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SEPARAÇÃO NÍQUEL-COBALTO DE PLS (PREGNANT LEACHING SOLUTIONS) POR EXTRAÇÃO POR SOLVENTES

Relatório Final do Projeto Separação Níquel-Cobalto de PLS (Pregnant Leaching Solution) por Extração por Solventes

Marcelo Borges Mansur[1]
Alexandre Silva Guimarães[1]
Georgio Patrício de Souza Resende[1]
Iranildes Daniel dos Santos[2]

Ouro Preto, MG
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RESUMO EXECUTIVO

A lixiviação ácida sulfúrica de minérios lateríticos de níquel resulta na obtenção de um PLS (Pregnant Leaching Solution) contendo Ni, Co e impurezas (Al, Ca, Cr, Cu, Fe, Mg, Mn, Zn, etc) cuja presença e concentração dependerá das características do minério e tipo de processo utilizado. Este projeto foi desenvolvido a partir de resultados obtidos por Ribeiro et al. (2021) e Silva et al. (2022), que obtiveram um PLS contendo Ni e Co a partir da sulfatação-tratamento térmico de minério laterítico de níquel, seguido de pré-tratamento do PLS para remoção seletiva de Fe, Al e Cr pelo método jarosita/goethita. A partir desses resultados, o objetivo do presente trabalho foi realizar a separação seletiva de Ni e Co das impurezas (Ca, Cu, Zn, Mg e Mn) do PLS purificado testando diferentes misturas de extratantes. Duas rotas conceituais foram desenvolvidas neste trabalho e ambas produziram soluções concentradas de Ni e Co (pureza superior a 99,9% Ni e 99,8% Co) adequadas para alimentar a etapa de eletrólise desses metais. A rota 1 (Capítulo 4) empregou reagentes comerciais típicos aplicados ao tratamento de licores sulfúricos de Ni, ácido versático, Cyanex 272, D2EHPA + TBP. A principal desvantagem desta rota é a extração parcial de Mn no primeiro circuito, o que faz com que ele fique circulando nos três circuitos da rota e, por ser um contaminante presente em concentração elevada, isso resulta em maior consumo de base para neutralização. A rota 2 (Capítulo 5) empregou combinação de reagentes inédita ao tratamento industrial de licores sulfúricos de Ni, LIX 860N-IC + ácido versático e, Cyanex 272. É possível proceder a remoção prévia de Cu (pH 2-2,5) contido no licor para evitar contaminação. A principal desvantagem desta rota seria operar em atmosfera inerte, porém a planta industrial, em Goro (com extratante Cyanex 301) opera usando atmosfera inerte. O reuso do refinado contendo Mg e Mn proveniente da rota 2, por estarem normalmente presentes em elevados teores no PLS, pode resultar em vantagens econômicas/ambientais. A rejeição de Ca é vantajosa por evitar a formação de gesso no processo. Logo, embora inédita, a rota 2 se mostrou mais promissora de futura aplicação industrial.

RESUMO

A lixiviação ácida sulfúrica de minérios lateríticos de níquel resulta na obtenção de um PLS (Pregnant Leaching Solution) contendo Ni, Co e impurezas (Al, Ca, Cr, Cu, Fe, Mg, Mn, Zn, etc) cuja presença e concentração dependerá das características do minério e tipo de processo utilizado. Este projeto foi desenvolvido a partir de resultados obtidos por Ribeiro et al. (2021) e Silva et al. (2022), que obtiveram um PLS contendo Ni e Co a partir da sulfatação-tratamento térmico de minério laterítico de níquel, seguido de pré-tratamento do PLS para remoção seletiva de Fe, Al e Cr pelo método jarosita/goethita. A partir desses resultados, o objetivo do presente trabalho foi realizar a separação seletiva de Ni e Co das impurezas (Ca, Cu, Zn, Mg e Mn) do PLS purificado testando diferentes misturas de extratantes. Os sistemas orgânicos que tiveram bom desempenho foram: (i) ácido versático (pH 6,5), (ii) Cyanex 301 + ácido versático (pH 1,5), (iii) LIX 84-I + ácido versático (pH 5) e (iv) LIX 860N-IC + ácido versático (pH 4). Como desvantagem, todos os sistemas orgânicos extraem 100% de Cu, embora este seja o contaminante de menor teor no PLS purificado. Os sistemas (i) e (ii) também extraem 100% de Zn, logo os sistemas (iii) e (iv) são os mais seletivos para Ni e Co. Outras desvantagens incluem: o sistema (i) apresenta extração parcial de Mn, os sistemas (ii), (iii) e (iv) requerem operação em atmosfera inerte, e o sistema (ii) usando apenas o Cyanex 301 já é utilizado industrialmente (Goro). Ainda, para o sistema (ii), há o desafio de proceder a reextração de Ni com solução eletrolítica de modo efetivo para obter uma solução concentrada em Ni que permita alimentar a eletrólise, visto que usou razões O/A relativamente baixas. E no caso do sistema (iii), o tempo de separação das fases é lento em pH > 3,5. Duas rotas conceituais foram desenvolvidas neste trabalho utilizando-se dois dos sistemas orgânicos investigados. Ambas produziram soluções concentradas de Ni e Co (pureza superior a 99,9% Ni e 99,8% Co) adequadas para alimentar a etapa de eletrólise desses metais. A rota 1 (Capítulo 4) empregou reagentes comerciais típicos aplicados ao tratamento de licores sulfúricos de Ni, ácido versático, Cyanex 272, D2EHPA + TBP. A principal desvantagem desta rota é a extração parcial de Mn no primeiro circuito, o que faz com que ele fique circulando nos 3 circuitos da rota. Como Mn é um contaminante presente em concentração elevada, isso resulta em maior consumo de base para neutralização, além do risco de contaminação cruzada. A rota 2 (Capítulo 5) empregou combinação de reagentes inédita ao tratamento industrial de licores sulfúricos de Ni (LIX 860N-IC + ácido versático, Cyanex 272). É possível proceder a remoção prévia de Cu (pH 2-2,5) contido no licor para evitar contaminação. A principal desvantagem desta rota seria operar em atmosfera inerte, porém a planta Goro (com extratante Cyanex 301) também opera industrialmente usando atmosfera inerte. O reuso do refinado contendo Mg e Mn proveniente da rota 2, por estarem normalmente presentes em elevados teores nos licores de lixiviação e por serem os contaminantes com os maiores teores no PLS, pode resultar em vantagens econômicas/ambientais. A rejeição de Ca é vantajosa por evitar a formação de gesso no processo. Logo, embora inédita, a rota 2 se mostrou mais promissora de futura aplicação industrial.

Palavras-chave: Níquel e cobalto. Extração por solventes. Extratores e sinergismo.

ABSTRACT

Sulfuric acid leaching of lateritic nickel ores results in a PLS (Pregnant Leaching Solution) containing Ni, Co, and impurities (Al, Ca, Cr, Cu, Fe, Mg, Mn, Zn, etc.). This project was developed based on the results obtained by Ribeiro et al. (2021) and Silva et al. (2022), who obtained a PLS from the sulfation-thermal treatment of lateritic nickel ore, followed by pretreatment of the PLS for Fe, Al, and Cr removal by the jarosite/goethite method. Based on these results, this work aimed to separate Ni, Co, and impurities (Ca, Cu, Zn, Mg, and Mn) from the purified PLS. Different mixtures of extractants were investigated. The organic systems that performed well were: (i) versatic acid (pH 6.5), (ii) Cyanex 301 + versatic acid (pH 1.5), (iii) LIX 84-I + versatic acid (pH 5) e, (iv) LIX 860N-IC + versatic acid (pH 4). As a disadvantage, all organic systems extract 100% Cu, although this is the lowest contaminant in purified PLS. Systems (i) and (ii) extract 100% Zn. Therefore, systems (iii) and (iv) are the most selective for Ni and Co. Other disadvantages include system (i) presents partial extraction of Mn, systems (ii), (iii), and (iv) require operation in an inert atmosphere, and system (ii) uses only Cyanex 301, which is already applied industrially (Goro). For system (ii), effectively Ni stripping is challenged. In system (iii), the phase separation is slow at pH > 3.5. Two conceptual routes were developed in this work using two of the organic systems investigated. Both produced concentrated solutions of Ni and Co (purity greater than 99.9% Ni and 99.8% Co) suitable for feeding the electrowinning step. Route 1 (Chapter 4) employed typical commercial reagents to treat Ni sulfuric liquors, versatic acid, Cyanex 272, D2EHPA + TBP. The main disadvantage is the partial extraction of Mn in the first circuit because Mn is a contaminant in high contents, resulting in greater base consumption for neutralization and the risk of cross-contamination. Route 2 (Chapter 5) used an unprecedented combination of reagents, LIX 860N-IC + versatic acid and Cyanex 272. Removing Cu (pH 2-2.5) contained in the liquor can avoid contamination. The main disadvantage would be operating in an inert atmosphere. However, the Goro plant (with Cyanex 301 extractant) also uses an inert atmosphere industrially. Reuse of refined products containing Mg and Mn from Route 2, usually present in high levels in PLS can result in economic/environmental advantages. Ca rejection is advantageous because it avoids the formation of gypsum in the process. Therefore, although new, route 2 seemed to be more promising for future industrial applications.

Keywords: Solvent extraction. Nickel. Cobalt. Extractants and synergism**.**

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1 INTRODUÇÃO

A lixiviação ácida sulfúrica de minérios lateríticos de Ni resulta na obtenção de um licor contendo Ni, Co e impurezas típicas (Al, Ca, Cr, Cu, Fe, Mg, Mn, Zn, etc) a depender das características do minério e da operação. Por meio de precipitação química seletiva, Fe, Al e Cr podem ser seletivamente removidos do licor sulfúrico (SILVA et al., 2022; KURSUNOGLU et al., 2017; CHENG et al., 2010; DONEGAN, 2006; FREYSSINET et al., 2005). A separação do Ni e Co entre si e das impurezas remanescentes é comumente realizada utilizando-se a técnica de extração por solventes (SX) (GUIMARÃES et al., 2020; GUIMARÃES e MANSUR, 2017;2018; GUIMARÃES et al., 2014; CHENG et al., 2010; ZHANG et al., 2012; KURSUNOGLU et al., 2017). Esse método é o único empregado industrialmente que permite separar Ni e Co (cujas características químicas são similares, o que dificulta a purificação de uma espécie em relação à outra), obtendo-se soluções aquosas com elevado teor de pureza de cada um destes metais, em condições apropriadas para obtenção de catodos por eletrorrecuperação (KURSUNOGLU et al., 2017). Como técnica de separação, a SX constitui operação unitária clássica aplicada no tratamento hidrometalúrgico de elementos como Zn, U, terras raras, por exemplo, logo detalhes operacionais encontram-se amplamente disponíveis na literatura, com destaque para aplicações metalúrgicas em Ritcey (2006), referência esta recomendada ao leitor não habituado à técnica.

O desenvolvimento de extratantes ácidos organofosforados como D2EHPA ($pK_a = 1{,}72$; ácido di-2-etilhexil fosfórico), PC 88A ($pK_a = 3{,}42$; ácido 2-etilhexil fosfônico éster mono-2-etilhexil) e Cyanex 272 ($pK_a = 6{,}37$; ácido 2,4,4-trimetil-pentil fosfínico) potencializaram a eficiência da separação Co/Ni em licores ácidos sulfúricos (FLETT, 1987). Esses reagentes orgânicos extraem preferencialmente Co em detrimento ao Ni numa faixa de pH de 4 a 6, aproximadamente. A eficiência de separação do Cyanex 272 ($\beta_{Co/Ni} = 7000$) é significantemente superior em relação ao PC 88A ($\beta_{Co/Ni} = 280$) e ao D2EHPA ($\beta_{Co/Ni} = 14$), em decorrência de uma alteração da natureza do complexo de Co na solução orgânica. Com o aumento da temperatura e/ou da concentração de Co, seus complexos octaédricos de coloração rosa hidratados se alteram para espécies poliméricas tetraédricas azuis anidras. Esse fato eleva o coeficiente de distribuição de Co na fase orgânica, aumentando o fator de separação $\beta_{Co/Ni}$, uma vez que os complexos de Ni permanecem em sua forma octaédrica hidratada (FLETT, 2005; 2004; 1987). Portanto, como consequência de sua elevada seletividade na separação Co/Ni, Cyanex 272 é utilizado em diversas plantas industriais de Ni, tais como: Bulong e Murin Murin (Austrália), Voisey's Bay (Canadá), Kasese Cobalt (Uganda), Votorantim (Brasil), Tati Nickel (Botsuana) e Hartley Pt (Zimbábue) (STEVENS et al., 2009; DONEGAN, 2006; SOLE et al., 2004).

Embora o Cyanex 272 seja extremamente eficiente na separação Co/Ni, sua seletividade em relação ao Ca, Mg e Mn é questionável, este último sendo praticamente coextraído com o Co. Já o Ca, além da tendência de formação de gesso, pode sofrer o efeito *crowding out* em licores concentrados de Ni (≈ 70-100 g/L) distribuindo-se entre as fases (GUIMARÃES et al., 2020; GUIMARÃES e MANSUR, 2018); em licores diluídos de Ni (≈1-6 g/L), Ca tende a permanecer com o Ni, dificultando a separação Ca/Ni (DONEGAN, 2006). Mg é coextraído com o Ni, reduzindo a seletividade da separação Mg/Ni ou Ni/Mg, e também com Co, dificultando etapas posteriores de obtenção de Co metálico (GUIMARÃES et al., 2014). Tais circunstâncias induzem ao uso de outro(s) extratante(s) visando remover/separar essas impurezas ou de extrair preferencialmente Ni e Co em detrimento desses contaminantes. Nesse contexto, além da necessidade de vários circuitos de separação, é frequente o emprego de ácidos carboxílicos e oximas (separadamente e/ou em misturas de extratantes) almejando-se a extração de Co e Ni em detrimento ao Ca, Mg e Mn (e outras impurezas) visando simplificar a separação Co/Ni com Cyanex 272.

O uso de sistemas extrativos sinérgicos (SSX), mistura de dois ou mais extratantes para maximizar determinadas separações, tais como LIX 63 (5,8-dietil-7-hidroxi-6-dodecanona oxima) + ácido versático (ácido neodecanóico), LIX 84-IC (2-hidroxi-5-nonilacetofenona oxima) + ácido versático, Acorga CLX 50 (di-éster de piridina 3-5-di-carboxilato) + ácido versático, etc., tem sido verificado com sucesso na separação (Co+Ni)/(Ca+Mg+Mn) em licores diluídos de Ni. Esse fato decorre da maximização da seletividade desta separação, facilitando etapas subsequentes de purificação de Co e Ni com Cyanex 272 (CHENG et al., 2015; CHENG et al., 2010; NDLOVU e MAHLANGU, 2008).

Diante desse contexto, são revisados no tópico a seguir, os principais estudos de extração por solventes direta (DSX) de Ni e Co utilizando-se extratantes comerciais, almejando-se estabelecer estratégias de purificação de licor sulfúrico de Ni e Co obtido a partir de processo piro-hidrometalúrgico (RIBEIRO et al., 2021).

2 REVISÃO DE LITERATURA: EXTRAÇÃO POR SOLVENTES DE NÍQUEL E COBALTO

2.1 PROCESSAMENTO HIDROMETALÚRGICO DE LICOR SULFÚRICO DE Ni e Co

A recuperação hidrometalúrgica de Ni e Co do licor ácido sulfúrico obtido na lixiviação HPAL (*High Pressure Acid Leaching*), ou AL (*Atmosferic Leaching*), ou HL (*Heap Leaching*), e após remoção seletiva de Fe, Cr e Al presentes no licor via precipitação química (SILVA et al., 2022), pode ocorrer mediante etapa intermediária de precipitação, a qual inclui a obtenção de um precipitado de sulfeto misto (MSP: *Mixed Sulphide Precipitate*) ou de um precipitado de hidróxido misto (MHP: *Mixed Hydroxide Precipitate*). Alternativamente, Ni e Co podem ser recuperados diretamente do licor sulfúrico utilizando-se a extração por solventes direta (DSX: *Direct Solvent Extraction*) (HARVEY et al., 2011; WHITTINGTON e MUIR, 2000).

A demanda da rota que envolve a obtenção dos produtos intermediários de Ni e Co, i.e., MSP ou MHP, ocorre quando a localização da planta industrial de lixiviação de minérios de Ni é, geralmente, distante da planta industrial de tratamento do licor, como é o caso da unidade da Votorantim no Brasil. Dessa forma, o MHP e MSP são transportados até as refinarias onde são relixiviados com ácido sulfúrico, obtendo-se um licor concentrado de Ni (70-100 g/L) e Co (1-5 g/L) contendo, ainda, impurezas, tais como Mn, Mg, Ca, Cu, Al, etc. Esses licores são tratados utilizando-se a técnica SX almejando-se separar Ni e Co entre si e também em relação aos contaminantes (WILLIAMS et al., 2013; CHONG et al., 2013; TAYLOR, 1995; GUIMARÃES et al., 2014).

A obtenção do MSP requer o uso de gás sulfídrico (H_2S) para precipitar Ni, Co e Cu em detrimento ao Ca, Mn, Zn e Mg. A rejeição desses metais alcalinos terrosos, Mn e Zn constitui a principal vantagem desse método. No entanto, a relixiviação do MSP é pressurizada com oxigênio gasoso, elevando os custos de operação. Adicionalmente, o consumo de H_2S também contribui para encarecer essa etapa, além de provocar prejuízos ambientais em decorrência da toxicidade desse gás, podendo ainda gerar outros gases tóxicos, como NO_2, SO_2, etc. (WILLIAMS et al., 2013; CHONG et al., 2013; TAYLOR, 1995).

A adição de MgO ao licor sulfúrico de lixiviação acarreta na obtenção do MHP (Ni,Co(OH_2)) o qual é facilmente ressolubilizado em meio ácido. O custo relativamente baixo do agente precipitante e da pronta dissolução em uma ampla faixa de pH caracterizam o MHP como uma rota segura e consolidada industrialmente. A relixiviação é realizada com H_2SO_4 na faixa de 40-80°C. Se a ressolubilização for realizada na ausência de oxidantes, geralmente obtém-se no licor sulfúrico Ni, Co, Ca, Mn, Mg, Zn e Cu. Se oxidante for usado, por exemplo, peroxidissulfato de sódio ($Na_2S_2O_8$), durante a relixiviação, então Ni, Ca, Mg e Zn são relixiviados seletivamente ao Co, o qual permanece no resíduo para posteriormente ser lixiviado separadamente com ácido sulfúrico e o licor obtido tratado para separar Co/(Mn+Cu) (WILLIAMS et al., 2013; CHONG et al., 2013). Como mencionado anteriormente, é importante ressaltar que a presença e a concentração de impurezas no licor dependem das características intrínsecas do minério de Ni, assim como da qualidade da etapa anterior de precipitação de Fe, Al e Cr.

Na extração por solventes direta (DSX), ao contrário, o licor de lixiviação é tratado diretamente por SX. A supressão das etapas de precipitação e ressolubilização acarretam em potencial redução dos custos de capital e de operação. Portanto, a separação de Ni e Co entre si e das impurezas é simplificada (CHENG et al., 2015). Ni e Co são concentrados durante a etapa de reextração obtendo-se soluções apropriadas à eletrólise de cada um desses metais com a finalidade de obtenção de catodos com elevada pureza (CHENG et al., 2015; CHENG et al., 2010). Nessa rota, é desejável que as plantas de lixiviação comercial de minérios de Ni e purificação do licor obtido estejam na mesma unidade industrial ou relativamente próximos entre si. A DSX tem sido testada nos últimos anos em escala piloto e/ou de bancada para separar Ni e Co das impurezas com diversos sistemas extrativos almejando-se seu emprego em escala comercial. Nesse contexto, destacam-se: (i) a extração por solventes sinérgica de Ni e Co com os extratantes ácido versático e 4PC (éster de n-decil-4-piridina carboxilato) deixando no licor Mn, Mg e Ca testada pela BHP Billiton; (ii) a extração sinérgica de Ni e Co com ácido versático e Acorga CLX 50 no processo Bulong; (iii) a SSX utilizando-se Cyanex 272 e LIX 84 (2-hidroxi-5-nonil-acetofenona oxima) para separar Cu e Zn em relação ao Co e Ni testado pela Minera Resources; (iv) a extração sinérgica de Co e Ni com ácido versático e LIX 63 deixando no refinado Ca, Mn e Mg investigado pela Baja Mining Corp.; (v) a SSX realizada pela Rio Tinto na extração seletiva de Co e Ni pelo sistema constituído de ácido versático, LIX 63 e TBP rejeitando Ca, Mn e Mg no refinado (CHENG et al., 2011). E há

2 unidades industriais com rota DSX (MYHAYLOV et al., 2000; DONEGAN, 2006): Bulong (Austrália) e Goro (Nova Caledônia).

Face à potencial redução dos custos de capital e de operação da DSX, assim como a possibilidade de desenvolver novos sistemas extrativos sinérgicos que possam maximizar a separação Co+Ni em relação às impurezas Ca+Mg+Mn, simplificando a etapa posterior de separação Co/Ni com Cyanex 272, uma revisão da literatura de DSX aplicada ao tratamento de licores sulfúricos de Ni e Co é apresentada a seguir. Os tópicos foram divididos conforme os sistemas orgânicos empregados. Para as rotas MSP e MHP, recomenda-se a literatura anteriormente citada.

2.2 EXTRAÇÃO POR SOLVENTES DIRETA (DSX) de Ni e Co

2.2.1 DSX utilizando-se Cyanex 272 e ácido versático

A refinaria Bulong localizada no oeste da Austrália (atualmente fora de operação) foi projetada para processar minérios lateríticos de Ni (e Co) visando-se a obtenção de catodos com elevado teor de pureza. Minério laterítico de Ni era lixiviado sob pressão com ácido sulfúrico e o licor obtido neutralizado ($4,5 \leq pH \leq 5,5$) para reduzir os teores de Fe, Al e Cr. A remoção de Fe era alcançada por meio de sua oxidação a Fe^{3+}, obtendo-se como precipitado $Fe(OH)_3$ em pH 4,5. A cinética de oxidação foi relatada como lenta, permanecendo cerca de 2 mg/L Fe no licor, sendo majoritariamente constituído por Fe^{2+} (DONEGAN, 2006). A composição química do licor obtido após pré-tratamento é mostrada na Tabela 2.1.

Tabela 2.1: Licor sulfúrico Bulong que alimenta a DSX.

Espécie	Ni	Co	Fe	Mn	Mg	Ca	Cl	Zn
Concentração (mg/L)	2800	210	2	750	16000	560	80000	30

*Al+Cr < 1 mg/L

Fonte: Donegan, 2006.

Esse licor alimentava o primeiro circuito SX com 16% v/v de Cyanex 272 (Figura 2.1) a 45°C a fim de separar Co+Cu+Mn+Fe+Zn de Ni+Ca+Mg em 5 estágios de extração em contracorrente. Não foi informada a razão volumétrica O/A da operação. Conforme a Tabela 2.2, o refinado obtido contém praticamente todo o Ni (2,8 g/L), indicando elevada seletividade da separação Co/Ni pelo Cyanex 272. A lavagem do extrato foi realizada essencialmente para remover o Ni coextraído nos estágios de extração e obter uma razão Co:Ni superior a 700 na solução orgânica. Para tal utilizou-se uma razão O/A = 20 e solução de lavagem com 5,5 g/L Co e 22 g/L Mn. A eficiência de lavagem de Ni era de 86% e a de Mg em torno de 10%, obtendo-se um refinado da lavagem contendo 0,3 g/L de Ni e 0,5 g/L de Co. A razão Co:Ni no extrato aumentou de 35 para 320, não atingindo, porém, a meta de 700 ou mais.

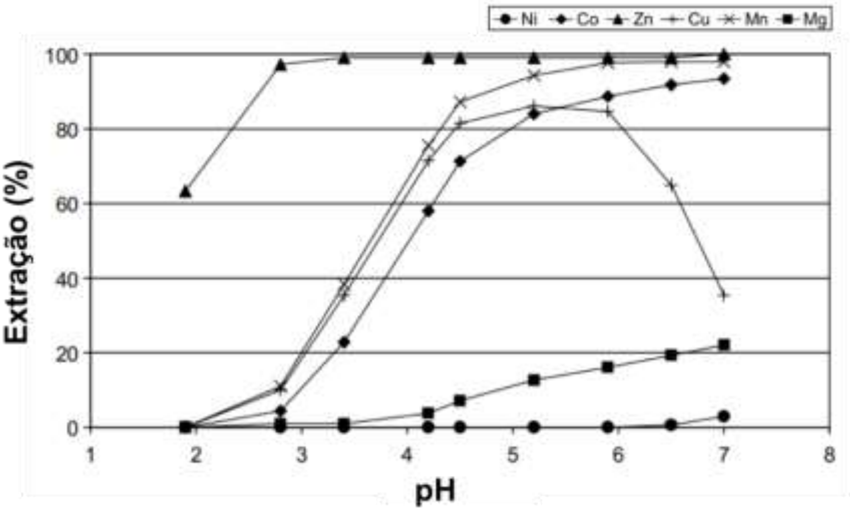

Figura 2.1: Extração dos metais do licor sulfúrico Bulong com Cyanex 272 (16% v/v, 45°C) (Adaptado de Donegan, 2006).

Tabela 2.2: Refinado da extração de Co com Cyanex 272 (16% v/v, 45°C).

Refinado	Ni	Co	Zn	Cu	Mn
Concentração (mg/L)	2800	3	0,1	0,6	1

Fonte: Donegan, 2006.

A reextração de Co, Mn e Mg do extrato foi realizada utilizando-se uma solução de reextração contendo 2 M de H_2SO_4 com a finalidade de se obter 9 g/L de Co no licor de reextração em pH correspondente a 1,7 controlando-se a razão O/A. Após 3 estágios, a reextração de Co, Mn e Mg excedeu 99,5%. No entanto, Mn e Mg foram concentrados no licor de reextração juntamente com o Co, conforme mostrado na Tabela 2.3, podendo dificultar etapas posteriores de purificação de Co. A separação do Co em relação ao Mn e Mg foi realizada por precipitação seletiva com NaOH e NaHS. Dessa etapa, cuja recuperação de Co foi superior a 99%, foi obtido um precipitado de sulfeto de Co, Cu e Zn (com a presença, em menor teor, de Ni e Fe). Após filtração, a solução contendo Mg e Mn foi direcionada ao rejeito, enquanto o precipitado de Co foi encaminhado para a refinaria para tratamento (separação Co/Cu+Zn) almejando-se a produção de catodos.

Tabela 2.3: Solução obtida na etapa de reextração de Co.

Licor	Co	Ni	Cu	Zn	Mn	Mg
Concentração (mg/L)	9000	30	100	1100	23000	28000

Fonte: Donegan, 2006.

O refinado da etapa de extração de Co, contendo Ni, Ca e Mg, era direcionado a um segundo circuito SX, desta vez com ácido versático como extratante. Ni foi extraído seletivamente em detrimento ao Mg e Ca usando-se 15% v/v de ácido versático em pH ≥ 6,5 a 45°C em uma dada razão de fases O/A em 4 estágios sucessivos. A recuperação de Ni no extrato foi de 98,2%, que foi lavado para a remoção de Mg e, principalmente, Ca, visando-se atingir uma relação Ni:Ca de 1800. A solução de lavagem foi obtida diluindo-se a solução eletrolítica de Ni para 8 g/L. Após 2 estágios, foram lavados 88% de Ca e 95% de Mg. Em seguida, o extrato foi lavado com água para remoção de cloreto visando-se reduzir sua concentração (< 50 mg/L) para não prejudicar a eletrólise do Ni, obtendo-se uma eficiência de lavagem superior a 99%. A razão de fases utilizada nas etapas de lavagem também não foi relatada por Donegan (2006). A reextração de Ni foi realizada utilizando-se uma solução eletrolítica de Ni (65 g/L) contendo 34 g/L de H_2SO_4 almejando-se a obtenção de 85 g/L de Ni (ΔNi = 20 g/L) na solução de reextração, em acidez correspondente a pH ≈ 3,2. A razão de fases O/A foi operacionalizada para esse propósito, além de se almejar que a concentração de Ni na solução orgânica após a reextração fosse inferior a 10 mg/L. Em 3 estágios, foram reextraídos cerda de 99,8% de Ni, obtendo-se 85 g/L de Ni em pH 3 no licor de reextração, o qual foi direcionado à etapa de eletrorrecuperação para obtenção de catodos de Ni. No entanto, Donegan (2006) ressalta que Fe e Cu contaminaram os depósitos de Ni, uma vez que suas concentrações no refinado da extração de Co e/ou durante a reextração de Ni, utilizando-se elevada razão O/A, ficaram acima das concentrações permissíveis ([Fe] < 5 mg/L e [Cu] < 5 mg/L). Ressalta-se, novamente, a relevância da qualidade da etapa de precipitação seletiva de Fe, Al e Cr no licor de lixiviação sulfúrico visando-se minimizar/evitar o envenenamento da solução orgânica e/ou contaminação dos produtos de Ni e Co.

Durante as etapas de lavagem e reextração, em ambos circuitos, houve precipitação de Ca em decorrência, principalmente, do uso de uma elevada razão de fases O/A. Esse fato é indesejável, visto que o Ca precipita nas tubulações, bombas, agitadores, etc e, consequentemente, limita/restringe o fluxo de soluções nos misturadores-decantadores, acarretando em perda de produtividade. Adicionalmente, foi relatada a presença de crud (solidificação da fase orgânica) nos dois circuitos de extração e na etapa de recuperação (tratamento) do ácido versático. A formação de crud no circuito de extração de Ni foi associada à precipitação de Ca na forma de gesso, enquanto no circuito de extração de Co em decorrência da presença de Si no licor de lixiviação. No caso do ácido versático, a formação do crud foi relacionada à transferência do ácido versático para a solução orgânica. A solidificação da fase orgânica dificulta a agitação e separação das fases aquosa e orgânica, podendo reduzir a eficiência de extração/lavagem/reextração dos metais de interesse. Além disso, sua formação implica em perdas de parte do extratante e do diluente (DONEGAN, 2006). Consequentemente, sua formação deve ser evitada por meio de um rigoroso controle operacional.

Em outro trabalho, Kursunoglu et al. (2017) avaliaram a separação de Ni e Co contidos em um licor obtido por lixiviação atmosférica sulfúrica, após precipitação de Fe (< 1 mg/L), Cr (< 0,5 mg/L) e Al (< 16 mg/L), utilizando-se a rota proposta por Donegan (2006) de maneira inversa, i.e., empregando-se ácido versático no primeiro circuito de extração e Cyanex 272 no segundo. A composição química do licor sintético sulfúrico similar ao obtido industrialmente a partir de minérios lateríticos de Ni de Caldag (na Turquia) é mostrada na Tabela 2.4.

Tabela 2.4: Licor sintético sulfúrico.

Metal	Ni	Co	Mn	Ca	Mg
Concentração (mg/L)	4100	240	1600	530	8750

Fonte: Kursunoglu et al. (2017).

Utilizando-se 20% v/v de ácido versático e 5% v/v de TBP (para prevenir a formação de terceira fase) foram extraídos 98% de Ni e Co, 94% de Mn, 65% de Ca e 12% de Mg em pH 7,26 a 40°C, conforme mostrado na Figura 2.2, em um único estágio na razão O/A = 1. Com a finalidade de remover Mn, Mg e Ca do extrato, foi utilizada uma etapa de reextração seletiva em 3 estágios com H_2SO_4 diluído, pH 5,6-5,8 (40°C, 10 min, razão O/A = 1). Os resultados estão mostrados na Tabela 2.5. Foram reextraídos 90,1% de Mg e apenas 15,7% de Ca e 2,1% de Mn do extrato em pH 5,6. Aumentando o pH para 5,8, a reextração seletiva de Mg e Ca diminuiu para 82,1% e 13,9%, respectivamente, enquanto a reextração de Mn permaneceu constante em 2,2%

(KURSUNOGLU et al., 2017). Embora a reextração de Ca e Mn tenha sido baixa, praticamente quase todo o Ni e Co permaneceram no extrato de ácido versático.

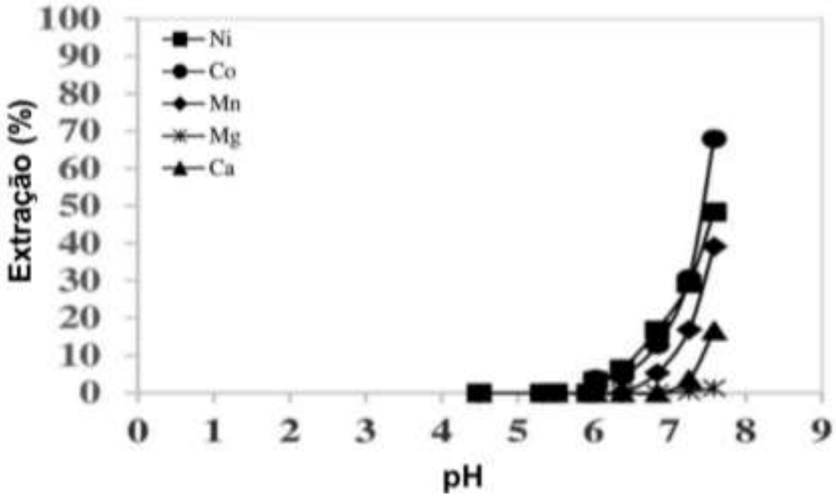

Figura 2.2: Extração dos metais do licor sintético sulfúrico utilizando-se 20% v/v de ácido versático e 5% TBP (40°C e razão O/A = 1, adaptado de KURSUNOGLU et al., 2017).

Tabela 2.5: Reextração seletiva do extrato de ácido versático (40°C e razão O/A = 1)

pH	Reextração (%)				
	Ni	Co	Mn	Ca	Mg
5,6	0,3	1,9	2,1	15,7	90,1
5,8	0,4	1,0	2,2	13,9	82,1

Fonte: Kursunoglu et al. (2017).

A reextração foi avaliada com o extrato lavado em pH 5,6 em um estágio de contatação utilizando-se H_2SO_4 em diferentes níveis de concentração (40°C, 10 min, razão O/A = 1). Por meio da Figura 2.3, verifica-se que a redução no pH aumenta a reextração dos metais, dada a maior disponibilidade de íons H^+ para promover a troca catiônica entre os metais. Até pH 0,75, os elementos Ni, Co, Ca, Mn e Mg são completamente reextraídos da solução orgânica (KURSUNOGLU et al., 2017).

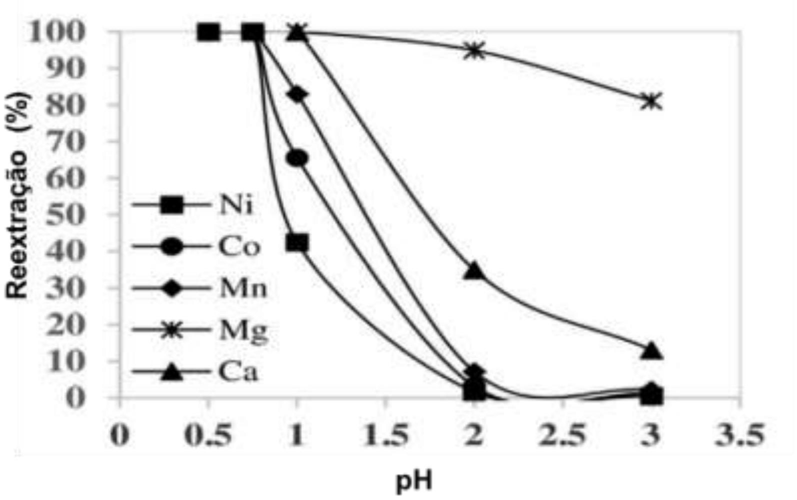

Figura 2.3: Reextração metálica do extrato de ácido versático (20% v/v) variando-se o pH (40°C e razão O/A = 1, adaptado de KURSUNOGLU et al., 2017).

O licor obtido com esses metais foi submetido a um circuito de extração utilizando-se 15% v/v de Cyanex 272 e 5% TBP (para evitar a formação de terceira fase) a 40°C, razão O/A =1. Conforme mostrado na Figura 2.4, nessas condições, foram extraídos 94% de Co e 98% de Mn com apenas 3% de coextração de Ni em pH 4,83 em um estágio de contatação. No entanto, 98% de Mn, 30% de Mg e 21% de Ca foram coextraídos com o Co, requerendo, dessa maneira, um circuito de lavagem. Nesse contexto, uma solução de lavagem contendo 20 g/L de Co em pH 5 (40°C, razão O/A = 1) foi utilizada para remover Mn, Mg, Ca e Ni. Em 2 estágios de contatação, Ni, Ca e Mg foram removidos completamente do extrato de Cyanex 272, enquanto 93% de Mn foram obtidos no licor de lavagem (KURSUNOGLU et al., 2017).

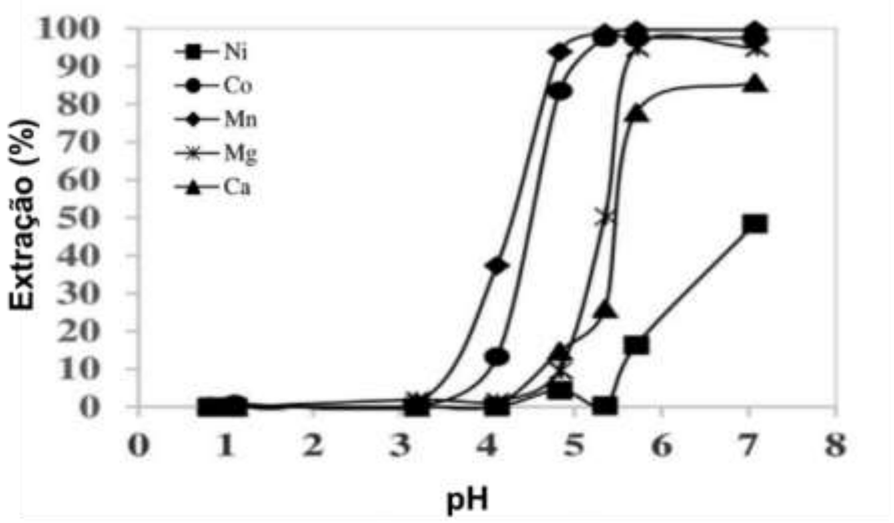

Figura 2.4: Extração dos metais do licor sintético sulfúrico utilizando-se 15% v/v de Cyanex 272 e 5% TBP (40°C e razão O/A = 1, adaptado de KURSUNOGLU et al., 2017).

O extrato lavado de Cyanex 272 contendo majoritariamente Co e Mn foi submetido a um estágio de reextração com H_2SO_4, conforme mostrado na Figura 2.5 (40°C, razão O/A = 1). Reextração superior a 99,9% de Co e Mn é obtida em pH 1, obtendo-se no licor 2,01 g/L de Co e 0,087 g/L de Mn. A concentração de Co aumentou no licor em comparação à concentração inicial (0,24 g/L) em decorrência da etapa de lavagem, uma vez que Co substituiu Mn, Mg, Ca e Ni no extrato de Cyanex 272, conforme mostrado pela Eq. 2.1 em que M representa Mn, Ca, Mg e Ni.

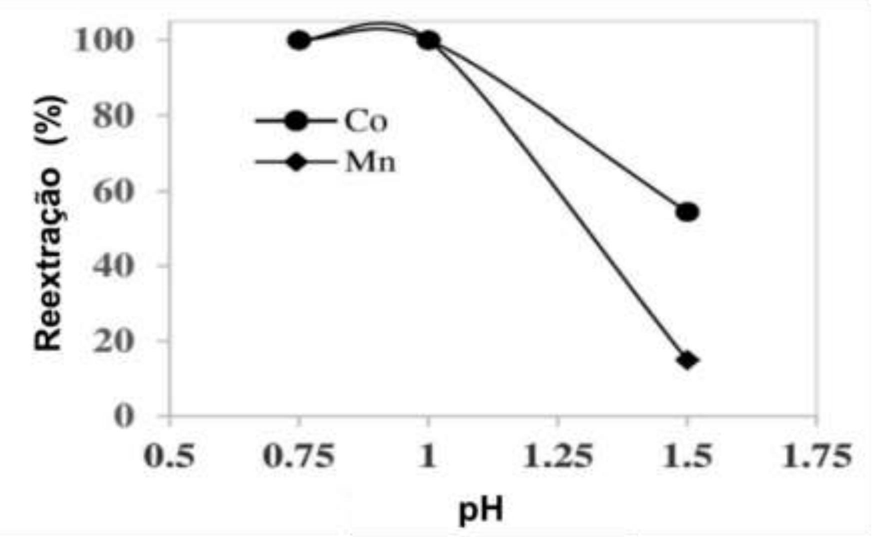

Figura 2.5: Reextração metálica do extrato de Cyanex 272 (15% v/v) variando-se o pH (40°C e razão O/A = 1, adaptado de KURSUNOGLU et al., 2017).

$$MR_{(org)} + CoSO_{4(aq)} \leftrightarrows CoR_{(org)} + MSO_{4(aq)} \qquad (2.1)$$

Considerando o preço elevado do Co (US$ 81340/ton em 01/04/22, London Metal Exchange, e mesmo com a flutuação intensa, atualmente da ordem de US$ 35000/ton), a principal desvantagem nos circuitos propostos por Kursunoglu et al. (2017) consiste no uso de uma solução de lavagem com elevada concentração desse metal, 20 g/L. Embora a destinação final de Ni e Co seja a produção de catodos, o refinado da extração de Co pelo Cyanex 272 contém Ni e a presença indesejável de Ca. Os circuitos de extração estão incompletos requerendo estudos adicionais para transferir Co e Ni para soluções eletrolíticas de forma a serem direcionadas à etapa de eletrorrecuperação. Nesse contexto, talvez seja necessário separar Ni e Ca no refinado da extração de Co de forma a minimizar ou evitar a formação de gesso, conforme relatado por Donegan (2006), durante a reextração de Ni para a solução eletrolítica. Ou adicionar estágios de lavagem do extrato de Cyanex 272 contendo Ni e Ca almejando-se a remoção de Ca antes da reextração de Ni. A principal vantagem da rota consiste no uso de reextração seletiva com H_2SO_4 para remover as impurezas (principalmente Mg) do extrato de ácido versático mantendo as espécies de interesse, Co e Ni.

2.2.2 DSX utilizando-se Cyanex 301 e ácido versático

Guan et al. (2016) avaliaram o desempenho do ácido versático e sua mistura com Cyanex 301 almejando-se separar Ni e Co em relação ao Ca e Mg contidos em um licor sintético sulfúrico similar ao obtido por lixiviação ácida pressurizada e subsequente precipitação seletiva de Fe, cuja composição química do licor encontra-se na Tabela 2.6.

Tabela 2.6: Licor sintético sulfúrico.

Metal	Ni	Co	Ca	Mg
Concentração (mg/L)	1900	220	390	14760

Fonte: Guan et al. (2016).

O efeito do pH inicial na extração de Ni, Co, Ca e Mg utilizando-se 20% v/v de ácido versático (50% saponificado) a 25°C na razão O/A = 1:4 é apresentado na Figura 2.6. Verifica-se que a redução da acidez favorece as extrações de Ni e Co que atingem um máximo de 95% e 85%, respectivamente, em pH inicial 2,5. Similarmente, as extrações de Mg e Ca se elevaram com o aumento do pH, atingindo um patamar de 5% e 10% de extração em pH $\geq$ 2, respectivamente. Baseando-se nesses resultados, Guan et al. (2016) selecionaram pH inicial de 2,5 e pH de equilíbrio correspondente a 6,85 (Figura 2.7) para a continuidade do estudo. Como os autores saponificaram parcialmente o extratante e decidiram não controlar o pH nos ensaios, o efeito real das variáveis estudadas pode ter sido mascarado pela variação considerável entre os valores reportados de pH inicial e de equilíbrio.

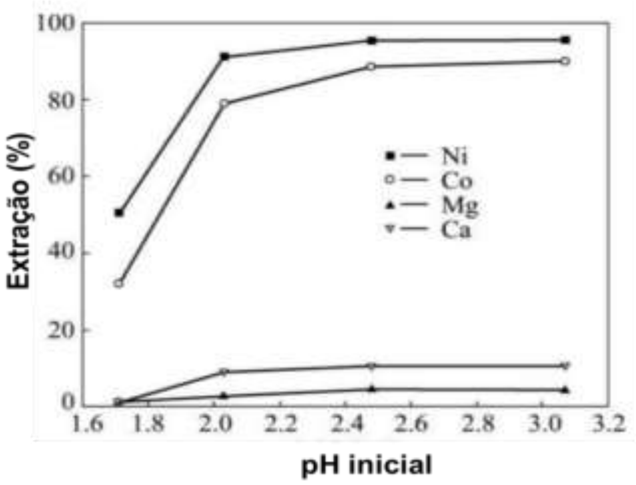

Figura 2.6: Extração com ácido versático (20% v/v) variando-se o pH (25°C, razão O/A = 1:4, 50% de saponificação, adaptado de GUAN et al., 2016).

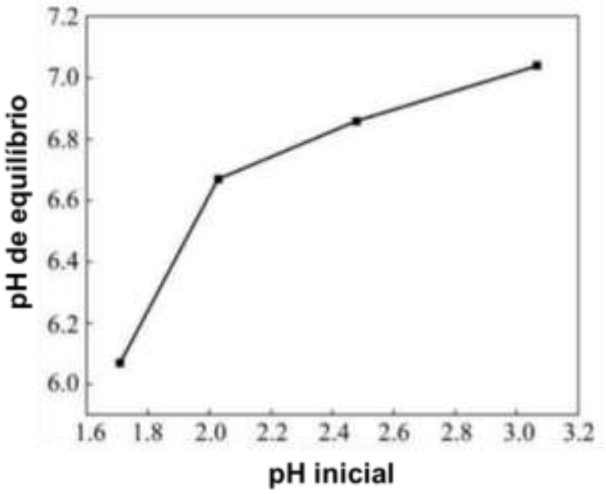

Figura 2.7: Efeito do pH inicial e de equilíbrio na extração com ácido versático (20% v/v) variando-se o pH (25°C, razão O/A = 1:4, 50% de saponificação, adaptado de GUAN et al., 2016).

Em seguida, avaliou-se a influência da razão O/A nas extrações de Ni, Co, Ca e Mg empregando-se pH inicial correspondente a 2,5 e 20% v/v de ácido versático (50% saponificado) a 25°C. Os resultados encontram-se na Figura 2.8. Tem-se que o aumento no volume de fase aquosa diminuiu a extração de Ni e Co de 98% e 95% na razão O/A = 1:3 para 84% e 65% ao se usar a razão O/A = 1:6, respectivamente. Esse fato decorre da manutenção da capacidade de carregamento da solução orgânica. Com o intuito de maximizar a extração de Ni e Co, foi selecionada a razão O/A = 1:3 para prosseguimento do trabalho (GUAN et al., 2016), apesar das maiores extrações de Ca e Mg.

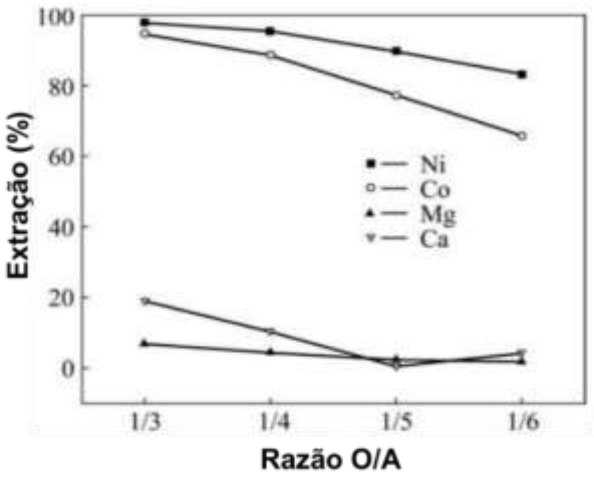

Figura 2.8: Efeito da variação da razão O/A na extração (20% v/v de ácido versático, 25°C, pH inicial = 2,5, 50% de saponificação, adaptado de GUAN et al., 2016).

