The free ligand model to describe and design cobalt extraction and nickel scrubbing in a base metal refinery

by M.J. Matsela[1], O.S.L. Bruinsma[2], and D.J. van der Westhuizen[1]

Affiliation:
[1]School for Chemical and Minerals Engineering, Hydrometallurgy Group, Faculty of Engineering, North-West University, Potchefstroom, South Africa

[2]Bruinsma Solutions (Pty) Ltd, Potchefstroom, South Africa

[3]Chemical Resource Beneficiation, Hydrometallurgy Group, Faculty of Natural and Agricultural Sciences, North-West University, Potchefstroom, South Africa

Correspondence to:
D.J. van der Westhuizen

Email:
derik.vanderwesthuizen@nwu.ac.za

ORCiD:
M.J. Matsela
http://orcid.org/0000-0002-3144-1074

O.S.L. Bruinsma
http://orcid.org/0000-0001-8428-4909

D.J. van der Westhuizen
http://orcid.org/0000-0001-6764-4132

Abstract

Solvent extraction (SX) is a widely used separation and purification technique in hydrometallurgy, enabling the selective transfer of target metal ions between aqueous and organic phases. The process relies on chemical equilibrium and the interaction between metal ions and extractants in the organic phase. The free ligand (FL) model enhances the understanding of SX by focusing on the availability of free ligands in the organic phase, a critical factor influencing extraction efficiency and purity. The FL model to calculate the equilibrium concentrations in solvent extraction (SX) based on the distribution coefficient (K_d) at infinite dilution and the fraction of free ligand available for extraction. In this work, the FL model is validated to account for co-extraction of Ni and for designing the extraction and scrubbing sections of Co/Ni separation in a base metal refinery. Cyanex 272 is employed as a selective Co extractant in the process to yield high purity Ni. To enhance the loading capacity of the extractant, 50 mol% of NaOH is pre-loaded into it. Experimental and FL modelling results show that four equilibrium stages are required to purify the 99% Ni feed to a 99.97% Ni raffinate. The 53.59% co-extract with 26.76% free ligand is purified with a reflux scrub of 30 g Co/L in one equilibrium stage to 99.01%, Co in the scrubbed extract. The FL model as well as the Co/Ni/Na-analysis of the aqueous phase confirm that in the scrubbing section, Ni in the extract is mainly replaced by Co. Finally, in the one stage stripper the Co concentration in the scrubbed extract is increased from 5.6 g Co/L in the extract to 30.5 g Co/L that is partially used as reflux scrub liquor.

Keywords

free ligand model, cobalt, nickel, Cyanex 272, extraction, scrubbing

Introduction

The primary objective of the free ligand (FL) model is to optimize the solvent extraction (SX) process by predicting the concentration of free ligands, which governs the equilibrium conditions. By understanding these dynamics, the model enables better control of the process, including the purity of the extracted product and the design of the scrubbing section. Conventionally the McCabe-Thiele graphical method has been the standard in designing the extraction section of SX plants. This approach is effective in determining the number of stages required to achieve the desired separation, however, it cannot predict the purity of the extract or aid in the design of the scrubbing section, which are both critical in achieving high quality outputs of the SX process. The free ligand model therefore addresses these limitations by determining the fraction of free ligands, which aids in determining the extract purity and consequently facilitates the design of the scrubbing section of the SX process.

Solvent extraction (SX) is a separation process that is used in hydrometallurgical plants to obtain one or more components of the aqueous solution into an immiscible organic phase, followed by stripping back into an aqueous solution (Nicol, 2008). This is done to obtain metals at the required purity levels or increase the concentration of the required metals (Kihlblom, 2021). A typical SX process has several stages of extraction, whereby the aqueous solution that contains the metals of interest is brought into contact with the organic solvent that contains the extractant. After extraction, the loaded organic also contains the other metals due to co-extraction. Consequently, a scrubbing section is required to eliminate the undesirable metals from the loaded organic (Kihlblom, 2021).

The conventional way to design the extraction section of an SX plant is by means of the McCabe-Thiele graphical method (Seader et al., 2011). However, this method is not able to predict the purity of the extract or to design the scrubbing section. In this paper a numerical method is demonstrated for the design of both the extraction and the scrubbing section with a limited number of parameters that all have a physical background.

