurgia e Materiais, 2002. p. 2306-2315.

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9. **Mendes**, F. D. ; **Costa**, R. S.. **Uso de resinas de troca iônica para a recuperação de Ni e Co**. In: *XX ENTMME, 2004, Florianópolis. Anais do XX ENTMME, 2004. v. CD.*

10. **Mendes**, F. D. ; **Martins**, A. H.. **Recuperação seletiva de níquel e cobalto de polpa ácida usando resina quelante de troca iônica.** In: *XXI ENTMME, 2005, Natal. Anais do XXI ENTMME, 2005. v. CD.*

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Anexo I - Resin-in-pulp application for nickel uptake

RESIN-IN-PULP APPLICATION FOR NICKEL UPTAKE

Flávia Dutra Mendes
Mineral Development Centre
Companhia Vale do Rio Doce
Rodovia BR 262 – km 296 – PO Box 09 - Santa Luzia – Minas Gerais - CEP: 33010-970 – Brazil
flavia.mendes@cvrd.com.br,

Abstract

Three 50-hour campaigns were performed to assess the viability of a chelating resin (CheRes – iminodiacetic group) continuous resin-in-pulp (cRIP) process, as applied to the recovery of nickel and cobalt from materials derived from a Brazilian laterite ore body. The campaign results were very encouraging, notably showing: (1) Highly effective removal of the nickel and cobalt from the liquid phases of the feed materials with very low residual concentrations. (2) Excellent resin loading for nickel and cobalt - a critical parameter in the quest for pregnant liquor of outstanding tenor and quality. (3) Evidence of rapid and complete desorption of both nickel and cobalt using either H_2SO_4 or HCl. (4) Samples of pregnant solution with high concentrations of nickel. (5) Low impurity levels, both on the resin and in the desorption samples.

These results support the ingoing hypotheses about the resin-in-pulp (RIP) technology's potential to revolutionise the overall flowsheet for recovery of nickel and cobalt from laterite ore bodies. The developing concept involves replacing the conventional CCD circuit with the RIP process. The concept is that material received from the acid leach process step would be converted into a pregnant liquor of sufficient tenor and purity that: (1) Downstream processing requirements would be greatly simplified. (2) The need for complicated recirculation circuits to deal with the iron present in CCD overflow solutions would be eliminated. (3) Total system recoveries will at least match, and probably exceed, those achieved by fully optimised conventional (CCD-based) processing schemes. (4) Capital intensity will be significantly reduced. (5) Total operating costs will be lower with the cost of resin replacement being more than offset by savings elsewhere in the system.

Introduction

The traditional methods commonly employed to remove heavy metals from effluents, such as chemical precipitation, oxidation/reduction, filtration, electrochemical processes, are not always convenient. In some cases either they are not effective enough due to the lack of selectivity or their cost is prohibitive.

In the last few years, nickel industry economy has pushed forward the development of alternative methods for nickel recovery in downstream flowsheet. This in turn has led to a growing interest in the use of sorption by ion-exchange resins for trapping nickel and cobalt from solution. These technologies are less aggressive to the environment and also economically promising but, in spite of much research effort, no ion exchange sorption process has reached commercial application in nickel laterite industry yet. A number of researchers have been investigating the feasibility of using chelating resins for nickel removal from high pressure acid leaching discharge pulps. CVRD studies began in a bench testwork program in order to evaluate the preliminary feasibility. As long as the results have been even more encouraging, it was observed the necessity to extend these results to larger-scale treatments of HPAL effluents in order to replicate the positive results.

This chapter aimed at the continuous resin-in-pulp process evaluation in a custom-built resin-in-pulp miniplant for nickel and cobalt recovery. Three 50-hour campaigns were performed to assess the viability of a chelating resin (defined in this text as CheRes) continuous resin-in-pulp (cRIP) process, as applied to the recovery of nickel and cobalt from materials derived from a Brazilian laterite ore body. CheRes is a non-comercial chelating resin and has an iminodiacetic acid functional group bonded to a macroporous styrene divinylbenzene matrix. A comparison between CheRes and Amberlite IRC 748® technical features showed that these resins are very similar regarding their performance in nickel sorption including load capacity and selectivity. In this case, CheRes was preferably tested in a continuous scale due to the large volume and suitable equipment availability by its manufacturer.

Methodology

CVRD is exploring a series of nickel/cobalt deposits. As part of its recent test work, three campaigns of the laboratory-scale continuous resin-in-pulp (cRIP) process were carried out. The first two runs processed autoclave leachate and the third treated overflow solution from CCD#1.

Feed Materials

For the Brazilian laterite ore laboratory-scale RIP campaigns, were prepared:

- 270 kg (or approximately 180 L) of autoclave pulp.
- 75 kg (or approximately 70 L) of CCD#1 overflow.

The pH, oxidation/reduction potential (ORP), maximum particle size, viscosity and temperature of the feed materials to its laboratory-scale cRIP test were managed.

- pH was adjusted to 4.5 by the addition of limestone 2-3 hours before the respective campaigns were due to begin. 66.8 kg and 29.1 kg of limestone slurry (with 20% solids on a w/w basis) were added to the pre-neutralised leachate and CCD#1 overflow solutions, respectively. Further small additions of limestone slurry were made during the course of the 50-hour runs as required to sustain the pH of the feed materials above 4.0. The total additional volumes were minor. The pH adjustment procedure is an important driver of total system recoveries and that no effort has been made at this point to optimise that process step. Further work is required to develop an appropriate pH adjustment methodology to optimise overall nickel and cobalt recoveries.
- During the initial pH adjustment, the oxidation reduction potential (ORP) was managed by the addition of small amounts of hydrogen peroxide.
- For these campaigns, sizing was not an issue. Neutralisation induced the expected precipitation of iron but the resulting solid particles were relatively small with the entire material passing a 200 micron mesh.

- The viscosity of the feed pulp was quite high, particularly for the neutralised autoclave leachate. An overhead mixer was used to stir the slurry in a 5L glass beaker. This allowed a closer watch over the viscosity and flow rate of the material entering the test rig. By monitoring the level in the glass beaker, it was possible to assure that pulp was flowing steadily into the feed vessel as well as out of it.
- Feed materials were heated to 60ºC using a titanium-sheathed heating rod and maintained at this temperature throughout each campaign. A 5 L glass beaker was positioned on a hot plate so that its contents were also maintained at 60ºC.

Laboratory-scale RIP Test

The laboratory-scale cRIP test procedure focuses primarily on the sorption process step. It was supplied the necessary equipment to perform continuous sorption and batch desorption for the three campaigns.