O efeito da saponificação na extração de Ni e Co e das impurezas Ca e Mg nas condições selecionadas (pH inicial 2,5 e razão O/A = 1:3) a 25°C foi investigado. Verifica-se por meio da Figura 2.9 que o aumento da taxa de saponificação de 40% para 70% favorece as extrações de Ni e Co, mas não de maneira significativa, obtendo-se um aumento médio de 2,5% de extração (97±2% para Ni e 95±3% para Co). Em relação às impurezas, verifica-se um aumento médio de 1,7% de extração (15±2% para Ca e 5±2% para Mg). Apesar disso, almejando-se maximizar a extração de Ni e Co, o uso de ácido versático (20% v/v) saponificado a 60% foi selecionado para prosseguimento do estudo (GUAN et al., 2016).

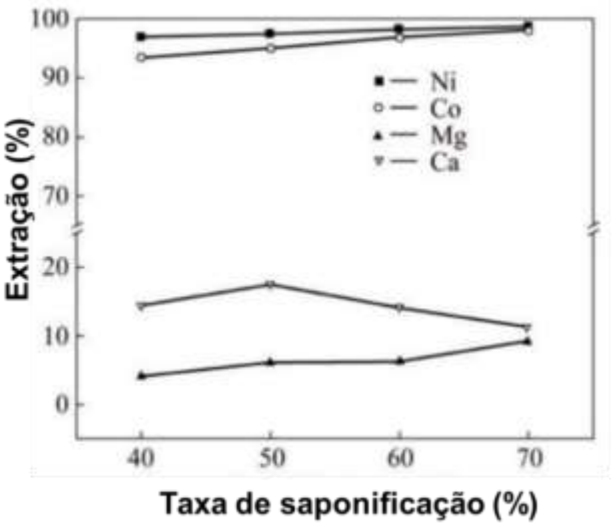

Figura 2.9: Efeito da saponificação do ácido versático na extração (20% v/v de ácido versático, 25°C, pH inicial = 2,5, razão O/A = 1:3, adaptado de GUAN et al., 2016).

Utilizando-se as condições “otimizadas” (pH inicial 2,5; razão A/O = 1:3; 60% de saponificação), 98,3% de Ni, 96,9% de Co, 13,9% de Ca e 6,3% de Mg foram extraídos. Visando-se remover Ca e Mg, o extrato foi contatado (1 estágio, 25°C, razão O/A = 1:1) com 2 soluções aquosas de reextração contendo H_2SO_4 diluído. Os resultados encontram-se na Tabela 2.7. O aumento do pH na solução de reextração seletiva sulfúrica de 3,04 para 4,34 foi insignificante na remoção de Ca e Mg do extrato, porém a co-reextração de Ni e Co foi aparentemente menor em pH 4,34. O uso de água deionizada (pH 6,5) em 2 estágios sucessivos apresentou resultado superior na lavagem de Mg, e similar na lavagem de Ca, Ni e Co. O resultado é interessante do ponto de vista de redução de custos operacionais, mas não se relatou se houve variação no pH (GUAN et al., 2016).

Tabela 2.7: Reextração seletiva com H_2SO_4 e lavagem com água deionizada na remoção de Ca, Mg, Ni e Co do extrato de ácido versático (20% v/v).

Metal	Reextração ou lavagem (%)		
	Solução H_2SO_4 (pH = 3,04)	Solução H_2SO_4 (pH = 4,34)	Água deionizada (pH = 6,50)
Ni	0,28	0,10	0,14
Co	0,31	0,11	0,32
Mg	74,8	73,9	93,6
Ca	98,5	98,5	98,1

Fonte: Guan et al., 2016.

Por fim, o extrato lavado com água foi contatado a uma solução de reextração otimizada por meio de planejamento fatorial (2 M de H_2SO_4 e razão O/A = 1:1), obtendo-se, em um estágio a 25°C, 99,5% e 99,8% de reextração de Ni e Co, respectivamente.

Ainda neste estudo, Guan et al. (2016) utilizaram a condição otimizada de extração (pH inicial 2,5; razão A/O = 1:3; 60% de saponificação) e adicionaram Cyanex 301 ao ácido versático. A soma da concentração total dos extratantes foi mantida em 20% v/v. Os resultados encontram-se na Figura 2.10.

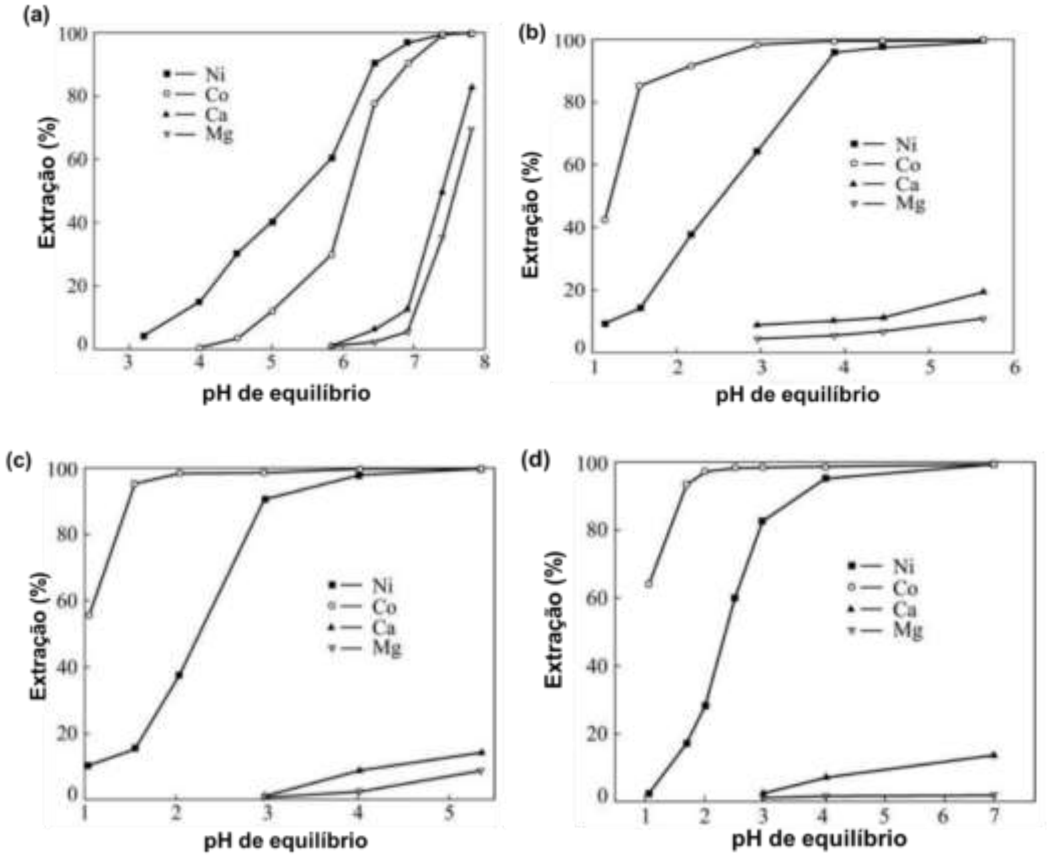

Figura 2.10: Extração metálica do licor sintético sulfúrico variando-se o pH e a composição da fase orgânica (25°C, razão O/A = 1:3, 60% de saponificação, adaptado de GUAN et al., 2016): (a) ácido versático (20% v/v) e misturas de ácido versático + Cyanex 301 na proporção de (b) 7:3, (c) 6:4 e (d) 5:5.

Verifica-se que a adição e o aumento da concentração de Cyanex 301 deslocaram significantemente as curvas de extração de Ni e, principalmente, de Co para condições mais ácidas, reduzindo os valores de $pH_{1/2}$, como mostrado na Tabela 2.8. Para $1 \leq pH \leq 2$, a faixa média extração de Co aumentou de 5% para 96%, e a de Ni de 8% a 96% para $1 \leq pH \leq 4$, respectivamente. Em contrapartida, as extrações de Mg e Ca diminuíram, em média, de 12,5% e 5% para 5% e 1% com o aumento da proporção de Cyanex 301 ao ácido versático, o que favorece à separação seletiva de Ni e Co em detrimento de Ca e Mg. Ressalta-se não ter sido relatado os valores dos fatores de separação, $\beta_{Ni/impurezas}$ e $\beta_{Co/impurezas}$. Utilizando-se ácido versático + Cyanex 301 na proporção de 5:5, as extrações de Co e Ni decresceram comparativamente à mistura na proporção de 6:4 para um mesmo valor de pH (Figura 2.10). Portanto, a proporção 5:5 foi selecionada para a continuidade do estudo, uma vez que as extrações de Ni e Co atingiram 90% e 99% (usando apenas ácido versático, estes foram de 3% e 1%), respectivamente, em pH 3 com apenas 1% de extração de Ca e Mg, resultado significantemente superior ao obtido anteriormente.

Tabela 2.8: Valores de pH de Ni e Co usando-se ácido versático e misturas de ácido versático e Cyanex 301 em diferentes proporções.

Sistema orgânico	$pH_{1/2}$	
	Ni	Co
20% v/v ácido versático	5,43	6,1
Ácido versático + Cyanex 301: proporção 7:3	2,55	1,22
Ácido versático + Cyanex 301: proporção 6:4	2,25	< 1
Ácido versático + Cyanex 301: proporção 5:5	2,35	< 1

Fonte: Guan et al., 2016.

A reextração de Ni e Co do extrato sinérgico, mostrada na Figura 2.11, diminuiu de 58% e 42% para 30% e 20%, respectivamente, ao se utilizar a mistura de ácido versático + Cyanex 301 na proporção de 6:4 (condição ótima identificada nos ensaios de extração) para 5:5 (25°C, razão O/A = 1:2, $[H_2SO_4]$ = 2,5 M). Logo, o aumento na concentração de Cyanex 301 na mistura sinérgica reduz as reextrações de Ni e Co do extrato. Assim, para aumentar a reextração desses metais, a proporção de ácido versático na extração foi aumentada na mistura com Cyanex 301 de 5:5 para 7:3, resultando em reextração de Ni e Co de 87% e 82%, respectivamente, utilizando-se 2,5 M de H_2SO_4. Resultado similar foi obtido usando-se a proporção de 8:2. Portanto, a mistura na proporção de 7:3 foi selecionada para avaliar o efeito da variação da razão O/A (25°C e 2 M de H_2SO_4) na reextração de Ni e Co, conforme apresentado na Figura 2.12.

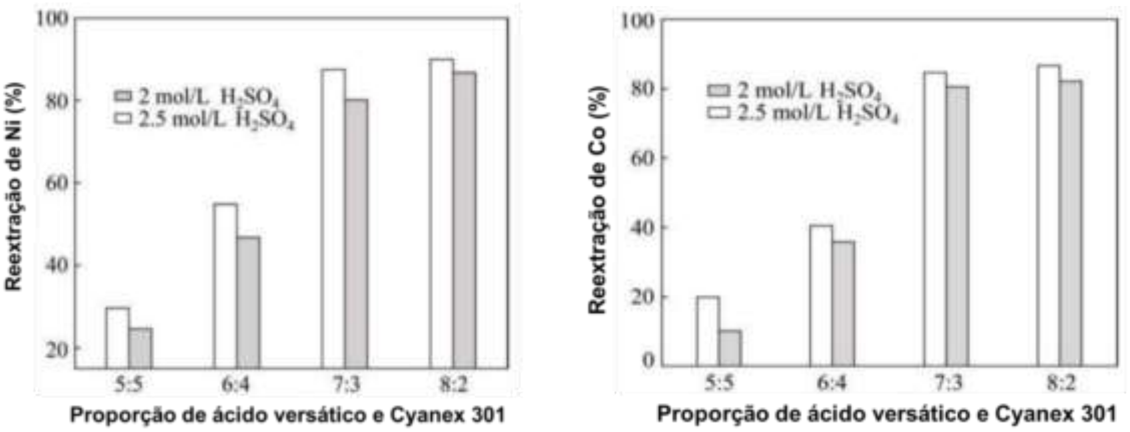

Figura 2.11: Reextração de Ni e Co variando-se H_2SO_4 em diferentes proporções de ácido versático e Cyanex 301 (25°C, razão O/A = 1:2, adaptado de GUAN et al., 2016).

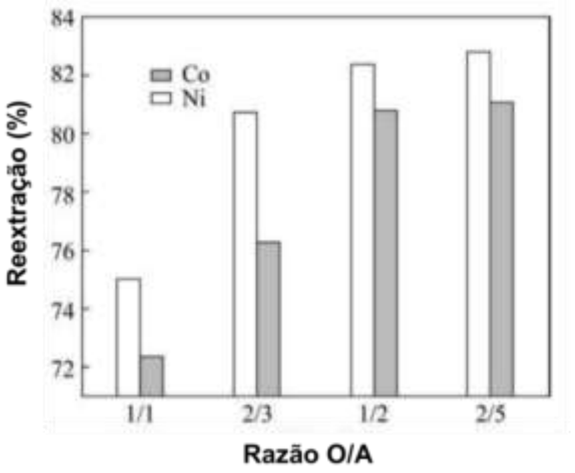

Figura 2.12: Reextração de Ni e Co variando-se a razão O/A (25°C, $[H_2SO_4]$ = 2 M, ácido versático + Cyanex 301 na proporção de 7:3, adaptado de GUAN et al., 2016).

Finalmente, importante reportar que o aumento no volume da solução reextratante não acarretou em variação significativa na recuperação de Ni e Co do extrato sinérgico, obtendo-se, em média, reextração de 75-83% de Ni e 72-81% de Co ao variar a razão O/A de 1:1 para 2:5, respectivamente. Depreende-se desses resultados que a reextração de Ni e Co do extrato sinérgico demanda operações estagiadas. A proporção ótima identificada por meio dos ensaios de extração de ácido versático + Cyanex 301 de 6:4 deve ser alterada para 7:3 com a finalidade de maximizar a reextração de Ni e Co do extrato sinérgico. Os valores das concentrações de Ni e Co no extrato sinérgico não foram relatados. Ressalta-se que o licor de reextração de Ni e Co não está em condições de ser utilizado na etapa de eletrólise visando-se a obtenção de catodos de Ni e Co. O efeito da reextração de Ni e Co do extrato sinérgico em solução eletrolítica de Ni não foi avaliado.

2.2.3 DSX utilizando-se Cyanex 302 e Cyanex 272

Tsakiridis et al. (2004) avaliaram dois circuitos de extração utilizando-se os extratantes Cyanex 302 (ácido di-2-4-4-trimetilpentil mono-tiofosfínico) e Cyanex 272 para purificar um licor sintético similar ao obtido por meio da lixiviação em pilhas de minérios oxidados de Ni empregando-se H_2SO_4 diluído a temperatura ambiente. A composição química do licor utilizado no estudo é mostrada na Tabela 2.9. O objetivo do trabalho foi a obtenção de soluções aquosas de Co e Ni com elevada pureza visando-se a produção de catodos nas cubas eletrolíticas.

Tabela 2.9: Licor sintético sulfúrico.

Metal	Ni	Co	Mg
Concentração (mg/L)	3800	630	5750

Fonte: Tsakiridis et al. (2004).

Inicialmente, o licor foi contatado a uma solução orgânica contendo 20% v/v de Cyanex 272 e 5% de TBP (para prevenir a formação de terceira fase) a 40°C. Os resultados encontram-se na Figura 2.13. Verifica-se que Mg e Co são coextraídos em detrimento ao Ni na faixa de pH de 2 a 5, corroborando Kursunoglu et al. (2017), vide Figura 2.4. Extrações superiores a 99% de Mn e Co são obtidas em pH 5,5 e 5,7, respectivamente, enquanto a extração de Ni é inferior a 5%. E, para separar Mg e Co, utilizou-se uma solução orgânica contendo 20% de Cyanex 302 e 5% de TBP, a 40°C. Observa-se na Figura 2.14 que Co é extraído seletivamente ao Mg na faixa de pH 1 a 4,5, com 99,9% de extração em pH 4,3. Baseando-se nesses resultados, um planejamento fatorial visando maximizar as extrações de Co, Mg e Ni com base nas seguintes variáveis foi aplicado: pH de extração (5,5 e 6,0), temperatura (25 e 40°C), concentração do extratante (5 e 20% v/v) e razão O/A (1:2 e 1:1). Os resultados nas condições otimizadas de extração são mostrados na Tabela 2.10. Logo, Cyanex 272 foi usado para extrair Co e Mn e também separar Ni, visando transferi-lo concentrado para a solução eletrolítica.

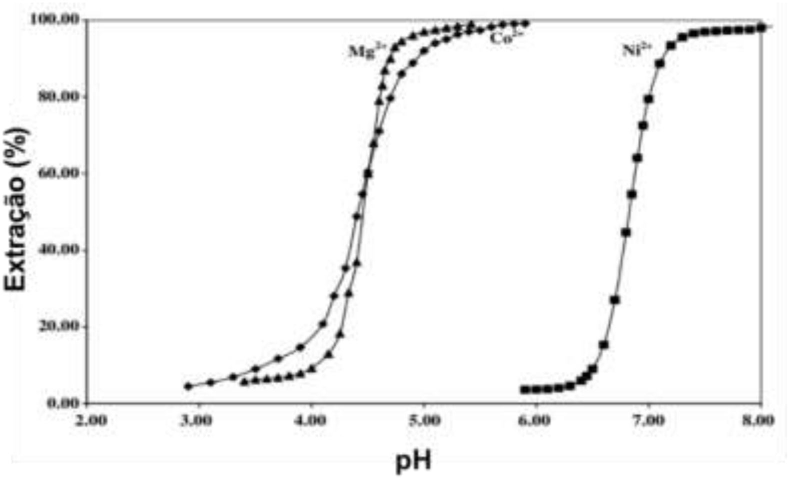

Figura 2.13: Extração de Co, Ni e Mg com 20% v/v de Cyanex 272 e 5% TBP a 40°C (Adaptado de TSAKIRIDIS et al., 2004).

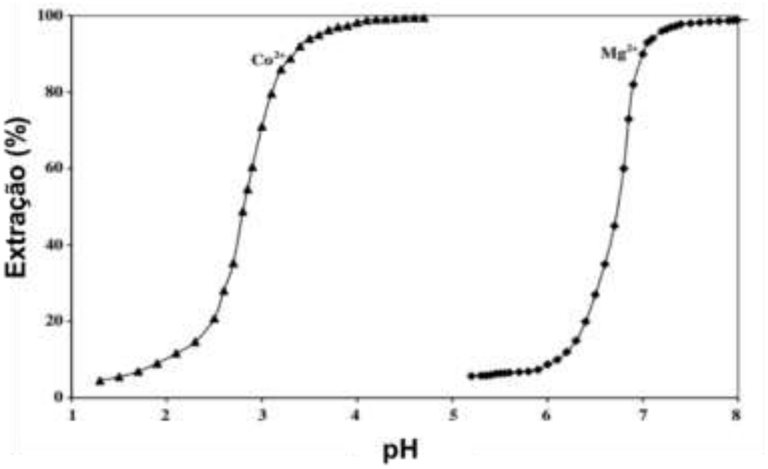

Figura 2.14: Extração de Co e Mg com 20% v/v de Cyanex 302 e 5% TBP a 40°C (Adaptado de TSAKIRIDIS et al., 2004).

Tabela 2.10: Condições otimizadas para extração e separação de Ni e Co.

Circuito de extração	Concentração do extratante (% v/v)	pH	T (°C)	razão O/A
Co e Mn pelo Cyanex 272	20	6,0	40	1
Ni pelo Cyanex 272	10	7,5	40	1
Co pelo Cyanex 302	20	5,0	40	1

Fonte: Tsakiridis et al. (2004).

O extrato de Cyanex 272 contendo Co e Mg foi submetido à reextração seletiva em H_2SO_4 diluído, pH 5,5, razão O/A = 4 a 40°C. A coextração de Ni após a reextração do extrato foi inferior a 0,3%. Similarmente, o extrato de Cyanex 302 contendo Co e Mg foi submetido à reextração seletiva em pH 4,5 (40°C e razão O/A = 4), obtendo-se apenas 0,05% de Mg no extrato lavado. O número de estágios não foi relatado. O extrato lavado de Cyanex 272 contendo Co e Mg foi submetido a uma etapa de reextração com 4 M de H_2SO_4 a 40°C e razão O/A = 2; foram necessários 2 estágios para a reextração de Co e 3 para o Mg, obtendo-se um licor de reextração com 1,57 g/L de Co e 14,3 g/L de Mg. Ni contido no outro extrato de Cyanex 272 foi reextraído contatando-se uma solução eletrolítica contendo 55,45 g/L de Ni e 2 M de H_2SO_4. Após 3 estágios, reextração superior a 99% foi obtida a 40°C e razão O/A = 2,4 (TSAKIRIDIS et al., 2004).

Co foi reextraído do extrato de Cyanex 302 utilizando-se uma solução eletrolítica com 30,8 g/L de Co e 0,5 M de H_2SO_4 a 40°C e razão O/A = 0,8. Nessas condições, reextração superior a 99% de Co foi obtida em 2 estágios. Esses resultados, em escala de bancada, corroboram a capacidade de reextração de Co e Ni dos extratos de Cyanex 302 e Cyanex 272, respectivamente, utilizando-se soluções eletrolíticas almejando-se a concentração dos metais para a produção de catodos. Em seguida, foi avaliada a separação de Co e Ni entre si e do Mg em escala contínua usando-se misturadores-decantadores, cujos volumes correspondiam a 185 e 364 mL, respectivamente. Utilizando-se as mesmas condições mostradas da Tabela 2.10, Co e Mg foram extraídos em 3 estágios com 20% v/v de Cyanex 272 e 5% v/v de TBP, obtendo-se 99,7% de extração de Co e 99,3% de Mg. A etapa de reextração seletiva foi desconsiderada. A reextração procedeu em 3 estágios em contracorrente. O licor obtido contém 1,6 g/L de Co e 14,3 g/L de Mg. Em seguida, esse licor foi submetido a um circuito com Cyanex 302 nas condições mostradas na Tabela 2.10. Foram extraídos cerca de 99,6% de Co em dois estágios. A etapa de reextração seletiva de Mg coextraído também foi descartada. Na reextração com solução eletrolítica de Co (30,8 g/L) e 0,5 M de H_2SO_4 reextraiu-se 99,5% de Co, aumentando a concentração da solução eletrolítica para 36,42 g/L de Co (ΔCo = 5,62 g/L). A extração de Ni (99,5%) ocorreu em 2 estágios, nas condições da Tabela 2.10. A reextração em 3 estágios promoveu a obtenção de solução eletrolítica contendo 77,25 g/L de Ni (ΔNi = 21,8 g/L). Ambas as soluções se encontram em concentrações apropriadas à eletrorrecuperação de Co e Ni para a produção de catodos (TSAKIRIDIS et al., 2004).

2.2.4 DSX utilizando-se LIX 1104-SM

Zhang et al. (2012) usaram ácidos hidroxâmicos alifáticos, LIX 1104 (33% de ácidos trialquil hidroxâmicos) e LIX 1104-SM (derivado do LIX 1104 com adição de álcool iso-C_{16}), visando avaliar seus desempenhos na separação de Ni e Co em relação a Ca, Mg e Mn. A composição química do licor sintético sulfúrico usado no estudo é mostrada na Tabela 2.11, similar aos obtidos na lixiviação HPAL de lateritas de Ni.

Tabela 2.11: Licor sintético sulfúrico.

Espécie	Ni	Co	Mn	Ca	Mg	Zn	Cu
Concentração (mg/L)	3000	190	1800	500	10000	200	200

Fonte: Zhang et al. (2012).

A extração dos metais com 0,25 M de LIX 1104 (40°C e razão O/A = 1) em função do pH apresentada na Figura 2.15 revela a seguinte sequência de extração: Cu > Zn > Ni e Co >> Mn >> Mg e Ca. Completa extração de Cu ocorre em pH 3. Zn, Co e Ni são extraídos juntos a partir de pH 3,5 atingindo 98% de extração em pH 5-6. A extração de Mn se inicia em pH 4,75 atingindo 85% em pH 7,2. Ca e Mg são rejeitados pelo LIX 1104 e permanecem no refinado, com extrações inferiores a 3%. A diferença no $pH_{1/2}$ do Mn em relação ao Ni, Co e Zn alcançou 1,9, 1,8 e 2,2, respectivamente, indicando facilidade na separação de Ni+Co+Zn e Cu em relação ao Mn e também Mg e Ca.

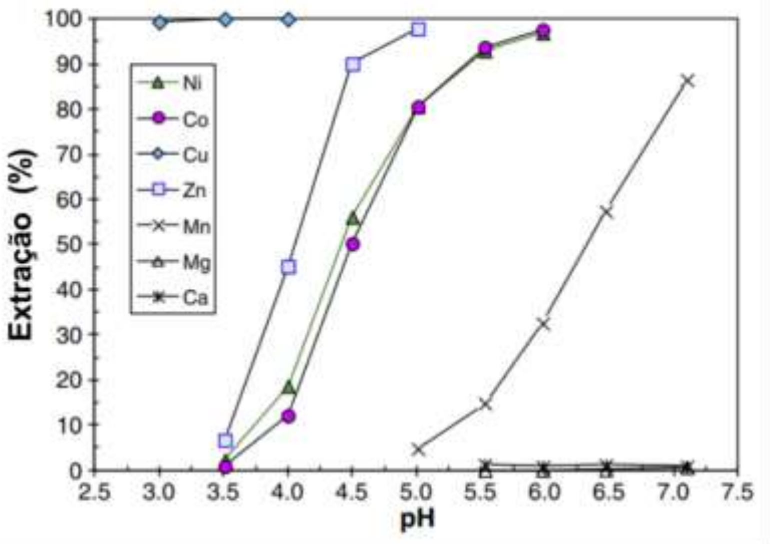

Figura 2.15: Extração metálica do licor sintético sulfúrico utilizando-se 0,25 M de LIX 1104 (40°C e razão O/A = 1, adaptado de ZHANG et al., 2012).

Nas mesmas condições do ensaio anterior, foi avaliado por Zhang et al. (2012) o desempenho do LIX 1104-SM na concentração de 0,38 M, tendo sido adicionado 0,15 g/L de Fe^{3+} a fim de verificar seu comportamento de extração. Os resultados encontram-se na Figura 2.16. A ordem de extração dos metais é similar à identificada pelo LIX 1104: Cu > Fe > Zn > Ni e Co >> Mn >> Mg e Ca. Aproximadamente 83% de Fe são extraídos em pH 3,5 e para pH ≥ 4 sua extração excede 98%. A eficiência de separação entre Ni, Co, Zn em detrimento de Mn usando LIX 1104-SM foi superior à verificada com LIX 1104; as curvas de extração de Ni, Co, Zn se deslocaram para condições mais ácidas, enquanto a de Mn para condições mais alcalinas, resultado em maiores diferenças de $pH_{1/2}$ para Ni, Co e Zn (2,1, 2,0 e 2,7, respectivamente). Portanto, LIX 1104-SM foi selecionado para a continuidade do estudo.

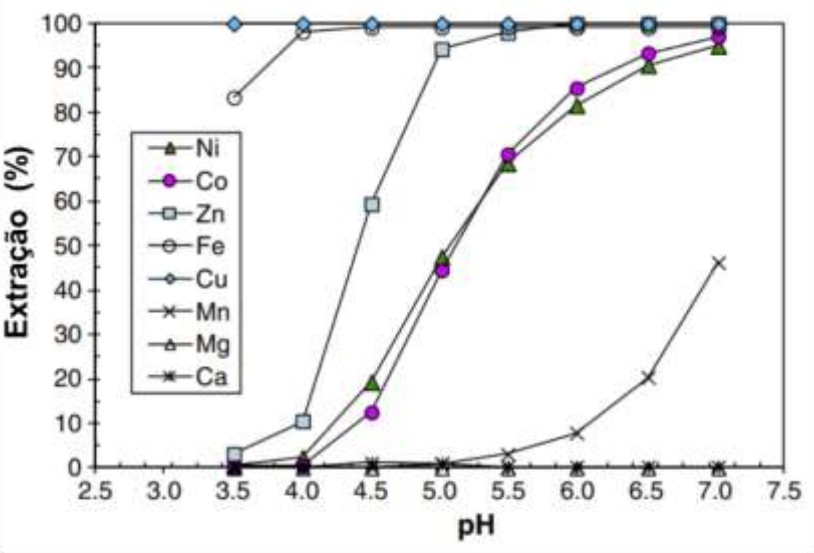

Figura 2.16: Extração metálica do licor sintético sulfúrico utilizando-se 0,38 M de LIX 1104-SM (40°C e razão O/A = 1, adaptado de ZHANG et al., 2012).

As isotermas de extração de Ni e Co foram obtidas em pH 6,5 a 40°C. Por meio do diagrama McCabe-Thiele mostrado na Figura 2.17, verifica-se que são necessários 2 estágios para extrair Ni e Co do licor sulfúrico utilizando-se uma razão O/A = 0,8.

A cinética de extração dos metais foi avaliada com 0,38 M de LIX 1104-SM a 40°C e razão O/A = 1. Conforme mostrado na Figura 2.18, a extração de Cu, Fe, Co e Zn é muito rápida alcançando o equilíbrio em apenas 30 s. Ni atingiu o equilíbrio em 1 min, com eficiência de extração correspondente a 89% (ZHANG et al., 2012). Esses resultados indicam que as extrações metálicas pelo LIX 1104-SM são rápidas o suficiente para esse reagente orgânico ser utilizado em escala industrial.

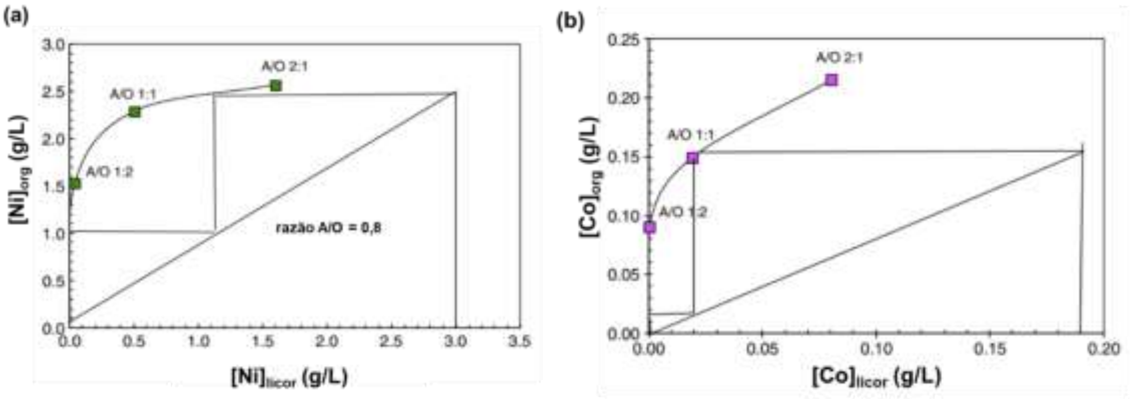

Figura 2.17: Diagramas McCabe-Thiele para (a) Ni e (b) Co utilizando-se 0,38 M de LIX 1104-SM a 40°C em pH 6,5 (Adaptado de ZHANG et al., 2012).

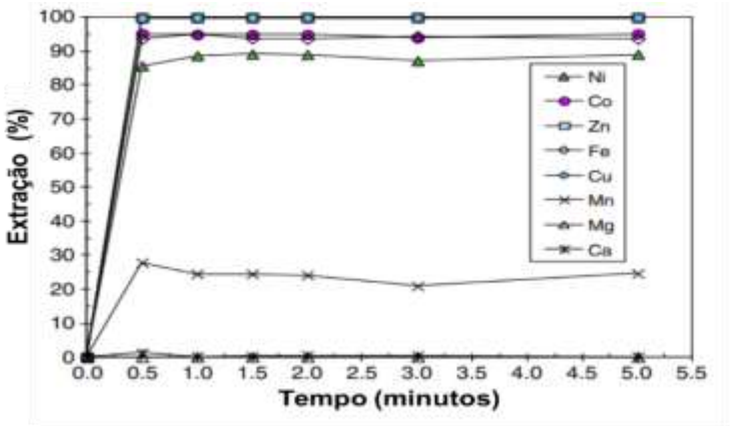

Figura 2.18: Cinética de extração de metais utilizando-se 0,38 M de LIX 1104-SM (40°C e razão O/A = 1, adaptado de ZHANG et al., 2012).

A cinética de reextração dos metais do extrato de LIX 1104-SM mostrada na Figura 2.19 foi avaliada usando-se uma solução de reextração eletrolítica contendo 30 g/L de Ni e 35 g/L (0,36 M) de H_2SO_4 a 40°C e razão O/A = 1. A reextração de Ni, Co, Zn e Mn é rápida alcançando o equilíbrio em 1,5 min, obtendo-se 91-95% de reextração. Em contrapartida, como não houve reextração de Fe e Cu nos 5 min avaliados, a remoção desses metais do extrato de LIX 1104-SM foi investigada variando-se a temperatura, o agente reextratante e sua concentração mantendo-se o tempo de reextração em 5 min; os resultados são mostrados na Tabela 2.12. Utilizando-se 100 g/L de H_2SO_4 a 23°C, obteve-se completa reextração de Cu. No entanto, a de Fe foi de apenas 0,17%, indicando a possibilidade de reextração seletiva. Aumentando a concentração de H_2SO_4 para 400 g/L (4 M) e a temperatura para 40°C, a reextração de Fe atingiu 79,7% enquanto à de Cu reduziu para 87,4%. Com 6 M de HCl a 40°C foram reextraídos 93,1% de Fe e 88,2% de

Cu. O motivo do decréscimo da reextração de Cu com o aumento da concentração de ácido não foi relatado.

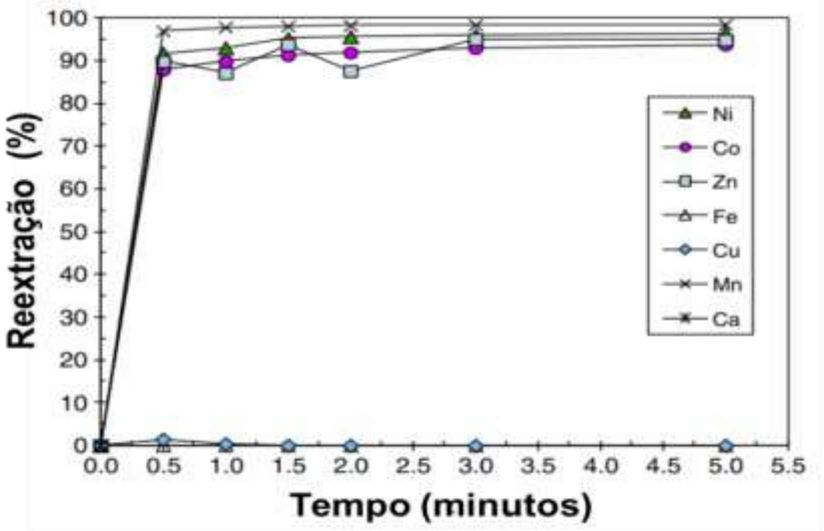

Figura 2.19: Cinética de reextração do extrato 0,38 M de LIX 1104-SM utilizando-se uma solução reextratante contendo 30 g/L de Ni e 35 g/L (40°C e razão O/A = 1, adaptado de ZHANG et al., 2012).

Tabela 2.12: Reextração de Cu e Fe utilizando-se diferentes níveis de temperatura e de concentrações de HCl e H_2SO_4.

Solução reextratante	T (°C)	Reextração (%)	
		Cu	Fe
30 g/L de Ni e 35 g/L de H_2SO_4	23	0	0
100 g/L de H_2SO_4	23	100	0,17
100 g/L de H_2SO_4	40	94,3	1,58
400 g/L de H_2SO_4	40	87,4	79,7
6 M HCl	40	88,2	93,1

Fonte: Zhang et al., 2012.

2.2.5 DSX utilizando-se misturas de LIX 63 e ácido versático

Cheng et al. (2010) utilizaram o licor sintético sulfúrico mostrado na Tabela 2.13 semelhante ao obtido na lixiviação HPAL para investigar o comportamento de extração sinérgica dos metais empregando-se LIX 63 + ácido versático.

Tabela 2.13: Licor sintético sulfúrico.

Espécie	Ni	Co	Mn	Ca	Mg	Zn	Si	Na	Cl
Concentração (mg/L)	5048	271	1573	486	30442	118	16	2839	8207

*Fe+Al+Cr+Cu < 0,2 mg/L

Fonte: Cheng et al. (2010).

Apenas com ácido versático (0,5 M), verifica-se por meio da Figura 2.20 que Ni, Co e Mn são coextraídos em 5,5 ≤ pH ≤ 7,0 a 40°C na razão A/O = 1,5. A extração de Ca e Mg foi inferior a 1%, indicando que esses metais são rejeitados pelo ácido versático. Infere-se desses resultados que seria possível separar Zn+Ni+Co+Mn em relação ao Ca e Mg em pH 7. No entanto, a separação Co/Mn foi difícil o que demandaria, ao menos, o uso de dois circuitos de extração, por exemplo, com Cyanex 272 para separar Zn+Co+Mn do Ni (Zn, Co e Mn são coextraídos pelo Cyanex 272, GUIMARÃES et al., 2014). E outro circuito de extração, por exemplo, com D2EHPA para separar Co de Mn e Zn.

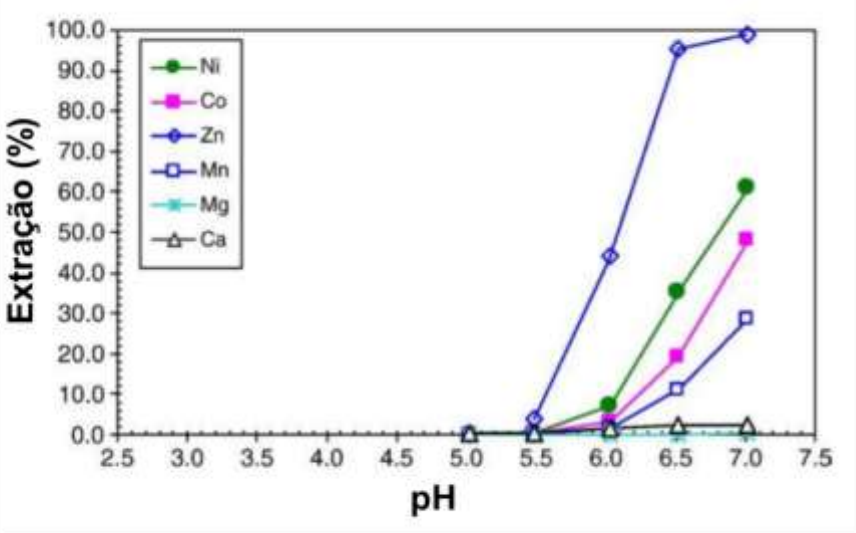

Figura 2.20: Extração metálica do licor sintético sulfúrico utilizando-se ácido versático (0,5 M) a 40°C e razão O/A = 1,0:1,5 (Adaptado de CHENG et al., 2010).

Em seguida, Cheng et al. (2010) avaliaram a extração dos metais utilizando-se a mistura sinérgica contendo 0,5 M de ácido versático + 0,45 M de LIX 63 + 1,0 M de TBP (para prevenir a formação de terceira fase e aumentar a cinética de reextração do Ni, conforme CHENG, 2006) a 40°C na razão O/A = 2. Os resultados encontram-se na Figura 2.21. Verifica-se que as curvas de extração de Ni e Co se deslocaram para condições mais ácidas, entre pH 3-5, enquanto a curva de extração de Mn se manteve na faixa de pH 5,5-7, indicando que Ni e Co podem ser separados do Mn, enquanto Ca e Mg permaneceram no refinado. As diferenças de $pH_{1/2}$ entre Ni e Co para Mn alcançaram 2,4 e 1,65, bem maior que quando somente ácido versático foi usado, de 0,35 e 0,33, respectivamente. Os valores dos fatores de separação $\beta_{Co/Mn}$ e $\beta_{Ni/Mn}$ do sistema sinérgico atingiram 534 e 7720 contra 6 e 15 do sistema não sinérgico, respectivamente. Infere-se desses resultados que o desempenho do sistema sinérgico contendo 0,5 M de ácido versático + 0,45 M de LIX 63 + 1,0 M de TBP é superior na separação de Ni e Co em relação as impurezas Mn, Ca e Mg, o que possibilita simplificar as etapas subsequentes de purificação. Portanto, esse sistema sinérgico foi selecionado para a continuidade do estudo.

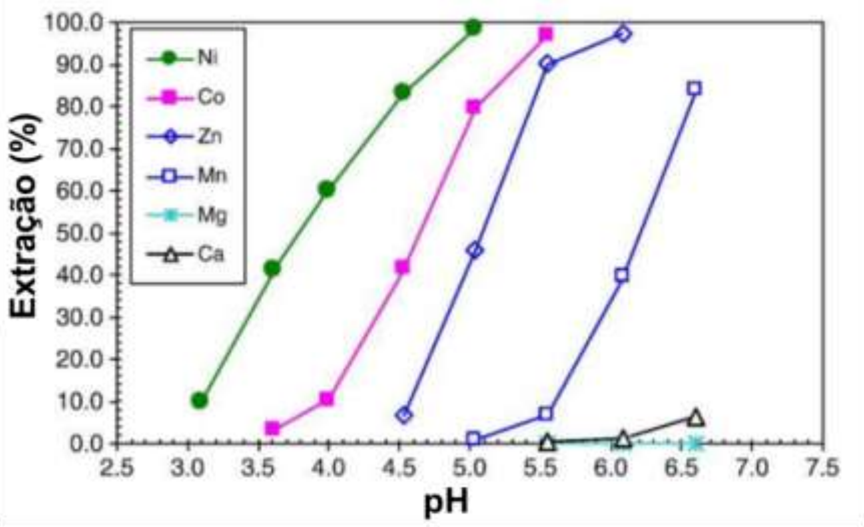

Figura 2.21: Extração metálica utilizando-se 0,5 M ácido versático + 0,45 M LIX 63 + 1,0 M TBP (40°C e razão O/A = 2, adaptado de CHENG et al., 2010).

As isotermas de extração e o diagrama McCabe-Thiele foram obtidos em pH 5,5, razão O/A = 2 a 40°C, conforme mostrado na Figura 2.22. Apenas um estágio teórico de extração é necessário para extrair aproximadamente 99,6% de Ni, enquanto dois estágios são requeridos para extração superior a 97% de Co. Apenas 33 mg/L de Mn, 14 mg/L de Mg e 4 mg/L de Ca foram coextraídos com o Ni e Co no extrato sinérgico. Utilizando-se uma solução de lavagem contendo 120 mg/L de Ni em pH 5, o extrato sinérgico foi lavado em um estágio, acarretando em remoção de 98,5% de Mn, 96,5% de Mg e 25,4% de Ca da solução orgânica. O extrato lavado contém menos de 1 mg/L de Mn e Mg e apenas 2 mg/L de Ca. A concentração de Ni no extrato aumentou de 2,46 g/L para 2,57 g/L e a de Co reduziu de 0,121 g/L para 0,110 g/L, correspondendo a uma lavagem de 8,9%. A solução de lavagem obtida contendo Co pode ser reutilizada nos estágios de extração visando a reciclagem de Co (CHENG et al., 2010).

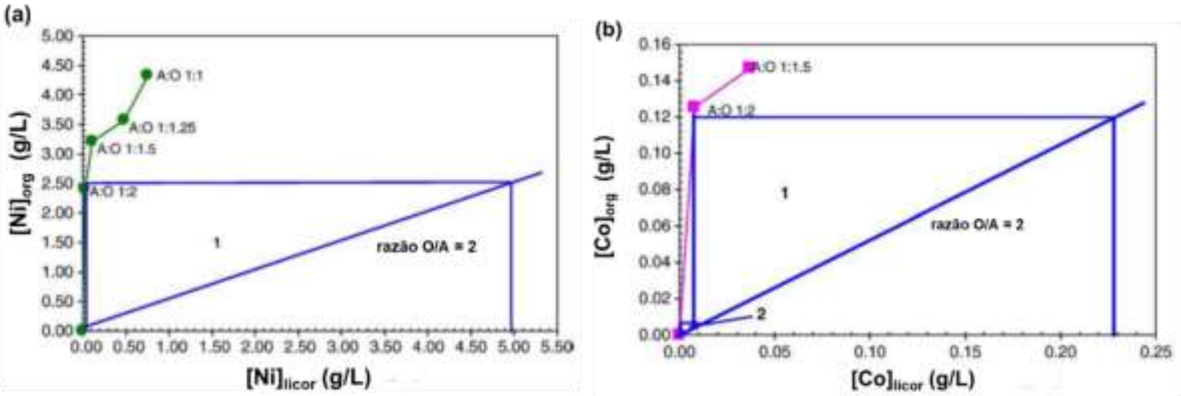

Figura 2.22: Diagramas McCabe-Thiele com 0,5 M ácido versático + 0,45 M LIX 63 + 1,0 M TBP a 40°C em pH 5,5 para (a) Ni e (b) Co (Adaptado de CHENG et al., 2010).

A reextração de Ni, Co e Mn foi avaliada usando solução de H_2SO_4 em $0,5 \leq pH \leq 3,0$. Conforme mostrado na Figura 2.23, a reextração de Ni, Co e Mn (40°C, razão O/A = 2, um estágio) é fácil e pode ser promovida em uma ampla faixa de pH. Assim, um extrato sinérgico de LIX 63 (0,45 M) + ácido versático (0,50 M) + TBP (1 M) contendo 2,25 g/L de Ni, 0,112 g/L de Co e 0,033 g/L de Mn foi submetido a estágios de reextração utilizando-se uma solução reextratante eletrolítica contendo 58 g/L de Ni e 70 g/L de H_2SO_4. As isotermas de extração e os diagramas McCabe-Thiele estão mostrados na Figura 2.24. Utilizando uma elevada razão O/A = 14 a 40°C, apenas 2 estágios teóricos de reextração são necessários para reextrair quase todo o Ni obtendo-se no licor 89 g/L ($\Delta Ni = 31$ g/L), e apenas um estágio teórico é requerido para a reextração de Co, obtendo-se no licor 1,75 g/L desse metal. O licor obtido é submetido a um circuito de extração com Cyanex 272 para a separação Co/Ni. O licor concentrado de Ni isento de Co é direcionado à eletrorrecuperação, e o extrato de Cyanex 272 reextraído com solução eletrolítica de Co para envio à eletrólise de Co (CHENG et al., 2010).