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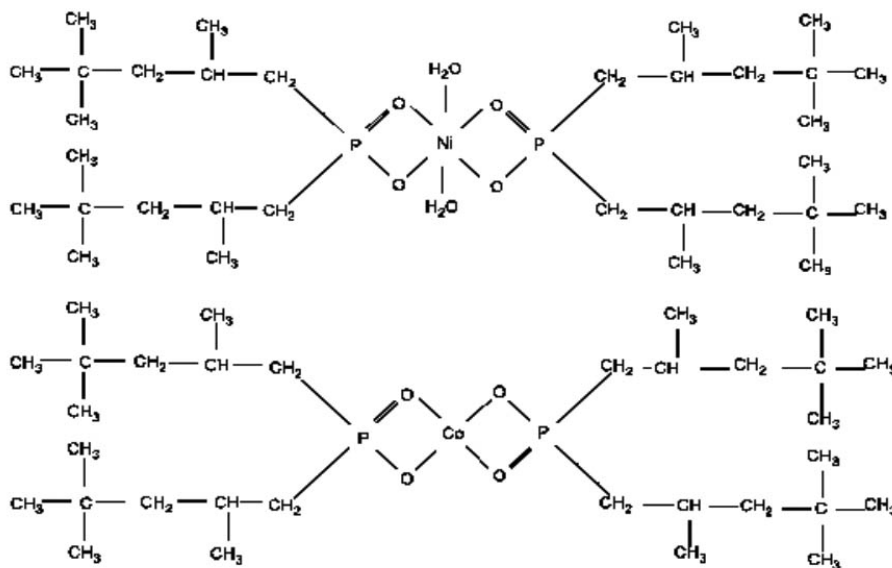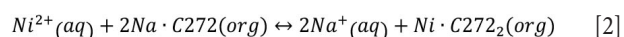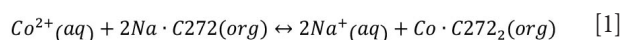

Figure 1—Structure formed during Co/Ni separation with C272 as the extractant

The system that was selected for this was cobalt/nickel (Co/Ni) purification using 50 mol% NaOH-preloaded Cyanex 272 (C272) as extractant (Mans, 2019). Metals are extracted by C272 via cation exchange mechanism (Rodrigues et al., 2022). The synthetic feed that was used contained 1 g Co/L and 100 g Ni/L corresponding with a composition of 99% Ni, as it occurs in a base metals refinery. Due to confidentiality restrictions, the aqueous feed solution from the industry was not accessible, therefore the use of the synthetic feed was employed for this study. The commercial purity of the raffinate is 99.95% Ni, and that of the scrubbed extract is 99% Co. Despite the high selectivity for Co, also Ni is co-extracted, both requiring the same stoichiometry of two C272 ligands per metal ion, however due to slightly larger ionic radius and higher electronegativity for Ni it can accommodate additional water molecules in its coordination sphere, as shown in Figure 1 (Santanilla et al., 2021).

The extraction reactions are shown by Equations [1] and [2], where (*aq*) and (*org*) represent the aqueous and the organic phases, respectively.

$$Co^{2+}(aq) + 2Na \cdot C272(org) \leftrightarrow 2Na^+(aq) + Co \cdot C272_2(org) \quad [1]$$

$$Ni^{2+}(aq) + 2Na \cdot C272(org) \leftrightarrow 2Na^+(aq) + Ni \cdot C272_2(org) \quad [2]$$

The free ligand (FL) model

The FL model assumes that there is a limited number of ligands in the solvent that are available for extraction, and this is the loading capacity of the solvent. The model provides the equilibrium concentration of component *i* in the solvent as follows:

$$y_{eq,i} = \alpha \cdot K_{do,i} \cdot x_i \quad [3]$$

In this equation, x_i (mol/L) is the concentration of metal *i* in the aqueous phase, $K_{do,i}$ (-) is the distribution coefficient of metal *i* at infinite dilution, and α (-) is the free ligand fraction still available for extraction and defined by:

$$\alpha = \frac{y^0 - \sum_j y_j}{y^0} \quad [4]$$

Table I

List of chemicals used for the experiments

Chemical	Purity	Supplier
$NiSO_4.6H_2O$	95%	Anyang General Chemical Company, Ltd
$CoSO_4.7H_2O$	99%	Sigma-Aldrich
H_2SO_4	98%	Labchem
NaOH	99.75%	Promark
Cyanex 272	85%	Solvay
1-Octanol	>99%	Sigma-Aldrich
Shellsol D70	–	SNF Chemicals

where y^0 (mol/L) is the maximum loading capacity of the solvent. It should be noted that in the FL model all concentrations are in mol/L. In the FL model the selectivity for a pair of metals, β_{ij}, is constant and equal to the ratio of the distribution coefficients at infinite dilution:

$$\beta_{ij} \equiv \frac{y_i/x_i}{y_j/x_j} = \frac{K_{do,i}}{K_{do,j}} = constant \quad [5]$$