The sorption equipment consisted of a series of ten (10) air-lift reactors made of borosilicate glass. Each reactor houses a basket made of stainless steel mesh and, for these campaigns, the baskets contained 100mL of chelating resin. Based on the previous experience, the speed of the slurry through the sorption circuit is determined by the feed pump. For these campaigns, the target throughput was set at 0.6 L/hour for the autoclave leachate and 0.9-1.0 L/hour for the CCD#1 overflow solution. Slurry migrates past the resin-filled basket and proceeds to the next reactor via a transfer tube.

The desorption equipment was a single glass column, diameter 40mm, height 750mm. The column was desorbed in a down flow regime at approximately 1 volume/volume resin/hour. The resin volume for each desorption was between 650 and 750ml.

Sorption

Sorption is the process of transferring targeted metals from the pulp to the resin using ionic forces. In cRIP, this occurs during the counter-current passage of pulp and resin through the glass reactors. Slurry was directed into the first reactor by the peristaltic pump and steadily made its way into the other reactors. Each batch of resin was left in its original reactor until the plant reached equilibrium. The first resin transfer was performed after the system had stabilised and nickel concentrations in the liquid fraction of reactor #8 had reached a predetermined concentration. Subsequently, resin was transferred roughly once every one to two hours but always depending on the level of nickel in the liquid fraction of the pulp in reactor #8.

Resin baskets were moved in the opposite direction to the flow of pulp. The basket from reactor #1 was removed and the fully-loaded resin it contained was prepared for desorption. The basket from reactor #2 was then moved into reactor #1; the basket from reactor #3 into reactor #2, and so on. A basket with fresh resin was then placed into reactor #10.

Desorption

Desorption involves the liberation of targeted metals from the resin to produce a pregnant liquor. The laboratory-scale cRIP test procedures were not designed to optimise desorption conditions and regimes. A series of batch desorption runs were performed with the following objectives:

- Obtain an indication of the resin loading capacities for the metals.
- Obtain an indicative figure of the pregnant liquor tenors.
- Test the hypothesis that hydrochloric acid can be used equally successfully as the more conventional desorption agent, sulphuric acid.
- Desorb metals from the resin fully and quickly, and return regenerated resin back into the sorption process (in to the 10th reactor).

Loaded resin from reactor #1 was thoroughly washed with tap water, removed from the basket and stored in a plastic container. After collecting several lots of fully loaded resin from reactor #1, the combined resin was placed into the desorption column and treated with measured volumes of desorption reagent. In total, ten batches of pregnant resin were pooled and desorbed in this way during the course of the three campaigns.

Table AI.1 shows the quantities of resin in each desorption batch, the type and volume of desorption reagent used and the desorption solution samples submitted for analysis.

Table AI.1 - Desorption batches

Campaign #	*Batch*	*Resin Volume (mL)*	*Desorption Reagent*		*Desorption Samples*	
			Type	*Total Volume (mL)*	*ID#*	*Cut Volume (mL)*
1	1.1	690	8% H_2SO_4	2590	RIP1/E1	420
					RIP1/E2	550
					RIP1/E3	700
					RIP1/E4	920
	1.2	750	8% H_2SO_4	2378	RIP1/E5	368
					RIP1/E6	1005
					RIP1/E7	1005
2	2.1	750	15% HCl	1980	RIP2/E1	530
					RIP2/E2	450
					RIP2/E3	580
					RIP2/E4	420
	2.2	750	15% HCl	1780	RIP2/E5	180
					RIP2/E6	310
					RIP2/E7	540
					RIP2/E8	750
	2.3	750	15% HCl	1550	RIP2/E9	1000
					RIP2/E10	550
	2.4	750	15% HCl	1660	RIP2/E11	360
					RIP2/E12	760
					RIP2/E13	540
	2.5	750	15% HCl	1290	RIP2/VII	850
					RIP2/VII	440
3	3.1	730	15% HCl	1450	RIP3/E1	200
					RIP3/E2	450
					RIP3/E3	800
	3.2	750	15% HCl	1550	RIP3/E4	1,000
					RIP3/E5	550
	3.3	770	15% HCl	1850	RIP3/E6	850
					RIP3/E7	1,000

Sampling regime

The sampling regime was designed to monitor the behaviour of target metals and impurities throughout the prospective cRIP process. Samples of feed, barren slurries and loaded, unloaded and in-process resin were taken to assess this behaviour and derive important information for flow sheet design.

- Samples of both of the original supplied materials—autoclave pulp and CCD#1 overflow - were taken before and immediately after the pH adjustment procedure.
- The pH-adjusted feed pulp was then monitored throughout the course of the campaign by taking grab samples every 4 hours for a total of thirteen samples.
- Grab samples of barren pulp were also taken every four hours but only once the system reached equilibrium in each campaign. Eleven grab samples of barren slurry were taken. In addition, composite samples of barren pulp were collected for rough mass balance calculations.
- At the end of each 50-hour campaign, samples of both slurry and resin were taken from each of the 10 sorption reactors. These "cut-off" samples provide insight into the loading profiles of the targeted metals and the relevant impurities.
- Desorption batch samples were collected as described in section above.

Slurries were tested for specific gravity, pH, ORP and percent solids before being separated into solid and liquid fractions for detailed elemental metal analysis. Solid fractions were analysed for targeted metals (Ni and Co) and major impurities (Fe, Mn, Mg, Cu, Zn, Al, Ca, Si, and Cr). Liquid phases were assayed for the same elements, and also for Fe^{++}. Liquors desorbed from the resin samples were also analysed. Analysis was done using an ICP and /or AA and resin loadings were calculated for the targeted metals and major impurities.

Results

Precipitation with pH adjustment

The pH of the slurries must be increased before they present to the sorption circuit. This is necessary to avoid iron sorption onto the resin. The pH adjustment process is intended to precipitate the iron out of solution, resulting in an increased percentage of solids in the slurry as shown in Tables AI.2 and AI.3 below.

Raising the pH is known to trigger a complex set of chemical reactions that must be managed in order to optimise total system recoveries. For the purpose of the laboratory-scale cRIP campaigns, the pH adjustment process has not been optimised. Further investigations will be required to determine the optimal pH for the feed slurry and the rate of limestone addition that achieves the target iron and aluminium concentrations (<5ppm Fe^{3+}, <20ppm Fe^{2+}, <10ppm Al^{3+}) with minimal co-precipitation of nickel and cobalt.