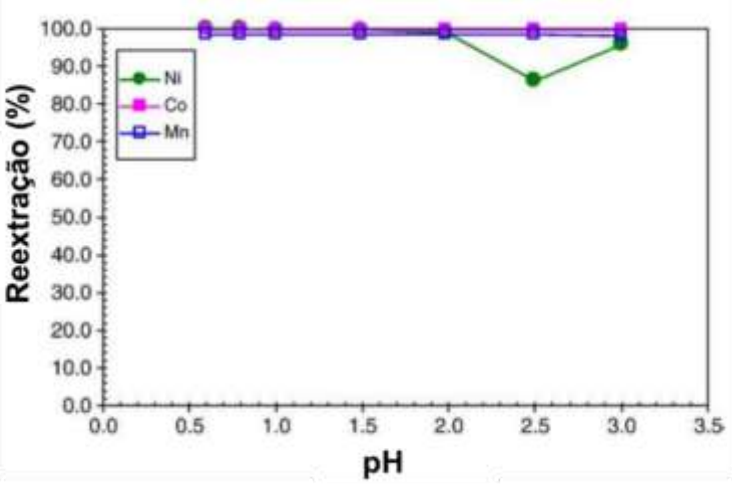

Figura 2.23: Reextração de Ni, Co e Mn utilizando-se 0,5 M ácido versático + 0,45 M LIX 63 + 1,0 M TBP a 40°C e razão O/A = 2 (Adaptado de CHENG et al., 2010).

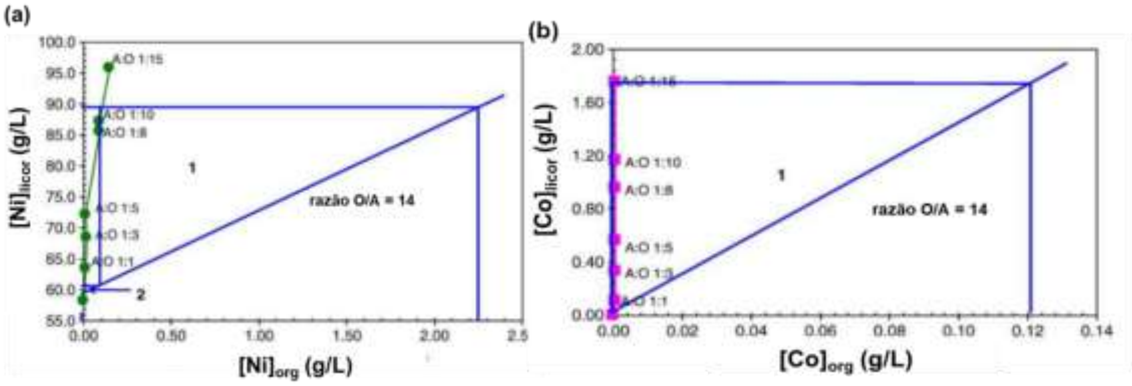

Figura 2.24: Diagramas McCabe-Thiele com solução eletrolítica reextratante (58 g/L de Ni e 70 g/L de H_2SO_4) a 40°C para (a) Ni e (b) Co (Adaptado de CHENG et al., 2010).

Por fim, a cinética de extração e reextração do sistema orgânico sinérgico contendo LIX 63 + ácido versático + TBP foi investigada para avaliar a possibilidade de sua implementação em escala industrial. Verifica-se na Figura 2.25 que 91% de Ni, 97% de Co e 13% de Mn são extraídos em apenas 30 s. A extração de Mn atinge 16% em 30 s e, em seguida, Mn sofre o efeito *crowding out* do Ni de 30 a 60 s e retorna ao licor, reduzindo sua concentração no extrato em torno de 2%. Dos 97% de extração de Co, 7% sofrem o efeito *crowding out* do Ni de 30 a 120 s. Em intervalo de tempo superior a 120 s, a extração de Co aumenta atingindo 95% em 5 min. Pode-se inferir que o tempo mínimo de agitação das fases pode corresponder a 5 min visando-se alcançar a máxima eficiência de extração de Co no extrato sinérgico.

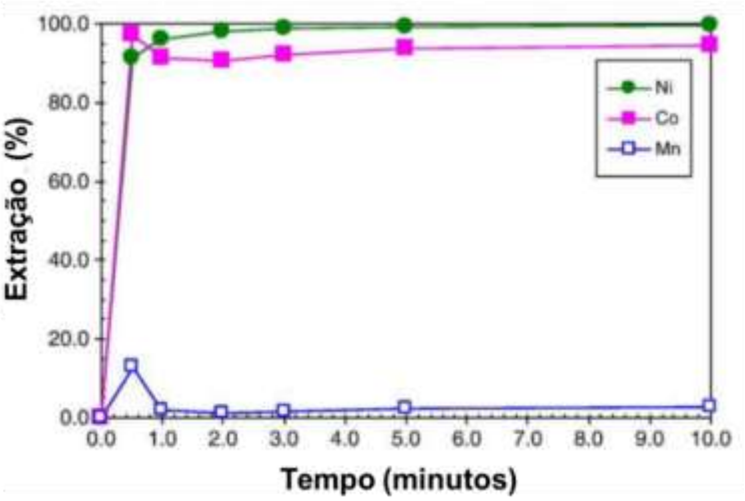

Figura 2.25: Cinética de extração de Ni, Co e Mn com 0,5 M ácido versático + 0,45 M LIX 63 + 1,0 M TBP a 40°C, pH 5,4 e razão O/A = 2 (Adaptado de CHENG et al., 2010).

A cinética de reextração foi avaliada com o extrato de LIX 63 + ácido versático + TBP contendo 2,25 g/L de Ni, 0,112 g/L de Co e 0,033 g/L de Mn usando-se uma solução de reextração eletrolítica contendo 7 g/L de Ni e 6 g/L de H_2SO_4 em um razão O/A = 1 (similar a solução de reextração industrial contendo 70 g/L de Ni e 60 g/L de H_2SO_4 a uma razão O/A = 10) a 40°C. Conforme mostrado na Figura 2.26, a reextração de Ni, Co e Mn é rápida. Em 5 min, obtém-se reextração superior a 99% desses metais. Portanto, a cinética de extração e reextração de Ni, Co e Mn é rápida favorecendo a aplicação do sistema sinérgico em escala piloto (CHENG et al., 2010).

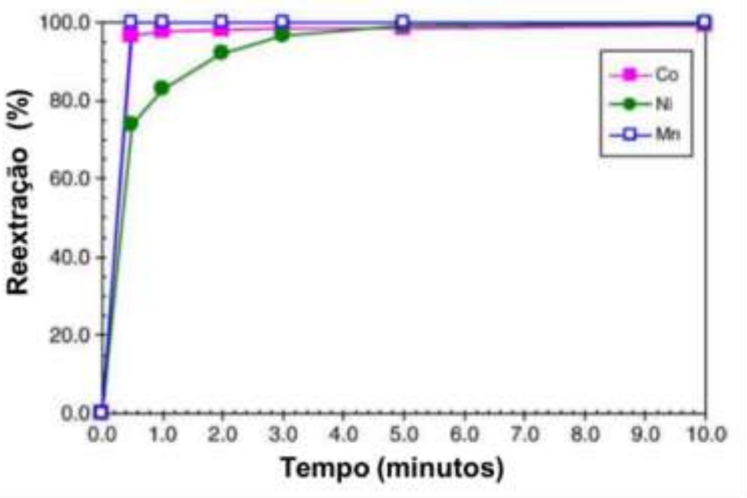

Figura 2.26: Cinética de reextração de Ni, Co e Mn do extrato 0,5 M ácido versático + 0,45 M LIX 63 + 1,0 M TBP utilizando-se uma solução reextratante contendo 7 g/L de Ni e 6 g/L de H_2SO_4 (40°C e razão O/A = 1, adaptado de CHENG et al., 2010).

2.2.6 DSX utilizando-se misturas de LIX 84-IC e ácido versático

Ndlovu e Mahlangu (2008) utilizaram uma mistura sinérgica de ácido versático e LIX 84-IC (2-hidroxi-5-nonilacetofenona oxima) visando separar Ni de Ca e Mg a partir de um licor sintético sulfúrico (composição química na Tabela 2.14), similar à obtida na lixiviação HPAL de lateritas de Ni após a separação de Co e outros metais.

Tabela 2.14: Licor sintético sulfúrico.

Metal	Ni	Ca	Mg
Concentração (mg/L)	3000	500	15000

Fonte: Ndlovu e Mahlangu (2008).

Verifica-se por meio da Figura 2.27 (a) e (b) a ordem de extração Ni > Mg > Ca se utilizando ácido versático (0,5 M) ou LIX 84-IC (0,5 M) a 40°C e razão O/A = 1. A faixa de extração de Ni (15-99%) com ácido versático ocorre em $4,5 \leq pH \leq 6,5$, e a de Ca e Mg (1-60%) em $6,5 \leq pH \leq 8,5$. Com LIX 84-IC, a extração de Ni (2-99%) se deslocou para condições mais ácidas ($3,8 \leq pH \leq 6$), assim como Ca e Mg (1-30% em $4,8 \leq pH \leq 7,8$). Ao misturar ácido versático (0,5 M) + LIX 84-IC (0,5 M), Figura 2.27 (c), a ordem de extração de Ca e Mg mudou para: Ni >> Ca > Mg. A extração de Ni (32-99%) se deslocou para condições ainda mais ácidas ($2,2 \leq pH \leq 4,8$), enquanto que a de Mg (6-50%) para condições mais alcalinas ($7,2 \leq pH \leq 8$). Em relação ao Ca, sua extração (2-70% e $6,3 \leq pH \leq 8$) é similar à de apenas ácido versático. Os valores de $\Delta pH_{1/2(Mg\text{-}Ni)}$ e $\Delta pH_{1/2(Ca\text{-}Ni)}$ com o sistema sinérgico atingiram 5,15 e 4,75 contra 1,95 e 2,1 utilizando-se apenas ácido versático, respectivamente. Portanto, a separação de Ni em relação ao Ca e Mg é facilitada pelo uso do sistema sinérgico. Por meio de um planejamento fatorial, concluiu-se que no mínimo 99% de Ni no extrato sinérgico em um estágio de contatação pode ser obtido utilizando-se 0,50 M de ácido versático + 0,45 M de LIX 84-IC a 40°C em pH 5 e razão A/O = 2. O extrato obtido nessas condições foi lavado em solução aquosa contendo 15 g/L de Ni na razão A/O = 4 sem ajuste de pH, porém a eficiência de lavagem de Ca e Mg, assim como o número de estágios não foram relatados.

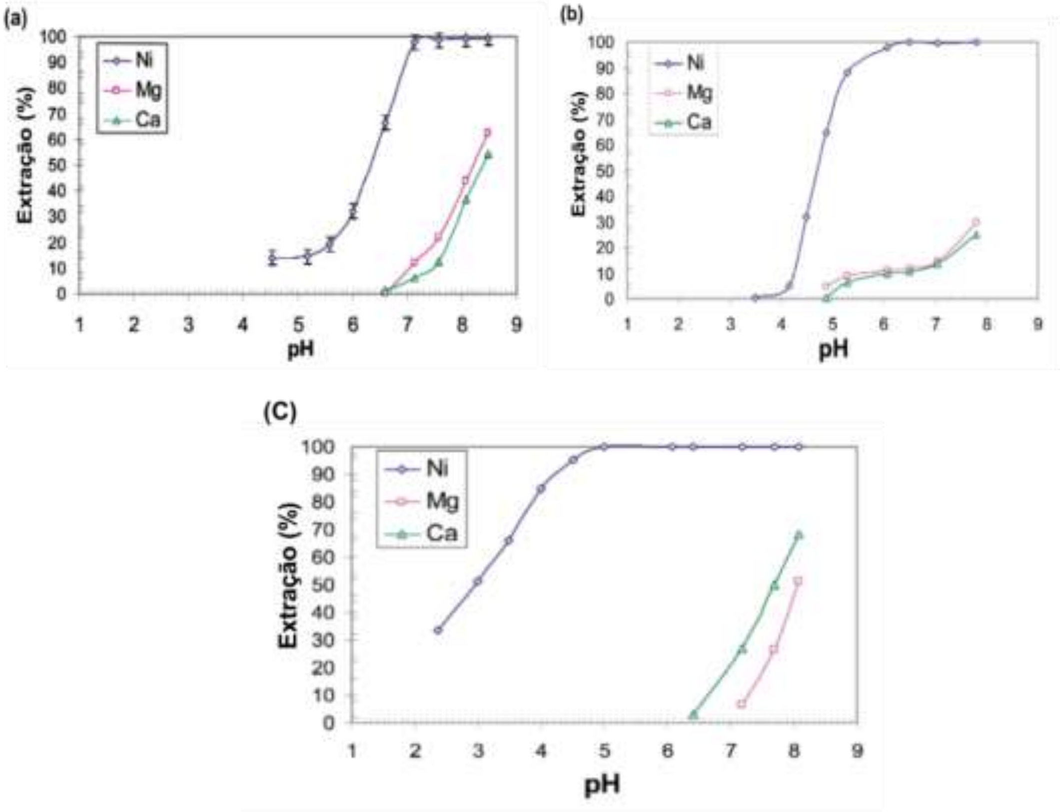

Figura 2.27: Extração de Ni, Ca e Mg usando (a) 0,5 M de ácido versático, (b) 0,5 M de LIX 84-IC e (c) 0,5 M de ácido versático + 0,5 M de LIX 84-IC (40°C e razão O/A = 1, adaptado de NDLOVU e MAHLANGU, 2008)

A cinética de extração e reextração foi investigada por Ndlovu e Mahlangu (2008) nas condições otimizadas e comparada ao sistema sinérgico 0,50 M de ácido versático + 0,35 M de LIX 63 proposto por Cheng (2006). Por meio da Figura 2.28, verifica-se que a extração de Ni é mais rápida com o sistema contendo 0,50 M de ácido versático + 0,45 M de LIX 84-IC, além de atingir o equilíbrio e extrair aproximadamente 95% em apenas 1 min. Em contrapartida, o sistema proposto por Cheng (2006) extraiu 60% de Ni em 1 min e atingiu o equilíbrio em 5 min com extração inferior próxima a 80%. A reextração de Ni com H_2SO_4 (40°C, razão O/A = 1, pH 5) é notavelmente superior do extrato de ácido versático + LIX 84-IC em comparação ao de ácido versático + LIX 63, como mostrado na Figura 2.29. De fato, atinge o equilíbrio em 5 min com eficiência de 95% de reextração contra 30% do extrato de ácido versático + LIX 63. Embora Ndlovu e Mahlangu (2008) não tenham avaliado o sistema sinérgico proposto na presença de Co, Mn, Zn e Cu, ficou evidenciando que misturas de ácido versático com LIX podem resultar em benefícios na separação de Ni em relação aos contaminantes Mg e Ca.

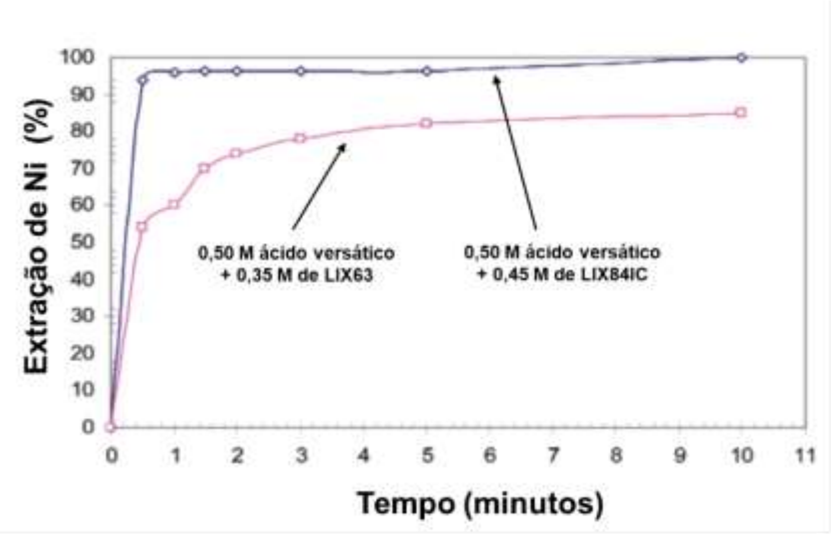

Figura 2.28: Comparação da cinética de extração de Ni utilizando-se 0,50 M ácido versático + 0,45 M LIX 84-IC (razão O/A = 1:2) e 0,50 M ácido versático + 0,35 M de LIX 63 (razão O/A = 1) a 40°C (Adaptado de NDLOVU e MAHLANGU, 2008).

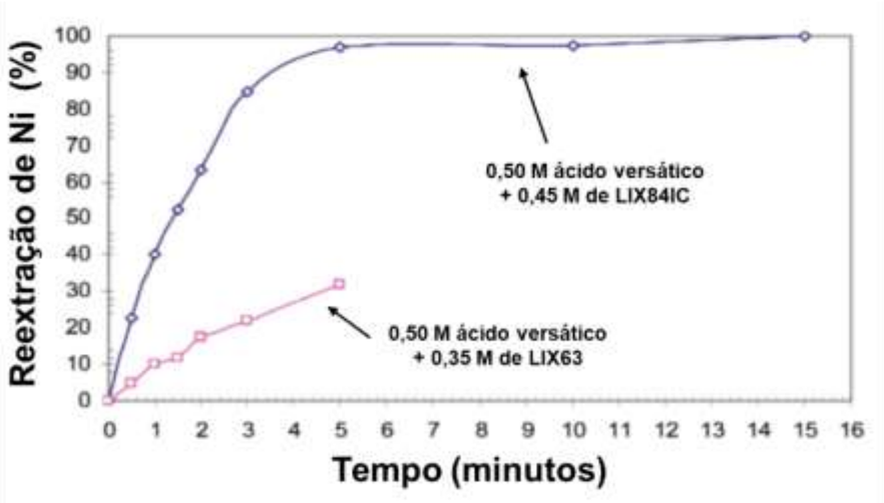

Figura 2.29: Comparação da cinética de reextração de Ni utilizando-se 0,50 M ácido versático + 0,45 M LIX 84-IC e 0,50 M ácido versático + 0,35 M de LIX 63 (40°C, razão O/A = 1, pH 5) (Adaptado de NDLOVU e MAHLANGU, 2008).

2.3. Considerações finais

Com base nos resultados relatados na literatura envolvendo a purificação de licores sulfúrico contendo Ni e Co frente às principais impurezas Ca, Mn, Mg, Fe, Zn e Cu, pode-se concluir que:

- Cyanex 272 deve ser utilizado na separação de Co em relação ao Ni;
- Cyanex 302 pode ser utilizado para separar Co e Mg;

- Ácido versático, LIX 1104 e LIX 1104-SM foram identificados como extratantes potenciais que permitem a extração preferencial de Ni e Co em detrimento ao Ca, Mn e Mg;
- Sistemas sinérgicos contendo ácido versático + LIX 63 e ácido versático + LIX 84-IC maximizam a seletividade da separação de Ni e/ou Co em relação a Ca, Mn, Mg;
- O reuso de Mg e Mn, por estarem normalmente presentes em elevados teores nos licores de lixiviação, pode resultar em vantagens econômicas/ambientais;
- O reuso de Cu e Zn requer avaliação pois estas espécies encontram-se nos licores normalmente em baixos teores. O ideal é que sejam removidos seletivamente, mas se concentrados, também podem apresentar vantagens econômicas/ambientais;
- A etapa de precipitação de Fe deve ser realizada de maneira que a concentração desse metal no licor de Ni seja praticamente nula (ou inferior a 1 mg/L).

Diante desse contexto, torna-se relevante avaliar o uso de extratantes da família LIX (LIX 63, LIX 84-IC, LIX 860-IC, etc.). Outro sistema potencial é Cyanex 301 com ácido versático, porém o único estudo disponível na literatura não foi realizado com controle de pH, embora Cyanex 301 já seja usado na planta Goro com rígidas restrições operacionais. No que tange a sistemas sinérgicos, observa-se o uso de ácido versático e TBP almejando-se maximizar a extração seletiva de Co e Ni em detrimento de Ca, Mg e Mn. Consequentemente, as etapas posteriores de purificação de Ni e Co entre si utilizando-se o Cyanex 272 podem ser simplificadas significantemente para a obtenção de soluções aquosas com elevado teor de pureza de Ni e Co, para posterior obtenção de catodos metálicos.

Face à ampla variação de condições operacionais nos diversos estudos reportados na literatura, é realizada a seguir uma avaliação comparativa entre diversos sistemas orgânicos constituídos por extratantes catiônicos comerciais, puros e em misturas sinérgicas com ácido versático. Tais sistemas foram aplicados ao licor ITV, nas mesmas condições operacionais, a fim de identificar sistemas orgânicos potenciais ao tratamento do licor nacional produzido por Ribeiro et al. (2021) via processo de sulfatação-tratamento térmico-lixiviação sulfúrica aplicada a um minério laterítico brasileiro de Ni, após pré-tratamento do licor para remoção seletiva de Fe, Al e Cr pelo método de precipitação jarosita/goethita (SILVA et al., 2022).

3 AVALIAÇÃO DE SISTEMAS EXTRATORES CATIÔNICOS CONTENDO VERSATIC 10 NA EXTRAÇÃO POR SOLVENTES DE METAIS A PARTIR DE UMA SOLUÇÃO SULFÚRICA LATERÍTICA DE NÍQUEL

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Evaluating cationic extractant systems containing Versatic 10 on the solvent extraction of metals from an Ni lateritic sulfuric solution

Alexandre Silva Guimarães[a,*], Georgio Patrício de Souza Resende[a], Iranildes Daniel dos Santos[b], Ysrael Marrero Vera[c], Marcelo Borges Mansur[a]

[a] Programa de Engenharia Metalúrgica e de Materiais, COPPE, Universidade Federal do Rio de Janeiro, Av. Horácio Macedo, 2030, Cidade Universitária, 21941-598 Rio de Janeiro, RJ, Brazil
[b] Instituto Tecnológico Vale, Rua Prof. Paulo Magalhães Gomes, S/N, Morro do Cruzeiro 35400-000, Ouro Preto, MG, Brazil
[c] Centro de Tecnologia Mineral (CETEM), Av. Pedro Calmon, 900, Cidade Universitária da UFRJ, 21941-908 Rio de Janeiro, RJ, Brazil

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ABSTRACT

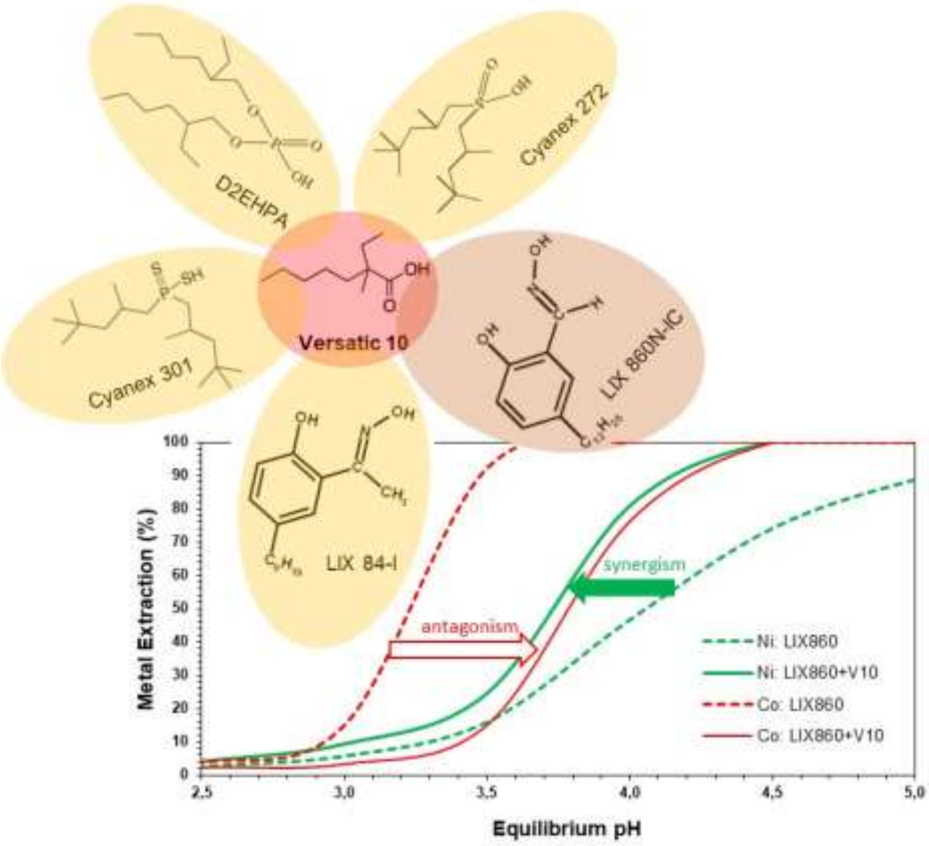
The solvent extraction of Ni, Co, Cu, Ca, Mn, Mg, and Zn was evaluated in this work using Versatic 10 and its mixture with D2EHPA, Cyanex 272, Cyanex 301, LIX 84-I, and LIX 860N-IC. The aqueous phase reproduces a liquor obtained by applying a sulfation-roasting-leaching process in an Ni lateritic ore after precipitation of Fe, Al, and Cr. Tests were conducted at 40 °C, A/O ratio = 1, and [extractant] = 0.5 M. It was found that Cu, Ni, Co, Zn, and Mn can be separated from Ca and Mg by Versatic 10 at pH 6.5. Similarly, Cu, Zn, Co, and Ni can be separated from Mn, Ca, and Mg by Versatic 10 + Cyanex 301 at pH 1.5, whose antagonism on Mn extractions favors Co/Mn and Ni/Mn separation at pH 1–2. Synergism was verified on Ni extractions with Versatic 10 + LIX 84-I and Versatic 10 + LIX 860 N-IC systems. Cu, Ni, and Co are preferentially extracted over Zn, Mn, Ca, and Mg by Versatic 10 mixed with LIX 860 N-IC and LIX 84-I at pH 4 and 5, respectively. Stripping tests using Ni electrolyte solution (50 g/L Ni + 1 M H_2SO_4) from the loaded Versatic 10 + LIX 860 N-IC resulted in the recovery of 80% Ni, 70% Co, and 42% Cu. These four organic systems may have potential applications in direct SX operations. Conversely, Versatic 10 + D2EHPA and Versatic 10 + Cyanex 272 preferentially extract some impurities over Co and Ni. At pH 3, Zn, Ca, Cu, and Mn can be removed over Co and Ni using Versatic 10 + D2EHPA; synergism was found to Mn extractions. Versatic 10 + Cyanex 272 separated Zn, Cu, and Mn at pH 3.5 leaving Co, Ni, Ca, and Mg in the raffinate; synergism was found to Ca extractions. Targeting the extraction of impurities over Co and Ni, Versatic 10 + D2EHPA is superior to Versatic 10 + Cyanex 272, with potential application to treat liquors obtained from the dissolution of MHP.

Abstract

The solvent extraction of Ni, Co, Cu, Ca, Mn, Mg, and Zn was evaluated in this work using Versatic 10 and its mixture with D2EHPA, Cyanex 272, Cyanex 301, LIX 84-I, and LIX 860N-IC. The aqueous phase reproduces a liquor obtained by applying a sulfation-roasting-leaching process in an Ni lateritic ore after precipitation of Fe, Al, and Cr. Tests were conducted at 40°C, A/O ratio = 1, and [extractant] = 0.5 M. It was found that Cu, Ni, Co, Zn, and Mn can be separated from Ca and Mg by Versatic 10 at pH 6.5. Similarly, Cu, Zn, Co, and Ni can be separated from Mn, Ca, and Mg by Versatic 10 + Cyanex 301 at pH 1.5, whose antagonism on Mn extractions favors Co/Mn and Ni/Mn separation at pH 1-2. Synergism was verified on Ni extractions with Versatic 10 + LIX 84-I and Versatic 10 + LIX 860N-IC systems. Cu, Ni, and Co are preferentially extracted over Zn, Mn, Ca, and Mg by Versatic 10 mixed with LIX 860N-IC and LIX 84-I at pH 4 and 5, respectively. Stripping tests using Ni electrolyte solution (50 g/L Ni + 1 M H2SO4) from the loaded Versatic 10 + LIX 860N-IC resulted in the recovery of 80% Ni, 70% Co, and 42% Cu. These four organic systems may have potential applications in direct SX operations. Conversely, Versatic 10 + D2EHPA and Versatic 10 + Cyanex 272 preferentially extract some impurities over Co and Ni. At pH 3, Zn, Ca, Cu, and Mn can be removed over Co and Ni using Versatic 10 + D2EHPA; synergism was found to Mn extractions. Versatic 10 + Cyanex 272 separated Zn, Cu, and Mn at pH 3.5 leaving Co, Ni, Ca, and Mg in the raffinate; synergism was found to Ca extractions. Targeting the extraction of impurities over Co and Ni, Versatic 10 + D2EHPA is superior to Versatic 10 + Cyanex 272, with potential application to treat liquors obtained from the dissolution of MHP.

Keywords: solvent extraction, Versatic 10, nickel, cobalt, synergism.

Graphical abstract



Fonte: próprio autor.

3.1 Introduction

The sulfuric acid leaching of lateritic Ni ores results in a liquor containing Ni, Co, and impurities such as Al, Ca, Cr, Cu, Fe, Mg, Mn, Zn, among others. In a typical purification flowsheet, Fe, Al, and Cr can be selectively removed by precipitation (DONEGAN, 2006; SILVA et al., 2022), followed by Direct Solvent Extraction (DSX) to obtain purified Ni and Co streams (CHENG et al., 2010; ZHANG et al., 2012; KURSUNOGLU et al., 2017; GUIMARÃES et al., 2022a), which are directed to produce Ni and Co salts, oxides, or metal cathodes by electrowinning (MANSUR et al., 2022; CASTRO et al., 2023). If mining and refinery plants are located distant enough from each other, precipitation of a mixed Ni-Co sulphide (MSP) or hydroxide (MHP) intermediates, followed by filtration, transport, and further refinery processing steps involving re-leaching of the precipitate, filtration, and Co-Ni separation by SX are required (GUIMARÃES et al., 2022b). Both strategies involve solvent extraction (SX) operations; however, DSX may imply lower capital and processing costs.

The Co/Ni separation efficiency from sulfuric liquors by SX has been potentiated due to the development of organophosphorus acid extractants, such as D2EHPA (di-2-ethylhexyl phosphoric acid; pKa 1.72; $\beta_{Co/Ni} = 14$), PC 88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester; pKa 3.42; $\beta_{Co/Ni} = 280$), and Cyanex 272 (2,4,4-trimethyl-pentyl phosphinic acid; pKa 6.37; $\beta_{Co/Ni} = 7000$) (FLETT, 2005). Due to the high Co/Ni selectivity, Cyanex 272 is preferred worldwide in several industrial Ni plants (40-50°C, pH ≈ 4-6): Bulong and Murin Murin (Australia), Voisey's Bay (Canada), Kasese Cobalt (Uganda), Votorantim (Brazil), Tati Nickel (Botswana), and Hartley Pt (Zimbabwe) (SOLE et al., 2004; DONEGAN, 2006). The explanation for Cyanex 272's high efficiency in Co/Ni separation relies on a change in the Co organocomplex nature. As evidenced by the FTIR analysis, with increasing temperature and/or Co concentration, its hydrated pink octahedral complexes change to anhydrous blue tetrahedral polymeric species, which raises the distribution coefficient of Co in the organic phase, since the Ni complexes remain in their hydrated octahedral form (FLETT, 2005).

Although Cyanex 272 has proven to be highly efficient to separate Co and Ni, its selectivity towards typical impurities, such as Ca, Mg, and Mn is questionable. In dilute Ni liquors (1-6 g/L), Ca tends to remain with Ni, making Ca/Ni separation difficult; while the crowding out effect was reported in concentrate Ni liquors (70-100 g/L) (DONEGAN, 2006; GUIMARÃES and MANSUR, 2017; GUIMARÃES et al., 2020). Depending on the operating conditions, Mg is partially distributed with Co and Ni, while Mn and Cu are fully extracted with Co. To overcome such difficulties, the flowsheet may demand various separation circuits and/or a combination of distinct extractants (separately and/or mixed). The use of synergistic extractive systems (SSX, the mixture of two or more extractants to maximize certain separations promoted by nonlinear effects) is common practice in hydrometallurgical operations, and organic systems combining acidic and/or chelating extractants have been proposed to separate (Co+Ni)/(Ca+Mg+Mn). Once Co and Ni are extracted together, leaving impurities in the raffinate, they are separated with Cyanex 272 (NDOLOVU and MAHLANGU, 2008; CHENG et al., 2010, 2015). In this context, some DSX strategies found in the literature to obtain Co and Ni from sulfuric liquors (compositions shown in Table 3.1) are depicted as follows.

Table 3.1: Composition of feed sulfuric solutions treated by DSX routes to obtain Co and/or Ni (in mg/L).

Liquor	**Ni**	**Co**	**Mn**	**Ca**	**Mg**	**Zn**	**Cu**	**others**	**Reference**
real	2,800	210	750	560	16,000	30	100*	[Cl] = 80,000; [Fe] < 2; [Al+Cr] < 1	Donegan (2006)
synthetic	4,100	240	1,600	530	8,750	-	-	[Fe] < 1; [Cr] < 0.5; [Al] < 16	Kursunoglu et al. (2017)
real	972	75	560.6	510	3,867	-		[Fe] < 0.1	Guimarães et al. (2022a)
synthetic	1,900	220	-	390	14,760	-	-	-	Guan et al. (2016)
synthetic	3,800	630	-	-	5,750	-	-	-	Tsakiridis and Agatzini-Leonardou (2004)
synthetic	3,000	190	1,800	500	10,000	200	200	-	Zhang et al. (2004)
synthetic	5,048	271	1,573	486	30,442	118	-	[Si] = 16; [Na] = 2,839; [Cl] = 8,207; [Fe+Al+Cr+Cu] < 0.2	Cheng et al. (2010)
synthetic	3,000	-	-	500	15,000	-	-	-	Ndlovu and Mahlangu (2008)

*estimated from

3.1.1 Organic systems based on acidic extractants

The Bulong Ni plant (Australia, decommissioned in 2005) consisted of 2 SX circuits to treat a sulfuric liquor that had been previously neutralized (pH 4.5-5.5) to remove Fe, Al, and Cr (DONEGAN, 2006). The feed liquor contains typical concentrations of Ni and Co, various impurities (Mn, Zn, Cu, Ca, Mg, Cl), and low contents of Fe, Al, and Cr. In the first SX circuit (5 stages, 45°C, A/O ratio not reported), Co, Zn, Cu, Fe, and Mn were separated from Ni, Mg, and Ca using Cyanex 272 (16% v/v). The extract was submitted to a scrubbing step (O/A = 20, [Co] = 5.5 g/L) to remove Ni and raise the Co/Ni ratio (target value > 700). The extract was stripped with H_2SO_4 (2 M), obtaining a rich-Co solution (9 g/L). This was then submitted to a precipitation step with NaOH and NaHS to selectively remove Mn and Mg (SICUPIRA et al., 2014), while the Co-sulfate precipitate obtained was further refined to remove Cu and Zn. The most difficult challenge reported was related to the gypsum formation in the scrubbing and stripping circuits due to the high O/A ratios. In the second SX circuit (4 stages, 45°C, pH $\geq$ 6.5, O/A = 4), Ni was separated from Mg and Ca using Versatic 10 (neodecanoic acid, 15% v/v), followed by a scrubbing step using a diluted Ni electrolytic solution, and then Ni stripping ([H_2SO_4] = 34 g/L, [Ni] = 65 g/L). Donegan (2006) also points out that Fe and Cu contaminated Ni deposits since their concentrations in the raffinate from Co extraction and/or during Ni stripping were above the permissible concentrations ([Fe] < 5 mg/L, [Cu] < 5 mg/L). In addition, the presence of crud was reported in both SX circuits (presence of Si in the first and gypsum formation in the second) and in the recovery step of Versatic 10.

Kursunoglu et al. (2017) inverted the SX circuit sequence of the Bulong plant to obtain Ni and Co from a synthetic sulfuric liquor simulating the Ni lateritic leach solution from the Çaldağ plant after the precipitation step, containing Ni, Co, Mn, Ca, Mg, and low contents of Fe, Cr, and Al. Ni and Co were extracted (98%) in the first SX circuit with Versatic 10 (20% v/v, 40°C, pH 7.3, A/O = 1) together with Mn (94%), Ca (65%), and Mg (12%). Only Mg was removed by selective stripping with H_2SO_4 (pH 5.6), while all remaining metals were stripped out together at pH 0.75. In the second SX circuit with Cyanex 272 (15% v/v, 40°C, pH 4.8, A/O = 1), Co (98%) and Mn (98%) were then extracted in detriment of Ni (3%) and Ca (21%). A scrubbing step ([Co] = 20 g/L) was applied to remove Ca and Ni; however, 7% Mn remained with Co in the scrubbed organic, and both metals were stripped out with H_2SO_4 (pH 0.75-1), producing a Co-rich solution

([Co] = 2 g/L; [Mn] = 0.087 g/L). A purified Ni-rich stream was not obtained. In both organic phases, TBP (tri-n-butyl phosphate) was added (5% v/v) to prevent third-phase formation.

Recently, Guimarães et al. (2022a) evaluated the extraction of Co and Ni with D2EHPA and Cyanex 272 (50°C, A/O = 1) from a real sulfuric Ni lateritic liquor after a precipitation step containing Ni, Co, Mn, Fe (residual), Ca, and Mg. Both extractants fully extracted Fe at pH > 3. While Mn was selectively separated from Co and Ni with D2EHPA (5% v/v, pH 3), it was co-extracted with Co with Cyanex 272, corroborating Kursunoglu et al. (2017). D2EHPA presented a high affinity to Ca at low pH conditions, while Cyanex 272 extracted Ca and Mg to similar extents but at higher pH levels. Therefore, two SX circuits at staged operations, the first with D2EHPA and the second with Cyanex 272, can produce Co and Ni rich-streams. It was verified that Fe, Mn, and Ca, as well as part of Mg may be removed from the liquor with D2EHPA (5% v/v, pH 3), while Co and the remaining Mg could be separated from Ni with Cyanex 272 (15% v/v, pH 4.5). Scrubbing and stripping conditions were not investigated.

It can be verified that Ca, Mg, and Mn actually complicated previous routes to purify Co and Ni. As such impurities are typically concentrated in Ni lateritic sulfuric leaching solutions, a plausible strategy involves leaving Ca, Mg, and/or Mn in the raffinate, as evaluated by Guan et al. (2016) with Versatic 10 + Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid). As pointed out by Mansur et al. (2008), thiophosphinic acids, like Cyanex 301 and Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid), were originally developed for selective Zn extraction at low pH levels from aqueous streams containing Mg and Ca in order to avoid the formation of gypsum precipitates. In fact, the replacement of oxygen by sulfur atoms in the molecular structure of the organophosphorus extractants results in stronger acid reagents for soft Lewis acid metal ions like Ag^+, Ni^{2+}, Zn^{2+}, Cu^+, Au^+, and platinum group metals, in accordance with the hard-soft acid-base principle, given that donor atoms of common bases contain electronegativities that increase in the sequence: S < Br < N < Cl < O < F (SOLE and HISKEY, 1995). Therefore, according to their characteristics of acidity, Cyanex 301 > Cyanex 302 > Cyanex 272, the pH extraction decreases with increasing sulfur substitution in the phosphinic acid, resulting in a more stable metal organocomplex. In their study, Guan et al. (2016) applied a synthetic liquor simulating an HPAL solution after Fe precipitation containing Ni, Co, Ca, and Mg. The optimum condition using solely Versatic 10 (60% saponified, pH 2.5, O/A = 3) was evaluated by adding Cyanex 301 (total extractant concentration = 20% v/v). It was found that Cyanex 301 significantly shifted the Ni extraction curves ($pH_{1/2}$ dropped from 5.4 to 2.4), mainly of Co ($pH_{1/2}$ dropped from 6.1 to below 1) to more acidic conditions. With the Versatic 10:Cyanex 301 ratio = 6:4 (initial pH 3), such an SSX system leads to high extractions of Ni (90%) and Co (99%), with only 1% extraction of Ca and Mg. However, in the stripping step, higher contents of Cyanex 301 required more acidic conditions; for the loaded organic obtained using the optimum extractant composition in the extraction step, for instance, Ni (58%) and Co (30%) stripping were obtained using $[H_2SO_4]$ = 2.5 M (25°C, O/A = 0.5).

Cyanex 301 is used in the Goro Ni project (New Caledonia) to selectively extract Ni, Co, and Zn (3 stages, pH < 2), leaving Mn, Mg, and Ca in the raffinate (RITCEY, 2006; GUIMARÃES et al., 2022a). After stripping with HCl (4 stages), Zn is removed by ion-exchange, and Co is recovered by SX with TOA (tertiary octylamine) in a small circuit. Finally, high purity Ni oxide is obtained by pyro-hydrolysis, and Co precipitated as a carbonate. Cyanex 301 is prone to metal-catalyzed degradation by air and heavily extracts the Ni and Co (VAHED et al., 2004; MIHAYLOV et al., 2000). Hence, the Goro process requires a rigorous elimination of Fe(III) and Cu before the SX step, operation under an inert atmosphere, periodic extractant regeneration, and concentrated HCl (6 M) in the stripping stage.

Tsakiridis and Agatzini-Leonardou (2004) applied two SX circuits (40°C, A/O = 1) using Cyanex 272 and Cyanex 302 to purify a synthetic sulfuric solution containing Ni, Co, and Mg. The study was conducted in batch and continuous mixer-settler operations. In the first circuit, Co and Mg (> 99%, pH 5.5) were extracted together with Cyanex 272 (20% v/v + TBP 5% v/v), leaving Ni in the raffinate (< 5%), followed by stripping ($[H_2SO_4]$ = 4 M, 40°C, O/A = 2). The liquor obtained ([Co] = 1.6 g/L, [Mg] = 14.3 g/L) was submitted to the second circuit, where Co (99.9%, pH 4.3) was separated from Mg using Cyanex 302 (20% v/v + TBP 5% v/v), and was then stripped out (> 99%) using a Co electrolyte solution ([Co] = 30.8 g/L, $[H_2SO_4]$ = 0.5 M, 40°C, O/A = 0.8) in 2 stages. Ni was also extracted with Cyanex 272 (10% v/v + TBP 5% v/v, 2 stages, 40°C, pH 7.5, O/A = 2.4), then stripped out (> 99%, 3 stages) using a Ni electrolytic solution ([Ni] = 55.5 g/L, $[H_2SO_4]$ = 2 M, 40°C, O/A = 2.4). Concentrate solutions of Co (30.8 g/L) and Ni (77.3 g/L) able to feed electrowinning operations were obtained.

3.1.2 Organic systems based on chelating extractants

Zhang et al. (2012) evaluated the performance of LIX 1104 (33% trialkyl hydroxamic acids) and LIX 1104-SM (LIX 1104 + iso-C16 alcohol) on the Co and Ni separation from Ca, Mg, Mn, Zn, and Cu. Metals are extracted according to the following pH sequence (0.25 M, 40°C, A/O = 1): Cu > Zn > Ni and Co >> Mn >> Mg and Ca with LIX 1104, and Cu > Fe > Zn > Ni and Co >> Mn >> Mg and Ca with LIX 1104-SM. Both reagents have high affinity to Cu, with Co, Ni, and Zn extracted together, leaving Mn, Ca, and Mg in the raffinate. Despite similar results, LIX 1104-SM was chosen for continuing study due to lower Mn extraction. Extraction isotherms with LIX 1104-SM (40°C, pH 6.5) using the McCabe-Thiele diagram revealed that 2 stages are required (O/A = 0.8) to extract Ni and Co. Stripping using a Ni electrolytic solution ([Ni] = 30 g/L, [H_2SO_4] = 0.36 M, 40°C, O/A = 1) has shown that Ni, Co, Zn, and Mn are quickly stripped out (91-95%, < 1.5 min) of the loaded organic phase, while Cu and Fe stripping are difficult and required more severe conditions ([H_2SO_4] = 4 M or [HCl] = 6 M, 40°C).

The SSX system LIX 63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime) + Versatic 10 was evaluated by Cheng et al. (2010) using a synthetic solution containing Ni, Co, Mn, Ca, Mg, Zn, Si, Na, Cl, and low contents of Fe, Al, Cr, and Cu. Using Versatic 10 alone (0.5 M, 40°C, A/O = 1.5), Zn, Ni, Co, and Mn are extracted together (pH 5.5-7), while Ca and Mg remained in the raffinate (< 1%). However, when LIX 63 (0.5 M + 1 M TBP) was added to Versatic 10 (0.5 M), Ni and Co extractions (40°C, A/O = 0.5) shifted to more acidic conditions (pH 3.5-5.5), surpassing Zn (extracted at pH > 4.5) and leaving Mn in the raffinate (extracted at pH > 5.5), as well as Mg and Ca. Under such conditions (pH 5.5) and using McCabe-Thiele, only 1 stage extracted 99.6% Ni while 2 stages extracted 97% Co. Co-extracted Mn, Mg, and Ca were scrubbed in 1 stage with $NiSO_4$ solution ([Ni] = 0.12 g/L, pH 5). The organic (in mg/L: [Ni] = 2,250; [Co] = 112; [Mn] = 33) was contacted with an Ni electrolyte solution ([Ni] = 58 g/L, [H_2SO_4] = 0.71 M), obtaining an aqueous solution containing 89 g/L Ni and 1.75 g/L Co (40°C, O/A = 14, 2 stages) to be submitted to a second SX circuit for Co and Ni separation with Cyanex 272.

Ndlovu and Mahlangu (2008) evaluated the SSX system LIX 84-IC (2-hydroxy-5-nonylacetophenone oxime) + Versatic 10 to separate Ni from Ca and Mg. Extraction tests revealed some Ca and Mg co-extraction when extractants were used alone (0.5 M, 40°C, A/O = 1). However, in the SSX system, a strong synergism was observed, with Ni being extracted (32-99%) at more acidic conditions (pH 2.2-4.8), while the Mg extraction curve (6-50%) shifted to more alkaline conditions (pH 7.2-8) and Ca extraction (2-70% at pH 6.3-8) presented a similar behavior to that of Versatic 10 alone. Fast Ni stripping (91% in 1 min) was achieved when the H_2SO_4 solution (40°C, O/A = 1, pH 5) was applied.

The works reported in the literature demonstrate that two main DSX separation strategies can be drawn to obtain purified Co and Ni streams, generally requiring two SX circuits, one for each metal. If Co and Ni are separated from each other in the first circuit, impurities distributed between both streams may require intermediate scrubbing steps to remove them. Crud and gypsum formation were reported. It is widely accepted that Cyanex 272 is the most efficient reagent to separate Co and Ni. The other strategy involves extracting Co and Ni together in the first circuit, thus leaving as many impurities as possible in the raffinate, mainly Ca, to avoid gypsum formation. SSX systems were investigated for both strategies, most of which used Versatic 10 in the organic mixture. In the works reviewed (operating conditions summarized in Table 3.2), the concentration of extractants, the number of metals and their concentrations in the aqueous phase (see Table 3.1) varied considerably, making comparisons between distinct flowsheets difficult, mainly concerning synergism and antagonism effects. In this context, the present work applied a multicomponent solution with a typical metal composition of Ni laterite sulfuric liquors after the precipitation step, with organic phases containing commercial extractants at the same concentration levels (alone and mixed with Versatic 10) in order to identify potential organic systems capable of promoting the Ni and Co separation in relation to the impurities Ca, Mg, Mn, Zn, and Cu.

Table 3.2: Main operating conditions of DSX circuits to obtain Co and/or Ni from sulfuric solutions reported in the literature.