Experimental

Methodology

Synthetic solutions were prepared using the chemicals in Table I. The solvent used in the experiments was 22 wt.% C272 (Mans et al., 2020), with 5% v/v of 1-Octanol as modifier and Shellsol D70 as the diluent. Prior to extraction the solvent was pre-neutralized with 50% mol/mol of NaOH. The aqueous and the organic phases were thoroughly mixed at room temperature in an orbital shaking incubator (Labcon) for 1 hour at a frequency of 150 rpm to guarantee equilibrium. By determining the concentrations of the metals in the aqueous solutions, it was observed that after an hour of mixing and settling, the distribution of metals between the two phases did not change with time, therefore this confirmed that equilibrium had been achieved within an hour.

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Analyses

Metal concentrations (Co, Ni and Na) of aqueous solutions were determined by ICP-OES (Agilent 5110). Metal concentrations in the solvent were calculated by mass balance. The pH was measured using a Metrohm 744 pH-meter with a calibrated 6.0258.010 electrode (Hanna instruments).

Application of the FL model in Co/Ni purification

The Co/Ni/C272 refinery

The block flow diagram (BFD) of a Co/Ni/C272 refinery is shown in Figure 2.

The 99% Ni feed is extracted counter currently with 22wt.%, C272 producing a 99.95% Ni raffinate. In the extraction section Co and Ni are exchanged with Na in the solvent. This composition includes only the metals of interest, specifically Co and Ni. The Co-extract that contains substantial amounts of Ni is scrubbed using a concentrated Co reflux from the stripper. In the scrubber, Ni in the solvent is exchanged with Co in the aqueous phase. The scrubbed extract is stripped with concentrated H_2SO_4 to produce a 99% Co at a typical concentration of 30 g Co/L. In this process all metals (Co, Ni and Na) are exchanged to bring the C272 back in the protonated form. Finally, the C272 is pre-loaded with 50 mol% using concentrated NaOH and the pre-loaded solvent enters the extraction section at the raffinate side. The aqueous return scrub streams are relatively small compared to the main streams as will be shown in the design paragraph.

FL model parameters for Co/Ni/C272

In a series of experiments with varying organic /aqueous (O/A)-ratios, the three FL model parameters were determined, as demonstrated in Table II. In these experiments, the pH of the aqueous solutions was maintained in the range of 5.0–5.5 and the (O/A)-ratios tested were in the range of 0.2–3.0, at room temperature (Mans, 2019). After mixing and settling, the concentration of metals in the aqueous solutions was determined

Table II

Free ligand parameters for Co/Ni/C272 (22 wt.%)

y^0 (mol Me/L)	0.119
$K_{do,Co}$	15
$K_{do,Ni}$	0.089

by ICP-OES and that, in the organic phase, was determined by mass balance. Subsequently, $K_{d, Co}$ and $K_{d, Ni}$ were calculated as the ratios of the concentration of Co and Ni in organic phase over aqueous phase, respectively, and plotted as shown in Figure 3.

The maximum loading of 0.119 mol Me/L corresponds with a total metal concentration of approximately 7 g/L (Co and Ni have about the same molecular weight). The Co/Ni selectivity calculated from the distribution coefficients at infinite dilution is $\beta_{Co/Ni} = 169$. The consistency of the model is shown in Figure 3, where for each experiment the distribution coefficients of Co and Ni were plotted for extraction conditions, that is 100 g Ni/L. As will be shown in the design, the Ni concentration in the extraction section only slightly reduced from feed to raffinate side. However, the co-extracted Ni results in an extract well below the 99% Co specification.