Following pH adjustment, both feed materials showed significant precipitation of hydroxide materials, as expected.

- The autoclave pulp's solid percentage rose from 29% to 36% as the pH was adjusted from 3.0 to 4.8. Note that the solid percentage in the feed samples for campaign #2 is roughly the same as that for campaign #1, indicating that the feed material is stable in this respect soon after the initial pH adjustment has been performed.

Table AI.2 - Feed material for campaigns #1 and #2 before and after pH adjustment

Autoclave leachate	*pH*	*ORP*	*SG*	*Solids % (w/w)*
Before pH adjustment	3.00	272	1.479	29.4
After pH adjustment	4.78	220	1.469	36.0

- Limestone addition to the CCD overflow solution also resulted in precipitation of the contained iron. Starting with an essentially solids-free solution, the pH adjustment from 1.0 to 4.6 produced a slurry containing some 9% solids.

Table AI.3 - Feed materials for campaign #3 before and after pH adjustment

CCD#1 overflow	*pH*	*ORP*	*SG*	*Solids % (w/w)*
Before pH adjustment	1.00	475	1.139	0
After pH adjustment	4.62	340	1.141	9.1

Nickel/cobalt reports to the solid fraction

As expected, a proportion of the nickel and cobalt reports to the solid fraction during the precipitation initiated by pH adjustment. The nickel content in the solid fraction rose sharply during the pH adjustment process as shown in Table AI.4 below.

Table AI.4 - Nickel and cobalt concentrations in solid fractions (mg/kg)

Sample	*Campaign #1*		*Campaign #2*		*Campaign #3*	
	Nickel	*Cobalt*	*Nickel*	*Cobalt*	*Nickel*	*Cobalt*
Pre-neutralised material	560	29	560	29	NA	NA
After neutralisation	1750	71	1750	71	3920	56
Feed slurry grab samples						
Average	2348	81	3534	109	4570	55
Maximum	2960	99	4460	133	6800	99
Minimum	1840	71	2640	82	1740	21

The data gathered fom the feed slurry grab samples suggests that there was further transfer of 15-20% of the nickel and cobalt from the liquid phase to the solid fraction over time. The feed slurry in campaign #1 contained an average of 2350 mg/kg of nickel in the solid fraction as compared to 1750 mg/kg immediately after pH adjustment. The corresponding set of feed slurry grab samples for campaign #2 -performed 3 days later with the same starting material - showed an average nickel concentration in the solid fraction of 3530 mg/kg. The average nickel tenors in the liquid phase of the feed samples for campaign #1 and campaign #2 were 7772 mg/L and 6466 mg/L respectively.

Under the conditions of the campaigns, only 15-20% of the co-precipitated nickel was recovered onto the resin as the slurry passed through the sorption reactors. The remainder reported to the solid fraction of the barren slurries.

The samples are matched up in Table AI.5 to allow for the time lag between the slurry's entry to the sorption circuit and its exit from the last reactor, although, this is only an approximation. The data gives a strong indication that at least some of the nickel present in the solids has been redissolved. Since there is practically no nickel in the liquid fraction of the barren slurry, it can be assumed that the redissolved nickel has reported to the resin.

Table AI.5 - Nickel concentrations (mg/kg) in solid fractions of feed/barren slurries.

Sample Timing		**Campaign #1**			**Campaign #2**			**Campaign #3**		
Feed	*Exit*[1]	*Feed*	*Exit*[1]	*%*[2]	*Feed*	*Exit*[1]	*%*[2]	*Feed*	*Exit*[1]	*%*[2]
0 hrs		1840			2640			3340		
4 hrs	8 hrs	2120	1700	19.8	3320	2320	30.1	1740	3180	****
8 hrs	12 hrs	2240	1870	16.5	3640	2520	30.8	4360	3600	17.4
12 hrs	16 hrs	2320	1770	23.7	3880	2900	25.2	5150	4480	13.0
16 hrs	20 hrs	2320	1950	16.0	4420	2940	33.5	5400	4300	20.4
20 hrs	24 hrs	2300	2040	11.3	4460	3400	23.8	6100	4200	31.1
24 hrs	28 hrs	2380	1700	28.6	3860	3320	14.0	5550	5000	9.9
28 hrs	32 hrs	2300	1960	14.8	3420	3080	9.9	6800	4880	28.2
32 hrs	36 hrs	2220	2060	7.2	3260	2760	15.3	5150	3780	26.6
36 hrs	40 hrs	2260	2080	8.0	3080	2820	8.4	4380	3080	29.7
40 hrs	44 hrs	2540	1940	23.6	3140	2720	13.4	3740	2800	25.1
44 hrs	48 hrs	2720	2060	24.3	2880	2620	9.0	3860	3060	20.7
48 hrs		2960			3940			3840		
Mean		2348	1921	17.6	3534	2855	19.2	4570	3851	15.7

Notes: 1) "Exit" = Barren slurry; 2) % = recovery percentage.

Total recovery of the available nickel, in the conditions that prevailed, was about 87% in the first two campaigns and about 91-92% in campaign #3. Co-precipitation of nickel and cobalt will be unacceptably high unless steps are taken to prevent these losses. The expectation is that the issue can be satisfactorily resolved and that total system recoveries can match or exceed those available from conventional flowsheets.

Nickel/cobalt recovery from liquid phase

Nickel and cobalt concentrations in the liquid phases of the feed and barren slurries were also monitored throughout each campaign. The data in Table AI.6 below indicates that virtually all of the nickel presenting to the cRIP system in solution is recovered onto the resin.

Table AI.6 - Nickel concentrations (mg/L) in liquid phases of feed/barren slurries.