SX circuit 1			**SX circuit 2**			**Additional comments**	**Reference**
Extraction	**Scrubbing**	**Stripping**	**Extraction**	**Scrubbing**	**Stripping**		
Cyanex 272 (16% v/v), 45°C, 5 stages	[Co] = 5.5 g/L, O/A = 20	$[H_2SO_4]$ = 2 M	Versatic 10, 45°C, 4 stages, pH $\geq$ 6.5, O/A = 4	dilute Ni electrolytic solution	$[H_2SO_4]$ = 34 g/L	crud and gypsum formation	Donegan (2006)
Versatic 10 (20% v/v), 40°C, pH 7.3, A/O = 1	-	H_2SO_4 (pH 5.6 and pH 0.75)	Cyanex 272 (15% v/v), 40°C, pH 4.8, A/O = 1	[Co] = 20 g/L (costly)	-	TBP added (5%), purified Ni-rich stream not obtained	Kursunoglu et al. (2017)
D2EHPA (5% v/v), 50°C, pH 3	-	-	Cyanex 272 (15% v/v), 50°C, pH 4.5	-	-	Ca extracted with D2EHPA	Guimarães et al. (2022a)
Versatic 10 + Cyanex 301 (6:4), initial pH 3	-	$[H_2SO_4]$ = 2.5 M, 25°C, O/A = 0.5	-	-	-	no pH control	Guan et al. (2016)
Cyanex 272 (20% v/v), 40°C, pH 5.5, A/O = 1	-	$[H_2SO_4]$ = 4 M, 40°C, O/A = 2	Cyanex 302 (20% v/v), 40°C, pH 4.3, A/O = 1	-	[Co] = 30.8 g/L, $[H_2SO_4]$ = 0.5 M, 40°C, O/A = 0.8, 2 stages	TBP added (5%)	Tsakiridis and Agatzini-Leonardou (2004)
LIX 1104-SM (0.25 M), 40°C, pH 6.5, A/O = 0.8, 2 stages	-	[Ni] = 30 g/L, $[H_2SO_4]$ = 0.36 M, 40°C, O/A = 1	-	-	-	difficult Cu and Fe stripping (40°C, $[H_2SO_4]$ = 4 M or [HCl] = 6 M)	Zhang et al. (2004)
LIX 63 (0.5 M) + Versatic 10 (0.5 M), 40°C, pH 5.5, A/O = 0.5, 2 stages	[Ni] = 0.12 g/L, pH 5	[Ni] = 58 g/L, $[H_2SO_4]$ = 0.71 M	-	-	-	TBP added (1 M)	Cheng et al. (2010)
LIX 84-IC (0.5 M) + Versatic 10 (0.5 M), 40°C, A/O = 1		H_2SO_4 (pH 5), 40°C, O/A = 1	-	-	-	-	Ndlovu and Mahlangu (2008)

3.2 METHODOLOGY

3.2.1 Chemicals and reagents

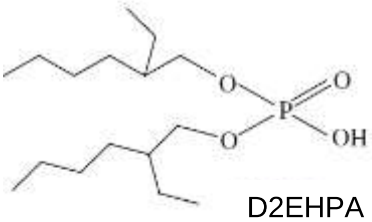
The aqueous phase consists of a synthetic sulfuric solution simulating a liquor obtained by a sulfation-roasting-leaching process (RIBEIRO et al., 2021) applied to a Brazilian laterite Ni ore after selective removal of Fe, Al, and Cr using the jarosite/goethite precipitation method (SILVA et al., 2022). The liquor composition is shown in Table 3.3 and all chemicals used were of analytical grade.

Table 3.3: Metal composition of the aqueous solution used in the SX tests.

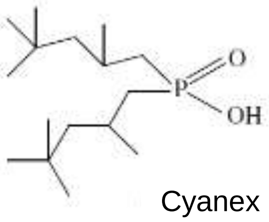
Metal	**Ni**	**Co**	**Mn**	**Mg**	**Ca**	**Zn**	**Cu**
Concentration (mg/L)	3,000	200	1,200	7,500	500	80	10

Fonte: próprio autor.

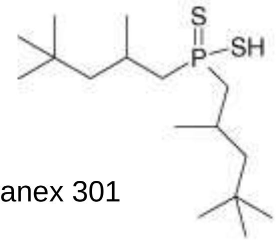
The organic phases were prepared by solubilizing the following extractants (0.5 M) in aliphatic kerosene Exxsol D80 (aromatic content < 0.5% w/w): D2EHPA (95% purity, Lanxess), Cyanex 272 (85% purity, Solvay), Cyanex 301 (75% purity, Solvay), Versatic 10 (90% purity, Brenntag), LIX 84-I (60% purity, BASF), and LIX 860N-IC (5-nonylsalicylaldoxime, 65% purity, BASF). The molecular structures of the extractants are shown in Figure 3.1. All chemicals used in the organic phases were commercial grade and used as received. No modifier agent was used.



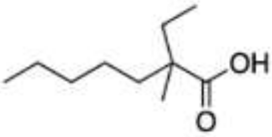
D2EHPA



Cyanex 272



Cyanex 301



Versatic 10

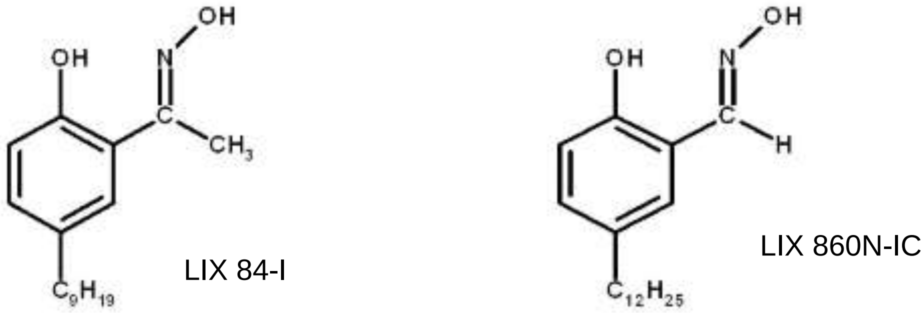


Figure 3.1: Molecular structure of extractants used in this work.

3.2.2 SX tests and chemical analysis

The SX tests were conducted in a 1 L glass reactor by contacting equal volumes of the aqueous and organic phases (400 mL each, A/O volume ratio = 1) at 40°C (lower temperature level normally used in Ni-Co separation with Cyanex 272). The reactor was placed in a digital water bath (Kacil, model RM-02), and the solutions stirred at 600 rpm using a stainless-steel impeller coupled to a mechanical stirrer (Ika, Euro ST-D model) for 5 min. The mixture was kept at rest for 3 min to obtain phase separation (MARTINS et al., 2020; MANSUR et al., 2003). The pH of the aqueous phase was measured using a pH-meter (Digimed, model DM-22). Aliquots of both phases were collected at given pH values to maintain the A/O ratio unchanged. The pH was adjusted by dropping an NaOH solution (1–10 M; Synth, analytical grade, 98% purity) during stirring. The concentration of metals in the aqueous samples was quantitatively accessed by energy dispersive X-ray fluorescence spectrometer (Shimadzu, model EDX-7000) using the calibration curve method, not including Cu, which was determined by atomic absorption spectroscopy (Varian, model ContrAA 55B). The metal content in the organic phase was obtained by mass balance. All aqueous solutions and dilutions for analytical analysis were prepared using distilled water.

3.2.3 SX operating parameters

The following operating parameters were applied to evaluate SX metal efficiency:

$$E_M = 100\frac{[M]_{org}}{[M]_{aq}^{0}} \qquad \text{percent metal extraction} \qquad (3.1)$$

$$\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}} = \frac{[M1]_{org}}{[M1]_{aq}}\frac{[M2]_{aq}}{[M2]_{org}} \qquad \text{separation factor} \qquad (3.2)$$

$$R_M = \frac{D_{M(\text{extractant1+extractant2})}}{D_{M(\text{extractant1})}+D_{M(\text{extractant2})}} \qquad \text{synergistic enhancement factor} \qquad (3.3)$$

where $[M]_{org}$ and $[M]_{aq}$ represent the metal concentration in the organic and aqueous phases, respectively, superscript 0 means initial condition, and D_M is the distribution coefficient of metals M1 and M2 between both liquid phases. From the SX theory, $R_M > 1$ indicates a synergistic effect, while $R_M < 1$ represents an antagonistic effect (RITCEY, 2006; COX, 2008).

3.3 Results and discussion

3.3.1 Metal extraction with Versatic 10

The metal extraction from the sulfuric liquor by Versatic 10 (0.5 M, 40°C, A/O = 1) is shown in Figure 3.2; metals are extracted according to the sequence: Cu > Zn > Ni > Co > Mn >> Ca ≈ Mg, corroborating Cheng et al. (2010, 2015) and Tsakiridis and Agatzini (2004). Cu extractions increased from 4.4% at pH 2 to 98% at pH 5.5. In contrast, the Zn, Ni, Co, and Mn extractions became appreciable solely at pH > 5, reaching 99.9, 93.2, 83.8, and 57.7% at pH 6.5, respectively. Extractions of Ca (< 12%) and Mg (< 5%) were comparatively low, indicating a rejection at pH 2-6.5.

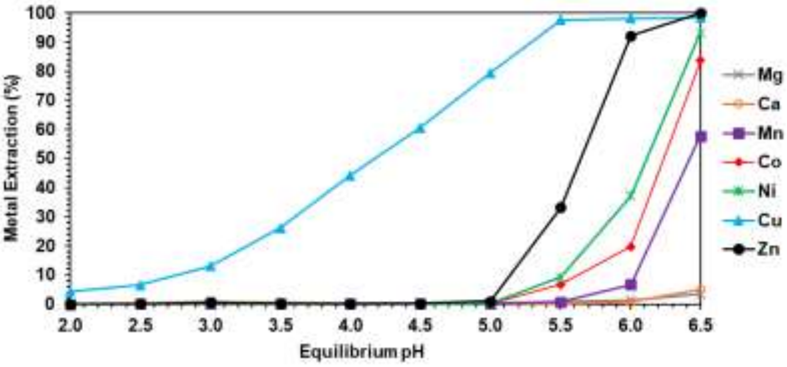


Figure 3.2: Metal extraction behavior by Versatic 10 (0.5 M, 40°C, A/O = 1). Fonte: próprio autor.

The Cu/Metal separation factor reached maximum value at pH 5 ($\beta_{Cu/Co}$ = 5,732; $\beta_{Cu/Ni}$ = 2,572; $\beta_{Cu/Mn}$ = 2,257; $\beta_{Cu/Ca}$= 1,535; $\beta_{Cu/Mg}$ = 1,211; $\beta_{Cu/Zn}$ = 452) revealing easy separation from Co, Ni, Mn, Ca, Mg, and Zn. The $pH_{1/2}$ difference of Mn in relation to Co, Ni, and Zn ($\Delta pH_{1/2(Mn\text{-}Metal)}$) was only 0.2, 0.3, and 0.8, respectively. Hence, these metals are simultaneously extracted from the liquor at $5 < pH \leq 6.5$. Consequently, the selectivity of the separation of Ni and Co in relation to Mn is low, $0.4 < \beta_{Co/Mn} \leq 3.8$ and $0.9 < \beta_{Ni/Mn} \leq 10$. However, at pH 6.5, Zn, Ni, Co, and Mn can be separated from Ca and Mg with good selectivity ($\beta_{Zn/Ca}$= 1.6x10^9; $\beta_{Ni/Ca}$ = 262; $\beta_{Co/Ca}$ = 98; $\beta_{Mn/Ca}$= 21; $\beta_{Zn/Mg}$ = 2.4x10^9; $\beta_{Ni/Mg}$ = 382; $\beta_{Co/Mg}$ = 143; $\beta_{Mn/Mg}$ = 38), due to the low Ca and Mg extractions that mostly remain in the raffinate. Operating at higher pH levels may enhance Ca and Mg extractions considerably, as found by Kursunoglu et al. (2017), and favor the solubility of this carboxylic acid extractant, considering that its recovery by acidifying the extraction raffinate at pH 3 is necessary, as found in Bulong (RITCEY, 2006).

3.3.2 SSX with Versatic 10

Synergistic systems containing Versatic 10 mixed with D2EHPA, Cyanex 272, Cyanex 301, LIX 84-I, and LIX 860N-IC were investigated to improve Ni and Co separation over Ca, Cu, Mg, Mn, and Zn. Metal extractions using the aforementioned extractants alone were also evaluated for comparison purposes.

3.3.2.1 Versatic 10 + D2EHPA system

The metal extraction using 0.5 M Versatic 10 + 0.5 M D2EHPA (40°C, A/O = 1) is shown in Figure 3.3. The sequence of metal extraction by this SSX system is similar to that of D2EHPA alone (0.5 M), in contrast to that found by Versatic 10 alone: Zn > Ca > Mn > Cu > Co > Mg > Ni (Mg was preferably extracted up to pH 4.1, then Co extraction surpassed this up to pH 6). Zn and Ca were fully extracted by the SSX system at pH 2.5 and pH 3.5, respectively, while Mn and Cu extractions increased from 34% and 22% at pH 2 to 99.9% at pH 4.5 and 5.5, respectively. Co extractions became appreciable at pH > 4, reaching 84% at pH 6. Mg and Ni extractions increased monotonically with pH, reaching 54% and 37% at pH 6, respectively. Based on this result, it can be inferred that this SSX system has a high affinity for Zn, Ca, Mn, and Cu over Co and Ni.

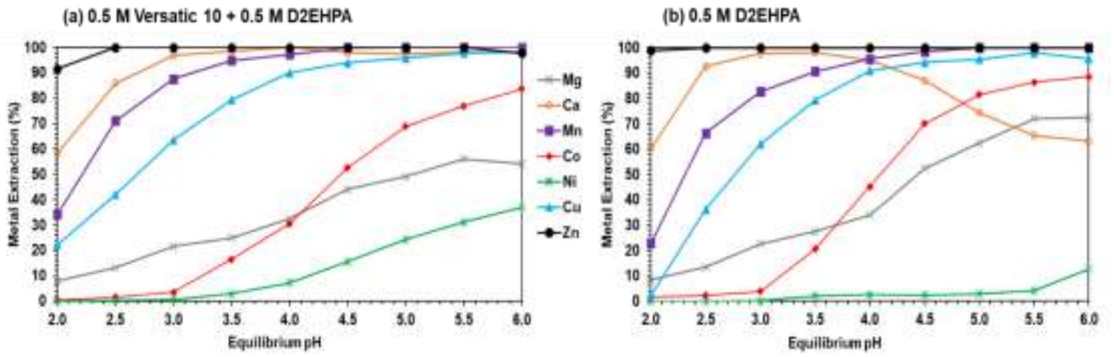


Figure 3.3: Metal extraction behavior by Versatic 10 + D2EHPA (a) and D2EHPA (b) ([extractant] = 0.5 M, 40°C, A/O = 1). Fonte: próprio autor.

Synergism was verified on the Ni extractions ($1.2 \leq R_{Ni} \leq 10$ at pH 2-5), as shown in Table 3.4. At pH > 5.5, this synergism changed to antagonism, since Ni extraction by Versatic 10 alone is higher than that by D2EHPA alone and by Versatic 10 + D2EHPA. Synergism also occurred on Mn extractions, reaching a maximum value of $R_{Mn} = 179$ at pH 4.5, given that $D_{Versatic\ 10\ +\ D2EHPA} \approx D_{D2EHPA} >> D_{Versatic\ 10}$, and the Mn extractions by the respective organic systems were 99.9%, 98.5%, and 0.24%. At pH > 4.5, R_{Mn} values dropped to 9.8 due to the rise in Mn extractions by Versatic 10 alone, obtaining higher values of $D_{Versatic\ 10}$. On the contrary, antagonism was seen on the Co, Mg, and Zn extractions, which is particularly significant for Co along the studied pH range. Regarding Cu and Ca, the synergistic effect was pH dependent; a similar result was reported by Guimarães and Mansur (2018, 2022). In the case of Cu extraction, synergism was verified at pH 2-2.5 ($1.1 \leq R_{Cu} \leq 4$), shifting to antagonism at pH > 3 ($R_{Cu} < 1$). While an opposite behavior with pH was observed for Ca, with an antagonism at pH 2-3 ($R_{Ca} < 1$), which shifted to a growing synergistic effect at pH > 3. This behavior can be attributed to an attenuation of the crowding out effect of the SSX system. Using D2EHPA alone, Mg and Ca extractions increased at pH 2-3.5, as shown in Figure 3.3(b); however, at pH > 3.5, the competition between them due to D2EHPA rose. Mg then scrubbed off 0.17 g/L Ca (difference on Ca concentration in the loaded D2EHPA at pH 3.5 and 6, Figure 3.4) from the organic solution promoting its return to the aqueous solution. The crowding out effect of Mg over Ca possibly occurred because the initial Mg/Ca concentration ratio in the liquor is 15. In the synergistic system, the presence of Versatic 10 minimized Mg extraction by D2EHPA (Figures 3.3(a) and 3.4). For example, at pH 6, the Mg concentration in the SSX organic solution was 4.2 g/L as compared to 5.7 g/L of that with D2EHPA alone. Consequently, Mg scrubbed off only 0.001 g/L of Ca (difference of Ca concentration in the loaded SSX at pH 4 and 6) from the loaded SSX, resulting in high values of R_{Ca} (Table 3.4), mainly at pH 4, reaching 2,400, due to the higher Ca extraction (99.9%) caused by the Versatic 10 + D2EHPA system compared to Versatic 10 (0.2%) and D2EHPA (95%) alone ($D_{Versatic\ 10\ +\ D2EHPA} > D_{D2EHPA} > D_{Versatic\ 10}$). At pH > 4, the crowding out effect of Mg in relation to Ca in the system containing only D2EHPA and in the SSX system reduced the Ca extractions (low D_{D2EHPA} and $D_{Versatic\ 10\ +\ D2EHPA}$), resulting in lower R_{Ca} values. The crowding out effect was reported by Hutton-Ashkenny et al. (2015), Guimarães et al. (2014, 2018), and Cheng (2000).

Table 3.4: Synergistic enhancement factor of metals with Versatic 10 + D2EHPA system at varying pH ([extractant] = 0.5 M, 40°C, A/O = 1).

pH	**R_{Zn}**	**R_{Cu}**	**R_{Ca}**	**R_{Mn}**	**R_{Co}**	**R_{Ni}**	**R_{Mg}**
2	0.1	4.0	0.9	1.8	0.2	1.2	0.9
2.5	0.9	1.1	0.5	1.3	0.7	1.4	0.9
3	0.9	1.0	0.7	1.5	0.9	1.4	0.9
3.5	0.9	0.9	1.3	1.9	0.8	1.3	0.9
4	0.9	0.8	2,400	1.7	0.5	2.9	0.9
4.5	0.9	0.9	7.0	179	0.5	7.1	0.7
5	0.9	0.9	12.8	9.8	0.5	10.1	0.6
5.5	0.9	0.5	28.4	9.8	0.5	3.1	0.5
6	< 0.1	0.8	29.4	9.8	0.6	0.8	0.4

Fonte: próprio autor.

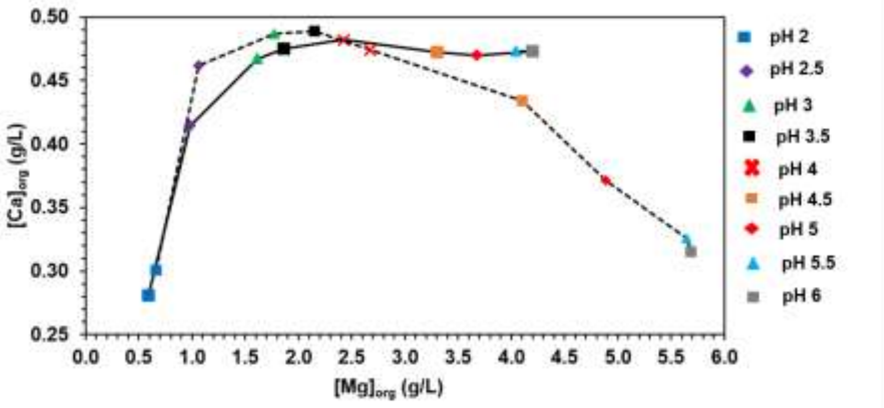


Figure 3.4: Influence of Mg concentration on Ca scrubbing from the loaded Versatic 10 + D2EHPA (continuous line) and D2EHPA alone (dotted line) systems ([extractant] = 0.5 M, 40°C, A/O = 1). Fonte: próprio autor.

Based on these results, Zn, Ca, Mn, and Cu can be separated from Co and Ni. The selectivities between these metals reach a maximum value at pH 3: $\beta_{Zn/Co}$ = 1.9x10^{9}; $\beta_{Ca/Co}$ = 839; $\beta_{Mn/Co}$ = 190; $\beta_{Cu/Co}$ = 47; $\beta_{Zn/Ni}$ = 1.2x10^{10}; $\beta_{Ca/Ni}$ = 5,100; $\beta_{Mn/Ni}$ = 1,200; and $\beta_{Cu/Ni}$ = 288. At pH > 3, $\beta_{Metal/Co}$ and $\beta_{Metal/Ni}$ decreased due to the higher Co and Ni extractions. Mg and Co can be practically extracted together from the aqueous solution by the SSX system, resulting in low $\Delta pH_{1/2(Mg-Co)}$ = 0.62 and $0.7 \leq \beta_{Mg/Co} \leq 1.7$ at pH 3.5-6. Consequently, Mg tends to remain in the raffinate with Co and Ni.

3.3.2.2 Versatic 10 + Cyanex 272 system

As shown in Figure 3.5, the metal extraction sequence by 0.5 M Versatic 10 + 0.5 M Cyanex 272 (40°C, A/O = 1) is similar to that of Cyanex 272 alone, except for the fact that Ca is preferentially extracted over Mg and Ni: Zn > Cu > Mn > Co > Ca > Mg > Ni, corroborating Guimarães et al. (2014). Similar to the Versatic 10 + D2EHPA, but to a lesser extent, some impurities are preferentially extracted in relation to Co and Ni, differing from the metal extraction sequence exhibited by the Versatic 10 alone (Figure 3.2). At pH 3, Zn is fully extracted. Cu and Mn extractions increased from 10% and 1% at pH 2 and 3, reaching 96% and 99% at pH 5, respectively. Co and Ca extractions increased from 6% and 3.5% at pH 3.5 to reach 98% and 81% at pH 5.5. Conversely, Mg and Ni tend to remain in the raffinate, with extractions ranging from 12% to 36% and 0.5% to 26% at pH 5-6, respectively.

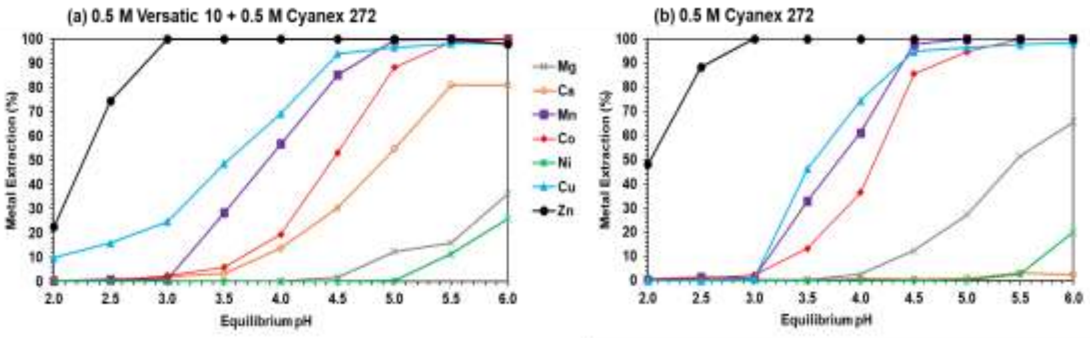


Figure 3.5: Metal extraction behavior by Versatic 10 + Cyanex 272 (a) and Cyanex 272 (b) ([extractant] = 0.5 M, 40°C, A/O = 1). Fonte: próprio autor.

Interestingly, while both Versatic 10 and Cyanex 272 alone rejected Ca in the raffinate, a strong synergism effect was verified using a mixture of such extractants, thus illustrating the nonlinear effect that synergistic systems may exhibit. The Ca extraction curve shifted significantly to the left with the SSX system, and, as shown in Table 3.5, its synergistic enhancement factor increased from 2-3 at pH 2-2.5 to 150 at pH 6. The high $86 \leq R_{Ca} \leq 150$ values at pH 4.5-6 are due to low Ca extraction by the Versatic 10 (0.02-2.8%) and Cyanex 272 (0.5-2.5%), as well as significant Ca extraction by the Versatic 10 + Cyanex 272 system (30-81%), resulting in $D_{\text{Versatic 10 + Cyanex 272}} >> D_{\text{Cyanex 272}} > D_{\text{Versatic 10}}$. Synergism was also found for Cu extractions at pH 2-3, then a shift to antagonism was observed. In contrast, antagonism was verified for Zn, Cu, Mn, Co, Mg, and Ni throughout the evaluated pH range.

It can be inferred from the results that Zn, Cu, and Mn can be separated from Co and Ni at pH 3.5 with the highest simultaneous values of $\beta_{Zn/Co}$ = 1.1x10^{9}, $\beta_{Cu/Co}$ = 15, $\beta_{Mn/Co}$ = 6.3, and $\beta_{Zn/Ni}$ = 1.0x10^{11}, $\beta_{Cu/Ni}$ = 1,400, $\beta_{Mn/Ni}$ = 576, despite co-extraction of 5.6% Co. The presence of Co in the extract with the impurities may require scrubbing steps with a rich-Co solution (20 g/L, for example, according to KURSUNOGLU et al., 2017). At pH > 4, Co extraction increases, thus reducing $\beta_{Zn/Co}$, $\beta_{Cu/Co}$ and $\beta_{Mn/Co}$ values. The small $pH_{1/2}$ difference between Co ($pH_{1/2}^{Co}$= 4.45) and Ca ($pH_{1/2}^{Ca}$= 4.90) results in a low $\Delta pH_{1/2(Ca\text{-}Co)}$ value (0.45), which indicates a simultaneous extraction of both metals, and if H_2SO_4 is used as stripping agent, Ca precipitation may occur at high O/A ratios. Therefore, this SSX system is not suitable to extract Co in the presence of Ca unless the stripping step is performed with HCl.

Table 3.5: Synergistic enhancement factor of metals with Versatic 10 + Cyanex 272 with pH ([extractant] = 0.5 M, 40°C, A/O = 1).

pH	R_{Zn}	R_{Cu}	R_{Ca}	R_{Mn}	R_{Co}	R_{Ni}	R_{Mg}
2	0.3	2.4	3.0	0.7	0.8	0.9	0.8
2.5	0.4	2.7	2.1	0.7	0.5	0.9	0.4
3	0.9	2.1	3.6	0.8	1.0	0.4	0.2
3.5	0.9	0.8	4.5	0.8	0.4	0.6	0.4
4	0.9	0.6	16.2	0.8	0.4	0.2	0.7
4.5	0.9	0.8	86.3	0.1	0.2	0.9	1.0
5	0.9	0.9	103	< 0.1	0.4	1.0	0.5
5.5	0.9	0.7	131	1.0	< 0.1	1.0	0.5
6	< 0.1	0.6	150	1.0	1.0	0.4	0.6

Fonte: próprio autor.

3.3.2.3 Versatic 10 + Cyanex 301 system

As shown in Figure 3.6, the sequence of metal extraction by the 0.5 M Versatic 10 + 0.5 M Cyanex 301 (40°C, A/O = 1) is similar to that of Cyanex 301: Cu ≈ Zn ≈ Co > Ni >> Mn >>> Ca ≈ Mg. It also resembles that of Versatic 10 but at a lower pH level (Figure 3.2), given that Cyanex 301 is a more acidic extractant due to the presence of S atoms in its molecule. The Cyanex 301 behavior was almost replicated in the SSX system. At pH 1, Cu, Zn, and Co were fully extracted, Ni extraction increased from 23% at pH 1 to 99% at pH 1.5-2, Mn extraction increased from 0-10% at pH 1 to 99.9% at pH 4, while Ca and Mg extractions were negligible (< 1%) along the studied pH range. It is interesting to note that this SSX system enhanced the capability of extracting Ni and Co selectively from Mn, mainly at pH 1.5, in comparison to that exhibited by Cyanex 301, while also being very selective over Mg and Ca, elements that constitute the main impurities in the liquor (Table 3.3).

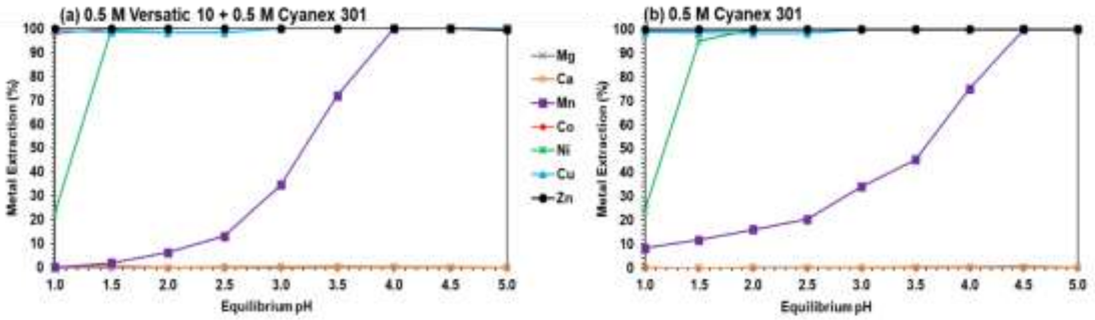


Figure 3.6: Metal extraction behavior by Versatic 10 + Cyanex 301 (a) and Cyanex 301 (b) ([extractant] = 0.5 M, 40°C, A/O = 1). Fonte: próprio autor.

As shown in Table 3.6, this SSX system had a very limited effect on Co and Ni extractions. Although a weak antagonism effect was detected in Zn and Cu extractions (almost null), it proved to be quite strong in Ca and Mg extractions, thus leaving them in the raffinate for the entire pH range. For Mn, by contrast, the effect varied with pH, with strong antagonism at pH 1-2.5 (extraction curve shifted to the right) and synergism at pH > 3 (extraction curve shifted to the left) because of $D_{\text{Versatic 10 + Cyanex 301}} > D_{\text{Cyanex 301}} + D_{\text{Versatic 10}}$. The strong synergistic effect at pH > 4.5 ($R_{\text{Mn}} \geq 906$) was due to the low Mn extraction by Versatic 10 alone (> 99.9%), as compared to Cyanex 301 alone (75%-99.9%) and the mixed system (0.3%-58%), resulting in $D_{\text{Versatic 10}} < D_{\text{Cyanex301}}$ and consequently $D_{\text{Versatic 10 + Cyanex 301}} > D_{\text{Cyanex 301}} + D_{\text{Versatic 10}}$. Thus, when compared to Cyanex 301, as performed in the Goro plant, this SSX system may improve Ni/Mn separation at pH < 2, maintaining high Co/Mn selectivity, given that $\beta_{Ni/Mn}$ may increase from 3.5 to 256 at pH 1, and from 150 to 6,330 at pH 1.5, leaving Ca, Mg, and Mn in the raffinate.

Table 3.6: Synergistic enhancement factor of metals with Versatic 10 + Cyanex 301 system at varying pH ([extractant] = 0.5 M, 40°C, A/O = 1).

pH	**R_{Zn}**	**R_{Cu}**	**R_{Ca}**	**R_{Mn}**	**R_{Co}**	**R_{Ni}**	**R_{Mg}**
1	0.9	1.0	0.1	0.3	1.0	1.0	0.6
1.5	0.9	1.0	0.1	0.3	1.0	1.0	0.6
2	0.9	1.0	0.1	0.3	1.0	1.0	0.6
2.5	0.9	1.0	0.6	0.6	1.0	1.0	0.8
3	0.9	0.9	0.7	1.0	1.0	1.0	0.5
3.5	0.9	0.9	0.1	3.1	1.0	1.0	0.9
4	0.9	0.9	0.5	906	1.0	1.0	1.0
4.5	0.9	0.9	0.7	909	1.0	1.0	0.3
5	< 0.1	0.9	0.3	909	1.0	1.0	0.2

Fonte: próprio autor.

3.3.2.4 Versatic 10 + LIX 84-I system

The extraction curves with 0.5 M Versatic 10 + 0.5 M LIX 84-I (40°C, A/O = 1), shown in Figure 3.7(a), resulted in the following metal extraction sequence: Cu > Ni > Co > Zn > Mn > Ca ≈ Mg. This is identical to that of LIX 84-I alone (Figure 3.7(b)) and similar to that of Versatic 10 alone (Figure 3.2), except for the fact that Ni and Co are preferentially extracted over Zn by the SSX system when compared to Versatic 10 alone. Cu was almost fully extracted (98.6%) at pH 2 by the SSX system. Ni and Co extractions increased from 5.7% and 2.5% at pH 3 and 3.5 to 99.9% at pH 5 and 5.5, respectively. Zn was extracted at pH ≥ 5 reaching 71.6% at pH 6. Mn extractions are low, ranging from 1.6-7.9% at pH 5.5-6. Ca and Mg extractions are negligible (< 0.9%) at pH 2-6, indicating that these metals remain in the raffinate. Similar results were found by Joo et al. (2016) in the extraction of Ni, Co, and Mn using 0.23 M LIX 84-I + 1.21 M Versatic 10.

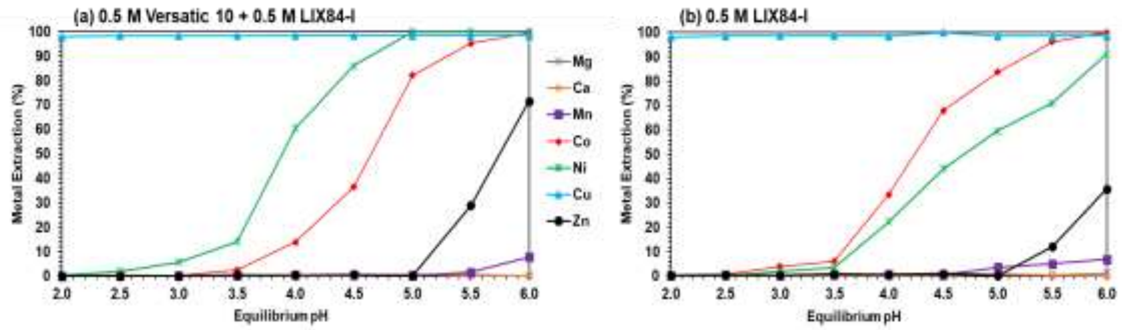


Figure 3.7: Metal extraction behavior by Versatic 10 + LIX 84-I (a) and LIX 84-I (b) ([extractant] = 0.5 M, 40°C, A/O = 1). Fonte: próprio autor.

An antagonism ($R_M < 1$) was verified in the Cu, Zn, Mn, Ca, Mg, and Co extractions (see Table 3.7). The synergistic behavior was only found in Ni extractions, corroborating Joo et al. (2016). R_{Ni} increased from 1.2 at pH 2 to 7.85 at pH 4.5; thereafter, a jump was observed at higher pH values due to the high Ni extractions by the SSX system resulting in $D_{\text{Versatic 10 + LIX 84-I}} >>> D_{\text{LIX 84-I}} >> D_{\text{Versatic 10}}$ at $4 < \text{pH} \leq 6$. In addition, Ni and Co $\text{pH}_{1/2}$ values by Versatic 10 + LIX 84-I were 3.9 and 4.6, respectively. Thus the $\Delta\text{pH}_{1/2(\text{LIX 84-I + Versatic 10 – LIX 84-I})}$ value for Ni was found to be 0.8, characterizing synergism (Ni extraction curve shifted to lower pH values), while for Co, it was -0.4, indicating antagonism (Co extraction curve shifted to higher pH values). Consequently, higher Versatic 10 contents in the SSX system may allow Ni and Co separation.

Table 3.7: Synergistic enhancement factor of metals with the Versatic 10 + LIX 84-I system at varying pH ([extractant] = 0.5 M, 40°C, A/O = 1).

pH	R_{Zn}	R_{Cu}	R_{Ca}	R_{Mn}	R_{Co}	R_{Ni}	R_{Mg}
2	0.08	0.9	0.3	0.6	0.1	1.2	0.7
2.5	0.04	0.9	0.7	0.4	0.2	6.3	0.3
3	0.03	0.8	0.3	0.3	0.07	2.7	0.2
3.5	0.4	0.8	0.6	0.4	0.4	4.5	0.6
4	0.6	0.9	0.4	0.4	0.3	5.3	0.4
4.5	0.5	0.01	0.4	0.7	0.3	7.9	0.6
5	0.1	1.0	0.9	0.04	0.9	2.0×10^5	0.5
5.5	0.6	0.6	0.4	0.3	0.8	1.1×10^5	0.2
6	0.2	0.6	0.6	0.6	0.01	2.7×10^5	0.5

Fonte: próprio autor.

It can be inferred that Cu can be selectively extracted at pH 2, leaving Zn, Ca, Mg, Ni, Co, and Mn in the raffinate. Hence, Co and Ni can be easily extracted at pH < 5, leaving Mn and Zn in the raffinate (at pH 5, $\beta_{Co/Mn}$ = 2.9x10^3, $\beta_{Ni/Mn}$ = 1.8x10^8, $\beta_{Co/Zn}$ = 2.6x10^3, and $\beta_{Ni/Zn}$ = 1.6x10^8). At pH > 5, Co and Ni selectivities decreased because Zn and Mn extractions increased. Ca and Mg remained in the raffinate. It is important to mention that at pH > 3.5, phase separation became slow (around 70-80 s to complete disengagement as compared to nearly 15 s at $2 \leq pH < 3.5$) with increasing Ni extractions. Similar behavior was verified for LIX 84-I at pH > 4 (around 300 s against nearly 15 s at $2 \leq pH < 4$, since metal extractions are lower in more acidic conditions, see Figure 3.7(b)). In both cases, however, no crud formation was verified.

3.3.2.5 Versatic 10 + LIX 860N-IC system

As shown in Figure 3.8(a), the extraction sequence of metals by 0.5 M Versatic 10 + 0.5 M LIX 860N-IC (40°C, A/O = 1) is very similar to that found by Versatic 10 + LIX 84-I (Figure 3.7(a)): Cu > Ni ≈ Co > Zn > Mn > Ca ≈ Mg. The main difference is that Ni and Co tend to be extracted closer together, as evidenced by the small $\Delta pH_{1/2(Ni-Co)}$ = 0.1. In addition, Cu extraction is almost complete, reaching 98.3% at pH 2. Ni and

Co extractions raise from 4.3% and 2.2% at pH 2.5 and reach 99.9% at pH 4.5. Zn extractions increase from 4.6% at pH 4.5 to 97.6% at pH 5.5. Mn extractions range from 4.4 to 39% at pH 5-6. Conversely, Ca and Mg remain in the raffinate with extractions below 1.4%.

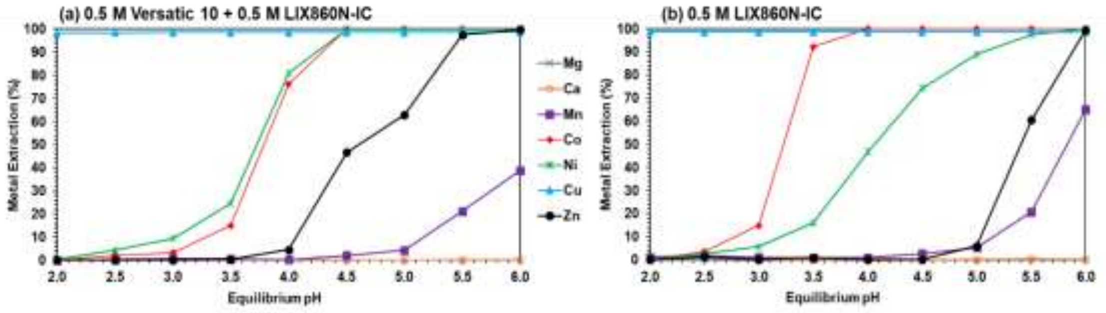


Figure 3.8: Metal extraction behavior by Versatic 10 + LIX 860N-IC (a) and LIX 860N-IC (b) ([extractant] = 0.5 M, 40°C, A/O = 1). Fonte: próprio autor.

Synergism was found on Ni extractions at pH 2-6, as shown in Table 3.8. The synergistic enhancement factor increased sharply from 4.8 at pH 4 to 1x10^9 at pH 4.5 due to increased Ni extraction from 80% to 99.9% by the SSX system as compared to 16%-46% by LIX 860N-IC alone and 0.07%-0.08% by Versatic 10 alone, thus obtaining $D_{\text{Versatic 10 + LIX 860N-IC}} >>> D_{\text{LIX 860N-IC}} >> D_{\text{Versatic 10}}$. At pH > 4.5, R_{Ni} decreased as a function of increased Ni extractions by LIX 860N-IC alone and Versatic 10 alone. Regarding LIX 860N-IC alone, the Ni curve of the Versatic 10 + LIX 860N-IC system shifted only 0.3 pH units ($\Delta pH_{1/2(\text{LIX 860N-IC – LIX 860N-IC + Versatic 10})}$), indicating synergism. The synergistic effect of Zn was pH dependent, with antagonism at pH 2-3.5 shifting to synergism at pH > 3.5 with a maximum of $R_{\text{Zn}} = 156$ at pH 4.5, followed by a decrease at $4.5 < pH \leq 6$ due to the rise in Zn extractions by LIX 860N-IC alone and Versatic 10 alone. By contrast, antagonism was identified for Mg, Ca, Mn, Cu (weak effect), and Co at pH 2-6. In addition, the Co extraction curve of the mixed system shifted -0.56 pH units ($\Delta pH_{1/2(\text{LIX 860N-IC – LIX 860N-IC + Versatic 10})}$) in relation to LIX 860N-IC alone, characterizing antagonism at pH < 4.5.

Table 3.8: Synergistic enhancement factor of metals with Versatic 10 + LIX 860N-IC system at varying pH ([extractant] = 0.5M, 40°C, A/O = 1).

pH	**R_{Zn}**	**R_{Cu}**	**R_{Ca}**	**R_{Mn}**	**R_{Co}**	**R_{Ni}**	**R_{Mg}**
2	0.01	0.6	0.09	0.01	0.3	1.3	0.2
2.5	0.08	0.8	0.1	0.2	0.6	1.4	0.2
3	0.2	0.9	0.3	0.6	0.2	1.6	0.3
3.5	0.3	0.9	0.3	0.7	0.01	1.7	0.03
4	14.8	0.9	0.2	0.2	0.01	4.8	0.2
4.5	156	0.9	0.6	0.7	1.0	1.0×10^9	0.2
5	23	0.9	0.06	0.8	1.0	3.6×10^8	0.1
5.5	20	0.6	0.1	1.0	1.0	7.4×10^7	0.2
6	2.0	0.7	0.06	0.3	1.0	101	0.5

Fonte: próprio autor.

Similarly, as obtained by the Versatic 10 + LIX 84-I system, Cu can be separated from Mn at pH 2 ($\beta_{Cu/Mn}$ = 2.8×10^6). Ni and Co can be separated from Mn and Zn at pH 4 ($\beta_{Ni/Mn}$ = 1,800, $\beta_{Co/Mn}$ = 1,400, $\beta_{Ni/Zn}$ = 88, and $\beta_{Co/Zn}$ = 68); such selectivities increase at pH > 4 because Co and Ni extractions by the SSX system are greater than 99.8%, resulting in even higher values of D_{Co} and D_{Ni} when compared to D_{Mn} and D_{Zn}. However, at pH 4.5-5.5, Zn extractions ranged from 46% to 97.6%, resulting in approximately 0.37 mg/L < $[Zn]_{org}$ < 0.77 mg/L in the loaded SSX organic. To minimize Zn concentration in the extract, it is suggested that Ni and Co separation over Mn and Zn should occur at pH 4 (only 3.6 mg/L Zn and 2.7 mg/L Mn in the loaded organic solution in one single contact). Thus, the raffinate contains the majority of the Mn and Zn as well as almost all of the Ca and Mg. The average time for phase separation of the SSX system was 50-55 s at pH 3.5-4.5. Since Versatic 10 + LIX 860N-IC presented faster phase separation when compared to that of Versatic 10 + LIX 84-I, the former system was selected to evaluate the stripping of Ni, Co, and Cu. The loaded Versatic 10 (0.4 M) + LIX 860N-IC (0.4 M) containing 3.2 g/L Ni, 0.186 g/L Co and 0.0105 g/L Cu was contacted with a synthetic Ni spent electrolyte under different acidity conditions (0.125 M and 1 M H_2SO_4 + 50 g/L Ni) at 40°C and A/O = 1. The results shown in Table 3.9 reveal that using 0.125 M H_2SO_4 in one stage, 90.8% Ni, 67.7% Co, and 1.4% Cu are stripped from the loaded Versatic 10 + LIX 860N-IC. It can be inferred that Ni and Co tend to be preferentially stripped over Cu. With the increase in H_2SO_4 concentration to 1 M, the Ni stripping decreased slightly to 81.1%. By contrast, Cu stripping increased to 42%, while that of Co increased smoothly to 70%. Although Cheng (2006) reported no difficulty in the Co stripping from the loaded Versatic 10 + LIX 63, as well as Flett and Titmuss (1969), Flett and West (1971), and Flett et al. (1974) using the LIX 63 + naphthenic acid and LIX 63 + Versatic 9-11 systems, further tests are required to ensure that Co is not being oxidized to Co^{3+} in the loaded SSX organic solution and poisoning the LIX 860N-IC, as reported by Ritcey (2006) for LIX systems from ammoniacal solutions.

Table 3.9: Stripping of Ni, Co, and Cu from the loaded Versatic 10 + LIX 860N-IC with Ni electrolyte solution (50 g/L + H_2SO_4) ([extractant] = 0.4 M, 40°C, O/A = 1).

[H_2SO_4] (M)	**Stripping (%)**		
	Ni	**Co**	**Cu**
0.125	90.8	67.7	1.4
1	81.1	70.0	42.0

Fonte: próprio autor.

At pH > 6, an increase in the viscosity and/or emulsion formation was observed in Versatic 10 mixture with D2EHPA, Cyanex 272, LIX 84-I, and LIX 860N-IC. Therefore, it is recommended that metal extraction by these SSX systems be performed at pH ≤ 6.

3.3.3 Comparison of organic systems and possible applications

According to the results shown in the previous sections, a comparison of organic systems (Versatic 10, Versatic 10 + Cyanex 301, Versatic 10 + LIX 84-I, and Versatic 10 + LIX 860N-IC) capable of simultaneously extracting Co and Ni in detriment of Ca and Mg (as well as Mn and Zn in some cases) is given in Table 3.10. It can be inferred that Ni and Co separation from impurities must be carried out in stages: (i) Ni and Co extraction at the optimum separation pH (Cu can be separated from Ni, Co, and impurities at pH 2 by the Versatic 10 + LIX 84-I and Versatic 10 + LIX 860N-IC systems, if necessary); (ii) scrubbing of the extract solution aiming to remove impurities co-extracted with Ni and Co; (iii) stripping of Ni and Co from the loaded organic solution with an Ni electrolytic solution containing H_2SO_4; (iv) separation of Co and Ni using Cyanex 272; (v) stripping of Co with Co electrolytic solution in H_2SO_4 medium; (vi) if necessary, Co separation from impurities (Zn, Cu, and Mn) using D2EHPA + TBP (KANI et al., 2021); and (vii) stripping of impurities from the loaded D2EHPA + TBP.