As illustrated in Figure 3, the maximum values of the distribution coefficients correspond with the values at infinite dilution and the slope is the inverse of the Co/Ni-selectivity. The observation that the experimental trend is not passing through the origin seems to suggest that Ni is also extracted by the other two components in the solvent. In the design sections this will be ignored. The competition between Co and Ni for free ligand is presented in Figure 4.

In Figure 4 the following can be observed. For the pure Co system, with increasing Co concentration in the aqueous phase, the Co concentration asymptotically approaches the maximum loading of y^0=0.119 mol Co/L. Adding 100 g Ni/L, reduces the maximum concentration in the solvent to 0.052 mol Co/L. This is the maximum loading using the real Co/Ni feed. For the design
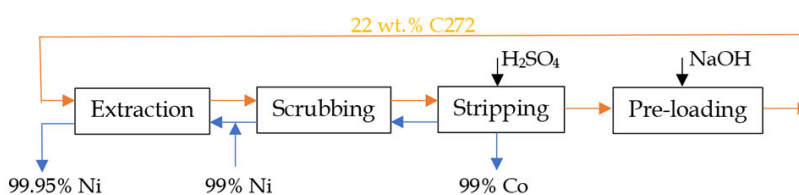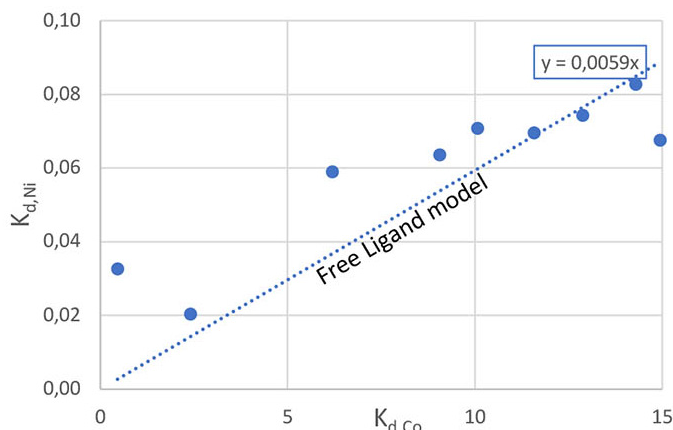

Figure 2—BFD of a Co/Ni refinery

Figure 3—Co and Ni distribution coefficients for 22 wt.% C272 at 100 g Ni/L and Co at different O/A-ratios

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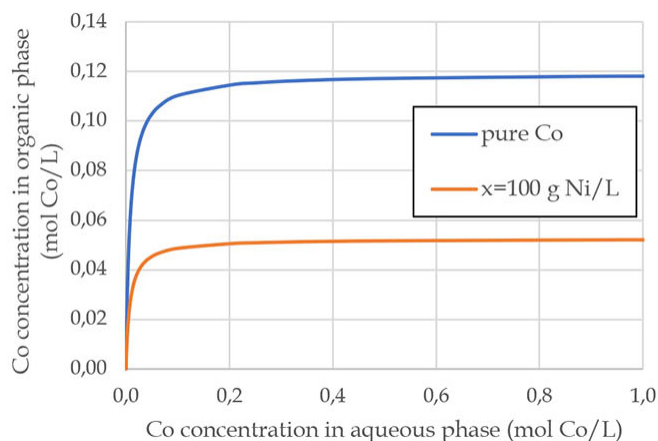

Figure 4—Co-isotherms according to the FL model for pure Co and Co with 100 g Ni/L
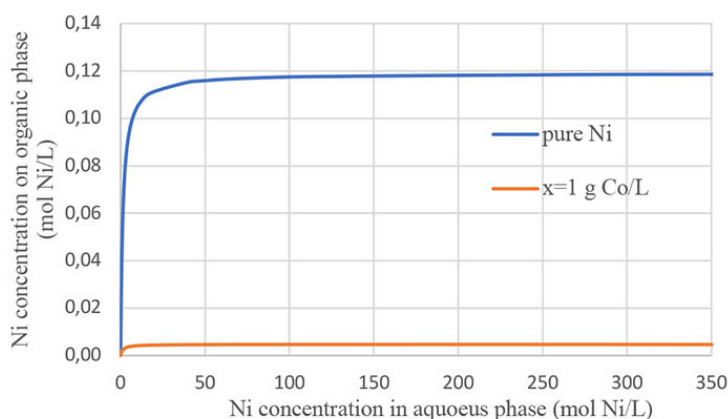

Figure 5—Ni isotherms according to FL model for pure Ni and Ni with 1 g Co/L

of n equilibrium stages and a binary system, this results in $2n$ mass balance and $1n$ equilibria. This set of $3n$ equations was conveniently solved using Excel-Solver. In Figure 5, for pure Ni system with increasing Ni concentration in the aqueous phase, the Ni concentration also approaches the maximum loading capacity of $y_0 = 0.119$ mol Ni/L. Adding 1 g Co/L reduces the loading capacity and the graph approaches a maximum of 0.005 mol Ni/L in the solvent. This is below that of Co and this is consistent as C272 has more affinity for Co over Ni.