Sample Timing		**Campaign #1**			**Campaign #2**			**Campaign #3**		
Feed	*Exit*[1]	*Feed*	*Exit*[1]	*%*[2]	*Feed*	*Exit*[1]	*%*[2]	*Feed*	*Exit*[1]	*%*[2]
0 hrs		7620			7545			4855		
4 hrs	8 hrs	7765	3.3	>99.9	5840	1.8	>99.9	4840	1.7	>99.9
8 hrs	12 hrs	7435	2.5	>99.9	6135	2.0	>99.9	4640	1.2	>99.9
12 hrs	16 hrs	7605	8.7	99.9	5795	2.8	>99.9	4655	5.4	99.9
16 hrs	20 hrs	7715	0.4	>99.9	5285	1.9	>99.9	4410	5.7	99.9
20 hrs	24 hrs	7955	0.2	>99.9	5465	5.7	>99.9	4440	5.9	99.9
24 hrs	28 hrs	8535	<0.1	>99.9	6195	5.8	>99.9	4470	4.6	>99.9
28 hrs	32 hrs	7780	1.3	>99.9	6965	5.6	>99.9	4280	4.0	>99.9
32 hrs	36 hrs	7975	0.9	>99.9	7180	5.9	>99.9	4430	3.3	>99.9
36 hrs	40 hrs	7885	3.5	>99.9	6810	4.4	>99.9	4400	2.2	>99.9
40 hrs	44 hrs	7735	2.6	>99.9	6905	3.6	>99.9	4715	7.0	99.9
44 hrs	48 hrs	7540	3.0	>99.9	7165	29.9	99.6	4765	2.6	>99.9
48 hrs		7485			6775			4895		
Mean		7772	2.4	>99.9	6466	6.3	99.9	4895	4.0	>99.9

Notes: 1) “Exit” = Barren slurry; 2) % = percent recovery.

At the end of each campaign, a profile of the removal of each metal from the liquid phase was established by taking a sample of slurry from each of the reactors. The results are shown in Figure A1.1 and Figure A1.2 below.

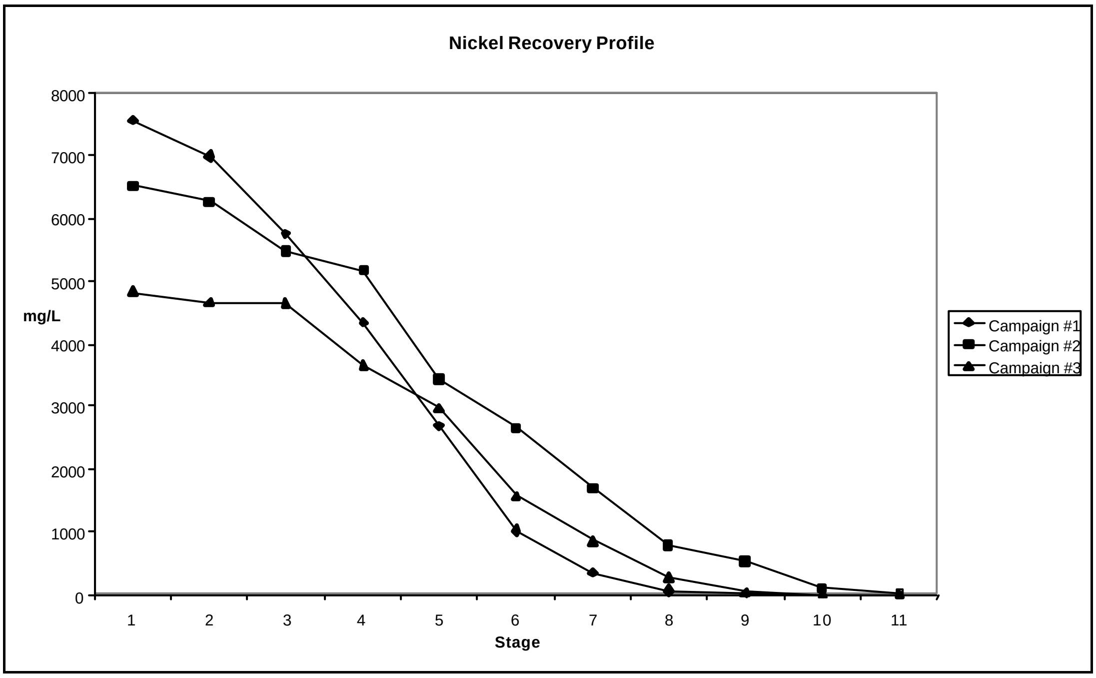

Figure A1.1 - Nickel recovery profile

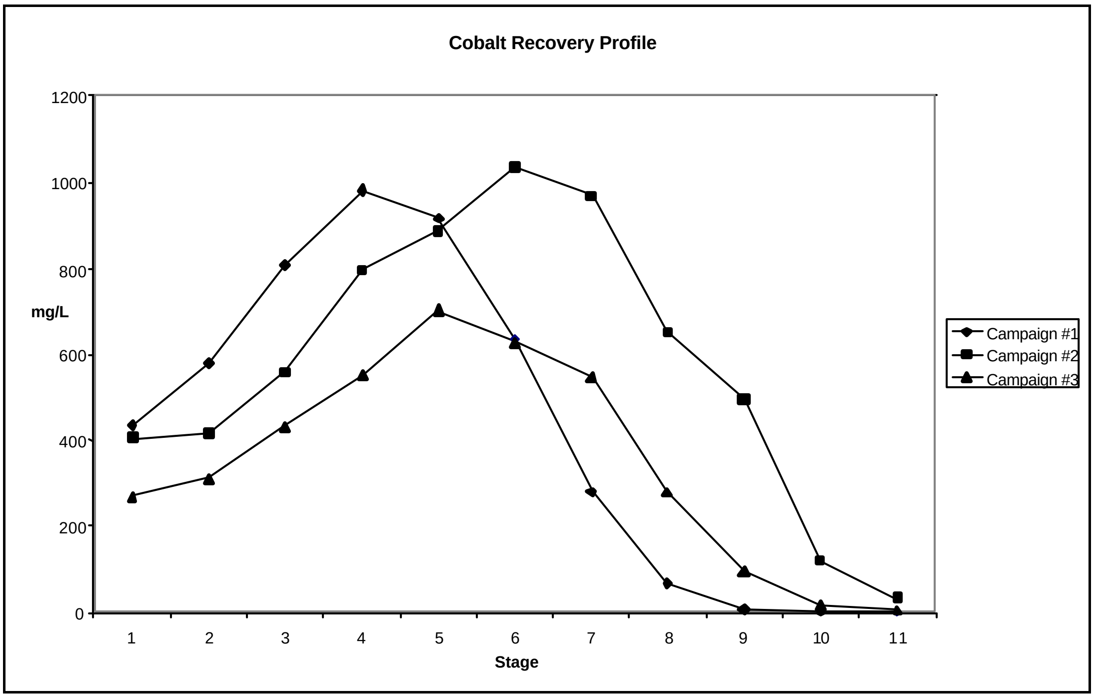

Figure A1.2 - Cobalt recovery profile

These results were very encouraging and showed that the process would recover virtually all of the nickel and cobalt that presented to the resin in solution. This holds for any quantity of targeted metal that might enter the system in the solid fraction and is redissolved as the slurry passes through the sorption reactors. The data indicates that this has happened for 15-20% of the nickel entering the system in the solid fraction in these campaigns.