The stripping of Ni and Co from the loaded Versatic 10 and Versatic 10 + Cyanex 301 systems is not problematic and can be performed with an H_2SO_4 solution as reported by Kursunoglu et al. (2017) and Guan et al. (2016). Regarding Versatic 10 + LIX 860N-IC, 70% Co, 81% Ni, and 42% Cu were stripped out using 1 M H_2SO_4 + 50 g/L Ni. However, additional tests must be performed to promote the full stripping of Ni, Cu, and especially Co, to ensure that Co^{3+} ions do not poison LIX 860N-IC reagent. Regarding the Versatic 10 + LIX 84-I system, Ni stripping from the loaded SSX system can be done with an H_2SO_4 solution (2 M) (JOO et al., 2016). Nevertheless, Ni was extracted over Co and Mn due to the increased concentration of Versatic 10 in the organic solution containing LIX 84-I. Consequently, as the evaluation of Co stripping from the loaded Versatic 10 + LIX 84-I system was not performed by Joo et al. (2016), stripping tests are required to assess the occurrence of Co oxidation in the organic phase containing LIX 84-I. All these systems may have potential applications in DSX operations as well as treat Li-ion battery leaching liquors containing dilute or moderate concentrations of Ni and Co (MANSUR et al., 2022; SANTOS et al., 2015). A conceptual flowsheet presenting the systematic recovery of metals in the loaded organic solution using the extractive systems investigated in this work capable of simultaneously extract Ni and Co over Ca, Mg, Mn, and/or Zn is shown in Figure 3.9.

Table 3.10: Comparison of organic systems that preferentially extract Ni and Co over impurities (Ca, Mg, Mn, and/or Zn) in terms of separation pH, selectivities ($\beta_{M1/M2}$), percentage extraction, and phase separation ([extractant] = 0.5 M, 40°C, A/O = 1).

Organic system	**Separation group**	**pH**	**(%) Extraction**	**Separation factor**				**Synergistic enhancement factor**	**Phase separation**
Versatic 10	Ni, Co, Cu, Mn, and Zn over Ca e Mg	6.5	Ni: 93% Co: 84% Cu: 98% Zn: 99% Mn: 58%	$\beta_{Cu/Ca}$ = 1,200 $\beta_{Co/Ca}$ = 98 $\beta_{Ni/Ca}$ = 261 $\beta_{Zn/Ca}$ = 1.6x10^{9} $\beta_{Mn/Ca}$ = 21		$\beta_{Cu/Mg}$ = 1,758 $\beta_{Co/Mg}$ = 143 $\beta_{Ni/Mg}$ = 382 $\beta_{Zn/Mg}$ = 2.4x10^{9} $\beta_{Mn/Mg}$ = 39		not applicable	fast
Versatic 10 + Cyanex 301	Ni, Co, Cu, and Zn over Mn, Ca, and Mg	1.5	Ni: 99% Co: 100% Cu: 100% Zn: 100%	$\beta_{Zn/Ca}$ = 7.8x10^{9} $\beta_{Cu/Ca}$ = 7,628 $\beta_{Co/Ca}$ = 2.3x10^{10} $\beta_{Ni/Ca}$ = 1.5x10^{4}	$\beta_{Zn/Mg}$ = 3.7x10^{10} $\beta_{Cu/Mg}$ = 3.6x10^{4} $\beta_{Co/Mg}$ = 1.1x10^{11} $\beta_{Ni/Mg}$ = 7.2x10^{4}	$\beta_{Zn/Mn}$ = 3.2x10^{9} $\beta_{Cu/Mn}$ = 3,200 $\beta_{Co/Mn}$ = 9.4x10^{9} $\beta_{Ni/Mn}$ = 6,330		R_{Ni} = 1.0 R_{Co} = 1.0 R_{Cu} = 0.9 R_{Zn} = 0.9	fast
Versatic 10 + LIX 84-I	Ni, Co, and Cu over Mn, Zn, Ca, and Mg	5	Ni: 99% Co: 82% Cu: 99%	$\beta_{Cu/Ca}$ = 8,392 $\beta_{Co/Ca}$ = 553 $\beta_{Ni/Ca}$ = 3.4x10^{7}	$\beta_{Cu/Mg}$ = 9,732 $\beta_{Co/Mg}$ = 641 $\beta_{Ni/Mg}$ = 4.0x10^{7}	$\beta_{Cu/Mn}$ = 1.5x10^{4} $\beta_{Co/Mn}$ = 2,900 $\beta_{Ni/Mn}$ = 1.8x10^{8}	$\beta_{Cu/Zn}$ = 4.0x10^{4} $\beta_{Co/Zn}$ = 2,637 $\beta_{Ni/Zn}$ = 1.6x10^{8}	R_{Ni} = 2.0x10^{5} R_{Co} = 0.9 R_{Cu} = 1.0	moderate
Versatic 10 + LIX 860N-IC	Ni, Co, and Cu over Mn, Zn, Ca, and Mg	4	Ni: 81% Co: 76% Cu: 99%	$\beta_{Cu/Ca}$ = 3.3x10^{4} $\beta_{Co/Ca}$ = 1,519 $\beta_{Ni/Ca}$ = 1,989	$\beta_{Cu/Mg}$ = 2.1x10^{5} $\beta_{Co/Mg}$ = 9,817 $\beta_{Ni/Mg}$ = 1.3x10^{7}	$\beta_{Cu/Mn}$= 3.0x10^{4} $\beta_{Co/Mn}$ = 1,400 $\beta_{Ni/Mn}$ = 1,800	$\beta_{Cu/Zn}$= 1.5x10^{4} $\beta_{Co/Zn}$ = 68 $\beta_{Ni/Zn}$ = 88	R_{Ni} = 4.8 R_{Co} = 0.01 R_{Cu} = 0.9	fast

Fonte: próprio autor.

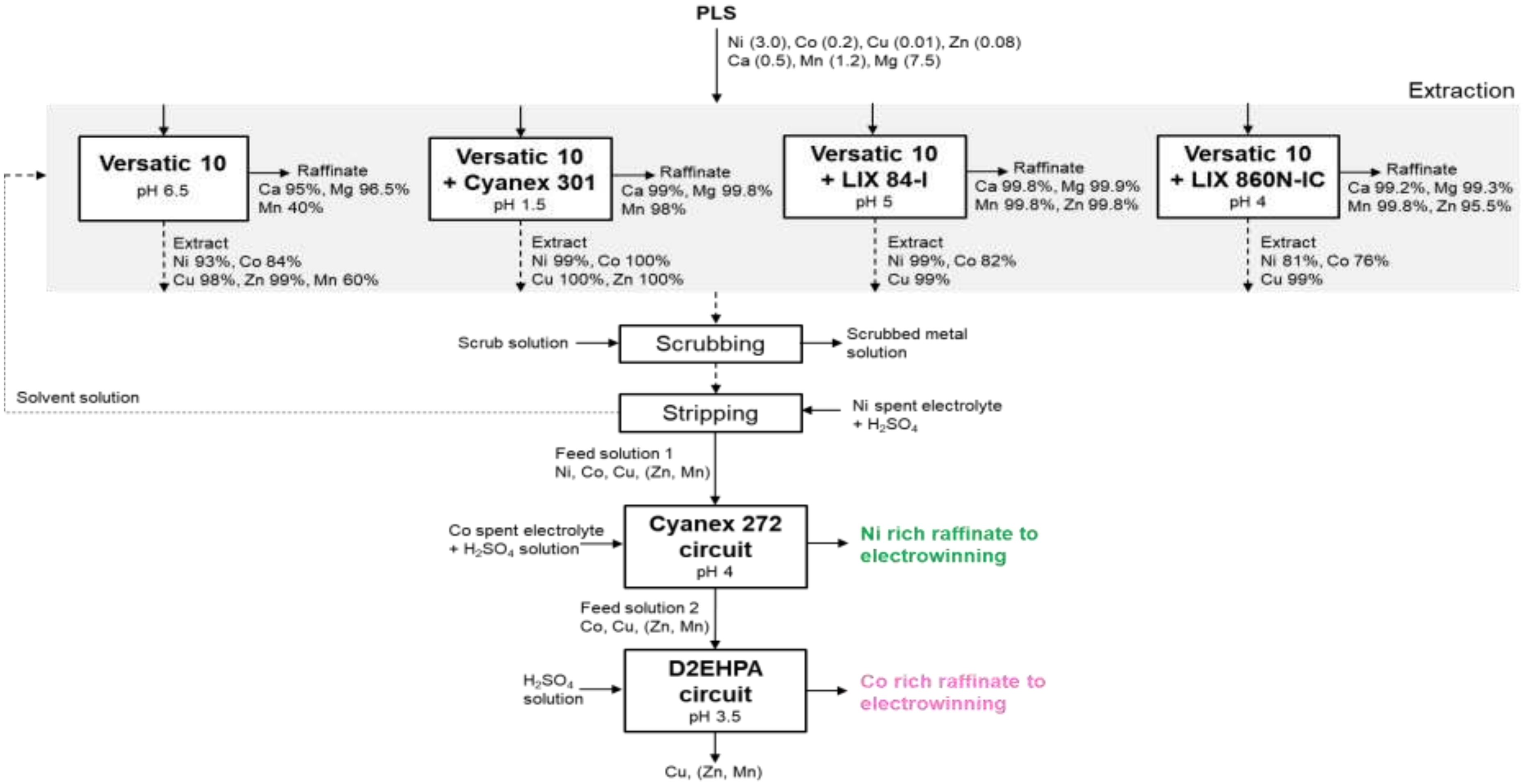


Figure 3.9: Conceptual flowsheet of recovery of Ni and Co using Versatic 10, Versatic 10 + Cyanex 301, Versatic 10 + LIX84-I, and Versatic 10 + LIX860N-IC (1 stage, 40°C, A/O = 1, concentration of metals in g/L). Fonte: próprio autor.

By contrast, the Versatic 10 + D2EHPA and Versatic 10 + Cyanex 272 systems preferentially extract Zn, Cu, and Mn over Ni and Co, as shown in Table 3.11. These systems behave similarly, but Versatic 10 + D2EHPA performs better because Ca is not extracted simultaneously with Co and Ni. The Versatic 10 + D2EHPA system seems to be interesting to treat NiMH spent battery liquors (RODRIGUES and MANSUR, 2010; MANTUANO et al., 2006; LE and LEE, 2020). The synergism obtained in the Mn extractions can facilitate the Mn/Ni separation. Another application for this system would be in the removal of impurities in liquors obtained from the dissolution of MHP since the high concentration of Ni (80-100 g/L) favors the removal of impurities in a preferential manner (GUIMARÃES et al., 2014; SOUZA and MANSUR, 2019). These operations can be performed in stages: (i) extraction of Mn, Zn, Ca, and Cu at suitable pH, (ii) scrubbing of co-extracted Ni and Co, (iii) stripping of impurities, and (iv) separation of Ni and Co with Cyanex 272 as illustrated in Figure 3.10. The Versatic 10 + Cyanex 272 system may demand a greater number of extraction circuits for purification of Ni and Co. However, as values shown in such flowsheets were obtained in one single extraction contact (A/O = 1), better results can be achieved by performing staged operations under optimized operating conditions.

Table 3.11: Comparison of organic systems that preferentially extract the impurities over Co and Ni in terms of separation pH, selectivities

<table>
<tr><th>Organic system</th><th>Separation group</th><th>pH</th><th>(%) Extraction</th><th colspan="4">Separation factor</th><th>Synergistic enhancement factor</th><th>Phase separation</th></tr>
<tr><td>Versatic 10 + D2EHPA</td><td>Ca, Zn, Cu and Mn (Mg) over Ni and Co</td><td>3</td><td>Ca: 97%
Zn: 100%
Cu: 64%
Mn: 88%
Mg: 21%</td><td colspan="2">$\beta_{Cu/Co}$ = 47
$\beta_{Zn/Co}$ = 1.9x10^9
$\beta_{Ca/Co}$ = 839
$\beta_{Mn/Co}$ = 190
$\beta_{Mg/Co}$ = 7.4</td><td colspan="2">$\beta_{Cu/Ni}$ = 288
$\beta_{Zn/Ni}$ = 1.2x10^{10}
$\beta_{Ca/Ni}$ = 5,100
$\beta_{Mn/Ni}$ = 1,200
$\beta_{Mg/Ni}$ = 45</td><td>R_{Cu} = 1.0
R_{Zn} = 0.9
R_{Ca} = 0.7
R_{Mn} = 1.5
R_{Mg} = 0.9</td><td>fast</td></tr>
<tr><td>Versatic 10 + Cyanex 272</td><td>Zn, Cu, Mn over Co, Ca, Mg, and Ni</td><td>3.5</td><td>Zn: 100%
Cu: 49%
Mn: 28%</td><td>$\beta_{Cu/Co}$ = 15
$\beta_{Zn/Co}$ = 1.1x10^9
$\beta_{Mn/Co}$ = 6.3</td><td>$\beta_{Cu/Ni}$ = 1,400
$\beta_{Zn/Ni}$ = 1.1x10^{11}
$\beta_{Mn/Ni}$ = 576</td><td>$\beta_{Cu/Ca}$ = 26
$\beta_{Zn/Ca}$ = 2.0x10^9
$\beta_{Mn/Ca}$ = 11</td><td>$\beta_{Cu/Mg}$ = 389
$\beta_{Zn/Mg}$ = 3.0x10^{10}
$\beta_{Mn/Mg}$ = 163</td><td>R_{Cu} = 0.8
R_{Zn} = 0.9
R_{Mn} = 0.8</td><td>fast</td></tr>
</table>

($\beta_{M1/M2}$), percentage extraction, and phase separation time ([extractant] = 0.5 M, 40°C, A/O = 1).

Fonte: próprio autor.

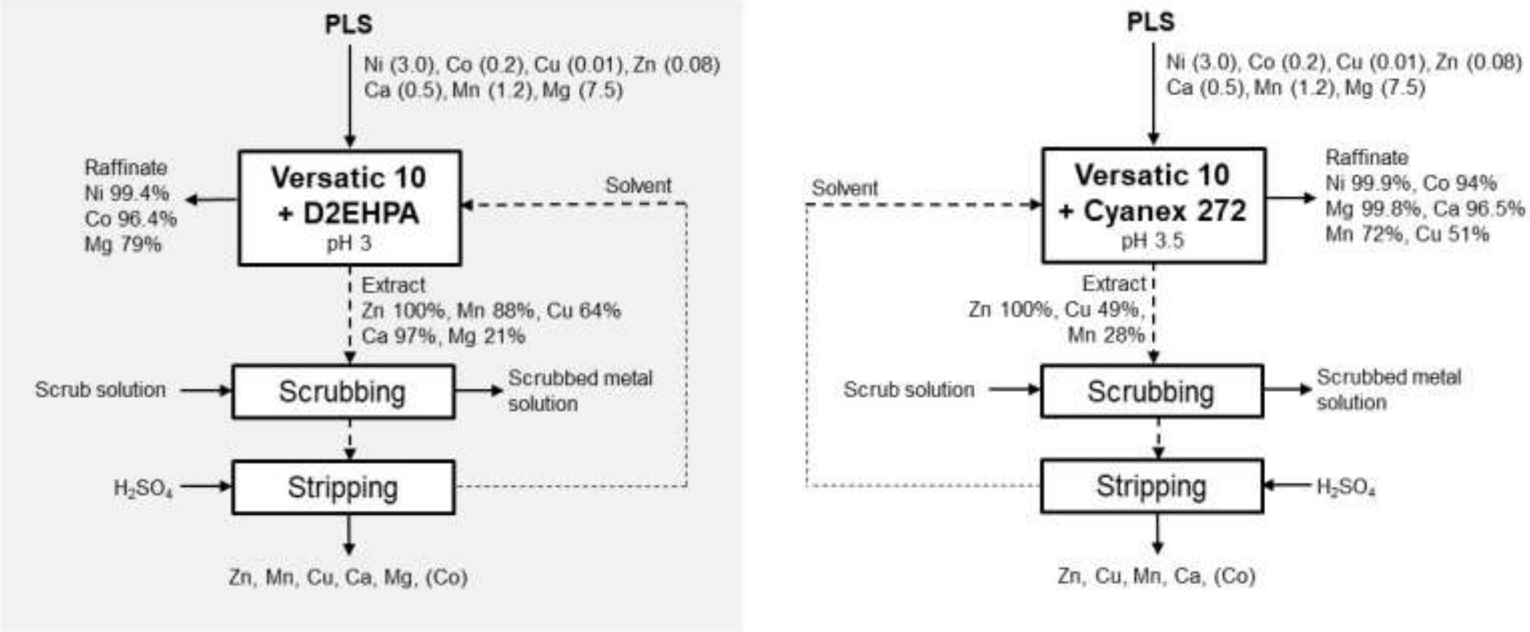


Figure 3.10: Conceptual flowsheet of recovery of Ni and Co using Versatic 10 + D2EHPA and Versatic 10 + Cyanex 272 (1 stage, 40°C, A/O = 1, concentration of metals in g/L). Fonte: próprio autor.

Finally, based on the Co/Ni selectivities shown in Table 3.12, Cyanex 272 alone has proven to be the most efficient organic system to separate Co over Ni in sulfate media at pH ≥ 3.5, thus confirming it as the globally dominant reagent used industrially for such a separation. Today, similar competing reagents, such as Ionquest 290 (Rhodia) and LIX 272 (Cognis), are on the market (SOLE, 2008). The following organic systems evaluated in this study are not shown in the table because $\beta_{Co/Ni} < 1$ was obtained at pH 2-5.5: Cyanex 301, Versatic 10 + Cyanex 301, Versatic 10 + LIX 84-I, and Versatic 10 + LIX 860N-IC.

Table 3.12: Selectivity Co/Ni at varying pH ([extractant] = 0.5 M, 40°C, A/O = 1).

pH	**Versatic 10**	**D2EHPA**	**Cyanex 272**	**LIX 84-I**	**LIX 860N-IC**	**Versatic 10 + D2EHPA**	**Versatic 10 + Cyanex 272**
2	0.1	45	7	3.5	0.5	2.8	2.5
2.5	0.2	22	9	18	1.3	6.0	2.5
3	1.2	17	34	2.1	2.8	6.1	23
3.5	1	11	380	1.8	62	6.5	91
4	2	32	139	1.8	∞	5.7	244
4.5	3	92	4679	2.7	∞	6.1	763
5	0.4	147	6474	3.5	∞	6.9	1646
5.5	0.7	147	∞	10	∞	7.4	626

∞: very high $\beta_{Co/Ni}$ was obtained because $[Co]_{aq} \approx 0$.
Fonte: próprio autor.

3.4 CONCLUSIONS

Versatic 10 and its mixture with D2EHPA, Cyanex 272, Cyanex 301, LIX 84-I, and LIX 860N-IC were studied to identify potential organic systems to separate Ni and Co over Ca, Cu, Mn, Mg, and Zn, typical impurities of lateritic sulfuric liquors after Al, Fe, and Cr removal by precipitation. For the evaluated operating conditions, extractions should be performed preferentially at pH < 6 so as to avoid emulsion formation and high viscous loaded organic phases. Two main organic system groups were identified:

(i) Systems capable of a selectively extract Ni and Co together over Ca and Mg, which may have a potential application in DSX operations, the main conclusions are:

- Versatic 10: Cu, Zn, Ni, Co, and Mn are preferentially extracted over Ca and Mg at pH 6. Cu can be selectively separated at pH 5. Ni, Co, Zn, and Mn are co-extracted due to the low $pH_{1/2}$ difference between them.
- Versatic 10 + Cyanex 301: high affinity for Cu and Zn; consequently, Ni, Co, Zn, and Cu are extracted over Mn, Ca, and Mg (favorable pH 1.5). Antagonism was verified for Mg, Ca, Ni, Cu, and Zn; for Mn, antagonism may enhance Co and Ni separation from Mn at pH 1-2, synergism occurred at $pH \geq 3$.
- Versatic 10 + LIX 84-I: Cu, Ni, and Co can be separated from Zn, Mn, Ca, and Mg at pH 5. Synergism found on Ni extractions and antagonism for Ca, Cu, Co, Mn, Mg, and Zn. Slow phase separation verified at $pH > 3.5$.
- Versatic 10 + LIX 860N-IC: preferential extraction of Cu, Ni, and Co over Zn, Mn, Ca, and Mg; separation can occur at pH 4 with synergism for Ni. Regarding Zn, synergism was found at pH 4-6 and antagonism at $2 \leq pH < 4$. Antagonism occurred for Ca, Cu, Co, Mn, and Mg at pH 2-6. A slightly faster phase separation, when compared to the Versatic 10 + LIX 84-I system, was verified. The stripping efficiency with an electrolytic Ni solution (1 M H_2SO_4 + 50 g/L Ni) was 81% Ni, 70% Co, and 42% Cu.

(ii) Systems with preferential extraction of impurities over Ni and Co, which may have potential applications to treat concentrated liquors of Ni and/or Co obtained from the dissolution of MHP concentrates, the main conclusions are:

- Versatic 10 + D2EHPA: Zn, Ca, Cu, and Mn can be separated from Ni and Co at pH 3. Synergism was found on Mn extractions and, for Cu, Ni, and Ca, it was pH dependent. Ca was not extracted simultaneously with Co and Ni.
- Versatic 10 + Cyanex 272: Zn, Cu, and Mn can be separated from Ca, Co, Ni, and Mg at pH 3.5. Synergism was verified on Ca extractions, for Cu it was pH dependent, while antagonism was verified throughout the evaluated pH range for Zn, Mn, Co, Ni, and Mg.

Acknowledgments

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4 DESENVOLVIMENTO DE UMA ROTA CONCEITUAL DE EXTRAÇÃO POR SOLVENTES DIRETA PARA PRODUZIR SOLUÇÕES CONCENTRADAS PURIFICADAS DE COBALTO E NÍQUEL A PARTIR DE UMA SOLUÇÃO SULFÚRICA LATERÍTICA DE NÍQUEL

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Development of a conceptual direct solvent extraction route to produce purified concentrated cobalt and nickel solutions from an Ni lateritic sulfuric solution.

Alexandre Silva Guimarães [1], Georgio Patrício de Souza Resende [1], Iranildes Daniel dos Santos [2] and Marcelo Borges Mansur [1],*

[1] Programa de Engenharia Metalúrgica e de Materiais, COPPE, Universidade Federal do Rio de Janeiro, Av. Horácio Macedo, 2030, Cidade Universitária, 21941-598 Rio de Janeiro, RJ, Brazil.

[2] Instituto Tecnológico Vale, Av. Juscelino Kubitschek, 31, Ouro Preto, MG, Brazil.

* corresponding author. E-mail: marcelo.mansur@metalmat.ufrj.br (M.B. Mansur), https://orcid.org/0000-0003-4916-5028

Abstract

Direct solvent extraction was applied to produce purified concentrated Ni and Co solutions from a synthetic sulfuric liquor containing Ca, Cu, Mg, Mn, and Zn as impurities, which simulates the solution obtained by the sulfation-roasting-leaching process after precipitation of Fe, Al, and Cr. The extractants – neodecanoic acid (Versatic 10), bis 2,4,4-trimethylpenthyl phosphinic acid (Cyanex 272), di-2-ethylhexyl phosphoric acid (D2EHPA), and tributyl phosphate (TBP) – were used in three different solvent extraction circuits. In the first, Versatic 10 (0.5 M) extracted Cu (99.9%), Zn (99.9%), Ni

(99.7%), Mn (54%), and Co (99%) in three theoretical stages (O/A = 2:1, 40°C, pH 6.5), leaving most of the Ca and Mg in the raffinate solution. The co-extracted Ca (15.8%) and Mg (6.9%) were fully scrubbed off the loaded Versatic 10 in two stages (O/A = 5:1, 40°C, pH 6.5). Ni, Co, Cu, Mn, and Zn were stripped out of the Versatic 10 extract using a synthetic Ni spent electrolyte (60 g/L Ni + 2 M H_2SO_4) in two stages (O/A = 9:1, 40°C). This loaded strip liquor was subjected to a second extraction circuit with Cyanex 272 (0.64 M). Three stages were required to extract Co (98.5%), Cu (99.9%), Mn (99.9%), and Zn (99.9%) (O/A = 2:1, 50°C, pH 4), whereas the raffinate solution (82 g/L Ni) was deemed suitable for electrowinning. Co-extracted Ni was completely scrubbed off the loaded Cyanex 272 in only one stage (O/A = 5:1, 50°C, pH 4). All Co, Cu, Mn, and Zn were stripped out from the scrubbed loaded Cyanex 272 in two stages (O/A = 10:1, 50°C), using a synthetic Co spent electrolyte (45 g/L Co + 1 M H_2SO_4). The concentrated Co liquor (58.4 g/L) was submitted to a third circuit using a D2EHPA (0.6 M) + TBP (0.73 M) synergistic system. Because the synergistic effect of Mn is pH dependent (antagonism at $2 \leq \text{pH} < 3$ and synergism at pH 3–6), the Mn/Co separation was maximized by antagonism in the Co extractions at pH 2–6. Zn was fully extracted by the D2EHPA + TBP system in two stages at pH 2 (O/A = 1:3, 50°C), while Mn and Cu were fully extracted from the Zn-depleted raffinate in two stages at pH 3.5 (O/A = 2:1, 50°C). The raffinate solution (58.3 g/L Co) was deemed suitable for Co electrowinning. Cu, Mn, and Zn were stripped out from the loaded D2EHPA + TBP in three stages (O/A = 2.5:1, 50°C), using 1 M H_2SO_4. A simplified flowsheet of the purification conceptual route is presented.

Keywords: solvent extraction; nickel; cobalt; lateritic leach solutions; synergism.

4.1 INTRODUCTION

A sulfation-roasting-leaching process was applied to a Brazilian lateritic Ni ore (RIBEIRO et al., 2021). To remove Al, Cr, and mainly Fe, the obtained liquor was subjected to a two-stage precipitation step using NH_4OH solution and calcium oxide (CaO) at 90°C (SILVA et al., 2022). Two main strategies could be applied to obtain an Ni-rich stream from this liquor.

In the first strategy, the pre-purified liquor can be precipitated with MgO and/or CaO to obtain an intermediate product called mixed hydroxide precipitate (MHP) (XU et al., 2022; CHENG et al., 2015; CHONG et al., 2013; MUBAROK and LIEBERTO, 2013; WILLIAMS et al., 2013; HARVEY et al., 2011; SIST and DEMOPOULOS, 2003). The

MHP is transported to a refinery plant and re-leached with H_2SO_4 solution, thus obtaining a concentrated liquor containing Ni (70–90 g/L), Co (1–2 g/L) and impurities, such as Ca, Mn, Cu, Mg, Zn (SANTANILLA et al., 2021; CHONG et al., 2013; SOLE and COLE, 2003). In this process route, solvent extraction (SX) with Cyanex 272 (0.64 M, bis(2,4,4-trimethylpenthyl) phosphinic acid) can be used to separate (Co+Cu+Mn+Zn)/Ni, leaving Ni, Ca, and Mg in the raffinate (GUIMARÃES et al., 2014). To meet the requirements for Ni electrowinning, Ca and Mg concentrations must be lowered, since the former can precipitate and disrupt the aqueous flow in the diaphragms that separate the catholyte and anolyte. At the same time, the latter can change the microstructure and morphology of the deposited Ni, and as a result, the mechanical properties of Ni cathodes can be altered, affecting the stripping and cutting operations (SANTOS et al., 2015; MOHANTHY et al., 2005; TRIPATHY et al., 2001). A synergistic solvent extraction (SSX, mixture of extractants to maximize the selectivity or extraction at a selected pH) circuit was applied to remove both Ca and Mg from the Ni-rich raffinate solution; under optimal conditions, Ca (98%) and Mg (98.4%) were extracted from the concentrated Ni liquor, using D2EHPA (0.3 M, di-2-ethylhexyl phosphoric acid) + Cyanex 272 (0.32 M) at pH 4 (O/A = 1.4:1, two stages, 50°C), thus obtaining a suitable raffinate solution for Ni conventional electrowinning (GUIMARÃES et al., 2020). Another SSX circuit may enable the preferential extraction of Mg (69%) from the Ni-concentrated liquor by using Cyanex 923 (0.13 M, a neutral extractant consisting of a mixture of four trialkyl-phosphine oxides, also called TRPO) + Cyanex 272 (0.64 M) at pH 5 (O/A = 1:1, one stage, 50°C), followed by a Ca extraction (51%) using D2EHPA at pH 3 (0.15 M, O/A = 1:1, one stage, 50°C). Both steps require staged operations (GUIMARÃES and MANSUR, 2022). The raffinate solution was therefore deemed adequate to obtain Ni cathodes by electrowinning.

The second strategy involves direct solvent extraction (DSX) to treat the pre-purified leach liquor. This route avoids intermediate precipitation, re-leach, and filtration steps, since the mining and refinery plants are integrated. Extractants with a strong affinity for Ni and Co, thus leaving the main impurities Ca, Mn, and Mg in the raffinate solution, are commonly used (KURSUNOGLU et al., 2017; CHENG et al., 2015; 2010; DONEGAN, 2006; MANSUR et al., 2022). Bulong (Australia, plant closed in 2003), the first DSX industrial plant to treat Ni lateritic liquor, consisted of three SX circuits. In the first, Cyanex 272 (16% v/v, 45°C) was used to preferentially extract Co (98.2%), Cu, Mn, and Zn from Ni, Ca, and Mg. After stripping, sulfide precipitation was applied to remove Mn. The obtained Co, Cu, and Zn sulfides were then re-leached and treated to remove Zn (second SX circuit, using D2EHPA as an extractant) and Cu (ion exchange), and finally recover Co by electrowinning. The Co-depleted raffinate was treated in a third SX circuit using Versatic 10 (neodecanoic acid) to extract Ni (98.5%). From the loaded Versatic 10, Ni was recovered, using an Ni spent electrolyte and electrowon. One reported disadvantage was the formation of gypsum (DONEGAN, 2006). PRESTON and du PREEZ (2000) proposed adding 4-(5-nonyl) pyridine to the Versatic 10 to improve the Ni/Ca separation; however, despite the excellent result found ($\Delta pH^{SSX}_{1/2(Ca-Ni)} \approx 3.5$), pyridine is not a commercially available reagent. In addition, crud formation was also reported by Donegan (2006). The high Mg concentration (16 g/L) in the liquor resulted in an additional consumption of anhydrous ammonia to neutralize the H^+ ions released during Mg co-extraction in the Co extraction circuit (DONEGAN, 2006).

DSX is currently applied in the Goro nickel-cobalt mine (New Caledonia) to treat a lateritic Ni liquor, using Cyanex 301 (bis(2,4,4-trimetylpentyl) dithiophosphinic acid). Ni, Co, and Zn are almost fully extracted at pH < 2, while Ca, Mg, and Mn are rejected by the raffinate. Ni, Co, and Zn are stripped out with HCl solution, which is treated by ion exchange for Zn removal. Co is extracted from the Zn-depleted solution using tertiary octylamine (TOA) and precipitated as a carbonate. Ni in the solution is recovered as an oxide by pyrohydrolysis (VAHED et al., 2004; MIHAYLOV et al., 2000). Since Cyanex 301 has a strong tendency to oxidize, Fe and Cu must be eliminated from the liquor before feeding the SX step in order to avoid its dimerization due to oxidation by redox coupling, as reported by Sole et al. (1993). Other problems identified in the Goro plant are related to the need to maintain an inert atmosphere to prevent Cyanex 301 oxidation, its constant regeneration in the SX circuit, as the high consumption of HCl (6 M) as a stripping agent.

Because DSX may involve lower capital and process costs when compared to the MHP route (WILLIS, 2008), Kursunoglu et al. (2017) applied it to treat the lateritic leach liquor from Çaldağ (Turkey). In the first SX circuit, practically all Ni and Co (> 98%) were extracted by Versatic 10 (20% v/v) + TBP (5% v/v, tributyl phosphate used as a modifier) at pH 7.2 (O/A = 1:1, 40°C). In addition, 94% Mn, 65% Ca, and 12% Mg were co-extracted. A selective stripping step, using dilute H_2SO_4 solution, was then applied to remove 90% Mg and 16% Ca from the loaded Versatic 10 in three stages at pH 5.6 (O/A = 1:1, 40°C). Ni, Co, Mn, Ca, and Mg were fully stripped out at pH 0.75, using an H_2SO_4 solution. In the second SX circuit, Co/Ni separation was achieved using Cyanex 272 (15% v/v) + TBP (5% v/v, used as a modifier). Co (94%) and Mn (98%) were extracted at pH 5 (O/A = 1:1, 40°C); however, a significant amount of Mg (40%) and Ca (41%) were co-extracted. To avoid gypsum formation during Co stripping, a scrubbing step, using a 20 g/L Co solution, was applied. Subsequently, 93% Mn and all Ca, Mg, and Ni were scrubbed off the loaded Cyanex 272 in two stages (O/A = 1:1). Co and Mn were fully stripped out from the scrubbed loaded Cyanex 272 with H_2SO_4 solution at pH 1 (KURSUNOGLU et al., 2017).

In this context, the present work aims to develop a conceptual DSX route to treat Ni lateritic sulfuric solutions similar to those obtained by using the aforementioned sulfation-roasting-leaching process, applied to a Brazilian lateritic Ni ore to produce purified/concentrated Co and Ni solutions. Using commercially available extractants, the route was designed to reject Ca and Mg in the raffinate of the first SX circuit in order to minimize gypsum formation, excessive base consumption for neutralization, and the deleterious effects in Ni electrowinning. This work includes the optimization of the main steps of the DSX route, which is presented in a simplified flowsheet.

4.2 EXPERIMENTAL

4.2.1 Aqueous and organic solutions

The aqueous solutions used in this work (extraction, scrubbing, and stripping tests) were prepared by dissolving the selected metal sulfates (analytical grade, Synth, minimum 98% purity) in distilled water. The chemical composition of the solution that fed the first SX circuit is shown in Table 4.1. This composition reproduces the liquor obtained by the sulfation-roasting-leaching process applied to a lateritic Brazilian Ni ore after the removal of Fe, Al, and Cr by chemical precipitation (SILVA et al., 2022). H_2SO_4 (Synth, 95% purity) was used to adjust the pH of the aqueous solutions and for the stripping tests.

Table 4.1: Chemical composition of the sulfuric synthetic liquor feed.

Metal	**Ni**	**Co**	**Mn**	**Ca**	**Mg**	**Zn**	**Cu**
Concentration (g/L)	3.0	0.2	1.2	0.5	7.5	0.08	0.01

Fonte: próprio autor.

The organic solutions were obtained by solubilizing the following extractants in aliphatic kerosene Exxsol D80 (aromatic content < 0.5% w/w): Versatic 10 (Lanxess, 95% purity), D2EHPA (Baysolvex-Lanxess, 95% purity), Cyanex 272 (Cytec Canada, 85% purity), and TBP (Sigma Aldrich, 97% purity). All organic reagents were used as received without further purification.

4.2.2 Solvent extraction and stripping tests

The SX tests were performed using a glass reactor (1 L) immersed in a temperature-controlled water bath. The aqueous and organic solutions were heated separately to reach the target temperature. At a given O/A volume ratio, the solutions were mechanically stirred using a stainless-steel impeller coupled to a mechanical stirrer (Kacil, model RM-02) for 10 min using a marine-type impeller. According to previous studies, the mixture was held to rest for 5 min to obtain phase disengagement (MARTINS et al., 2020; LOBATO et al., 2016; MANSUR et al., 2003). The pH was measured using a pH electrode (Digimed, model DM-22, with temperature corrector). At a selected pH, aliquots of both phases were withdrawn to keep the O/A ratio constant. The pH adjustment was carried out by dropping NaOH solution (1, 2.5, 5, and 10 M; Synth, analytical grade, 99% purity) during stirring. Extraction/stripping distribution isotherm tests were performed at changing O/A ratios by mixing the organic and aqueous solutions at a given pH/acidity and temperature.

4.2.3 Chemical analysis and operating parameters

The metal concentration in the aqueous solution samples was quantitatively accessed by an energy-dispersive X-ray fluorescence spectrometer (Shimadzu, model EDX-7000, calibration curve method). The content of Cu and other metals at comparatively low concentration levels in selected samples were determined by atomic absorption spectroscopy (Agilent, model 55B). The metal contents in the organic solution were quantified by mass balance.

To determine the extraction efficiency (E_M), the distribution coefficient (D_M), the separation factor ($\beta_{M1/M2}$), and the synergism enhancement factor (R_M) in the SX circuits, the following equations were used:

$$E_M = 100\frac{[M]_i-[M]_f}{[M]_i} \tag{4.1}$$

$$D_M = \frac{[M]_i-[M]_f}{[M]_f}$$

(4.2)

$$\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}}$$

(4.3)

$$R_M = \frac{D_{M(TBP+D2EHPA)}}{D_{M(\text{TBP})}+D_{M(D2EHPA)}} \tag{4.4}$$

wherein $[M]_i$ and $[M]_f$ are the initial and final metal concentrations in the aqueous solution, respectively. $D_{M(TBP+D2EHPA)}$, $D_{M(TBP)}$, and $D_{M(D2EHPA)}$ refer to the distribution coefficients of metal M extracted by the SSX, consisting of TBP + D2EHPA, TBP, and D2EHPA, respectively. According to the SX theory, $R_M > 1$ indicates a synergistic effect, while $R_M < 1$ represents an antagonistic effect (RITCEY and ASHBROOK, 1984).

4.3 RESULTS AND DISCUSSION

4.3.1 Circuit 1: Co and Ni extraction with Versatic 10

The metal extraction behavior from the sulfuric synthetic liquor using 0.4 M and 0.5 M of Versatic 10 (O/A = 1:1, 40°C) is shown in Figure 4.1. As expected, the higher the extractant content the higher the metal extractions, according to the following pH sequence: Cu > Zn > Ni > Co > Mn >> Ca ≈ Mg. Cu extractions increased from 25% to 40% at pH 2 when Versatic 10 concentration was raised, then reached 98% at pH 5.5. Compared with 0.4 M Versatic 10, Zn extractions increased by 32% and 33% ($\Delta E_{Zn} = E_{Zn}^{0.5\ M\ Versatic\ 10} - E_{Zn}^{0.4\ M\ Versatic\ 10}$) at pH 5.5 and 6, using 0.5 M Versatic 10, and reached 99.9% extraction at pH 6.5. Similarly, the increase in the Ni, Co, and Mn extractions by varying the Versatic 10 concentration from 0.4 M to 0.5 M was found to be ΔE_{Ni} = 9%, 25%, and 23%; ΔE_{Co} = 6.7%, 19%, and 34%; and ΔE_{Mn} = 0.16%, 0.59%, and 5.3% at pH 5, 5.5, and 6, respectively. At pH 6.5, the respective extractions reached 70%, 50%, and 22% as compared to 93%, 84%, and 58%, using 0.4 M and 0.5 M Versatic 10, respectively. Ca and Mg were rejected by Versatic 10 and the extractions at changing Versatic 10 concentrations from 0.4 M to 0.5 M were relatively low: $0.01 \leq \Delta E_{Ca}\ (\%) \leq 4.6$ and $0.01 \leq \Delta E_{Mg}\ (\%) \leq 2.6$ at pH 4-6.5. At pH ≥ 7, emulsion and crud formation in the organic solution occurred. For this reason, it is recommended that Ni and Co extractions be performed at pH < 7, which also favors the minimization of Ca and Mg co-extractions.

The separation factors of Co and Ni in relation to Mn, Ca, and Mg are shown in Table 4.2. It can be seen that $\beta_{Co/Mn}$ and $\beta_{Ni/Mn}$ values were comparatively low (≤ 10) at pH 6.5 for both levels of the Versatic 10 concentration evaluated in this study, thus demonstrating that Mn was co-extracted with Co and Ni as a consequence of the low values of $\Delta pH_{1/2(Mn-Co)}$ = 0.2 and $\Delta pH_{1/2(Mn-Ni)}$ = 0.3, using 0.5 M Versatic 10. In contrast, the separation factor values of Co and Ni in relation to Ca and Mg increased significantly with the increase in Versatic 10 concentration from 0.4 M to 0.5 M as a result of relatively higher Co and Ni extractions, thus showing the higher affinity of Versatic 10 by Ni and Co over Ca and Mg. At pH 6.5, by raising Versatic 10 concentration from 0.4 M to 0.5 M, $\beta_{Co/Ca}$ and $\beta_{Co/Mg}$ values increased from 217 and 101 to 1 592 and 2 802, as well as $\beta_{Ni/Ca}$ and $\beta_{Ni/Mg}$ from 526 and 245 to 4 246 and 7 473, respectively. Based on these results and targeting the highest Ni and Co extractions, 0.5 M Versatic 10 and pH 6.5 were selected for further investigation.

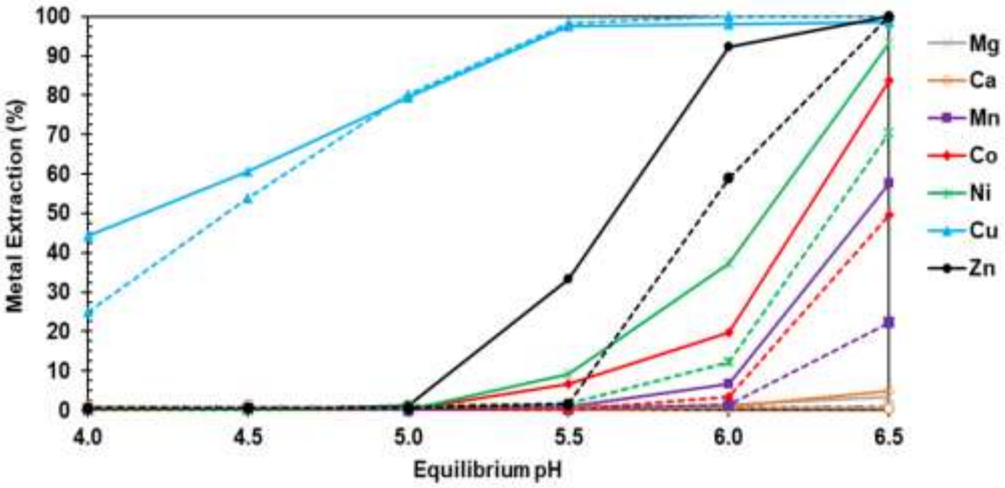

Figure 4.1: Effect of pH on metal extractions from the sulfuric synthetic liquor using 0.4 M (dotted) and 0.5 M (continuous) Versatic 10 (O/A = 1:1, 40°C). Fonte: próprio autor.

Table 4.2: Effect of pH on Co and Ni selectivity compared with Mn, Ca, and Mg at different Versatic 10 concentrations (O/A = 1:1, 40°C).

[Versatic 10] (M)	**pH**	$\beta_{Co/Mn}$	$\beta_{Ni/Mn}$	$\beta_{Co/Ca}$	$\beta_{Ni/Ca}$	$\beta_{Co/Mg}$	$\beta_{Ni/Mg}$
0.4	5	11	21	4	7	1.1	2
	5.5	0.5	7	3	34	0.12	2
	6	3	10	8	32	6	22
	6.5	4	8	217	526	101	245
0.5	5	0.39	0.88	0.30	0.60	0.20	0.47
	5.5	9	12	68	96	10	14
	6	3	8	86	208	195	470
	6.5	4	10	1 592	4 246	2 802	7 473

Fonte: próprio autor.

The extraction distribution isotherms of Co and Ni were conducted by placing the sulfuric synthetic liquor in contact with 0.5 M of Versatic 10 at pH 6.5, 40°C, and O/A ratios of 2:1, 1:1, 1:2, and 1:5. The number of theoretical counter-current extraction stages was determined using the McCabe–Thiele method. It can be seen from Figure 4.2 that 99.7% Ni and 99% Co could be extracted from the liquor using an operation O/A ratio of 2:1 with 2 and 3 extraction stages, respectively. The Co concentration reaches a maximum of 0.15 g/L at an O/A ratio of 1:2 and smoothly decreases to 0.14 g/L at an O/A ratio of 1:5. This is because Ni crowded Co out of the organic solution with the decreasing O/A ratio, since there is more volume of sulfuric synthetic liquor for the same volume of organic solution, implying less Versatic 10 available for a greater amount of metal. Consequently, Ni and Co competition for Versatic 10 increased, and Ni could displace the Co loaded in the organic solution. Similar behavior was reported by Guimarães and Mansur (2018), Souza and Mansur (2019), Hutton-Ashkenny et al. (2015), and Cheng et al. (2010). Regarding Cu and Zn, it was verified that their removal from the sulfuric synthetic liquor required only one theoretical stage with 99.9% of extraction efficiency. Nearly 54% Mn, 3% Ca, and 0.7% Mg were co-extracted with Ni and Co in the three extraction stages, thus obtaining only 0.01 g/L Ni, 0.002 g/L Co, and less than 0.001 g/L of Cu and Zn in the final raffinate solution.

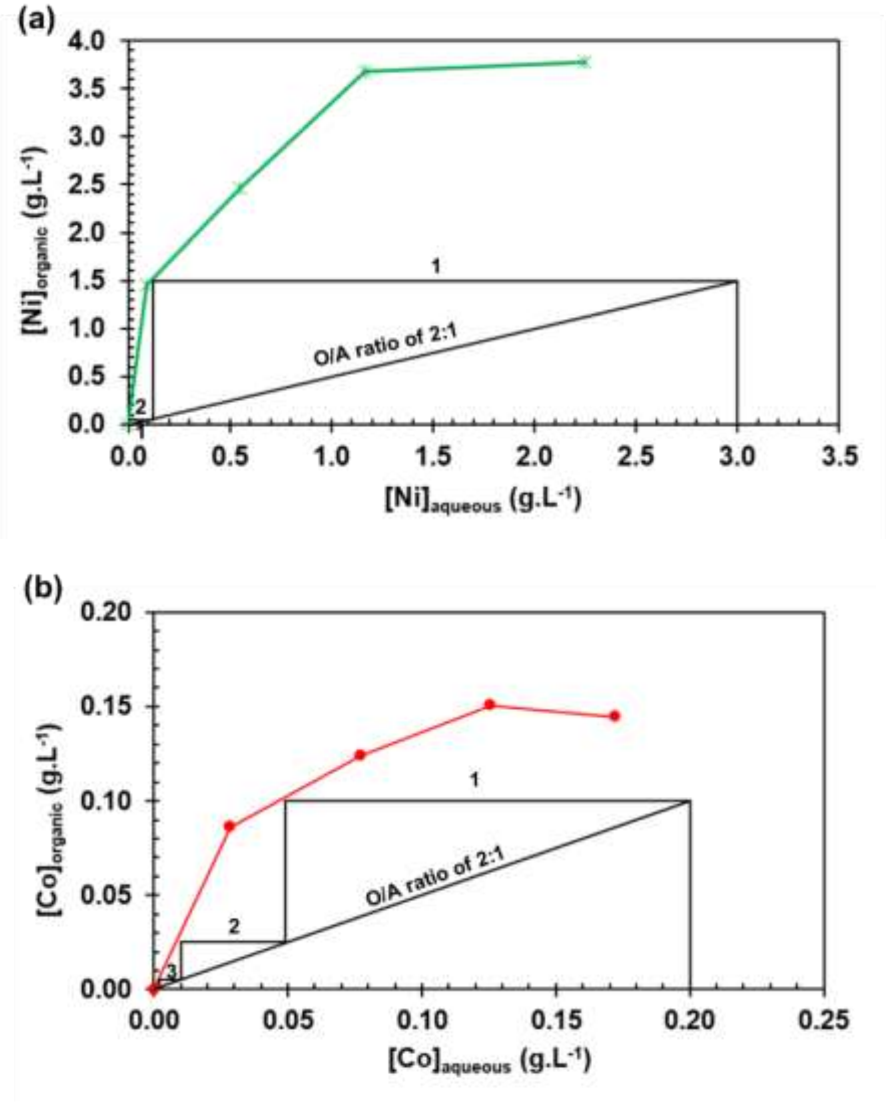

Figure 4.2: McCabe–Thiele diagrams for (a) Ni and (b) Co extractions from the sulfuric synthetic liquor with Versatic 10 (0.5 M, 40°C). Fonte: próprio autor.