Design of the co-extraction section

The basis of design is a feed containing 1 g Co/L and 100 g Ni/L that needs to be purified to 99.95% Ni and 99.0% Co, respectively. The conventional method (Seader et al., 2011) is used for the flash calculations to determine the number of equilibrium stages to purify 99% Ni to 99.95% Ni in the raffinate. In a flash calculation it is assumed that both streams leaving the stage are in equilibrium, as described by the FL model in Equation [3]. This is combined with the mass balance over the equilibrium stage:

$$\frac{\Delta x_i}{\Delta y_i} = \frac{O}{A} \qquad [6]$$

The minimum (O/A) ratio is calculated by assuming that: a) the solvent is in equilibrium with the feed, and b) all Ni is extracted. For this case, it is (O/A)$_{min}$= 0.294. Details of the calculation, using the FL model, are shown in Table III.

The minimum O/A ratio required to achieve the desired metal separation is 0.294, with a free ligand fraction of 22.7% and the Co

extract purity of 62.8%. To achieve equilibrium between solvent and feed, an infinite number of stages would be required. In the conceptual design phase, a 20% higher value is used to reduce the number of stages to an acceptable level:

$$\frac{O}{A} = 1.2x \left(\frac{O}{A}\right)_{min} = 0.352 \qquad [7]$$

The method outlined in the following was used to predict the purity of the calculated stages. Firstly, estimate the concentrations of Co and Ni in the aqueous phase (x_i). Next, use these estimates to determine the organic phase composition (y_i) through mass balance calculations. Subsequently, calculate the free ligand fraction (α) using Equation [4] and the parameters in Table II. Following that, determine x_i at equilibrium using Equation [3] and compare

Table III

Minimum O/A ratio

	O/A$_{min}$		
mol Co/L	0.0578		0
mol Ni/L	0.0342	O/A$_{min}$ 0.294	0
Co purity	62.80%	N infinite	
		α 22.7%	
		Ψ_{raf} 100.00%	
mol Co/L	0.0170	Ψ_{extr} 62.80%	0.0000
mol Ni/L	1.7038		1.6937
Ni purity	99.01%		100.00%

Table IV

Four equilibrium stages for co-extraction to pure Ni raffinate

	4-stage, O/A=0.352								
mol Co/L	0.0467		0.0316		0.0172		0.0072		0
mol Ni/L	0.0405	E1	0.0489	E2	0.0567	E3	0.0609	E4	0
Co purity	53.59%		39.22%		23.22%				
		α 26.76%		α 32.35%		α 37.93%		α 42.78%	
mol Co/L	0.0170		0.0116		0.0066		0.0030		0.000508
mol Ni/L	1.7038		1.7068		1.7095		1.7110		1.689525
Ni purity	99.01%		99.32%		99.62%		99.82%		99.97%

it with the x_i from the mass balance. Finally, use a Solver in Excel to adjust x_i until y_i matches both the mass balance and equilibrium composition. When the Solver converges it will accurately determine y_i, and yield the correct α.

At this O/A ratio, the number of stages, the purity, and the free ligand fraction in the extract to obtain pure Ni raffinate are four (4) equilibrium stages to produce raffinate with Ni purity of 99.97%. This leads to Co purity of 53.59% in the extract and the free ligand fraction of 26.8%. The detailed results per stage are presented in Table IV.