Nickel/cobalt concentrations in desorption samples

The laboratory-scale cRIP plant was not designed to provide continuous desorption capability - the process that would optimise nickel and cobalt concentrations in the pregnant liquor. The batch desorption samples do, however, provide data that allow calculations of resin loading capacities for the targeted metals and estimations of impurity loadings. Nickel and cobalt tenors in the desorption samples are presented in Table AI.7.

Nickel/cobalt loading on resin

The laboratory-scale cRIP campaigns were designed to achieve high loading of resin with nickel, as this is a critical driver of the economics of the overall processing scheme. The higher the resin loading capacity, the greater the chances of producing a pregnant liquor that contains in excess of 60 g/L of nickel.

Resin loading capacity was assessed in two ways.

1. At the conclusion of each campaign, a small sample of resin was collected from each sorption reactor and assayed for loading with the targeted metals. The data derived from the resin in the first reactor gives a preliminary indication of what can be achieved. The nickel resin loading capacities were calculated as 38.2, 37.0 and 32.5 g/L for campaigns #1, #2 and #3 respectively.
2. The volume of loaded resin used in each of the batch desorption runs was divided by the total mass of nickel and cobalt collected in the desorption samples. The data are shown in Table AI.8.

Table AI.7 - Nickel and Cobalt tenors (mg/L) in batch desorption samples.

Campaign #	**Batch**	**Desorption Samples**		**Targeted Metal Concentrations**	
		ID#	*Volume (mL)*	*Nickel (g/L)*	*Cobalt (mg/L)*
1	1.1	RIP1/E1	420	11.2	360
		RIP1/E2	550	14.9	400
		RIP1/E3	700	21.6	290
		RIP1/E4	920	1.7	17
	1.2	RIP1/E5	368	17.8	480
		RIP1/E6	1005	13.6	620
		RIP1/E7	1005	4.3	59
2	2.1	RIP2/E1	530	23.5	1030
		RIP2/E2	450	46.0	1210
		RIP2/E3	580	1.7	36
		RIP2/E4	420	2.7	1
	2.2	RIP2/E5	180	0.4	21
		RIP2/E6	310	17.5	830
		RIP2/E7	540	42.4	1090
		RIP2/E8	750	0.5	37
	2.3	RIP2/E9	1000	29.5	1100
		RIP2/E10	550	2.2	69
	2.4	RIP2/E11	360	3.0	180
		RIP2/E12	760	38.0	1400
		RIP2/E13	540	2.9	71
	2.5	RIP2/VII-1	850	36.5	1290
		RIP2/VII-2	440	3.9	115
3	3.1	RIP3/E1	200	9.9	506
		RIP3/E2	450	36.0	1460
		RIP3/E3	800	8.4	213
	3.2	RIP3/E4	1000	26.6	1310
		RIP3/E5	550	1.5	70
	3.3	RIP3/E6	850	32.3	1450
		RIP3/E7	1000	0.9	41

Table AI.8 - Resin loading capacity for nickel

Desorption Sample (Batch #)[1]	*Resin Volume (mL)*	*Desorption Volume (mL)*	*Nickel Mass (g)*	*Resin Loading Capacity (g/L)*
1.1	690	2590	30.8	44.7
1.2	750	2378	29.3	39.1
2.1	750	1980	34.1	45.5
2.2	750	1780	28.7	38.3
2.3	750	1550	30.7	41.0
2.4	750	1660	31.5	42.1
2.5	750	1290	32.7	43.6
3.1	730	1450	24.9	34.1
3.2	750	1550	27.4	36.5
3.3	770	1850	28.3	36.8

Note: 1) see Table AI.5 for full description of desorption samples.

The data indicates that the optimised resin loading capacity for nickel in a cRIP system processing a Brazilian Laterite ore leachate will be in excess of 40 g/L.

It should be noted that the resin loading profile for nickel and cobalt is quite different, as shown in Figure A1.3 e Figure A1.4. The resin used in these campaigns is designed to optimise for nickel loading. Accordingly, the highest resin loading for nickel is always seen in the first reactor. Peak loading capacities for cobalt were measured in the cut-off samples from reactor #6 for the first and third campaigns and reactor #4 for the second campaign. Subsequently, cobalt is pushed off the resin, along with several of the impurities, as further nickel is loaded on. Optimisation for the combined loading of targeted metals, nickel and cobalt, is one of several objectives that would be addressed in the future.