Scrubbing tests were performed to scrub out, as much as possible, Mn, Mg, and Ca, which were co-extracted with Ni and Co in the extraction stages. The loaded Versatic 10 (chemical composition in Table 4.3) was contacted twice successively (O/A = 5:1, 40°C, 10 min) with a scrubbing solution consisting of 3 g/L Ni + 0.2 g/L Co (concentration similar to feed solution, Table 4.1). It can be seen from Table 4.3 that Mg and Ca were scrubbed out by Ni and Co. Mg was completely scrubbed off of the loaded Versatic 10 in one stage, while Ca scrubbing efficiency increased from 96% in the first stage to 100% in the second stage. Regarding Mn, partial scrubbing reached 67% of efficiency in two stages. In contrast, Cu and Zn were not scrubbed off since $pH_{scrubbing}$ > $pH^{Zn}_{extraction}$ > $pH^{Cu}_{extraction}$ (Figure 4.1). As a consequence of the scrubbing step, Ni and Co concentrations in the loaded Versatic 10 increased, resulting in a scrubbed organic solution containing 2.40 g/L Ni, 0.13 g/L Co, 0.22 g/L Mn, 0.005 g/L Cu, and 0.04 g/L Zn (Table 4.3). The obtained scrubbed liquor containing Ni and Co (Table 4.3) can be recycled with the feed liquor (Table 4.1) in the extraction stages.

Table 4.3: Scrubbing metal efficiency from the loaded Versatic 10 (0.5 M) in two successive stages using a scrubbing solution containing 3 g/L Ni + 0.2 g/L Co (O/A = 5:1, 40°C, pH 6.5).

Metal	Composition of loaded Versatic 10 (g/L)	Scrubbing efficiency (%)		Composition of scrubbed organic solution (g/L)	Composition of scrubbed liquor (g/L)	
		First stage	Second stage		First stage	Second stage
Mg	0.055	100	-	0	0.275	-
Ca	0.025	96	100	0	0.12	0.0047
Mn	0.650	37	67	0.220	1.21	0.95
Co	0.106	-23	-17	0.130	0.13	0.27
Ni	1.630	-33	-47	2.400	0.73	2.06
Cu	0.005	0	0	0.005	0	0
Zn	0.040	0	0	0.040	0	0

Fonte: próprio autor.

The scrubbed organic solution shown in Table 4.3 was placed in contact with a synthetic Ni spent electrolyte (60 g/L + 2 M H_2SO_4) to obtain the stripping distribution isotherms (40°C) at varying O/A ratios of 1:1, 2:1, 4:1, 8:1, and 10:1. According to the McCabe–Thiele diagrams (Figure 4.3), two counter-current theoretical stages were enough to fully strip Ni and Co, using an operation O/A ratio of 9:1, obtaining a strip liquor containing 83 g/L Ni and 1.35 g/L Co. The variation of Ni concentration (ΔNi) in the loaded strip liquor was found to be 33 g/L, indicating that Ni can be concentrated in an electrolytic matrix from the loaded Versatic 10, implying potential application on an industrial scale. The stripping of Cu, Mn, and Zn was also complete, obtaining 0.045 g/L, 1.94 g/L, and 0.36 g/L in the loaded strip liquor of Ni and Co, respectively.

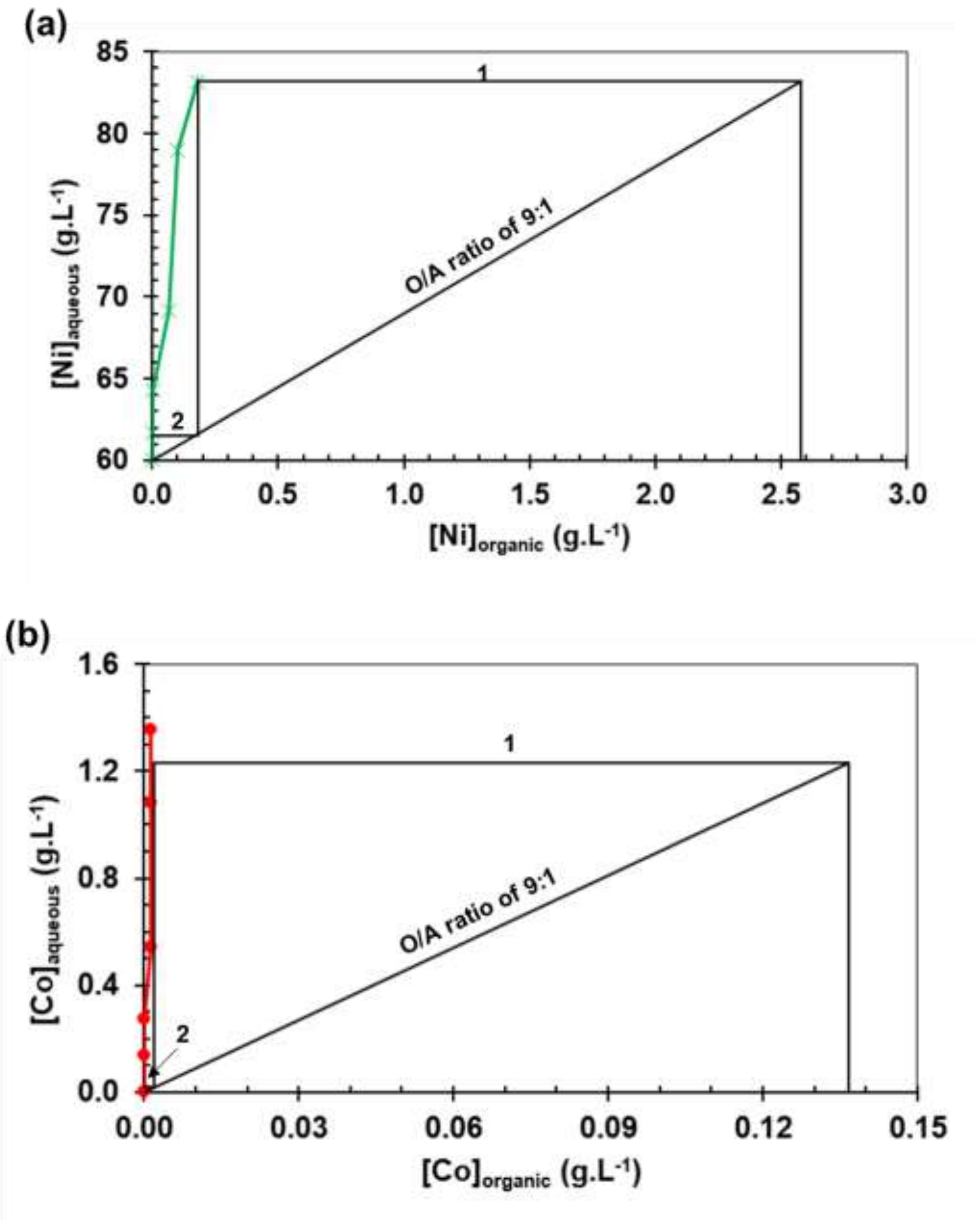

Figure 4.3: McCabe–Thiele diagrams for (a) Ni and (b) Co stripping from the scrubbed loaded Versatic 10 (0.5 M), using a synthetic Ni spent electrolyte (60 g/L Ni + 2 M H_2SO_4) at 40°C. Fonte: próprio autor.

4.3.2 Circuit 2: Co extraction with Cyanex 272

The Ni-rich solution obtained in the stripping stages from the loaded Versatic 10 was submitted to a second circuit with Cyanex 272, aiming to selectively extract Co, Mn, Zn, and Cu, thus leaving Ni in the raffinate stream. The choice for this reagent is due to its high selectivity in the Co/Ni separation, as verified by Guimarães et al. (2024a), Kursunoglu et al. (2017), Donegan (2006), and Flett (2005). Guimarães et al. (2014)

investigated the optimal concentration of Cyanex 272 and pH for the extraction of Zn, Cu, Mn, and Co, using a concentrated Ni liquor with a chemical composition similar to that obtained in the current work (see Table 4.4). It was found that 0.64 M Cyanex 272, pH 3.9–4.0 at 50°C, is an adequate operating condition to promote favorable (Zn+Cu+Co+Mn)/Ni separation ($\beta_{Zn/Ni}$= 11 865 at pH 2.5, $\beta_{Mn/Ni}$= 455, $\beta_{Cu/Ni}$= 829, and $\beta_{Co/Ni}$= 173). Hence, these conditions were adopted in the current work.

Table 4.4: Comparison of chemical compositions of concentrated Ni sulfuric liquors to be treated by DSX using Cyanex 272 as an extractant.

Metal	Ni	Co	Mn	Ca	Mg	Zn	Cu	Reference
Concentration (g/L)	83	1.35	1.94	0	0	0.36	0.045	Current study
	75	2.10	0.55	0.5	3.5	0.06	0.250	Guimarães et al. (2014)

Fonte: próprio autor.

The Co, Mn, Cu, and Zn extraction distribution isotherms were evaluated using different O/A ratios (2:1, 1:1, 1:2, 1:5, and 1:10) at 50°C and pH 4. As shown in Table 4.5, decreasing the O/A ratio from 2 to 0.2 resulted in a higher metal concentration in the loaded Cyanex 272, although $\beta_{Metal/Ni}$ values decreased due to the simultaneous effect of increasing Ni extractions and lower Co, Cu, and Mn extractions as a result of the limited capacity of the organic solution. Similar to the loading Versatic 10 (Figure 4.2), the crowding out effect of Ni can limit the Co loading up to 1.4 g/L. The Metal/Ni separation efficiency reached its maximum at an O/A ratio of 2:1, obtaining $\beta_{Mn/Ni}$ = 2.4×10^5, $\beta_{Co/Ni}$ = 5 700, $\beta_{Cu/Ni}$ = 18 000, and $\beta_{Zn/Ni}$ = 2.5×10^9. To avoid a high number of extraction stages and to minimize the crowding out effect of Ni (only 0.03 g/L of Ni was co-extracted with about 0.52 g/L of Co), the O/A ratio of 2:1 was chosen as the operating ratio. The McCabe–Thiele diagram for Co extraction, shown in Figure 4.4, revealed that three theoretical stages were required to extract 98.5% Co at an operational O/A ratio of 2:1. In addition, only one theoretical stage was necessary to extract all Zn and Mn, while total Cu removal required two stages. The raffinate solution contained approximately 82 g/L of Ni, suitable for electrowinning to obtain Ni cathodes (DONEGAN, 2006).

Table 4.5: Effect of O/A ratio on metal extractions, metal concentration in the extract, and Metal/Ni selectivities ([Cyanex 272] = 0.64 M, 50°C).

O/A ratio	**Extraction (%)**					**Metal concentration in the loaded Cyanex 272 (g/L)**					**Separation factor**			
	Mn	**Co**	**Ni**	**Cu**	**Zn**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	$\boldsymbol{\beta_{Mn/Ni}}$	$\boldsymbol{\beta_{Co/Ni}}$	$\boldsymbol{\beta_{Cu/Ni}}$	$\boldsymbol{\beta_{Zn/Ni}}$
2:1	99.5	82.0	0.08	93.5	100	0.97	0.52	0.03	0.03	0.10	2.4×10^{5}	5 700	18 000	2.5×10^{9}
1:1	89.1	62.7	0.21	87.6	100	1.73	0.80	0.16	0.05	0.20	4 000	814	3 400	9.7×10^{8}
1:2	67.1	42.7	0.26	60.6	100	2.60	1.09	0.41	0.07	0.40	779	285	589	7.7×10^{8}
1:5	42.5	21.9	0.32	34.2	100	4.13	1.39	1.23	0.10	1.00	232	88	163	6.3×10^{8}
1:10	28.3	10.9	0.41	18.2	100	5.49	1.4	3.18	0.11	2.00	96	30	54	4.9×10^{8}

Fonte: próprio autor.

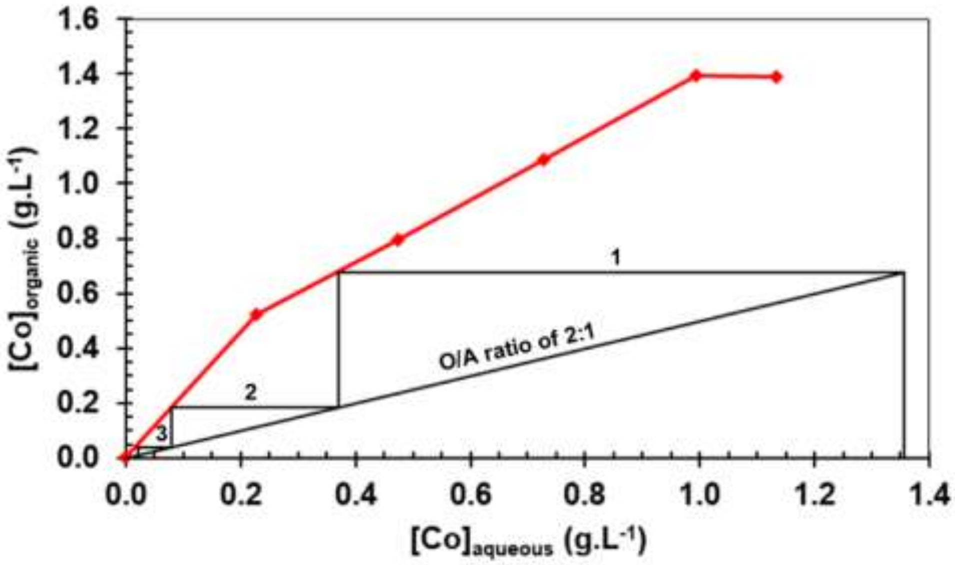

Figure 4.4: McCabe–Thiele diagrams for Co extraction from Ni-rich liquor ([Cyanex 272] = 0.64 M, pH 4, 50°C). Fonte: próprio autor.

To evaluate the removal of co-extracted Ni from the loaded Cyanex 272, scrubbing tests were conducted (O/A = 5:1, pH 4, 50°C), the results of which are shown in Table 4.6. It can be seen that all Ni was scrubbed off from the organic phase in one contact stage by using a scrub solution containing 5 g/L Co. Mn and Cu were slightly scrubbed off in the first stage (11% and 0.5%, respectively). In the second scrubbing stage, Mn removal efficiency reached 26%, implying a greater displacement of Co by the loaded Mn, resulting in a higher concentration of Co in the organic solution. Zn was not scrubbed off because $pH_{scrubbing} > pH^{Zn}_{extraction}$, as reported by Guimarães et al. (2014). The scrubbed organic solution containing 1.3 g/L Co, 0.05 g/L Cu, 0.74 g/L Mn, and 0.19 g/L Zn (Table 4.6) was directed to the stripping tests, while the loaded scrub liquor could be recycled to the extraction stage with Cyanex 272.

A synthetic spent electrolyte containing 45 g/L Co + 1 M H_2SO_4 was contacted with the scrubbed loaded Cyanex 272 at 50°C using different O/A ratios (1:1, 2:1, 4:1, 8:1, and 10:1) in order to obtain the stripping distribution isotherms of Co. The McCabe–Thiele diagram, shown in Figure 4.5, revealed that two theoretical stages were required to strip 99.9% Co at an operational O/A of 10:1, obtaining 58.4 g/L Co in the strip liquor. Only one theoretical stage was required to strip out all Mn, Cu, and Zn. The loaded strip liquor contained 58.4 g/L Co (ΔCo = 13.4 g/L), 7.4 g/L Mn, 0.5 g/L Cu, and 1.8 g/L Zn;

therefore, a further SX step was required to obtain a suitable solution for Co electrowinning.

Table 4.6: Metal scrubbing efficiency from the loaded Cyanex 272 (0.64 M) in two successive stages using a scrubbing solution with 5 g/L Co (O/A = 5:1, 50°C, pH 4).

Metal	**Composition of loaded Cyanex 272 (g/L)**	**Scrubbing efficiency (%)**		**Composition of scrubbed organic solution (g/L)**	**Composition of loaded scrub liquor**	
		First stage	**Second stage**		**First stage**	**Second stage**
Mn	0.83	10.6	25.9	0.74	0.44	0.64
Co	0.62	-104.5	-143.6	1.30	2.02	4.0
Ni	0.089	100	0	0	0.45	0
Cu	0.05	0.5	0.1	0.05	0.001	0.002
Zn	0.19	0	0	0.19	0	0

Fonte: próprio autor.

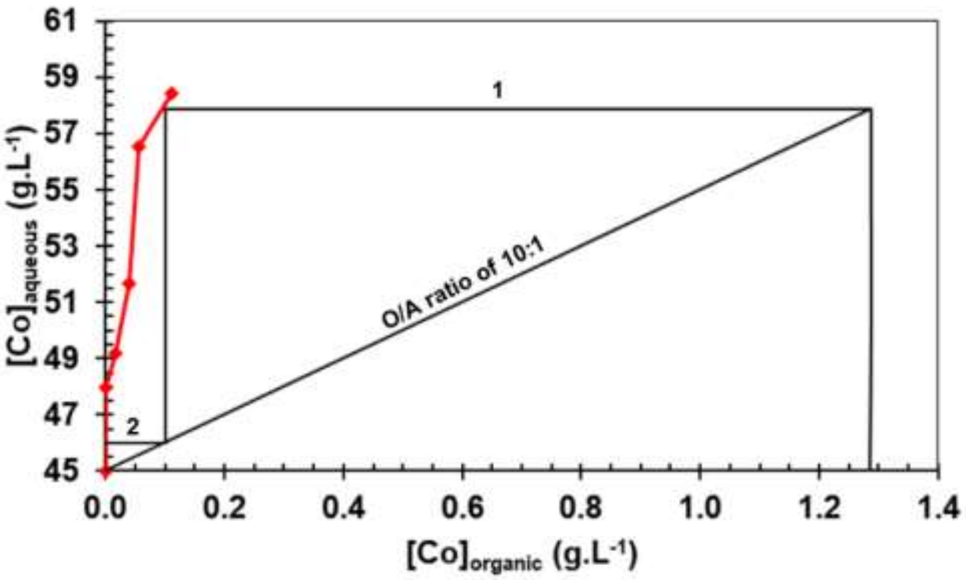

Figure 4.5: McCabe–Thiele diagrams for Co stripping from the scrubbed loaded Cyanex 272 using a synthetic Co spent electrolyte (45 g/L Co + 1 M H_2SO_4) at 50°C.

Fonte: próprio autor.

4.3.3 Circuit 3: Cu, Mn, and Zn extraction with organophosphorous extractants

The extraction behavior of Zn (1.8 g/L), Cu (0.5 g/L) and Mn (7.4 g/L) contained in the Co concentrated liquor (58.4 g/L, obtained from the SX circuit with Cyanex 272, see **section 3.2**) was evaluated using TBP (0.73 M), D2EHPA (0.6 M), and D2EHPA (0.6 M) + TBP (0.73 M) systems to select an organic phase favorable to extracting the maximum of impurities with the minimum of Co (O/A = 1:1, 50ºC). It can be seen in Figure 4.6(a) that TBP rejected mostly Co (E_{Co} < 1.2%), Cu (E_{Cu} < 3.8%), Zn (E_{Zn} < 3.8%), and Mn (E_{Mn} < 8.5%) in the raffinate solution, since it is a neutral organophosphorous extractant whose extraction mechanism occurs through the solvation of neutral inorganic species (BATCHU et al., 2014). Therefore, it can be inferred from these results that there is a weak tendency to form neutral aquocomplexes in the Co-rich sulfuric liquor (MSO_4), thus resulting in low metal extractions with TBP. In addition, as the separation factor values are comparatively low (see Table 4.7), TBP alone is not able to separate Zn, Cu, and Mn over Co as expected. Opposite extraction behavior was verified for Zn, Cu, and Mn when using D2EHPA and D2EHPA + TBP systems (Figure 4.6(b)). The following extraction sequence was found for both systems: Zn >> Cu > Mn > Co, with significant differences in the extractions of Cu, Mn, and Co when the two organic systems are compared. Zn is fully extracted at pH 2 by both systems. Cu extraction by D2EHPA increases by 5% at pH 2 and reaches 100% at pH 3.5. Similarly, Mn extractions by D2EHPA increased by 18% at pH 2, reaching an extraction plateau of 84% at pH 4.5-5.5 and then decreased to 82% at pH 6 due to the crowding out effect of Co. D2EHPA rejected Co ($0.4\% \leq E_{Co} \leq 0.9\%$) in the raffinate solution at pH 2–3; however, at pH > 3, Co extraction increased, with pH reaching 21% at pH 6. Crud formation was observed at pH ≥ 4.5.

It can be seen from Figure 4.6(b) that the addition of TBP to D2EHPA shifted the Cu extraction curve towards higher pH values, obtaining $\Delta pH_{1/2(D2EHPA + TBP - D2EHPA)}$ of 0.3 pH units, characterizing antagonism ($R_{Cu} < 1$) at pH 2–6, as shown in Table 4.8. A different behavior was observed for Mn, whose extractions by the SSX system resulted in antagonism ($R_{Mn} < 1$) at $2 \leq pH < 3$ because $D_{D2EHPA} > D_{D2EHPA + TBP}$ and synergism at pH 3–6 ($R_{Mn} > 1$, $D_{D2EHPA + TBP} > D_{D2EHPA}$), corroborating Kani et al. (2021). The synergistic effect is pH dependent for Mn. Similar behavior was reported by Guimarães et al. (2020) and Guimarães and Mansur (2018) on the extraction of Ca, Mg, and Ni by the D2EHPA + Cyanex 272 system in a concentrated Ni liquor. Antagonism ($R_{Metal} < 1$)

is verified on Zn and Co extractions at pH 2–6, since $D_{D2EHPA} >> D_{D2EHPA + TBP}$ (Table 4.8). Nevertheless, adding TBP to D2EPHA did not affect the Zn extraction behavior (Figure 4.6(b)), but it did affect the extraction behavior of Co by increasing its rejection in the loaded D2EHPA + TBP system (Figure 4.6(b)). As a consequence, the selectivity of the Mn/Co separation increases, reaching its maximum value at pH 3.5, $\beta_{Mn/Co}$= 479 as compared to 24 when using D2EHPA alone, as shown in Table 4.7. At pH > 3.5, $\beta_{Mn/Co}$ decreased due to the higher Co extractions performed by the SSX system. The Zn/Co selectivity increased from 2.4×10^5 (D2EHPA) to 3.3×10^6 (D2EHPA + TPB) due to lower Co extractions at pH 3.5. At pH ≥ 5, crud formation was observed, indicating that extractions must be performed at pH < 5. Although $\beta_{Cu/Co}$ values decreased due to antagonism on Cu extractions (though this does not affect its extraction by the SSX system), the D2EHPA + TBP system and the optimal pH 3.5 with higher $\beta_{Mn/Co}$ values (Table 4.7) were selected for the continuation of the study.

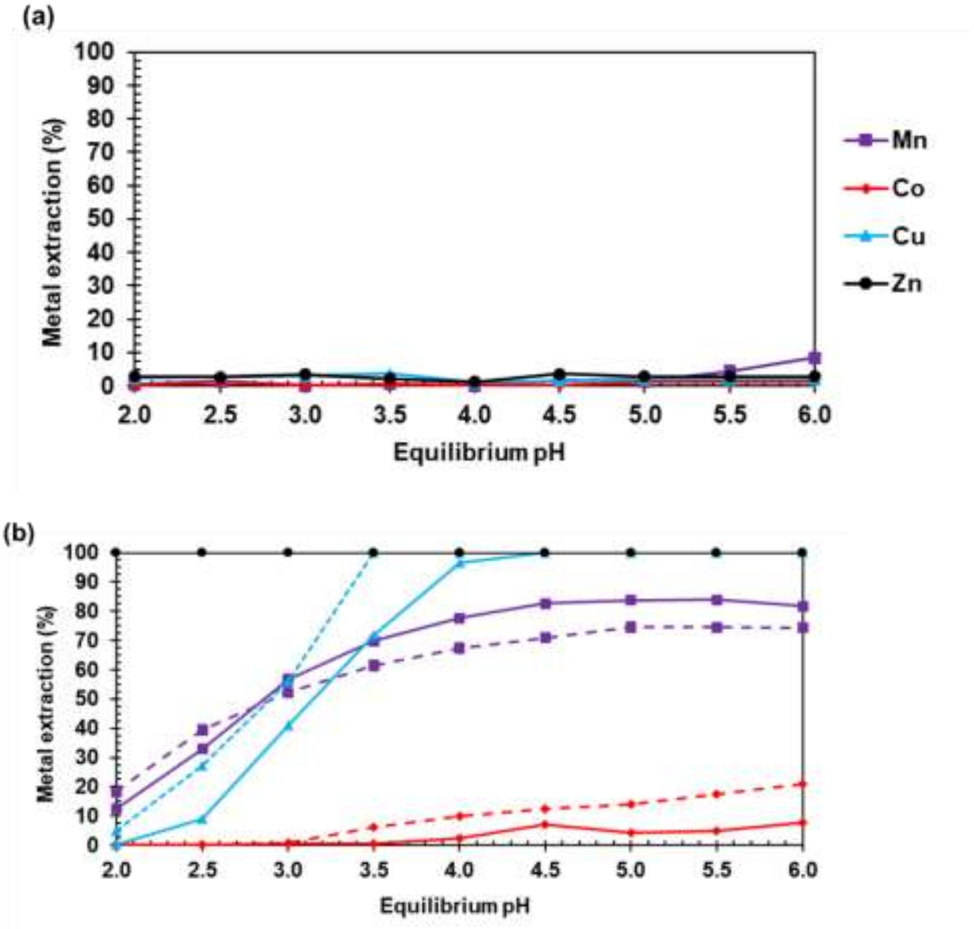

Figure 4.6: Effect of pH on the metal extraction from a synthetic Co-rich sulfuric liquor using (a) TBP (0.73 M), (b) D2EHPA (0.6 M, dotted line), and D2EHPA (0.6 M) + TBP (0.73 M) (continuous line) (O/A = 1:1, 50°C). Fonte: próprio autor.

Table 4.7: Effect of pH on the selectivity of Zn, Cu, and Mn over Co, using TBP (0.73 M), D2EHPA (0.6 M), and TBP (0.73 M) + 0.6 M D2EHPA (0.6 M) (50°C, O/A = 1:1).

pH	**Organic system**								
	TBP (0.73 M)			**D2EHPA (0.6 M)**			**D2EHPA (0.6 M) + TBP (0.73 M)**		
	$\beta_{Zn/Co}$	$\beta_{Cu/Co}$	$\beta_{Mn/Co}$	$\beta_{Zn/Co}$	$\beta_{Cu/Co}$	$\beta_{Mn/Co}$	$\beta_{Zn/Co}$	$\beta_{Cu/Co}$	$\beta_{Mn/Co}$
2.0	45	36	6	4.5×10^{6}	14	63	1.1×10^{7}	2	98
2.5	2	3	1	5.0×10^{6}	117	204	1.1×10^{7}	71	350
3.0	25	22	2	1.8×10^{6}	144	123	4.2×10^{6}	186	352
3.5	5	8	1	2.4×10^{5}	4.3×10^{4}	24	3.3×10^{6}	524	479
4.0	11	10	2	1.5×10^{5}	2.6×10^{4}	19	6.2×10^{5}	1 090	138
4.5	21	9	10	1.1×10^{5}	2.0×10^{4}	17	2.0×10^{5}	3.6×10^{4}	62
5.0	3	2	1	9.8×10^{4}	1.8×10^{4}	18	3.6×10^{5}	6.4×10^{4}	118
5.5	3	2	4	7.6×10^{4}	1.4×10^{4}	14	3.1×10^{5}	5.5×10^{4}	103
6.0	3	2	9	6.0×10^{4}	1.1×10^{4}	11	1.9×10^{5}	3.3×10^{4}	53

Fonte: próprio autor.

Table 4.8: Effect of pH on synergistic enhancement factor of Zn, Cu, Mn, and Co using D2EHPA (0.6 M) + TBP (0.73 M) (50°C, O/A = 1:1).

pH	R_{Zn}	R_{Cu}	R_{Mn}	R_{Co}
2.0	0.99	0.05	0.63	0.30
2.5	0.99	0.25	0.74	0.10
3.0	0.99	0.53	1.20	0.36
3.5	0.99	0.0009	1.44	0.07
4.0	0.99	0.01	1.68	0.23
4.5	0.99	0.97	1.95	0.53
5.0	0.99	0.97	1.75	0.25
5.5	0.99	0.97	1.76	0.23
6.0	0.99	0.97	1.50	0.31

Fonte: próprio autor.

The Zn, Cu, and Mn extraction distribution isotherms were obtained by varying the O/A ratio (2:1, 1:1, 1:2, 1:5, and 1:10) at pH 3.5 and 50°C. It can be seen from Figure

4.7 that the Zn loading capacity by the D2EHPA + TBP system was high (16.1 g/L) due to the very strong affinity that the SSX system has for this metal (Figure 4.6(b)). As a result, Zn crowded Mn and Cu out of the loaded D2EHPA + TBP system at an O/A ratio $\leq$ 1:2, decreasing the loadings of Mn and Cu in the organic solution from 5.75 g/L and 0.28 g/L to 2.66 g/L and 0.09 g/L, respectively, at an O/A ratio = 1:10 (Figure 4.7). Similar behavior was identified by Cheng (2000) using D2EHPA and a solution containing Zn, Cu, Mn, Mg, Co, and Ni. To minimize the crowding out effect of Zn, its removal from the Co-rich sulfuric liquor was evaluated at pH 2, 50°C, using O/A ratios of 2:1, 1:1, 1:1, 1:5, and 1:10. From the McCabe-Thiele diagram (Figure 4.8), it can be seen that two stages were enough to remove all Zn from the Co-rich solution when using an operating O/A ratio of 1:3. The Zn depleted raffinate contains practically all Cu, Mn, and Co.

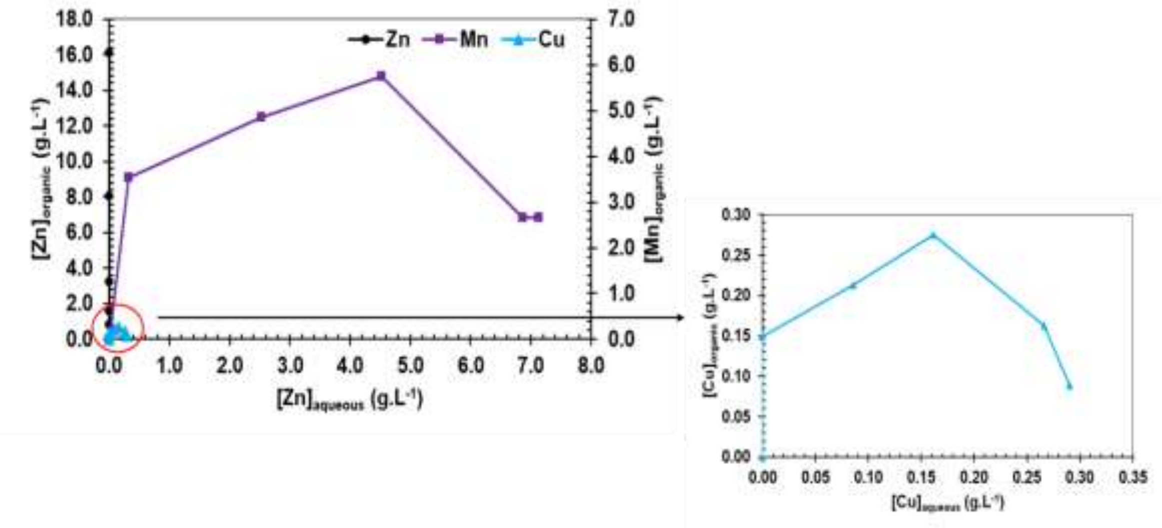

Figure 4.7: Extraction distribution isotherms of Zn, Mn, and Cu from a Co-rich sulfuric solution using TBP (0.73 M) + D2EHPA (0.6 M) at varying O/A ratios (pH 3.5, 50°C).

Fonte: próprio autor.

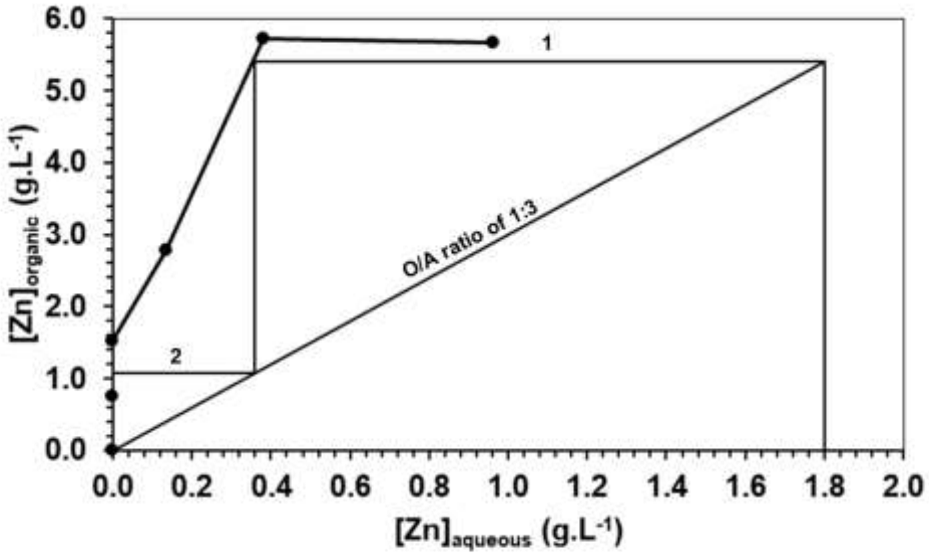

Figure 4.8: McCabe–Thiele diagram for Zn extraction from a Co-rich sulfuric solution using TBP (0.73 M) + D2EHPA (0.6 M) at varying O/A ratios (pH 2, 50°C). Fonte: próprio autor.

This solution was used to evaluate the Cu and Mn extraction distribution isotherms by the SSX system at pH 3.5 and 50°C using different O/A ratios (2:1, 1:1, 1:2, 1:5, and 1:10). The McCabe–Thiele diagrams of Cu and Mn are shown in Figure 4.9. At an operating O/A ratio of 2:1, approximately 99% Mn and 100% Cu are removed from the Co-rich sulfuric solution after two theoretical extraction stages. The raffinate solution contains practically all Co (58.3 g/L), adequate to Co electrowinning. No scrubbing was required because Co extraction by the D2EHPA + TBP system was below 0.12%. The stripping of Zn, Cu, and Mn from the loaded D2EHPA + TBP was evaluated considering that Zn loading obtained at pH 2 was mixed with the loading of Cu and Mn at pH 3.5. By mass balance, the following chemical composition was found in the final extract: 2.9 g/L Mn, 0.12 g/L Cu, 0.77 g/L Zn, and 0.022 g/L Co. An aqueous solution was prepared with the metal concentrations of interest to load the D2EHPA + TBP system at 50°C. The extract obtained was placed in contact with a strip solution containing 1 M H_2SO_4 at 50°C in order to evaluate the stripping distribution isotherms of Zn, Cu, and Mn, using different O/A ratios (1:1, 2:1, 4:1, 8:1, and 10:1). The McCabe-Thiele diagram for each metal is shown in Figure 4.10. Two theoretical stripping stages were required to fully strip out Mn and Zn, and three theoretical stages were needed to strip all Cu at an operational O/A ratio of 2.5:1. The strip liquor obtained contained 7.3 g/L Mn, 0.3 g/L Cu, 1.93 g/L Zn, and 0.06 g/L Co. At an O/A ratio $\geq$ 4:1, the concentration of Mn and Zn tends to remain high in the organic solution. This is because the concentration of metals in the loaded organic solution is at least four times higher when compared with the O/A ratio of 1:1, implying a higher concentration of H_2SO_4 to obtain a greater stripping efficiency.

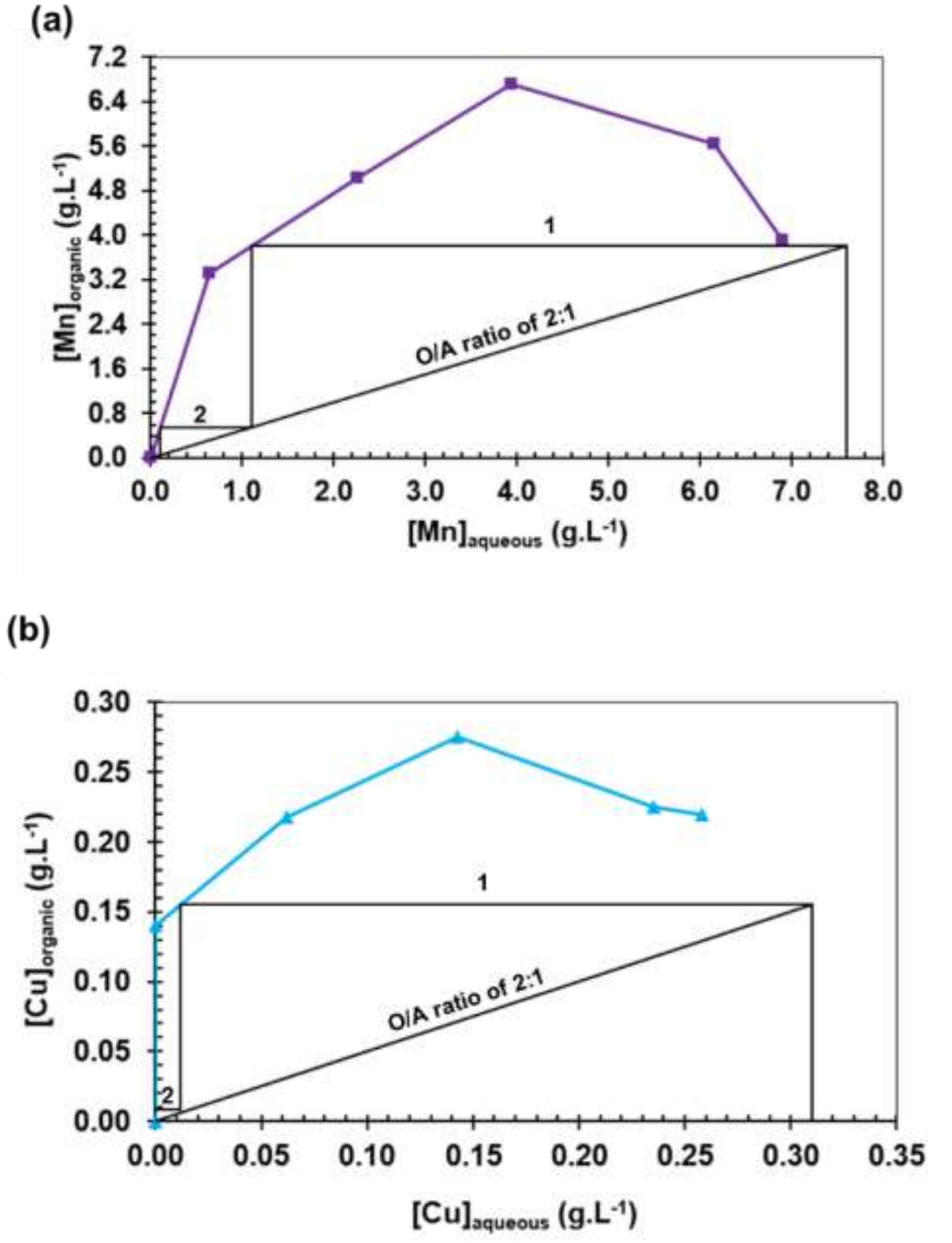

Figure 4.9: McCabe–Thiele diagrams for (a) Mn and (b) Cu extractions from the Zn depleted raffinate solution, using 0.73 M TBP + 0.6 M D2EHPA at varying O/A ratios (pH 3.5, 50°C). Fonte: próprio autor.

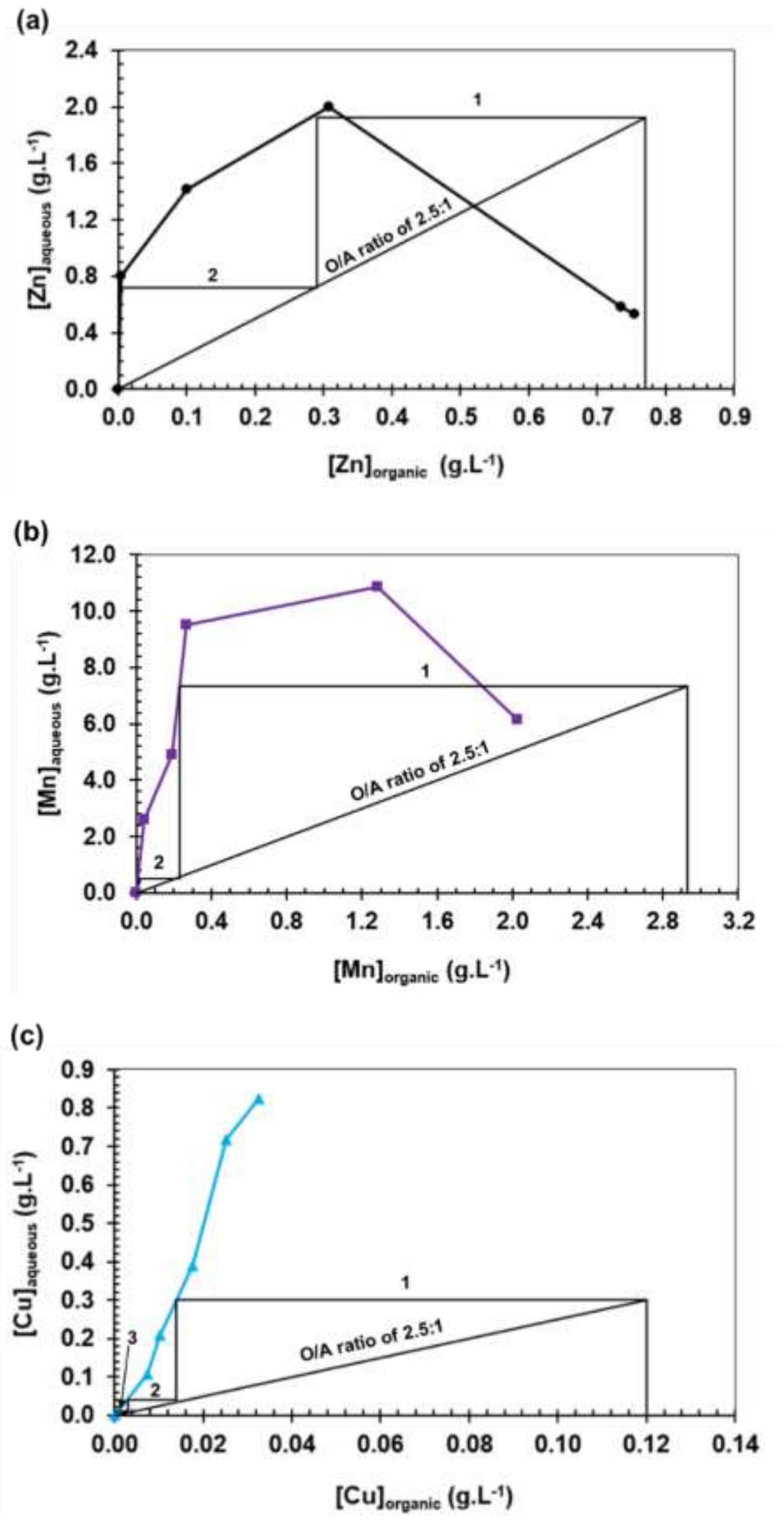

Figure 4.10: McCabe–Thiele diagrams for Zn, Mn, and Cu stripping from the loaded TBP (0.73 M) + D2EHPA (0.6 M), using 1 M H_2SO_4 at 50°C. Fonte: próprio autor.

4.3.4 DSX conceptual route for the purification of Ni and Co

Based on the results obtained in this study, Ni and Co can be separated from each other and impurities using three SX circuits. The simplified flowsheet of the DSX conceptual route developed in this work is shown in Figure 4.11. After Fe, Al, and Cr precipitation treatment, the liquor obtained by the sulfation-roasting-leaching process is fed to the first SX circuit, operated with Versatic 10, targeting the extraction of Ni and Co over Ca and Mg. All Ca and Mg co-extracted with Co and Ni are scrubbed off from the loaded Versatic 10. Complete stripping of Ni and Co (Zn and Cu are also co-extracted) was achieved using a synthetic Ni spent electrolyte (60 g/L + 2 M H_2SO_4). The loaded strip liquor containing approximately 83 g/L Ni and 1.35 g/L Co is submitted to a second SX circuit with Cyanex 272, aiming to separate (Co+Cu+Zn+Mn)/Ni. All Ni co-extracted with Co is scrubbed off from the loaded Cyanex 272 using a scrub solution containing 5 g/L Co. The raffinate solution contains practically all Ni and it can be sent to electrowinning, seeking to produce the Ni cathode. Co (as well as Cu, Mn, and Zn) is recovered from the loaded Cyanex 272 using the Co spent electrolyte (45 g/L Co + 1 M H_2SO_4). The loaded strip liquor is submitted to a third SX circuit using the D2EHPA + TBP synergistic system. All impurities (Zn at pH 2, Cu, and Mn at pH 3.5) are extracted by the SSX system, thus leaving almost all Co in the raffinate, which can be sent to electrowinning. A stripping solution containing 1 M H_2SO_4 was used to recover Mn, Zn, and Cu. The loaded strip liquor containing Mn (7.3 g/L), Zn (1.93 g/L), and Cu (0.3 g/L) can be subjected to a precipitation step using Na_2S to selectively remove Zn and Cu from Mn at pH 5–6 and 25°C, obtaining ZnS and CuS, while Mn remains in the solution (ZHANG and CHENG, 2007; HANNAY and WALSH, 1944; SICUPIRA et al., 2014). Therefore, the proposed conceptual route can produce purified Ni, Co, and Mn concentrated solutions. The circuits consist of closed cycles, seeking to reduce water consumption and decrease environmental pollution. It should be mentioned that the solubility of Versatic 10 at the operating pH (6.5) can be minimized (< 0.006 M) as a consequence of the high concentration of $M'SO_4$ (1.02 M, where M' = Mg, Ca, Zn, Mn, Ni, Co, Cu) in the pregnant leach solution and by adding an inert salt, such as Na_2SO_4, which is inexpensive (RITCEY and ASHBROOK, 1984). Therefore, the losses of this extractant from the raffinate are expected to be low. The additional base (e.g., NaOH, NH_4OH) consumption due to the co-extraction of Cu, Zn, and especially Mn (the main co-extracted impurity that demands a high base consumption, since its concentration in pregnant leach solution is high, 1.2 g/L, Table 4.1) is a concern in the three SX circuits. To minimize base consumption, the Ni and Co stripping steps can be further optimized to consume less H_2SO_4 so as to obtain a strip solution with an acidity in the range of 2.5–3.5 and consequently reduce the costs of neutralizing H^+ ions from the co-extraction (or extraction of) impurities in Ni and Co SX circuits, whose operating pH are 4 and 3.5, respectively. Strict control of these operating conditions can prevent/eliminate Na build-up in the recirculating spent electrolyte solution between the SX circuits and electrowinning tankhouse. If Na builds up in the solutions, a bleed can be done by withdrawing the spent electrolyte stream and by dilution in order to reduce the concentration of Na and Ni (or Co) and return to the leaching/stripping stage (CRUNDWELL et al., 2011). Moreover, the co-extraction of Mn can be decreased in an DSX operation by reducing the concentration of Versatic 10 to 0.4 M, Figure 4.1. This lower entry of Mn into the Cyanex 272 and D2EHPA + TBP circuits would result in a lower base consumption and a lower concentration of Na in the spent electrolyte solution for Ni/Co stripping. To prevent/minimize contamination of extractants between the three circuits, a scrubbing stage of the raffinate solution with a diluent should be added as a recirculating stream of the diluent (DONEGAN, 2006). A carbon column can also be implemented to recover the extractant and minimize/avoid the cross-contamination of reagents among the three SX circuits (RITCEY and ASHBROOK, 1984). The recovered extractant can be transferred to the organic feed solution of each circuit in the solvent make-up stage, as reported by Donegan (2006) at the decommissioned Bulong plant. Additionally, Mg in the raffinate solution containing Ca from the first SX circuit could be recovered through adequate treatment, for instance, by SX with D2EHPA as an extractant (GUIMARÃES and MANSUR, 2017) or calcination to produce reactive MgO to be used as a precipitating agent to recover Ni and Co in the form of MHP (SOUZA et al., 2021).