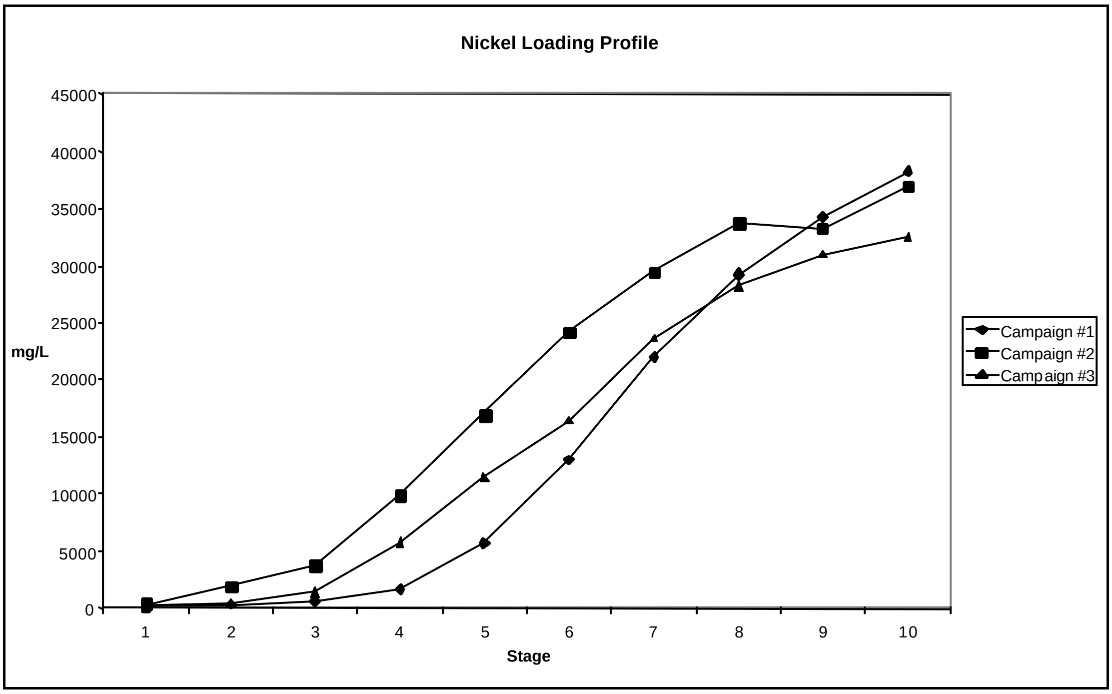

Figure A1.3 - Nickel loading profile

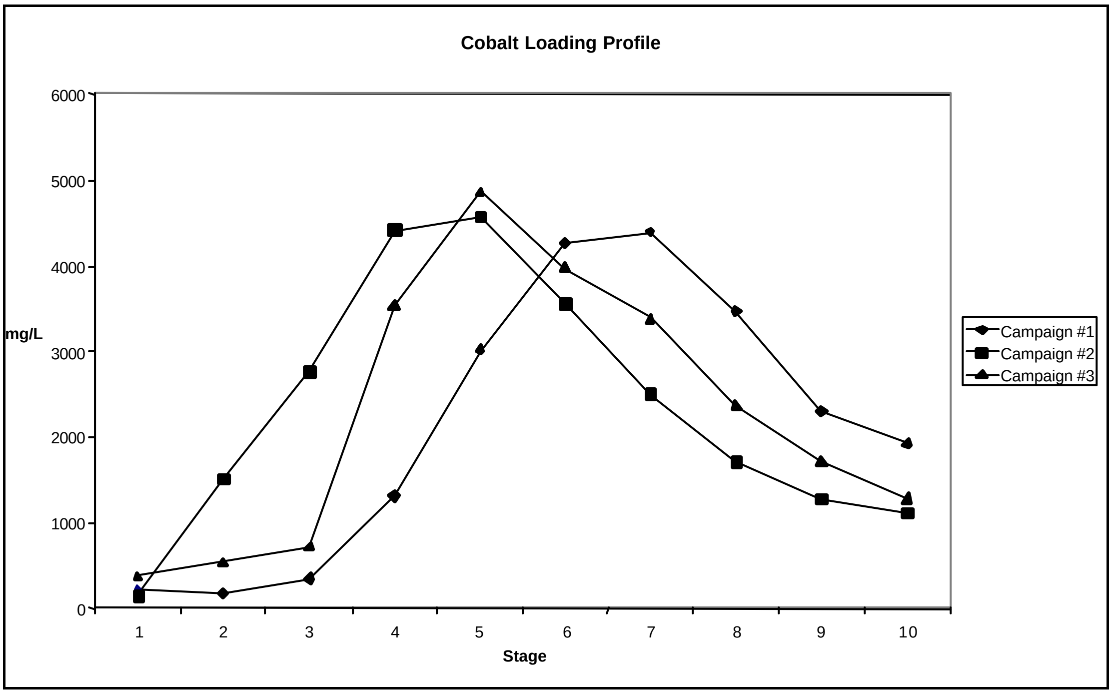

Figure A1.4 - Cobalt loading profile

Impurity behaviour

Prior experience with laterite nickel slurries and knowledge of the behaviours of various metals in a cRIP system suggests that it is necessary to manage the following impurities to achieve the desired quality of pregnant liquor: Fe, Mg, Mn, Cu, Zn, Al, Ca, Cr and Si.

In respect of impurities, each of the campaigns produced very encouraging results. The various metals behaved as they were expected and there is every indication that a pregnant liquor of very high quality could leave a cRIP circuit processing the slurry. The graphs below show the behaviour of the relevant metals during sorption and desorption. Comparison of the metal tenors in the liquid phases of feed and barren pulps versus the loading capacity of each metal provides a visual comparison of the extent of extraction of nickel and cobalt versus other metals.