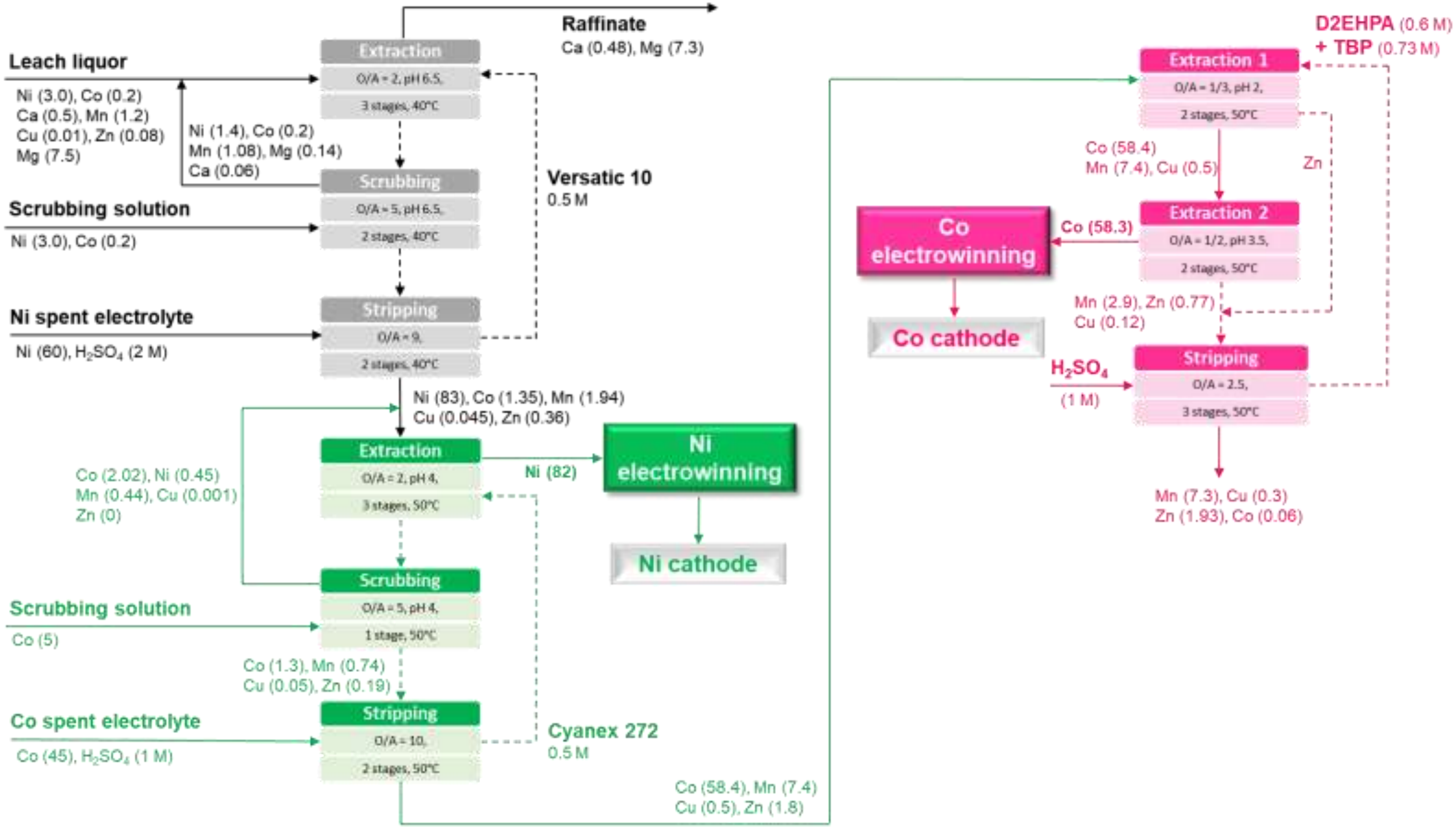

Figure 4.11: Simplified flowsheet of the conceptual route for the purification of Ni and Co (metal concentrations in g/L; continuous lines: aqueous streams; dotted lines: organic streams).

Fonte: próprio autor.

4.4 CONCLUSIONS

In the present work, a DSX conceptual route was developed to produce Ni and Co purified/concentrated streams from an aqueous solution, simulating a sulfuric liquor obtained from a sulfation-roasting-leaching process applied to a lateritic Brazilian Ni ore after the removal of Fe, Al, and Cr by chemical precipitation. Three SX circuits were evaluated to obtain suitable solutions for Ni and Co electrowinning:

- In the first SX circuit, three theoretical stages are required to extract 99% Co and practically all Ni, Cu, and Zn (O/A = 2:1, pH 6.5, 40°C) with Versatic 10 (0.5 M). Cu and Zn were co-extracted due to their very strong affinity for Versatic 10. Approximately 93% Mg and 84% Ca were rejected in the raffinate solution. The extraction operation must occur at pH < 7 in order to avoid emulsion and crud formation. All Mg, Ca, and 66.5% Mn were scrubbed off from the loaded Versatic 10 in two stages, using a scrubbing solution containing 3 g/L Ni and 0.2 g/L Co (O/A = 5:1, 40°C, pH 6.5). Complete stripping of Ni, Co, Cu, Mn, and Zn from the scrubbed loaded Versatic 10 is achieved in two theoretical stages (O/A = 9:1, 40°C) using a synthetic Ni spent electrolyte (50 g/L Ni + 2 M H_2SO_4);
- The loaded strip liquor containing 83 g/L Ni, 1.35 g/L Co, and co-extracted Zn and Cu was subjected to a second SX circuit with Cyanex 272 (0.64 M) to separate (Co+Cu+Zn+Mn)/Ni. Three theoretical stages were required to remove practically all Mn, Cu, Zn, and Co (O/A = 2:1, pH 4, 50°C). Approximately 99.9% Ni was rejected, and the raffinate solution containing Ni (82 g/L) could be sent to the electrowinning step to obtain Ni cathodes. All Ni co-extracted was scrubbed off the loaded Cyanex 272 in only one stage, using a scrubbing solution containing 5 g/L Co (O/A = 5:1, 50°C, pH 4). Co, Zn, Cu, and Mn were fully stripped out from the scrubbed loaded Cyanex 272, using a synthetic Co spent electrolyte (45 g/L Co + 1 M H_2SO_4) in two theoretical stages (O/A = 10:1, 50°C);
- The loaded strip liquor containing Co (58.4 g/L), Mn, Cu, and Zn was subjected to a third SX circuit using the SSX system D2HEPA (0.60 M) + TBP (0.73 M). At pH 3–6, synergism was found on Mn extractions and antagonism at $2 \leq pH < 3$. The Mn/Co separation was favored by the antagonism verified in Co extractions at pH 2–6. Antagonism was observed on Cu and Zn extractions throughout the pH range evaluated in this study. The metal extractions must occur at pH < 5 in order to avoid crud formation. Zn is fully removed from the liquor at pH 2, using two

theoretical stages (O/A = 1:3, 50°C). Zn was first removed from the liquor to minimize its crowding out effect on Mn and Cu at O/A ≤ 1:2. From the Zn depleted raffinate, two theoretical stages were needed for fully extract Cu and Mn at pH 3.5 (O/A = 2:1, 50°C). Co was rejected and the raffinate ([Co] = 58.3 g/L) is suitable for Co electrowinning. All Zn, Mn, and Cu were stripped out in three theoretical stages, using 1 M H_2SO_4 (O/A = 2.5:1, 50°C).

- Although this conceptual DSX route was designed to produce Ni and Co purified/concentrated streams, the recovery of other elements that constitute the liquor, such as Mg, Zn, and Mn can also be performed through adequate treatment.

Acknowledgments

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5 EXTRAÇÃO POR SOLVENTES SELETIVA DE NÍQUEL E COBALTO A PARTIR DE UMA SOLUÇÃO SULFÚRICA LATERÍTICA DE NÍQUEL USANDO O SISTEMA SINÉRGICO LIX860N-IC + VERSATIC 10

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Status em 10.11.2023: em revisão após os seguintes comentários da revista/revisores (“this is a well written study about a potentially useful synergistic solvent extraction system. The introduction is through, the results are presented clearly and conditions were selected that are of industrial relevance. The conclusions are appropriate and based on the studies completed. Some comments to help with final polishing of the article.”)

Selective solvent extraction of nickel and cobalt from a Ni lateritic sulfuric solution using synergism caused by LIX860N-IC and Versatic 10

Alexandre Silva Guimarães [1], Georgio Patrício de Souza Resende [1], Iranildes Daniel dos Santos [2] and Marcelo Borges Mansur [1]*

[1] Programa de Engenharia Metalúrgica e de Materiais, COPPE, Universidade Federal do Rio de Janeiro, Av. Horácio Macedo, 2030, Cidade Universitária, 21941-598 Rio de Janeiro, RJ, Brazil.

[2] Instituto Tecnológico Vale, Rua Prof. Paulo Magalhães Gomes, S/N, Morro do Cruzeiro 35400-000, Ouro Preto, MG, Brazil.

* corresponding author. E-mail: marcelo.mansur@metalmat.ufrj.br (M.B. Mansur), https://orcid.org/0000-0003-4916-5028

Abstract

This work investigated the efficiency of the LIX860N-IC + Versatic 10 synergistic system (pH range 2-6, 40°C) to treat an aqueous sulphate solution containing Ca, Co, Cu, Mg, Mn, Ni, and Zn, which mimics a liquor obtained by the sulfation-roasting-leaching process applied to a lateritic Brazilian Ni ore, after precipitation of Fe, Al, and Cr. Almost complete extraction of Cu was observed at pH 2 (1 stage, A/O = 1:1), while a rise in the selectivity of Ni/(Mn+Zn) and Co/(Mn+Zn) was identified at pH 2-6 and pH > 5, respectively. By varying both extractant concentrations, an organic phase containing 0.4

M LIX860N-IC + 0.4 M Versatic 10 was selected to obtain high Ni and Co extractions with low Mn and Zn extractions. At the studied pH range, antagonism occurred for Ca, Cu, and Mg extractions, while synergism was found for Ni and Zn extractions. For Co and Mn, such an effect was pH dependent: antagonism at pH 2-5 and below 4.5, respectively, otherwise synergism was identified. The stoichiometry of Co and Ni extractions with the LIX860N-IC + Versatic 10 system were obtained by data fitting supported by statistical analysis. Ni and Co were complete and selectively extracted together (> 99.9%) at pH 4.5 (2 stages, A/O = 1:1.1) with low extractions of Mn (3.3%) and Zn (20%), leaving Ca and Mg in the raffinate. In the sequence, while Zn was completely scrubbed off from the loaded organic using a scrub solution containing 3.5 g/L Ni and 0.2 g/L Co at pH 4.5 (1 stage, O/A ≤ 15), Mn scrubbing efficiency achieved from 85.6% to 97.8% at an O/A ratio ranging from 5 to 25, which can be attributed to possible Mn oxidation in the extract. Finally, Ni was completely stripped out (3 stages, A/O = 10:1), using a synthetic Ni spent electrolyte (50 g/L Ni + 1 M H_2SO_4), while Co stripping increased from 70% in the first stage to 75.4% in the second, and to only 76% in the third stage, indicating that Co oxidation might have occurred in the loaded organic solution. The remaining Co in the extract was stripped out with 5 M HCl (2 stages, A/O = 1:1). Consequently, to avoid Mn and Co oxidations in the loaded organic solution, the solvent extraction circuit with LIX860N-IC + Versatic 10 requires an operation under an inert atmosphere.

Keywords: solvent extraction, nickel, cobalt, LIX860N-IC, Versatic 10, synergism.

5.1 INTRODUCTION

Solvent extraction (SX) has proven to be a highly efficient method for separating, concentrating, and purifying Ni and Co through hydrometallurgical processing of lateritic ores (HUTTON-ASHKENNY et al., 2015; GUIMARÃES et al., 2014; CHENG et al., 2015; 2010; ZHU et al., 2012). After leaching, Fe, Al, and Cr are precipitated to obtain liquor for further treatment (SILVA et al., 2022). Depending on the downstream processing route, three industrial methods for Ni production can be applied: (i) mixed hydroxide precipitation (MHP), (ii) mixed sulphide precipitation (MSP), and (iii) direct solvent extraction (DSX) (WHITTINGTON and MUIR, 2000; BARD et al., 1985). In the first two methods, Ni and Co are precipitated from the pregnant leach solution (PLS), obtaining an intermediate product that can then be transported to a refinery for further processing. The MHP is obtained using MgO and/or CaO as a precipitated agent, while the MSP is processed using H_2S gas (WILLIANS et al., 2013; TAYLOR, 1995). At the refinery, the MSP is re-leached under pressure with O_2. Ni and Co can then be separated from each other through a solvent extraction method using Cyanex 272 (bis(2,4,4-trimethylpenthyl) phosphinic acid) (HARVEY et al., 2011). The MHP can be re-leached with an H_2SO_4 solution or in the ammonia-ammonium carbonate medium. If H_2SO_4 is used, the liquor obtained contains approximately 70-100 g/L Ni; 1-3 g/L Co; and impurities, including Ca, Cu, Mn, Mg, and Zn. Cyanex 272 is used to separate (Zn+Cu+Co+Mn)/(Ni+Ca+Mg) at pH 3.9-4 and 50°C (GUIMARÃES and MANSUR, 2017; GUIMARÃES et al., 2014; WILLIANS et al., 2013; HARVEY et al., 2011; SIST and DEMOPOULOS, 2003; SOLE and COLE, 2003). Synergistic solvent extraction (SSX, a mixture of two or more extractants to maximize certain separations promoted by nonlinear effects) with 0.32 M Cyanex 272 + 0.3 M D2EHPA (di-2-ethylhexyl phosphoric acid) (A/O = 0.7, pH 4, 50°C) is employed to remove Ca and Mg from the concentrated MHP liquor (GUIMARÃES et al., 2020; SANTOS et al., 2015). Ni in the raffinate solution can be electrowon (DONEGAN, 2006). At the Cawse plant in Australia, the MHP is re-leached with ammonia-ammonium carbonate solution. Ni is selectively extracted over Ca, Co, Mg, Mn, and Zn with LIX84-INS (2-hydroxy-5-nonylacetophenone oxime). To increase the Ni/Co selectivity, Co^{2+} is oxidized to Co^{3+} with air in the ammonia re-leaching tanks. Co in the raffinate is separated from Mn, Mg, Ca, and Zn by sulphide precipitation. Ni is stripped out from the loaded LIX84-INS using a stripping solution containing $NiSO_4$ and H_2SO_4. Ni contained in the loaded strip liquor (70-100 g/L) is electrowon. Since the oxidation of Co is partial in the ammonia-ammonium carbonate medium, some Co is co-extracted with Ni. In the loaded LIX84-INS solution, Co (and some co-extracted Mn) is oxidized to R_3Co chelate. After stripping of Ni, the Co^{3+} (and Mn^{3+}) in the loaded organic solution is stripped out, using H_2SO_4 solution and Fe as a reductant solid. Alternatively, an HCl solution can be used without a reductant to strip out Co (and Mn) from the loaded LIX84-INS solution (MACKENZIE et al., 2006).

By contrast, the DSX operation is generally used when leaching and refining plants are integrated. The advantage consists of avoiding precipitation and re-leaching steps, since the SX step is applied directly to the PLS to separate Ni and Co from each other and/or over impurities. Consequently, another potential benefit is related to the reduction of capital and processing costs in the DSX route. The Bulong industrial plant in Western Australia (closed in 2003) was the first commercial route to apply DSX targeting Ni/Co separation from the PLS. In the first extraction circuit, Cyanex 272 (16% v/v, 45°C) was used to selectively extract Co, Mn, Cu, and Zn, thus leaving Ni, Ca, and Mg in the raffinate. After stripping, Co, Cu, and Zn were precipitated as sulfides and separated from Mn and Mg in the loaded strip liquor. The metal sulfides were re-leached and purified, targeting the electrowinning of Co, while Zn was recovered by SX with D2EHPA. In a third SX circuit, Ni was selectively extracted by Versatic 10 (neodecanoic acid), leaving Ca and Mg in the raffinate. After scrubbing small quantities of both co-extracted Ca and Mg, a spent Ni electrolyte (65 g/L Ni + 34 g/L H_2SO_4) was used to strip out Ni from the scrubbed loaded organic solution, and the loaded strip liquor (85 g/L Ni) was suitable for electrowinning. The main problems identified in this plant were related to gypsum formation, additional anhydrous ammonia consumption due to high Mg and Ca co-extractions in the SX circuits, and crud formation. Many of these difficulties were overcome by the time the plant closed, and the Bulong operation met most design parameters (DONEGAN, 2006).

At the Goro plant (New Caledonia), DSX is commercially applied with the Cyanex 301 (bis(2,4,4-trimetylpentyl) dithiophosphinic acid) as an extractant to selectively extract Ni and Co from the PLS at pH < 2, while Ca, Mg, and Mn are rejected in the raffinate. The plant operates in an inert atmosphere seeking to reduce the concentration of O_2 in the loaded Cyanex 301 in order to avoid oxidation of any co-extracted Fe or Cu by redox coupling, thus minimizing the formation of Cyanex 301 dimers (SOLE et al., 1993). Ni and Co are stripped out from the loaded Cyanex 301 with 6 M HCl at 60°C. Zn is separated from Ni and Co by ion-exchange resin. Alamine 336 is then used to extract Co, leaving Ni in the loaded strip liquor; Ni oxide is obtained with high purity by pyro-hydrolysis, while Co is stripped out and then precipitated to obtain Co carbonate (VAHED et al., 2004; MIHAYLOV et al., 2000).

DSX was studied by Zhang et al. (2012) by applying hydroxamic acid derivative reagents to treat a synthetic lateritic liquor containing Fe. Using 0.38 M LIX1104SM, it was found that Fe, Cu, Zn, Ni, and Co can be selectively extracted over Mn, Mg, and Ca. At pH 6.5, practically all Ni (3 g/L) and Co (0.19 g/L) were extracted from the liquor (2 stages, A/O = 0.8, 40°C). A synthetic Ni spent electrolyte (30 g/L + 35 g/L H_2SO_4) was used to evaluate the metal stripping behavior from the loaded LIX1104SM at 40°C. It was found that Ni, Co, Mn, and Zn were stripped out (91-95%). No, Cu, and Fe stripping was observed at 23°C and 40°C, using the spent electrolyte solution. Using an aqueous solution containing 100 g/L H_2SO_4 at 23°C, all Cu was stripped out, along with negligible Fe stripping (0.17%), which was stripped out with 6 M HCl at 40°C, obtaining 93.1% efficiency. It was concluded that after Ni, Co, Zn, and Mn stripping, Cu can be selectively stripped out from the loaded LIX1104SM in relation to Fe. The advantage of using LIX1104SM would be to avoid the Fe precipitation step after lateritic ore leaching, reducing reagent consumption and operating costs. Despite promising results, LIX1104SM is not commercially available.

The study of potential SSX systems to be applied in DSX operations has shown promising results in the separation of Ni and Co over Ca, Mg, and Mn, benefiting Ni and Co stripping using high O/A ratios (GUIMARÃES et al., 2024a,b; CHENG et al., 2015; 2010; ZHU et al., 2012; HUTTON-ASHKENNY et al., 2015). A high (Co+Ni)/(Mn+Mg+Ca) selectivity was verified by Cheng et al. (2010) using 0.45 M LIX63 (5,8-diethyl-7-hydroxydodecan-6-oxime) + 0.5 M Versatic 10 + 1 M TBP (tributyl phosphate). The $pH_{1/2}$ difference of Mn in relation to Ni and Co ($\Delta pH_{1/2(Mn-Metal)}^{SSX\ system}$) was found to be 2.4 and 1.65. The separation factor of Ni and Co over Mn was 7,720 and 534, respectively, indicating that the separation (Ni+Co)/Mn is easy. At pH 5.5, 99.6% Ni and 96.9% Co are extracted from the synthetic sulfuric liquor with one and two stages (A/O = 1:2, 40°C), leaving almost all Ca, Mg, and Mn in the raffinate. After the Mn, Mg, and Ca scrubbing step, Ni and Co were stripped out using a synthetic Ni spent electrolyte (60 g/L Ni + 70 g/L H_2SO_4) at 40°C. It was found that stages two and one are required to strip almost all Ni and Co (O/A = 14:1), obtaining 89 g/L Ni and 1.75 g/L Co in the loaded strip liquor. Despite promising results, the main challenges identified for this SSX system are related to the use of high concentrations of TBP to speed up the Ni stripping kinetic and the instability of LIX63 at high temperatures when placed in contact with organic acids (BARNARD and TURNER, 2011; CHENG 2006).

In the present work, the SSX system LIX860N-IC (5-nonylsalicylaldoxime) + Versatic 10 consisting of commercially available reagents was investigated to treat a synthetic sulfuric liquor similar to those obtained through the sulphation-roasting-leaching process applied to a lateritic Brazilian Ni ore after removal of Fe, Al, and Cr by chemical precipitation (SILVA et al., 2022; RIBEIRO et al., 2021). As recently identified by Guimarães et al. (2024a), this SSX is a potential organic system to be applied in a DSX route to treat such sulfuric liquors presenting preferential extraction of Cu, Ni, and Co over Zn, Mn, Ca, and Mg. The best operating conditions for the extraction, scrubbing, and stripping steps of an SX circuit to obtain a purified stream containing Ni and Co were evaluated. An effort was made to adjust the concentration of extractants in the SSX system to identify a pH value < 5 that would enable a reduction in hydroxide consumption in the simultaneous Ni and Co extraction step. A simplified flowsheet of the conceptual SSX circuit is presented.

5.2 EXPERIMENTAL

5.2.1 Aqueous and organic solutions

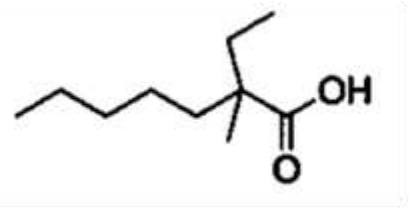
A sulfuric synthetic solution was prepared to mimic a typical leach liquor obtained by the sulphation-roasting-leaching process applied to a lateritic Brazilian Ni ore after removal of Fe, Al, and Cr by chemical precipitation (SILVA et al., 2022; RIBEIRO et al., 2021). Metal sulfates of analytical grade (Synth, minimum 98% purity) were dissolved in distilled water to obtain a working solution containing different concentrations of Ni, Co, Cu, Mn, Ca, Mg, and Zn, as shown in Table 5.1. H_2SO_4 (Synth, 95% purity) or HCl (Synth, 36.5% purity) were used as stripping agents.

Table 5.1: Chemical composition of the sulfuric synthetic working solution.

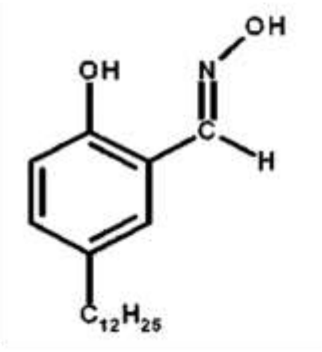
Metal	**Ni**	**Co**	**Mn**	**Ca**	**Mg**	**Zn**	**Cu**
Concentration (g/L)	3.0	0.2	1.2	0.5	7.5	0.08	0.01

Fonte: próprio autor.

The organic solutions were prepared by solubilizing LIX860N-IC (BASF, 65% purity) and/or Versatic 10 (Lanxess, 95% purity) in aliphatic kerosene Exxsol D80 (aromatic content < 0.5% w/w). Such reagents were used as received, without further purification. No modifier agent was used in the organic phase. The molecular structure of the extractants is shown in Figure 5.1.



Versatic 10



LIX860N-IC

Figure 5.1: Molecular structure of extractants Versatic 10 and LIX860N-IC.

5.2.2 Solvent extraction and stripping tests

Once heating the solutions separately to 40°C, extraction tests were performed by placing in contact equal volumes of the synthetic sulfuric solution ($pH_{initial} = 2$, adjusted with H_2SO_4) and the organic solution in a glass reactor (1 L) immersed in a temperature-controlled water bath. Both phases were mechanically stirred with the aid of a stainless-steel impeller coupled to a mechanical stirrer (Kacil, model RM-02) for 10 min using a marine-type impeller. The mixture was allowed to stand for 5 min to obtain phase disengagement. The pH was measured using a pH electrode (Digimed, model DM-22, with temperature corrector). At a given pH value of interest, aliquots of both phases with similar volumes were withdrawn to keep the A/O ratio constant. The pH adjustment was carried out by dropping NaOH solution (1, 2.5, 5, and 10 M; Synth, analytical grade, 99% purity) during stirring. The extraction and stripping distribution isotherms were obtained by mixing the aqueous and organic solutions at changing A/O ratios in a given acidity/pH at 40°C. This procedure has been adopted in a series of previous SX studies (GUIMARÃES et al., 2024a; 2020; GUIMARÃES and MANSUR, 2022; 2017; HUTTON-ASHKENNY et al., 2015; CHENG et al., 2015; 2010).

5.2.3 Chemical analysis and operating parameters

The concentration of Ni, Co, Ca, Mn, Mg, and Zn in the aqueous samples was determined quantitatively by an energy dispersive X-ray fluorescence spectrometer (Shimadzu, model EDX-7000) using the calibration curve method. The Cu concentration in the aqueous phase and other metals at comparatively low concentration levels in selected samples were analyzed quantitatively by atomic absorption spectroscopy (Agilent, model 55B). In the organic phase, the metal concentrations were assessed by mass balance.

The extraction efficiency (E_M), distribution coefficient (D_M), separation factor ($\beta_{M1/M2}$) and synergism enhancement factor (R_M) at a selected pH were respectively calculated according to the following equations:

$$E_M = 100\frac{[M]_i - [M]_f}{[M]_i} \tag{5.1}$$

$$D_M = \frac{[M]_i - [M]_f}{[M]_f} \tag{5.2}$$

$$\beta_{M1/M2} = \frac{D_{M1}}{D_{M2}} \tag{5.3}$$

$$R_M = \frac{D_{M(LIX860N-IC+Versatic\ 10)}}{D_{M(\mathrm{LIX860N-IC})}+D_{M(Versatic\ 10)}} \tag{5.4}$$

in which $[M]_i$ and $[M]_f$ are the initial and final metal concentrations in the aqueous solution, respectively. $D_{M(\mathrm{LIX860N\text{-}IC\ +\ Versatic\ 10})}$, $D_{M(\mathrm{Versatic\ 10})}$, and $D_{M(\mathrm{LIX860N\text{-}IC})}$ refer to the distribution of metal M coefficients using LIX860N-IC + Versatic 10, Versatic 10 alone, and LIX860N-IC alone, respectively. According to the SX theory, $R_M > 1$ indicates a synergistic effect, while $R_M < 1$ represents an antagonistic effect (RITCEY and ASHBROOK, 1984).

5.3 RESULTS AND DISCUSSION

5.3.1 Metals extraction

5.3.1.1 Effect of pH and organic composition

Metal extractions with pH of the synthetic sulfuric feed liquor using 0.4 M Versatic 10 at 40°C and an A/O ratio of 1:1 are shown in Figure 5.2. It can be seen that the extraction sequence found, Cu >> Zn > Ni > Co ≈ Ca ≈ Mn ≈ Mg, is similar to that reported by Guimarães et al. (2024a), Kursunoglu et al. (2017), Cheng et al. (2010), and Cheng (2006). Due to the lower concentration of Versatic 10 used in the present study (0.4 M) in comparison to that used in the aforementioned works (0.5-1 M), lower metal extractions were obtained, mainly Co and Mn. Consequently, the extraction of Co, Mn, Ca, and Mg was practically the same at pH 2-6. Regarding the extraction performance, it can be seen from Figure 5.2 that Cu extractions gradually increased from 2.6% at pH 2.5 to 25% at pH 4, and then reached 98.3% at pH 5.5 and 99.9% at pH 6. By contrast, Zn and Ni extractions increased from 1.6% and 1.7% at pH 5.5 to 59% and 12.2% at pH 6, respectively, while Co (≤ 3.5%), Mn (≤ 1.5%), Ca (≤ 0.5%), and Mg (≤ 2.1%) were rejected by 0.4 M Versatic 10 in the raffinate solution at pH ≤ 6.

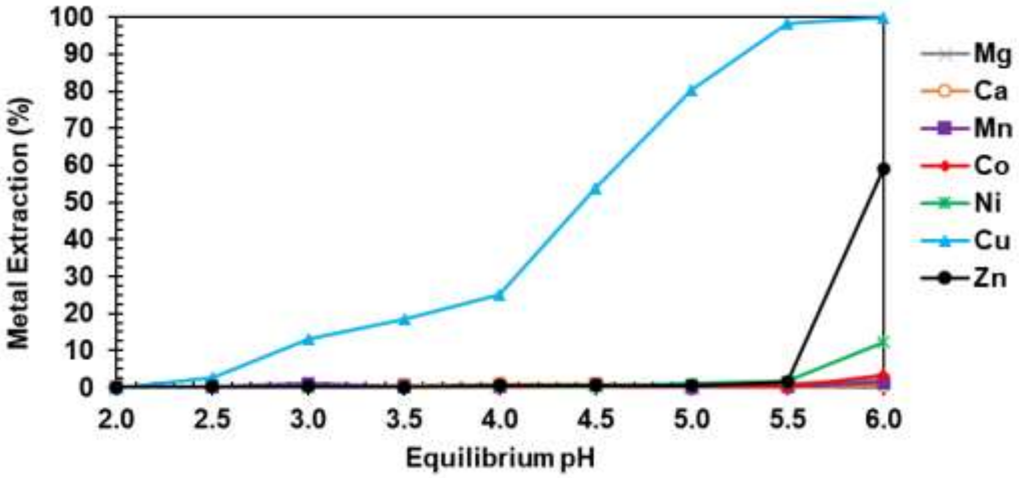


Figure 5.2: Metal extraction from the synthetic sulfuric liquor by 0.4 M Versatic 10 (A/O = 1:1, 40°C). Fonte: próprio autor.

A very distinct metal extraction sequence with pH was found using 0.4 M LIX860N-IC at 40°C and A/O ratio of 1:1, mainly for Zn, Co, and Ni, as shown in Figure 5.3: Cu >> Co > Ni > Zn > Mn > Ca ≈ Mg. LIX860N-IC has shown a very strong affinity for Cu, resulting in 99.9% extraction at pH 2, corroborating Willner et al. (2015). Co extraction increased from 3.4% at pH 2.5 to 99.9% at pH 4.5, while Ni extractions became appreciable at pH > 4 with 26% extraction at pH 4.5 reaching 76% at pH 6. Zn and Mn extractions increased from 1.3% and 2.4% at pH 5 to 60% and 26% at pH 6, respectively. Regarding Ca and Mg, negligible extractions (≤ 4.2%) were found, indicating a rejection of the raffinate solution at pH 2-6.

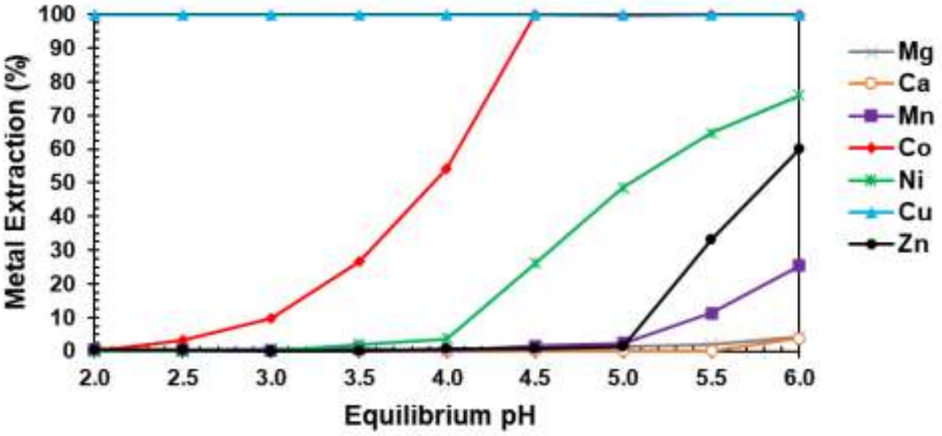


Figure 5.3: Metal extraction from the synthetic sulfuric liquor by 0.4 M LIX860N-IC (A/O = 1:1, 40°C). Fonte: próprio autor.

The effect of adding 0.4 M LIX860N-IC to the 0.4 M Versatic 10 in metal extraction with pH is shown in Figure 5.4 for the same operating conditions. It can be seen that the extraction sequence is similar to that found using LIX860N-IC alone, except for the fact that the Ni extraction curve shifted to lower pH values due to the higher affinity of the SSX system for this metal, while the Co extraction curve remained practically unchanged when compared to 0.4 M LIX860N-IC (Figure 5.3). Consequently, both metals are extracted together since $\Delta pH_{1/2(Ni-Co)}$ is only 0.05 pH units: Cu >> Ni ≈ Co > Zn > Mn > Ca ≈ Mg. Almost all Cu was extracted (98.3%) at pH 2. Ni and Co extractions gradually increase from 3.3% and 2.1% at pH 2.5 to 57% and 53% at pH 4, reaching 99.9% at pH 5, respectively. Zn and Mn extractions increase from 16% and 2% at pH 5 to 99% and 38% at pH 6, respectively. By contrast, Ca (≤ 4.4%) and Mg (≤ 6.2%) were rejected by the SSX system in the raffinate solution at pH 2-6.

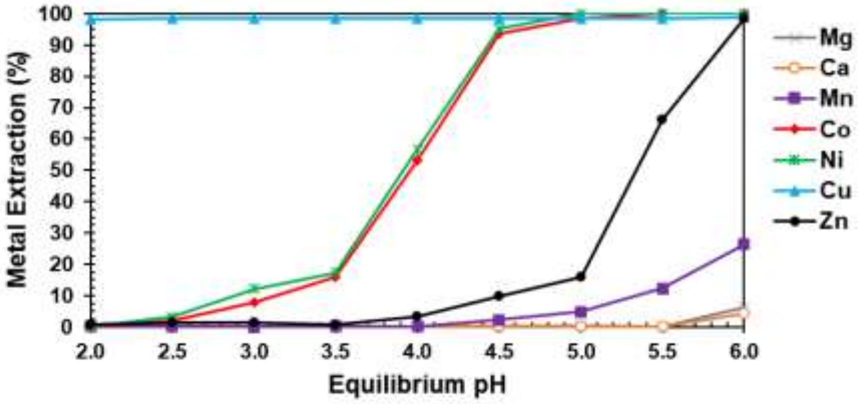


Figure 5.4: Metal extraction from the synthetic sulfuric liquor by 0.4 M LIX860N-IC + 0.4 M Versatic 10 (A/O = 1:1, 40°C). Fonte: próprio autor.

The influence of f LIX860N-IC and Versatic 10 (keeping constant [LIX860N-IC] + [Versatic 10] = 0.8 M) concentrations on the behavior metal extraction as a function of pH of the synthetic sulfuric feed liquor at 40°C and A/O ratio of 1:1 is displayed in Figure 5.5. To facilitate the comparison, the Cu, Ca, and Mg results were omitted because they are very similar to those found in Figure 5.4.

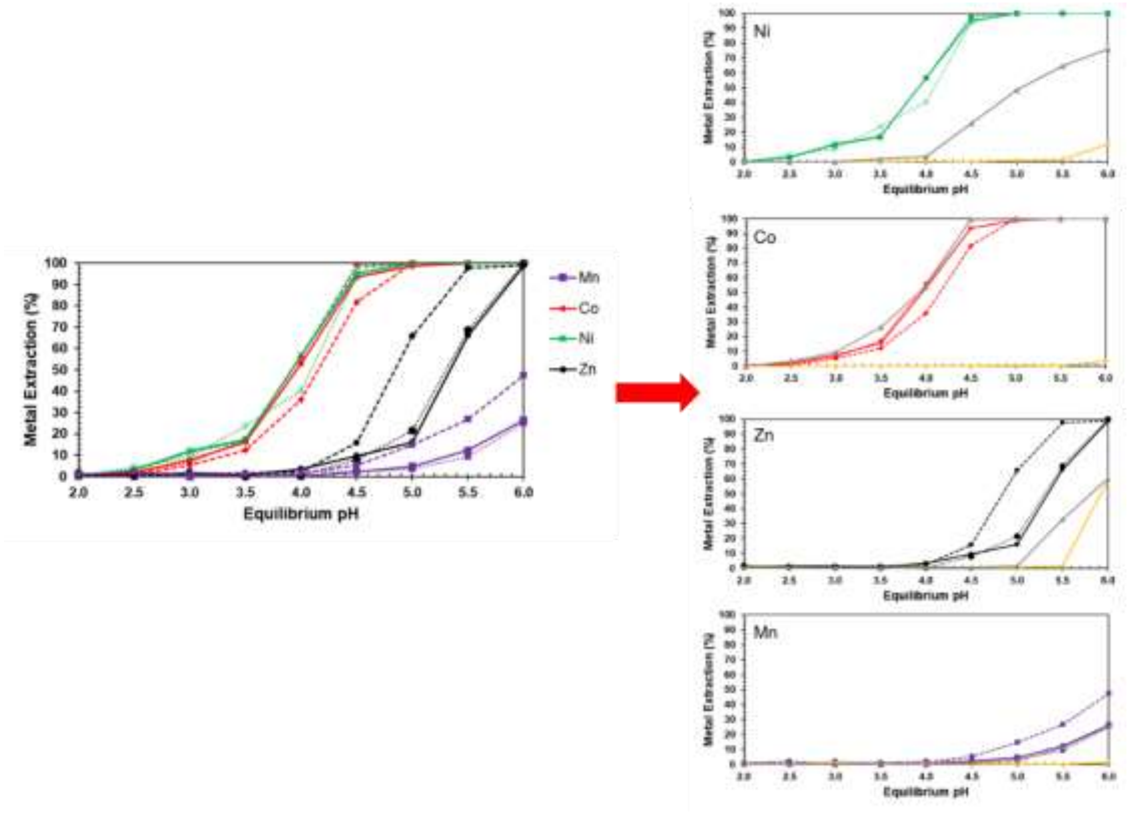


Figure 5.5: Effect of varying the concentration of LIX860N-IC + Versatic 10 (total extractant concentration = 0.8 M) on the metal extraction from sulfuric synthetic liquor (A/O = 1:1, 40°C): dashed line = 0.3 M LIX860N-IC + 0.5 M Versatic 10; continuous line = 0.4 M LIX860N-IC + 0.4 M Versatic 10; dotted line = 0.5 M LIX860N-IC + 0.3 M Versatic 10; for comparison purposes, the curves of 0.4 M Versatic 10 (yellow line) and 0.4 M LIX860N-IC (gray line) were added to the figures for each individual metal). Fonte: próprio autor.

In general, Ni and Co extraction behavior was not markedly affected by the variation in the concentration of extractants. Compared to the 0.4 M Versatic 10 + 0.4 M LIX860N-IC system, increasing the concentration of LIX860N-IC to 0.5 M (and decreasing the concentration of Versatic 10 to 0.3 M) smoothly shifted the Ni extraction curve towards higher pH values, resulting in a $pH_{1/2}$ difference of only 0.2 units. Regarding Co, it was practically unaffected, with the extraction curve being shifted to a lower $pH_{1/2}$ difference of -0.01 units. Likewise, no effect was found for Ni by decreasing the concentration of LIX860N-IC to 0.3 M (and increasing the concentration of Versatic 10 to 0.5 M), with a null $pH_{1/2}$ difference. On the contrary, a shift to the Co extraction curve towards higher pH values with a $pH_{1/2}$ difference of 0.3 was found, indicating that higher Versatic 10 concentration can promote Ni/Co separation, as observed by Joo et al. (2016) using the 0.23 M LIX84-I + 1.21 M Versatic 10. Regarding Mn and Zn extractions, increasing the concentration of LIX860N-IC in the SSX system from 0.3 M to 0.4 M resulted in lower metal extractions, which remained practically unaffected when raised to 0.5 M. Moreover, regarding the synergistic effect in terms of the extraction curve shifts based on the $pH_{1/2}$ values shown in Figure 5.5, it can be seen that synergism was clearly verified to Ni and Zn. In the case of Ni, the SSX curves shifted around 1-1.2 pH units to the left when compared to the curve with LIX860N-IC 10 alone. For Zn, the SSX curves shifted 0.6-1 pH units to the left, while a relatively weak synergistic effect was found for Mn, despite extractions being lower than 50%. On the contrary, antagonism was observed for Co, based on $pH_{1/2}$ values, with SSX curves shifted 0-0.3 to the right.

Regarding the selectivity in terms of the separation factor, Table 5.2 shows that $\beta_{Co/Mn}$ values increase with increasing concentrations of LIX860N-IC in the SSX system from 0.3 M to 0.5 M, obtaining $78 \leq \beta_{Co/Mn} \leq 1.1\text{x}10^7$, $607 \leq \beta_{Co/Mn} \leq 1.6\text{x}10^7$, and $5844 \leq \beta_{Co/Mn} \leq 5.2\text{x}10^7$, as well as $76 \leq \beta_{Co/Zn} \leq 1.0\text{x}10^6$, $135 \leq \beta_{Co/Zn} \leq 1.1\text{x}10^6$, and $1605 \leq \beta_{Co/Zn} \leq 7.0\text{x}10^6$ at pH 4.5-6, except at pH 6 for $\beta_{Co/Zn}$, given that since almost all Co and Zn were extracted from the liquor (99.9%), resulting in high D_{Co} and D_{Zn} and low $\beta_{Co/Zn}$. This is because an increasing Versatic 10 concentration increases Co rejection in the loaded LIX860N-IC + Versatic 10, corroborating Joo et al. (2016). Regarding the Ni/Mn and Ni/Zn separations, the effect of LIX860N-IC and Versatic 10 concentrations was not relevant, obtaining an average range corresponding to $797 \leq \beta_{Ni/Mn} \leq 5.1\text{x}10^8$ and $213 \leq \beta_{Ni/Zn} \leq 9.1\text{x}10^7$ at pH 4.5-6, respectively (Table 5.2). Compared to Versatic 10 alone and LIX860N-IC alone, the $\beta_{Ni/Mn}$ and $\beta_{Ni/Zn}$ values of the SSX systems were at least 97 and 1937 times higher, respectively, at pH 2-6. Similarly, the Co/Mn and Co/Zn selectivity of the SSX systems were at least 199 and 961 times greater when compared to using Versatic 10 alone at pH 4.5-6. Due to the strong affinity that LIX860N-IC alone has for Co, the Co/Mn and Co/Zn selectivity is at least 366 and 325 times higher when compared to the SSX systems at pH 4.5-5. At pH > 5, the $\beta_{Co/Mn}$ and $\beta_{Co/Zn}$ values of the SSX systems are at least 1047 and 32-fold higher when compared to that using LIX860N-IC alone as a result of the greater extractions of Co (> 99.99% against 99.8%, respectively), obtaining $D_{Co}^{LIX860N-IC+Versatic\,10} > D_{Co}^{LIX860N-IC}$. For the SSX systems (Table 5.2), at pH > 4.5, $\beta_{Ni/Mn}$, $\beta_{Ni/Zn}$, $\beta_{Co/Mn}$ and $\beta_{Co/Zn}$ values increased because Ni and Co extractions increased (E_{Ni} > 94% and E_{Co} > 82%), obtaining D_{Ni} and D_{Co} >

D_{Mn} and D_{Zn}. However, the Mn and Zn extractions also increased ($E_{Mn} > 4\%$ and $E_{Zn} > 7.8\%$) and their high content in the extract can make subsequent scrubbing steps difficult. Moreover, it is important to report that the extraction behavior and selectivity of Ni and Co over Mn and Zn was also evaluated using 0.5 M LIX860N-IC + 0.5 M Versatic 10 (GUIMARÃES et al., 2024a) and 0.6 M LIX860N-IC + 0.6 M Versatic 10 systems. Nevertheless, Zn and Mn extractions increased with varying extractant concentrations from 0.4 M to 0.5-0.6 M, shifting their extraction curves to lower pH values and consequently increasing their co-extraction with Ni and Co. As Mn is a difficult impurity to separate from Co after removing them from the concentrated Ni liquor with Cyanex 272 (GUIMARÃES et al., 2014), the SSX systems containing 0.5-0.6 M of LIX860N-IC and Versatic 10 were discarded.

Cu can be separated from Ca, Co, Mn, Mg, Ni, and Zn at pH 2 (Figure 5.4) with $\beta_{Cu/Mn} = 3.1\text{x}10^4$, $\beta_{Cu/Co} = 1.0\text{x}10^5$, $\beta_{Cu/Ni} = 3.5\text{x}10^5$, $\beta_{Cu/Zn} = 7{,}400$, $\beta_{Cu/Ca} = 1.9\text{x}10^4$, and $\beta_{Cu/Mg} = 8.5\text{x}10^5$. Targeting the simultaneous extraction of Ni and Co with minimal Zn, Mn, Ca, and Mg co-extractions, and considering decreasing costs with LIX860N-IC, the system containing 0.4 M LIX860N-IC + 0.4 M Versatic 10 at pH 4.5 (with $\beta_{Co/Mn} = 607$, $\beta_{Co/Zn} = 135$, $\beta_{Ni/Mn} = 848$, and $\beta_{Ni/Zn} = 188$, shown in Table 5.2, and $\beta_{Co/Ca} = 3{,}900$, $\beta_{Co/Mg} = 3.5\text{x}10^5$, $\beta_{Ni/Ca} = 5{,}400$, and $\beta_{Ni/Mg} = 4.8\text{x}10^5$) was selected as the optimal composition and pH for further tests. At pH 4.5, Mg extraction is only 0.004%, implying a reduction in hydroxide consumption for pH adjustment, since Mg co-extraction is very low. In addition, Ca extraction is also low (0.3%), which reduces the chances of gypsum formation during scrubbing and/or stripping using high O/A ratios. The values of the synergistic enhancement factor for the selected SSX system is shown in Table 5.3. Antagonism ($R_{Metal} < 1$) was verified for the extractions of Cu, Ca, and Mg and synergism ($R_{Metal} > 1$) for Ni and Zn at pH 2-6. At pH ≥ 5, $R_{Ni} > 10^6$, considering that the SSX system extracted practically all Ni, thus resulting in $D_{LIX860N\text{-}IC\ +\ Versatic\ 10} >> D_{LIX860N\text{-}IC} + D_{Versatic\ 10}$. Antagonism was found for Co extractions at pH 2-5, given that $D_{LIX860N\text{-}IC} > D_{LIX860N\text{-}IC\ +\ Versatic\ 10}$, and synergism at $5 < \text{pH} \leq 6$, since $D_{LIX860N\text{-}IC\ +\ Versatic\ 10} > D_{LIX860N\text{-}IC} + D_{Versatic\ 10}$. Similar behavior was obtained for Mn, with antagonism at $2 \leq \text{pH} < 4.5$ (the low Mn extractions by organic systems at this pH range resulted in $D_{LIX860N\text{-}IC\ +\ Versatic\ 10} < D_{LIX860N\text{-}IC} + D_{Versatic\ 10}$) and synergism at pH 4.5-6. The synergistic effect dependent on the pH was also verified by Guimarães et al. (2020) and Guimarães and Mansur (2018) in the extractions of Ca, Mg, and Ni from the MHP liquor.