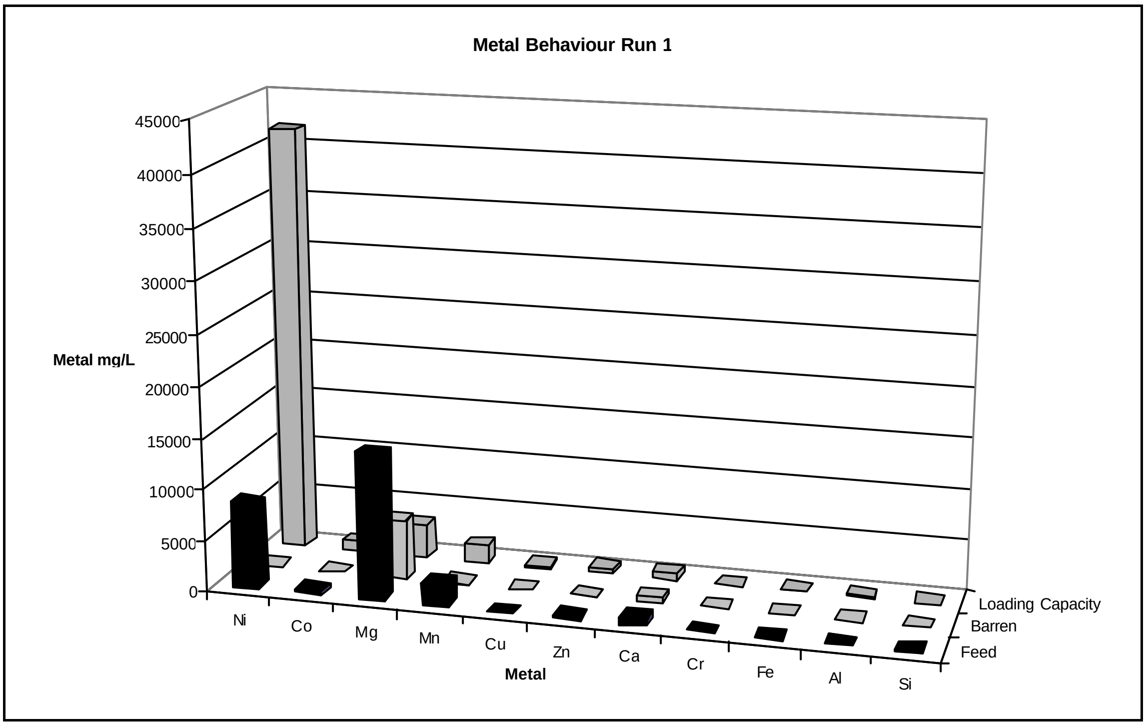

Figure A1.5 - Metal behaviour Run 1

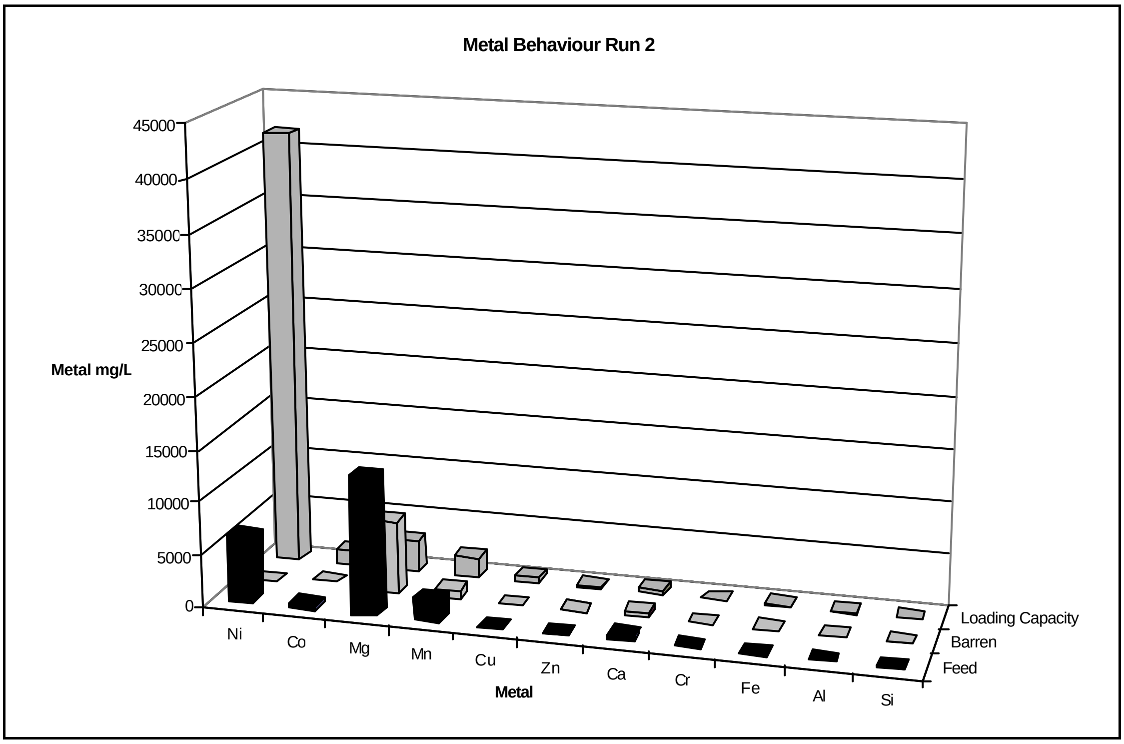

Figure A1.6 - Metal behaviour Run 2

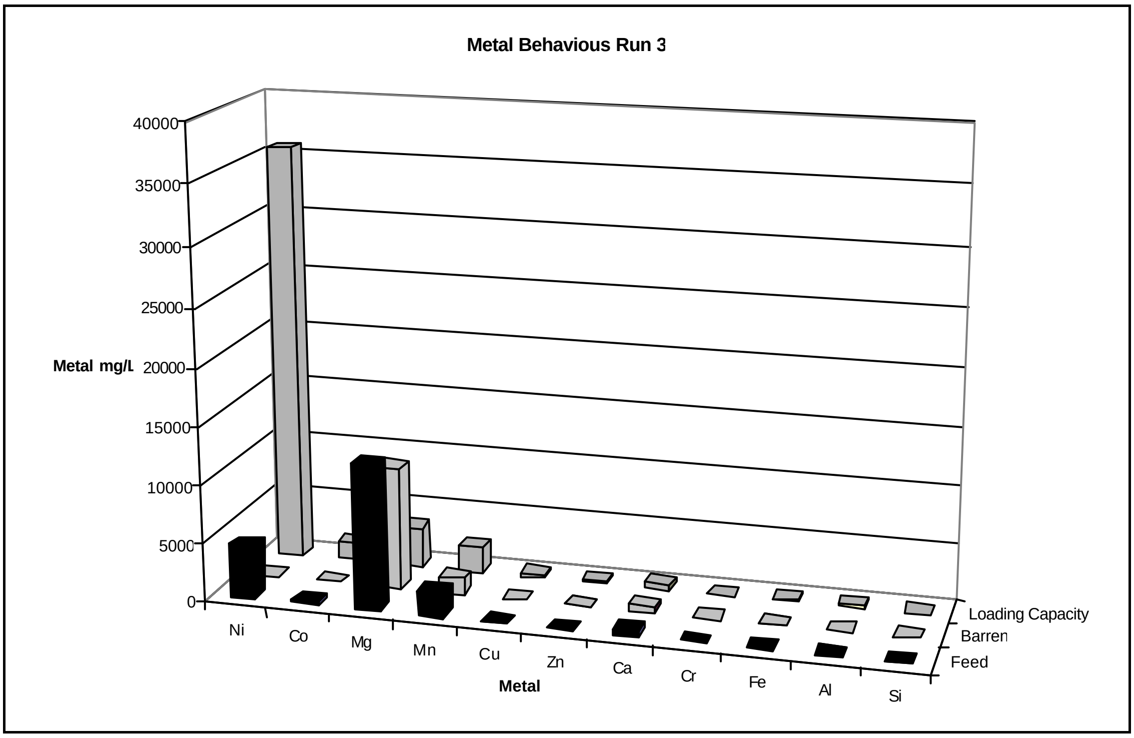

Figure A1.7 - Metal behaviour Run 3

- Iron, in the soluble ferric or ferrous form, will sorb onto the resin reducing its capacity to load the targeted metals. The pH and ORP adjustment step is performed on the feed materials to ensure that all iron is oxidised to the ferric form and precipitated as ferric hydroxide. Table AI.9 shows that the iron virtually disappears from the liquid fraction of the feed material following pH adjustment. As a result, very little iron is found on the resin or in the batch desorption samples.

Table AI.9 - Iron content in liquid fraction of feed materials before and after ?pH

Feed material (campaigns)	*Total Fe (mg/L)*		*Fe^{++} (mg/L)*	
	Before ?pH	*After ?pH*	*Before ?pH*	*After ?pH*
Autoclave pulp (#1, #2)	1325	16	1474	<6
CCD#1 overflow (#3)	11750	20.5	4635	<6

- Magnesium has affinity for the resin and initially loads onto the resin in reactors 5 - 10 where nickel concentrations are low. At the higher nickel concentrations found in reactors 1-5, nickel displaces magnesium and magnesium reports to the barren slurry. The loading capacity for magnesium is around 2-3g/L. The desorption regime will be optimised to desorb magnesium in a different fraction to the nickel.

- Manganese acts in a similar way to magnesium and so loads through the middle stages of the system but it too is pushed off as nickel concentration in the liquid phase peaks. A loading capacity of 1-2 g/L may be found for manganese. Desorption regimes will be optimised as for magnesium.

- Copper and zinc will both be sorbed onto the resin as they have a high affinity for this type of resin. The flowsheet downstream of the cRIP process needs to allow for removal of these metals using either solvent extraction or ion exchange.

- Calcium is also partially sorbed by the resin but the loading capacity is well below the critical point (1 g/L) for downstream processing. Calcium may be desorbed along with magnesium and manganese in a modified desorption regime during optimisation.

- Chromium has the potential, over time, to cause resin fouling. However, it is precipitated during the pH adjustment stage and, as long as the ORP is not high (>600mV) causing oxidation to Cr^{6+}, it will not be problematic. At no point does the chromium concentration in the liquid phase of the slurry inside the sorption reactors exceed 2 mg/L. The ICP resin assays show chromium readings rising up to a maximum of 0.7 mg/L.

- Aluminium is a potentially problematic metal, having an affinity similar to nickel for the resin. However at the pH used in these campaigns it has not loaded onto the resin.

- Silica has not been sorbed by the resin and reports fully to the barren slurry.

Discussion and conclusion

In interpreting the results from the campaigns, the limitations of the experimental system must be recognised. The equipment is not automated, mass balance loops are not fully closed, pH adjustment is not optimised and the system does not allow for continuous desorption. Given this context, the campaign results were very encouraging, notably showing:

1. Highly effective removal of the nickel and cobalt from the liquid phase of the feed materials with residual concentrations consistently below 10 and 5 ppm respectively.
2. Excellent resin loading for nickel and cobalt - a critical parameter in the quest for pregnant liquor of outstanding quality.

3. Evidence of rapid and complete desorption of both nickel and cobalt using either H_2SO_4 or HCl.
4. Samples of pregnant solution with high concentrations of nickel.
5. Low impurity levels, both on the resin and in the desorption samples.

Together, these results provide the foundation for a very robust cRIP-based flowsheet. The implication of these results is that the technology has the potential to revolutionise the overall flowsheet for recovery of nickel and cobalt from laterite ore bodies. The developing concept involves replacing the conventional CCD circuit with the cRIP process. Material received from the acid leach process step would be converted into a pregnant liquor of sufficient tenor and purity that:

1. Downstream processing requirements would be greatly simplified.
2. The need for complicated recirculation circuits to address iron removal would be eliminated. Management of iron has caused major difficulties for a number of laterite nickel processors, notably with respect to CCD operation.
3. Total system recoveries will at least match, and probably exceed, those achieved by fully optimised conventional (CCD-based) processing schemes. Extrapolation of previous R&D work suggests that total system recoveries of up to 95% could be achieved.
4. Capital intensity will be significantly reduced.
5. Total operating costs will be lower with the cost of resin replacement being more than offset by savings elsewhere in the system.

Clearly, a series of technical risks still need to be addressed before the technology is ready for commercial-scale application. The next steps in the process of validating the technology need to focus on three key areas:

- Management of nickel and cobalt losses to the solid fraction during pre-treatment of the feed material.
- Pregnant liquor tenors. Using a specified proprietary desorption process, it is expected to produce pregnant liquor containing target of 60 g/L nickel.

- Resin attrition rates are of paramount importance in evaluating the economic potential of the cRIP process for any laterite nickel project.

Management of nickel/cobalt losses during neutralisation

The problem of targeted metal (nickel and cobalt) loss as the pH of laterite HPAL pulps is adjusted is well known but still relatively poorly understood. Each operation needs to understand the nature and scope of the problems this issue will generate and develop a situation-specific solution that optimises the trade-off between total system recoveries and lifecycle costs.

The objectives during these laboratory-scale cRIP campaigns were to:

- Scope the technical problem and the potential economic impact.
- Determine how much of the nickel and cobalt would be recovered through contact with resin in the reactors in the simplest sorption regime.

The magnitude of the nickel and cobalt co-precipitation with iron was somewhat higher and the degree of unassisted recovery was somewhat lower than expected. The data suggests that about 15-20% of the nickel made available by the leaching process had reported to the solid fraction by the time the slurries entered the first sorption reactor. About 80% of this “lost” metal remained in the solid fraction, reporting to the barren slurry. This is an unacceptable basis on which to design a commercial flowsheet. The expectation is that total system recoveries of an optimised cRIP scheme will at least match, and probably exceed, those can be achieved by a conventional, CCD-based, flowsheet.

Pregnant liquor tenors

The conventional approach to desorption in resin-based ion exchange is a batch process. Metals that have accumulated on the resin are desorbed on the same column, generally in the reverse direction. Such desorption schemes produce a desorption liquor with typical target metal concentrations of 50-75% of the resin loading capacity. With 40 g of nickel loaded on a litre of resin, this would deliver a pregnant liquor with a nickel tenor of 20-30 g/L. Pregnant liquor with nickel content in excess of 60 g/L and low impurity levels would allow the development of a greatly simplified downstream flowsheet.

Optimisation of the pregnant liquor is a function of the desorption reagent to be used. This in turn will be determined by the overall processing scheme. For instance, contemplate HCl-based desorption coupled with a chloride recycling circuit. This scheme could lend itself to direct electrowinning, eliminating a number of complex and expensive downstream processing steps.

Attrition rates

One of the major stumbling blocks in the quest to extend the application of resin-based ion exchange has been high attrition rates of expensive resins. In a continuous resin-in-pulp process, resin beads are subjected to two major types of shock: mechanical and osmotic. The former arises from the repeated mixing and separation of the resin with and from the particulate matter in the slurry. The latter results from the chemical reactions that take place during sorption and desorption.

As the process of technology validation unfolds, it has been systematically gathered the evidence that will prove, or disprove, the economic viability of the resin. Thus far, it is noted that:

- Mechanical grinding tests show that the resin is considerably stronger than commercially available resins with functional groups targeting nickel and cobalt.
- The resin at the electroplating plant has been circulating for several months with no breakage.
- The resin that was used in the campaigns has already performed half a dozen similar tests with no breakage.

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