Table 5.2: Effect of pH and composition of organic systems on the separation factor of Co and Ni in relation to Mn and Zn (A/O = 1:1, 40°C).

Organic system	**pH**	$\beta_{Co/Mn}$	$\beta_{Co/Zn}$	$\beta_{Ni/Mn}$	$\beta_{Ni/Zn}$
0.4 M Versatic 10	4.5	0.6	0.47	0.45	0.4
	5	11	1.02	21	1.9
	5.5	0.5	0.08	7	1.1
	6	2.6	0.03	10	0.1
0.4 M LIX860N-IC	4.5	2.9x10^{4}	7.8x10^{4}	23	62
	5	7,518	1.4x10^{4}	38	72
	5.5	5,034	1,309	14	4
	6	1,778	404	9	2
0.3 M LIX860N-IC + 0.5 M Versatic 10	4.5	78	24	853	262
	5	1.1x10^{7}	1.0x10^{6}	1.7x10^{8}	1.5x10^{7}
	5.5	5.3x10^{6}	4.2x10^{4}	8.0x10^{7}	6.5x10^{5}
	6	2.0x10^{6}	1.8x10^{4}	3.2x10^{7}	2.7x10^{5}
0.4 M LIX860N-IC + 0.4 M Versatic 10	4.5	607	135	848	188
	5	1,440	383	5.8x10^{8}	1.5x10^{8}
	5.5	1.4x10^{7}	1.0x10^{6}	2.1x10^{8}	1.5x10^{7}
	6	5.6x10^{6}	2.7x10^{4}	8.0x10^{7}	3.9x10^{5}
0.5 M LIX860N-IC + 0.3 M Versatic 10	4.5	5,844	1,605	690	189
	5	5.2x10^{7}	7.0x10^{6}	7.8x10^{8}	1.1x10^{8}
	5.5	1.9x10^{7}	9.0x10^{5}	2.8x10^{8}	1.4x10^{7}
	6	5.8x10^{6}	2.4	8.7x10^{7}	36

Fonte: próprio autor

Table 5.3: Effect of pH on the synergistic enhancement factors with 0.4 M LIX860N-IC + 0.4 M Versatic 10 (A/O = 1:1, 40°C).

pH	R_{Mg}	R_{Ca}	R_{Mn}	R_{Co}	R_{Ni}	R_{Cu}	R_{Zn}
2	0.03	0.28	0.39	0.57	1.57	0.0008	1.99
2.5	0.005	0.67	0.27	0.60	12	0.0009	2.08
3	0.03	0.35	0.03	0.78	84	0.0009	3.92
3.5	0.004	0.63	0.12	0.52	9	0.0009	2.81
4	0.04	0.10	0.40	0.96	31	0.0009	2.96

4.5	0.003	0.41	1.15	0.03	56	0.0009	9.33
5	0.27	0.66	2.0	0.39	$3.1\text{x}10^7$	0.0009	10
5.5	0.004	0.43	1.08	3099	$1.6\text{x}10^7$	0.0009	3.84
6	1.00	0.99	1.01	3294	$8.8\text{x}10^6$	0.0001	25

Fonte: próprio autor.

5.3.1.2 Stoichiometry of Co and Ni extractions with LIX860N-IC and Versatic 10

The extraction of Co and Ni by the synergistic system containing LIX860N-IC (HL) and Versatic 10 (HV) followed the generic equilibrium reaction given by:

$$M^{2+} + \mathrm{xHL} + \mathrm{y}(HV)_2 = \mathrm{M} \cdot L_x \cdot (HV)_{2y} + nH^+ \qquad (5.5)$$

where Versatic 10 was presumed to exist predominantly as dimers in aliphatic organic phases (KOLARIK, 1982; RITCEY and ASHBROOK, 1984; JOO et al., 2016). To perform data fitting, the equilibrium equation assuming activity coefficients of 1.0 and apparent equilibrium constant K_M was written in logarithm form as:

$$\log(D_M) = \log(K_M) + n\,pH + \mathrm{x}\log(\mathrm{HL}) + \mathrm{y}\log[(HV)_2] \qquad (5.6)$$

Experimental data for Co and Ni at pH range 2-6 obtained at changing concentrations of LIX860N-IC and Versatic 10 (0.3-0.6 M, together and separated) were fitted to Eq. (6) using the Statistica software, applying the Gauss-Newton estimation method and loss function of least squares. The concentration of metals in the organic phase was calculated by mass balance. The fitted parameters are summarized in Table 5.4, and the scatter of the predicted and experimental values of $\log(D_M)$ shown in Figure 5.6 reveals that a satisfactory fit was achieved. It must be emphasized that no correlation between the estimates was found as p-values below 0.05 were obtained in the fit. Therefore, all parameters are statistically significant (95%) to reproduce the experimental behavior and, based on the estimates, the respective equilibrium reactions for Co and Ni extraction by the synergistic system LIX860N-IC and Versatic 10 were proposed:

$$Co^{2+} + L^- + \mathrm{HL} + (\mathrm{HL})_2 \cdot 2(HV)_2 = \mathrm{Co}L_2 \cdot (HL)_2 + 2(HV)_2 + H^+ \qquad (5.7)$$

$$Ni^{2+} + L^- + \mathrm{HL} + (\mathrm{HL})_2 \cdot 2(HV)_2 + (HV)_2 = \mathrm{Ni}L_2 \cdot (HL)_2 \cdot 3(HV)_2 + H^+ \qquad (5.8)$$

Based on the model, LIX860N-IC plays the role of the extractant for both metals, while Versatic 10 acts as an adduct (synergist) solely in the case of Ni extraction. Such assumptions corroborate the experimental behavior depicted in Figure 5.5 that a much higher affinity of LIX860N-IC alone by Co and Ni was observed in comparison to that of Versatic 10 alone. Consequently, the aldoxime based reagent has a larger $\log(K_M)$ value than the neodecanoic acid, as observed also by Joo et al. (2016) for the LIX84-I + Versatic 10 system. Moreover, a higher rejection was observed for Co upon increasing Versatic 10 concentration in the organic mixture (resulting in an antagonistic effect), while an opposite behavior was obtained for Ni extraction (synergism).

Table 5.4: Fitting results of Co and Ni extraction with LIX860N-IC and Versatic 10.

Co	$n = 1.06 \approx 1$	$x = 4.2 \approx 4$	$y = -1.7 \approx -2$	$\log(K_{Co}) = -5.9 \pm 0.1$	$R^2 = 0.8959$
Ni	$n = 0.79 \approx 1$	$x = 3.8 \approx 4$	$y = 1.3 \approx 1$	$\log(K_{Ni}) = -6.90 \pm 0.09$	$R^2 = 0.8626$

Fonte: próprio autor.

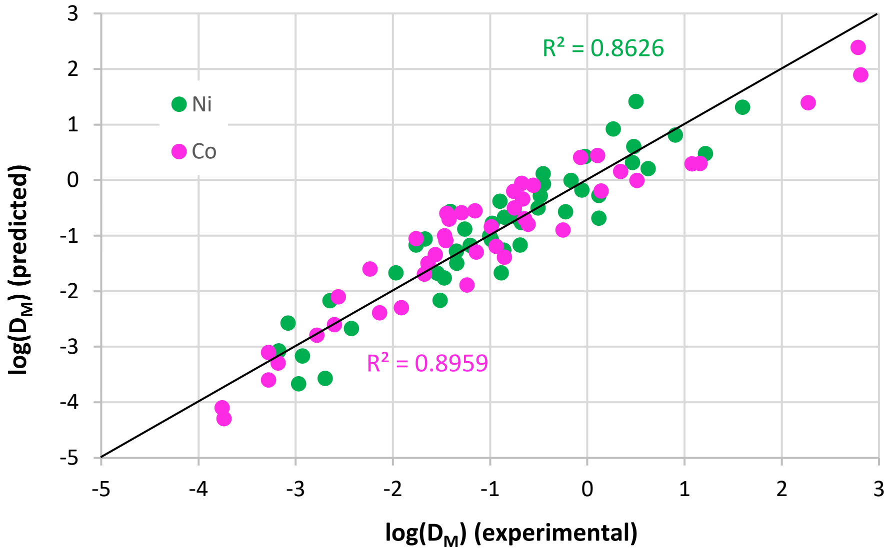


Figure 5.6: Comparison between predicted and experimental $\log(D_M)$ values for Co and Ni extraction with LIX860N-IC and Versatic 10. Fonte: próprio autor.

The stoichiometry obtained in the present work reasonably agrees with that reported by Joo et al. (2016). Each mol of Co or Ni requires 4 mols of aldoxime and 4 mols of neodecanoic acid to be extracted, with one proton being released. Perhaps a 1:1 mixed-extractant structure could be formed in the organic phase, but further investigations are required to validate the organic species involved. However, to fulfill the estimates obtained in the present work and based on previous knowledge available in the literature, a plausible mechanism to explain Co and Ni extractions with the LIX860N-IC + Versatic 10 system could be inferred as follows. According to Flett (1977), the classical description of metal chelate extraction requires the partition of the chelating agent from the organic phase into the aqueous phase, ionization of the chelating agent in the aqueous phase, sequential stepwise chelate formation, and finally the partition of the neutral chelate back into the organic phase.

It is well known that chelating self-aggregation (as well as other interactions, such as association with adduct molecules) may occur in the bulk organic phase, and these species are less surface active when compared to the monomer, partly due to steric hindrances, and partly due to reduced interfacial tension (VASILYEV et al., 2017). When the organic is contacted with the aqueous solution, the hydrophilic head of the chelating monomer extractant is adsorbed at the liquid-liquid interface; the concentration of the ligand in the aqueous side L^- depends on the partition of the extractant in the two-phase system $[HL]_{org} = [HL]_{aq}$ and, at a certain pH range, on its dissociation $[HL]_{aq} = [H^+][L^-]$. In the present work, NaOH (1-10 M) was added to pH adjustments and, under such conditions, the following reaction was proposed by Joo et al. (2016) for the extraction of Ni with LIX84-I alone that might occur in the vicinity of the interface, on the aqueous side of the interface:

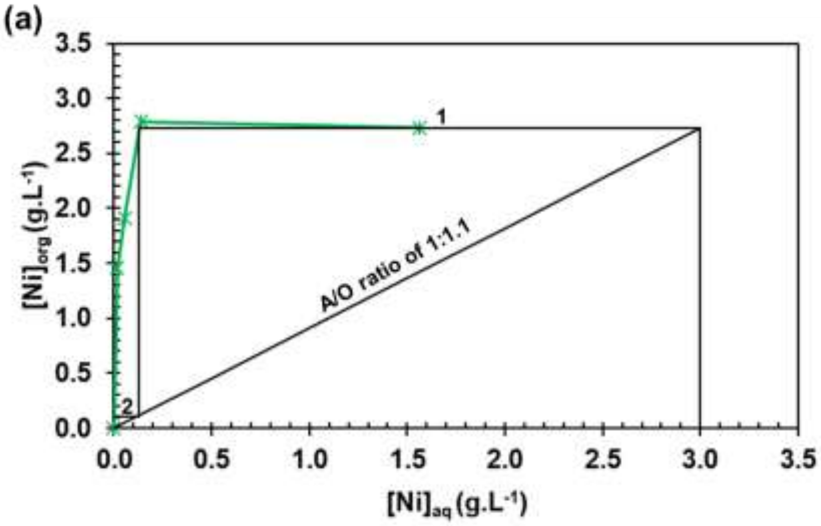
$$Ni^{2+} + L^- + \mathrm{HL} = \mathrm{Ni} \cdot 2\mathrm{L} + H^+ \qquad (5.9)$$

Once a neutral metal-complex has been formed, it is then transferred from the aqueous to the organic phase. As pointed out by Narbutt (2008), the partition may be accompanied by complete or partial dehydration of its molecules, and the aqueous-phase interactions that affect partition of neutral metal complexes are: (i) water structuring around nonpolar hydrocarbon regions of the solute (hydrophobic hydration); (ii) coordination of water molecule(s) to the central metal ion in coordinatively unsaturated chelates (inner-sphere hydration); and (iii) hydrogen bonding of water molecule(s) to ligands in the chelate molecule (outer-sphere hydration).

Finally, as previously mentioned, adduct formation in the organic phase may occur involving the chelating self-aggregate and adduct molecules resulting in the metal-complexes shown in equations (7) and (8) for Co and Ni extractions, respectively.

5.3.1.3 Extraction distribution isotherms of Co and Ni

The extraction distribution isotherms of Co and Ni were evaluated by contacting the 0.4 M LIX860N-IC + 0.4 M Versatic 10 system with the synthetic sulfuric feed liquor at different A/O ratios (1:2, 1:1.5, 1:1, and 2:1), at pH 4.5 and 40°C. The McCabe-Thiele diagrams were drawn to determine the number of theoretical counter-current extraction stages, the results of which are shown in Figure 5.7. It can be verified that the Ni isotherm is steeper when compared to that of the Co. This is because Ni has a strong affinity for the SSX system and due to the fact that Ni crowds Co out of the loaded organic solution. At an A/O ratio of 2:1, the maximum loading capacity of Ni is reached, around 2.8 g/L, implying that Ni and Co competition for LIX860N-IC and Versatic 10 extractants increases at 1:1.5 ≤ A/O ratio ≤ 2:1 and as the Ni concentration is 15-fold higher than that of Co in the synthetic sulfuric liquor, Ni can scrub off some Co from the loaded organic phase resulting in a lesser slope isotherm of Co. The crowding out effect of Ni in relation to Co was also observed by Cheng et al. (2015; 2010). Despite that, it can be seen from Table 5.5 that Ni and Co extractions at varying A/O ratios are consistent, since a decrease from 99.4% and 99.9% to 46.7% and 79.7% was observed with increasing A/O ratio from 1:2 to 2:1, respectively, as a result of limited organic capacity. According to the McCable-Thiele diagrams (Figure 5.7), two theoretical extraction stages are needed to extract all Ni and Co (> 99.99%) at an operational A/O ratio of 1:1.1. Cu was fully (> 99.99%) extracted in one theoretical stage. Approximately 3.3% Mn, 20% Zn, 0.02% Ca, and 0.01% Mg were co-extracted with Ni, Co, and Cu, thus obtaining a raffinate containing 0.49 g/L Ca, 7.4 g/L Mg, 0.64 g/L Zn, 1.16 g/L Mn, and less than 0.001 g/L of Ni, Co, and Cu.



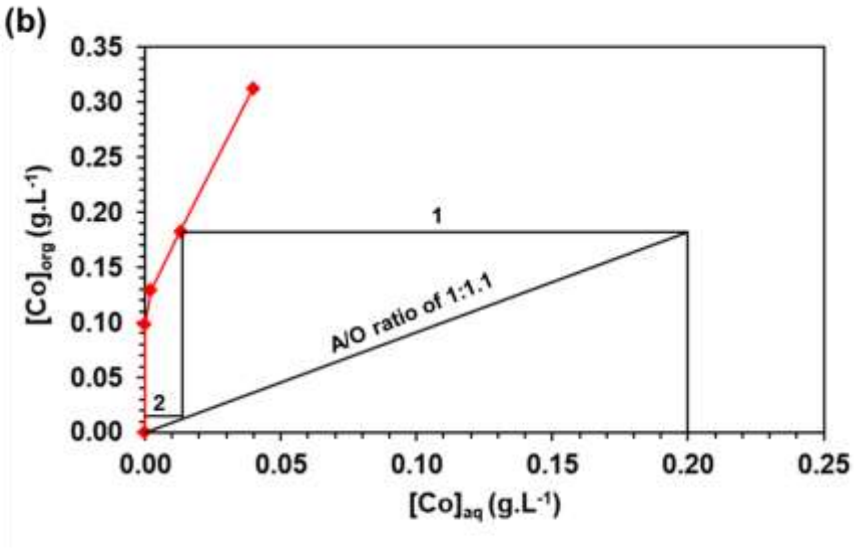


Figure 5.7: McCabe-Thiele diagrams for (a) Ni and (b) Co extractions with 0.4 M LIX860N-IC + 0.4 M Versatic 10 system at pH 4.5 and 40°C. Fonte: próprio autor.

Table 5.5: Effect at varying the A/O ratio on the extraction of Co and Ni with 0.4 M LIX860N-IC + 0.4 M Versatic 10 system ($[Ni]_{initial}$ = 2.93 g/L, $[Co]_{initial}$ = 0.19 g/L, 40°C)

A/O ratio	**Concentration in organic phase (g/L)**		**Concentration in aqueous phase (g/L)**		**Metal extraction (%)**	
	Ni	**Co**	**Ni**	**Co**	**Ni**	**Co**
1:2	1.45	0.098	0.017	< 0.001	99.4	99.9
1:1.5	1.91	0.13	0.055	0.002	98.1	98.9
1:1	2.79	0.18	0.14	0.013	95.3	93.4
2:1	2.73	0.31	1.56	0.040	46.7	79.7

Fonte: próprio autor.

5.3.2 Scrubbing of Zn and Mn

Scrubbing tests were performed to remove Mn and Zn co-extracted in the extraction stages and obtain a purified Ni and Co extract stream. A scrubbing solution containing 3.4 g/L Ni and 0.2 g/L Co (mimicking the concentration of sulfuric feed liquor, Table 5.1) was mixed with the loaded LIX860N-IC + Versatic 10 ([Ni] = 3.44 g/L, [Co] = 0.22 g/L, [Mn] = 0.04 g/L, [Zn] = 0.016 g/L, [Cu] = 0.01 g/L, and [Ca+Mg] < 0.002 g/L) in different O/A ratios (25:1, 20:1, 15:1, 10:1 and 5:1) at pH 4.5 and 40°C in one stage. Table 5.6 shows that the negative scrubbing efficiency of Ni and Co implies that both metals scrubbed off the loaded Zn and Mn from the loaded organic solution. Decreasing the O/A ratio from 25:1 to 5:1 increased the Zn scrubbing efficiency from 97.2% to 100%. These results are consistent because at low O/A ratios there is a higher amount of Ni and Co available to displace the loaded Zn. The opposite behavior was verified for Mn as its scrubbing efficiency decreased from 97.8% to 85.6% by decreasing the O/A ratio from 25:1 to 5:1. These results indicate that some Mn^{2+} may be oxidized to Mn^{3+} in the loaded organic solution as reported by Mackenzie et al. (2006) on an extraction circuit with LIX84-ISN (2-hydroxy-5-nonylacetophenone oxime). If Mn^{3+} forms a more stable complex with extractants LIX860N-IC and/or Versatic 10, its scrubbing by Ni and Co becomes difficult. As these tests were conducted in room atmosphere, the O_2 from the air might contribute to the oxidation of Mn. It seems that the longer the loaded organic solution is in contact with air, the higher the rate of Mn oxidation. For the sake of clarity, the test at an A/O ratio of 25:1 was performed immediately after loading the organic solution. Meanwhile, the stock loaded organic solution was kept warm at 40°C in a water bath separated from the scrubbing solution. The average time to perform each scrubbing test including the phase separation time was approximately 18 minutes. After about 72 minutes, the test at an A/O ratio of 5:1 was started. During this resting time of the organic solution, the Mn could have been oxidized, decreasing its scrubbing efficiency. A similar result was obtained by Cheng et al. (2010) with Versatic 10 + 4PC (2-ethylhexyl 4-pyridinecarboxylate ester) during scrubbing and stripping of Mn from the loaded organic solution. According to the authors, Mn oxidation was attributed to the probable presence of impurities contained in the 4PC extractant that may have catalyzed the reaction from Mn^{2+} to Mn^{3+}. It has to be emphasized that the purity of the commercial reagent LIX860N-IC used in the present study is 65%.

In another test, a scrubbing solution containing 0.53 g/L of Ni and 0.035 g/L Co (mimicking a 7-fold dilution of the feed liquor, Table 5.1) was contacted twice successively with the organic solution immediately after loading at an A/O ratio of 5:1, 40°C, and pH 4. Table 5.6 shows that all Zn was scrubbed off in the first stage, while Mn scrubbing efficiency was 80.5%. In the second stage, no Mn was scrubbed off from the loaded organic solution due to its probable oxidation to Mn^{3+}, which occurred during the first and second tests. Since the remaining Mn in the organic solution was oxidized to Mn^{3+}, the available Ni in the scrubbing solution displaced the Co loaded, promoting its return to the aqueous solution, obtaining a scrubbing efficiency of +2%. These results suggest that the Co and Ni extraction circuit should be carried out in an inert atmosphere to reduce the O_2 contact from the air and prevent Mn oxidation in the loaded organic solution; the use of a purified LIX860N-IC must be evaluated as well. In addition, Ca and Mg were completely scrubbed off in all tests. Cu was not scrubbed off because $pH_{scrubbing} > pH_{extraction}^{SSX\ system}$.

Table 5.6: Effect at varying O/A ratio on Mn and Zn scrubbing from the loaded 0.4 M LIX860N-IC + 0.4 M Versatic 10 in a changing composition of the scrubbing solution (40°C).

Composition of the scrubbing solution (g/L)	**O/A ratio**	**Scrubbing efficiency (%)**			
		Mn	**Co**	**Ni**	**Zn**
3.4 g/L Ni + 0.2 g/L Co pH 4.5 (one stage)	25:1	97.8	-2.7	-2.2	97.2
	20:1	95.4	-3.9	-2.4	97.8
	15:1	94.7	-4.9	-2.5	100
	10:1	88.5	-8.1	-2.5	100
	5:1	85.6	-6.0	-2.3	100
0.53 g/L Ni + 0.035 g/L Co pH 4	5:1 (first stage)	80.5	-3.2	-2.8	100
	5:1 (second stage)	0	2.0	-2.8	0

Fonte: próprio autor.

5.3.3 Metal stripping of Co, Cu, and Ni

The stripping tests were carried out by placing into contact the loaded organic solution containing 3 g/L Ni, 0.2 g/L Co, and 0.01 g/L Cu with a synthetic Ni spent electrolyte (50 g/L) in different acidity conditions (0.05-3 M H_2SO_4) at an A/O ratio of 1:1 and 40°C. Table 5.7 shows that, in general, increasing H_2SO_4 concentration in the spent electrolyte from 0.05 to 0.5 M resulted in higher Ni stripping from 7.9% to 100%, thus indicating that Ni stripping from the loaded LIX860N-IC + Versatic 10 is easy. Regarding Cu, it was verified that its stripping is below 10% at $0.05 \leq H_2SO_4\ (M) \leq 1$, suggesting that Ni and Co can be selectively stripped out from the loaded LIX860N-IC +

Versatic 10 with $6 \leq \beta_{Ni/Cu} \leq 152$ and $17 \leq \beta_{Co/Cu} \leq 42$ (at $[H_2SO_4] \geq 0.25$, $\beta_{Ni/Cu} > 10^5$ due to the complete stripping of Ni, and $\beta_{Co/Cu}$ decreases as a result of higher Cu stripping). At $2 \leq H_2SO_4$ (M) ≤ 3, Cu stripping ranged from 42% to 90.5%, indicating that its recovery from the loaded organic solution is not problematic. This result is consistent with experimental expectation since Cu was almost completely extracted at pH 2 (Figure 5.4), thus its recovery using diluted H_2SO_4 solution is expected to be low. In fact, $[H_2SO_4] \geq 1$ M was required for Cu stripping to become appreciable. In relation to Co, it was observed that its stripping behavior follows an opposite tendency to that of Ni and Cu. Its stripping efficiency decreased from 37.8% to 25.8%, with an increasing H_2SO_4 concentration from 0.05 M to 3 M. Similar to Mn, this behavior may indicate the occurrence of Co oxidation in the loaded organic solution, as the prolonged contact with air may favor the oxidation of Co^{2+} to Co^{3+} in the loaded organic solution, resulting in difficult stripping due to the higher chemical stability of such organocomplexes as reported elsewhere (JEFFRERY et al., 1989). The stock loaded organic solution was kept at 40°C in a water bath for around three hours during the tests, and tests were carried out from the lowest concentration of H_2SO_4 to the highest one. The results in Table 5.7 reveal this trend in the stripping behavior of Co. During this time, part of the Co^{2+} in contact with the atmosphere may have oxidized to Co^{3+}, resulting in a decrease in its stripping efficiency as mentioned earlier.

Table 5.7: Effect of H_2SO_4 concentration variation in the synthetic Ni spent electrolyte (50 g/L Ni) on Ni, Co, and Cu stripping at (O/A = 1:1, 40°C).

$[H_2SO_4]$ (M)	**Stripping efficiency (%)**			$\beta_{Ni/Cu}$	$\beta_{Co/Cu}$
	Ni	**Co**	**Cu**		
3	100	25.8	90.5	4.5×10^5	0.04
2	100	21.0	85.7	7.1×10^5	0.04
1	100	27.6	41.9	6.4×10^6	0.53
0.5	100	27.4	8.5	4.4×10^7	4
0.25	100	27.5	8.6	4.2×10^7	4

0.125	78.8	28.7	2.4	152	17
0.063	44.2	30.2	2.0	38	21
0.05	44.1	32.3	1.7	45	27
0.016	14.8	33.5	2.0	9	25
0.005	7.9	37.8	1.4	6	42

Fonte: próprio autor.

To evaluate the effect of time on a possible Co oxidation, an aqueous solution containing 3.3 g/L Ni and 0.186 g/L Co was used to load the organic phase, consisting of LIX860N-IC + Versatic 10. After phase separation, the load LIX860N-IC + Versatic 10 was kept at room temperature for seven days. The stripping distribution isotherms were then evaluated by mixing the loaded LIX860N-IC + Versatic 10 with a synthetic Ni spent electrolyte containing 50 g/L Ni + 1 M H_2SO_4 in different A/O ratio (1:1, 2:1, 4:1, 8:1, and 10:1) at 40°C. The McCabe-Thiele diagrams for Ni and Co are shown in Figure 5.8. It can be observed that the stripping behavior of the Ni isotherm is usual, obtaining greater Ni recovery from 83.4% to 99.6% with the decrease of the O/A ratio from 10:1 to 1:1 (Table 5.8). In addition, Figure 5.8(a) confirms that three stages are required to strip out all Ni from the loaded organic solution using an operational O/A ratio of 10:1. The load strip liquor contains 80 g/L Ni, which corresponds to $\Delta Ni = 30$ g/L. Regarding Co, Figure 5.8(b) shows that the isotherm shape is unusual due to the oxidation of Co^{2+} to Co^{3+}, which occurred during the seven days standing of the loaded organic phase. In fact, the concentration of Co in the organic phase remained practically constant (approximately 0.18 g/L) when varying the O/A ratio from 1:1 to 10:1 (Table 5.8), indicating that approximately 97.4% of Co was oxidized, which made its stripping difficult. Since antagonism was found for the Co extractions for the 0.4 M LIX860N-IC + 0.4 M Versatic 10 system (Table 5.3) at pH ≤ 5 and observing the behavior of its extraction by the 0.4 M Versatic 10 alone and 0.4 M LIX860N-IC alone (Figures 5.2 and 5.3), it is reasonable to infer that its extraction by the SSX system occurs mainly by the LIX860N-IC. With prolonged contact with O_2 from the air, the formation of a stable Co^{3+} chelate complex in the organic solution may have indeed occurred as reported by Preston (1975a,b), resulting in a complicated stripping without reduction (MACKENZIE et al., 2006).

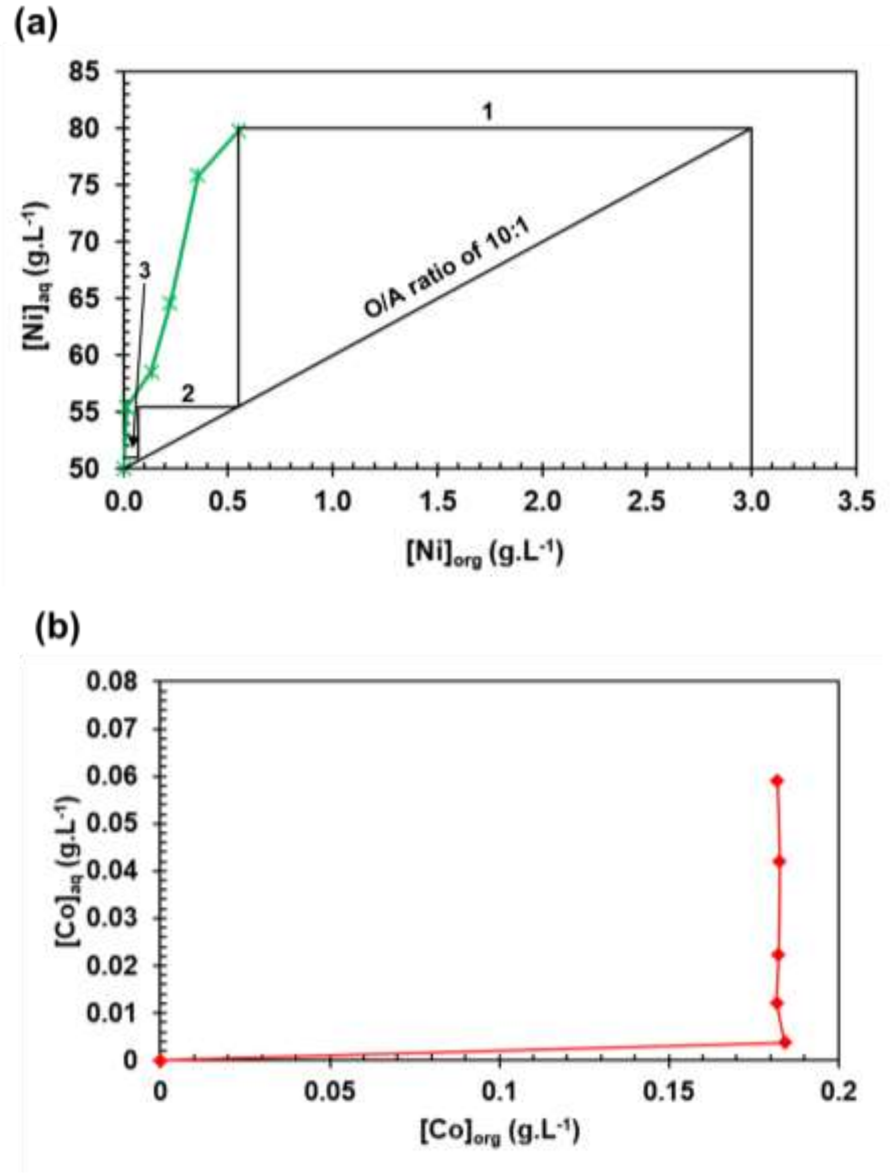


Figure 5.8: Stripping distribution isotherms and McCabe-Thiele diagrams for (a) Ni and (b) Co from the loaded 0.4 M LIX860N-IC + 0.4 M Versatic 10 after seven days standing using a synthetic Ni spent electrolyte (50 g/L Ni + 1 M H_2SO_4) at 40°C. Fonte: próprio autor.

Table 5.8: Effect of O/A ratio on Ni and Co stripping using a synthetic Ni spent electrolyte (50 g/L Ni + 1 M H_2SO_4) at 40°C from the loaded organic phase containing 0.4 M LIX860N-IC + 0.4 M Versatic 10 after seven days standing.

O/A ratio	Concentration in the organic phase (g/L)	Stripping efficiency (%)

	Ni	Co	Ni	Co
1:1	0.014	0.185	99.6	1.4
2:1	0.132	0.182	96.0	3.0
4:1	0.221	0.183	93.3	2.8
8:1	0.356	0.183	89.3	2.7
10:1	0.551	0.182	83.4	3.1

Fonte: próprio autor.

In another series of tests, the organic solution containing LIX860N-IC + Versatic 10 was loaded with 3 g/L Ni and 0.18 g/L Co, and the stripping tests were carried out immediately after loading, thus avoiding leaving the organic stock solution for a long time at 40°C in a water bath. Using only an aqueous solution containing 0.005 M H_2SO_4 at 40°C and an A/O ratio of 1:1, 51% Co and 5.3% Ni were stripped out from the loaded LIX860N-IC + Versatic 10 in the first stage (Table 5.9). Co stripping efficiency increased to 67%, while that of Ni rose to 6.1% in the second stage. The variation in the Co stripping from the first to the second stage was only 16%, most likely due to the formation of Co^{3+} while the organic stock solution was maintained at 40°C in a water bath. The results of the first stage show that the shorter the time the organic solution containing Co remains in contact with the atmosphere, the greater the stripping of Co. In another test, Ni (3 g/L) and Co (0.18 g/L) were loaded into the SSX system and stripping tests were immediately conducted using a synthetic Ni spent electrolyte containing 50 g/L + 1 M H_2SO_4 at an O/A ratio of 10:1 and 40°C in three successive stages. Table 5.9 shows that 80% Ni and 70% Co were stripped out from loaded LIX860N-IC + Versatic 10 in the first stage. In the second and third stages, Ni stripping efficiency increased from 95.4% to 99.8%, while that of Co rose from 75.4% to only 76%, indicating that approximately 24% of Co oxidized to Co^{3+} during stripping tests. The loaded organic solution containing the remaining Co was contacted with HCl solution (5 M, A/O ratio of 1:1 and 40°C) obtaining 82.7% of the stripping in the first stage and 100% in the second stage. It can be inferred from these results that Co has a strong tendency to oxidize in the loaded organic solution, and once oxidized, its stripping is not easy and requires the use of a highly concentrated HCl solution. The operational conditions (extraction, scrubbing, and stripping) identified in the current work must be investigated in an inert atmosphere, as similarly done in the Goro industrial plant operation with Cyanex 301 (VAHED et al., 2004; MIHAYLOV et al., 2000) to avoid Mn and Co oxidation problems in the loaded LIX860N-IC + Versatic 10.

Table 5.9: Ni and Co stripping immediately after loading the 0.4 M LIX860N-IC + 0.4 M Versatic 10 ([Ni] = 3 g/L and [Co] = 0.18 g/L), using different stripping solutions at 40°C.

Stripping solution	O/A ratio	Stages	Concentration in organic phase (g/L)		Stripping efficiency (%)	
			Ni	Co	Ni	Co
0.005 M H_2SO_4	1:1	1	2.83	0.088	5.3	51
		2	2.81	0.060	6.1	67
50 g/L Ni + 1 M H_2SO_4	10:1	1	0.57	0.054	80	70
		2	0.14	0.044	95.4	75.4
		3	0.007	0.043	99.8	76
6 M HCl	1:1	4	0	7.5	-	82.7
		5	0	0	-	100

Fonte: próprio autor.

5.3.4 Flowsheet of conceptual SX circuit

With the results obtained in the present work, the flowsheet of a conceptual route using the SSX system containing 0.4 M LIX860N-IC + 0.4 M Versatic 10 was proposed to recover Ni and Co directly from the PLS after the precipitation of Fe, Al, and Cr. The route shown in Figure 5.9 consists of two SX circuits. The first SX circuit uses the SSX system to obtain Cu and Co+Ni streams, while Ca, Mg, Mn, and Zn are directed to the raffinate. Two distinct strategies can be drawn to selectively separate Cu, as schematically shown in Figure 5.9. In the first, Cu is removed from the liquor by 0.4 M LIX860N-IC + 0.4 M Versatic 10 at pH 2 (A/O = 1:1, 40°C), then H_2SO_4 solution can be used to strip it from the loaded organic solution, as no scrubbing step is required. From the Cu depleted raffinate solution, Ni and Co are extracted simultaneously by 0.4 M LIX860N-IC + 0.4 M Versatic at pH 4.5, 40°C, and an O/A ratio of 0.9, leaving almost all Ca, Mg, Mn, and Zn in the raffinate. After scrubbing co-extracted Zn and Mn (O/A = 25:1, pH 4, 40°C), Ni and Co are stripped out from the loaded organic solution using an Ni spent electrolyte (50 g/L Ni + 1 M H_2SO_4), thus obtaining approximately 80 g/L Ni and 1.8-2 g/L Co in the strip liquor. This stream can be directed to a second SX circuit that uses Cyanex 272 as an extractant to separate Co from Ni, obtaining a raffinate solution suitable for Ni electrowinning. Co can be recovered from the loaded Cyanex 272 with a Co spent electrolyte (45 g/L Co + 1 M H_2SO_4) to obtain a loaded strip liquor for Co electrowinning, as demonstrated by Guimarães et al. (2024b). Based on the present study, selective stripping can be alternatively used to obtain a Cu-rich stream. Such a separating configuration consists of simultaneous extraction of Cu, Ni, and Co at pH 4.5 (A/O = 1:1.1, 40°C) in a first SX circuit, then scrubbing of Mn and Zn, followed by a selective stripping of Ni and Co using the spent Ni electrolyte (50 g/L Ni + 1 M H_2SO_4), and finally Cu stripping.

Mn and Co are the major concern on the evaluated route; however, according to Mackenzie et al. (2006), Mn and Co oxidized in the loaded organic solution can be stripped out using an acidic solution with a reductant solid or by being placed in contact with an aqueous solution with a high concentration of HCl. In the current work, 5 M HCl was required to strip out all the remaining Co in the loaded LIX860N-IC + Versatic 10. Further tests must be carried out using an inert atmosphere to minimize and/or avoid the contact of O_2 from the air with the loaded LIX860N-IC + Versatic 10, seeking to reduce or eliminate oxidations of Co and Mn in the loaded organic solution.

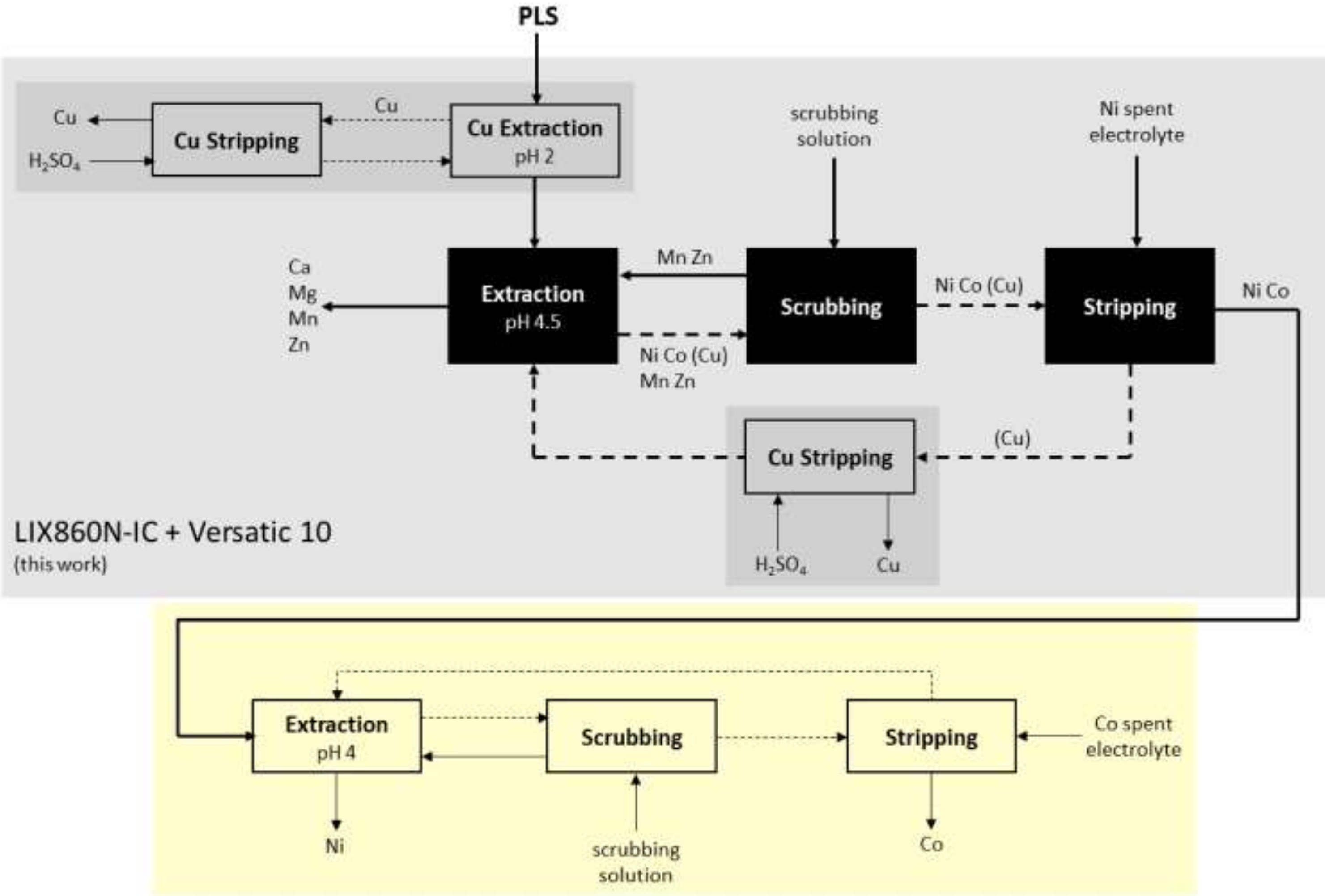


Figure 5.9: Conceptual generic flowsheet to obtain Ni and Co from the PLS after the precipitation of Fe, Al, and Cr using two SX circuits.

Fonte: próprio autor.

5.4 CONCLUSIONS

A synergistic system consisting of LIX860N-IC + Versatic 10 was studied in a DSX operation at 40°C using a liquor similar to those obtained by the sulfation-roasting-leaching process after precipitation of Fe, Al, and Cr. The main conclusions are:

- The addition of LIX860N-IC to Versatic 10 enables the simultaneous extraction of Ni and Co over Mn, Zn, Ca, and Mg at pH 4-4.5 and increases the selectivity of (Ni+Co)/(Mn+Zn) when compared to LIX860N-IC alone and Versatic 10 alone;
- The system 0.4 M LIX860N-IC + 0.4 M Versatic 10 operated at pH 4.5 was selected as an optimal condition to separate Ni and Co over Mn, Zn, Ca, and Mg. Alternatively, Cu can be selectively separated at pH 2-2.5;
- Antagonism was identified in the extractions of Ca, Cu, and Mg, and synergism for Ni and Zn at pH 2-6. The synergistic effect was pH dependent for Co and Mn, creating an antagonism at pH 2-5 and $2 \leq pH < 4.5$, otherwise synergism, respectively;
- The stoichiometry of Co and Ni extractions with LIX860N-IC + Versatic 10 system were obtained by data fitting supported by statistical analysis;
- Ni and Co are fully extracted together (99.99%) in 2 stages (A/O = 1:1.1, pH 4.5). In this condition, 96.7% Mn, 80% Zn, and 99.9% Ca and Mg are rejected in the raffinate;
- Zn is fully scrubbed off from the loaded extract solution at pH 4.5 and O/A ratio ≤ 15 using a scrubbing solution containing 3.4 g/L Ni and 0.2 g/L Co. The partial Mn scrubbing (85.6% at O/A = 5, and 97.8% at O/A = 25) was attributed to possible oxidation and/or the presence of impurities in the LIX860N-IC reagent that may have accelerated/catalyzed Mn oxidation;
- Ni and Co can be selectively stripped out in relation to Cu from the loaded 0.4 M LIX860N-IC + 0.4 M Versatic 10 at $0.005 \leq H_2SO_4\ (M) \leq 0.25$. Ni is fully stripped out using a Ni spent electrolyte (50 g/L Ni + 1 M H_2SO_4) in 3 stages (O/A = 10:1), thereby producing a loaded strip liquor with 80 g/L Ni. Regarding Co, 70% stripping occurred in the first stage, with a low efficiency in the next two stages (75.4% and 76%) attributed to Co oxidation. The remaining Co in the extract solution was fully stripped out using 5 M HCl (2 stages, A/O = 1:1);
- To avoid/reduce Mn and Co oxidations in the organic solution, an inert atmosphere operation is recommended in order to minimize the O_2 contact from the air.

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6 CONSIDERAÇÕES FINAIS

Baseado nos resultados obtidos com o desenvolvimento do presente projeto voltado à purificação de licor produzido via sulfatação-tratamento térmico-lixiviação sulfúrica aplicada a um minério laterítico brasileiro de Ni (RIBEIRO et al., 2021), após pré-tratamento do PLS para remoção seletiva de Fe, Al e Cr por precipitação pelo método jarosita/goethita (SILVA et al., 2022), é importante frisar, além das considerações apresentadas ao final de cada capítulo, que:

- Os seguintes sistemas orgânicos demonstraram potencial para a aplicação pretendida (elevada extração de Ni e Co, associada com rejeição de Ca, Mg e Mn) e podem ser selecionados para tratar o licor num eventual primeiro circuito de extração por solventes (Capítulo 3, vide Figura 3.9): (i) ácido versático (pH 6,5), (ii) Cyanex 301 + ácido versático (pH 1,5), (iii) LIX 84-I + ácido versático (pH 5) e (iv) LIX 860N-IC + ácido versático (pH 4);
- Como desvantagem, todos os sistemas orgânicos extraem 100% de Cu, embora este seja o contaminante de menor teor no licor. Os sistemas (i) e (ii) também extraem 100% de Zn, logo os sistemas (iii) e (iv) são os mais seletivos para Ni e Co. Outras desvantagens incluem: o sistema (i) apresenta extração parcial de Mn, os sistemas (ii), (iii) e (iv) requerem operação em atmosfera inerte, e o sistema (ii) usando apenas o Cyanex 301 já é utilizado industrialmente (Goro). Ainda, para o sistema (ii), há o desafio de proceder a reextração de Ni com solução eletrolítica de modo efetivo para obter uma solução concentrada em Ni que permita alimentar a eletrólise, visto que Guan et al. (2016) usou razões O/A relativamente baixas. E no caso do sistema (iii), o tempo de separação das fases é lento em pH > 3,5;
- Dentre todos os reagentes e suas misturas com ácido versático avaliados, Cyanex 272 (pH 4) é o extratante mais eficiente para a extração seletiva de Co em relação ao Ni;
- Duas rotas conceituais foram desenvolvidas neste trabalho utilizando-se dois dos sistemas orgânicos investigados. Ambas produziram soluções concentradas de Ni e Co (pureza superior a 99,9% Ni e 99,8% Co) adequadas para alimentar a etapa de eletrólise desses metais;
- A rota 1 (Capítulo 4) empregou reagentes comerciais típicos aplicados ao tratamento de licores sulfúricos de Ni (ácido versático, Cyanex 272, D2EHPA + TBP). A principal desvantagem desta rota é a extração parcial de Mn no primeiro circuito, o que faz com

que ele fique circulando nos 3 circuitos da rota. Como Mn é um contaminante presente em concentração elevada, isso resulta em maior consumo de base para neutralização, além do risco de contaminação cruzada;

- A rota 2 (Capítulo 5) empregou combinação de reagentes inédita ao tratamento industrial de licores sulfúricos de Ni (LIX 860N-IC + ácido versático, Cyanex 272). É possível proceder a remoção prévia de Cu (pH 2-2,5) contido no licor para evitar contaminação. A principal desvantagem desta rota seria operar em atmosfera inerte, porém a planta Goro (com extratante Cyanex 301) também opera industrialmente usando atmosfera inerte;
- O reuso do refinado contendo Mg e Mn proveniente da rota 2, por estarem normalmente presentes em elevados teores nos licores de lixiviação e por serem os contaminantes com os maiores teores no PLS, pode resultar em vantagens econômicas/ambientais. A rejeição de Ca é vantajosa por evitar a formação de gesso na unidade. Logo, embora inédita, a rota 2 se mostrou mais promissora de futura aplicação industrial.

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