Design of the Ni-scrubbing section

The basis of design for the scrubbing section is the extract, which is to be scrubbed from 53.59% Co to 99.0% Co with the scrubbing liquor of 30 g Co/L at 99.0% purity (reflux from the stripper). The design results from the scrubber showed that the O/A ratio needed to scrub all Ni from the extract is 13.48 using 20% excess. One (1) equilibrium stage is required to increase the extract purity from 53.59% to 99.01% and the free ligand fraction in the extract decreases further from 20.76% due to high Co affinity at the concentration of 30 g Co/L. The scrub return to the extraction section contains 37.2% Co. The Ni-rich scrub return is only 2.5% of the feed. Therefore, it can be conveniently added to the feed as shown in the BFD (Figure 2). A more detailed mass balance of the 1-stage scrubber is presented in Table V.

It should be noted that, with the available data, the H_2SO_4-stripper cannot be designed with the FL model. For this, the H^+ exchange with Co^{2+} should be included in shakeout tests. The same is true for the pre-loading, where H^+ is exchanged with Na^+.

Validation of the method

The method was validated by shakeout tests that correspond with the design O/A ratios of extraction, scrubbing, and stripping. The Co-Ni-Na ICP data were used to verify if only Na was exchanged with Co and Ni. This was done by comparing the total ionic values of the aqueous phase, $\sum z_i x_i$, before and after shakeout, as well as the pH, where i is the summation over Co, Ni and Na. In Table VI, the Ni purity increases from 98.99% to 99.78% in a single stage. The Co purity in the extract increases from 1% in the feed to 38% in the extract. Additionally, the free ligand fraction decreases from 100% in the fresh solvent to 20.22% in the extract. These results validate the FL model, as they closely align with the results from Table IV, stage 1. The slight difference in the available free ligand fraction for extraction is likely due to a slight variation in the feed purity.

In the scrubbing section, the free ligand fraction further decreases from 20.22% in the extract to 18.75% in the scrubbed

Table V

Mass balance for one-stage scrubber

	1-stage scrub, O/A=13.48	
mol Co/L	0.0467	0.0825
mol Ni/L	0.0405	0.0008
Co purity	53.59%	99.01%
	Scrub1	
	α 20.76%	
mol Co/L	0.0265	0.5091
mol Ni/L	0.0447	0.0051
Co purity	37.20%	99.01%

extract, with results that are closely aligned with the scrubber design in Table V. The minor differences in the results may be attributed to variations in the composition of the scrubbed extract.

The results are demonstrated in Table VI.

In the extraction shakeout at O/A=1.2x(O/A)$_{min}$=0.352, the $\sum z_i x_i$, changes slightly from 3.121 mol/L in the feed to 3.262 mol/L in the raffinate. Since also the pH hardly changes, the assumption that Co and Ni only exchange with Na is valid. The observation that the nickel concentration in the raffinate is slightly higher than in the feed shows that some water is absorbed by the solvent. The nickel purity increases from 98.99% to 99.78% in one stage. The cobalt purity of the extract increases from 1% in the feed to 38% in the extract. The free ligand fraction reduces from 100% in the fresh solvent to 20.22% in the extract.

In the scrubbing shakeout at O/A=1.2x(O/A)$_{min}$=8.63, the $\sum z_i x_i$, changes slightly from 1.086 mol/L in the scrub liquor to 1.077 mol/L in the scrub reflux. Since also the pH hardly changes, the assumption that Co and Ni only exchange with Na is valid. The free ligand fraction decreases from 20.22% in the extract to 18.75% in the scrubbed extract, indicating that some of the Na in the extract is replaced with Co from the scrub liquor.

In the stripping shakeout at O/A=6.00, the objective is to produce a 30 g Co/L solution that can partially be refluxed to the scrubber. The results for the rich liquor show that it contains 30.33 g Co/L and thus can be used for reflux scrubbing. The $\sum z_i x_i$, = 3.269 mol Me/L, which is essentially equal to the feed, shows that the ion balance is correct. The pH=-0.30, which makes it less useful for reflux scrubbing. This problem can be bypassed by using less concentrated acid and two stripping stages. The first stripping stage is operated with a low O/A ratio to produce reflux scrub liquor at a higher pH, and the second with the rest of the acid to recover all Co and to produce metal-free solvent for pre-loading.

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Table VI

Validation of the method

Stage	O/A	Stream	Co (g/L)	Ni (g/L)	Na (g/L)	Σzixi (mol/L)	pH	Purity (wt(%)	a (-)
Extraction	0.352	Feed	0.920	90.54	0.095	3.121	5.22	98.99%	
		Solvent	0	0	*10.876*				100%
		Raffinate	0.197	90.88	3.616	3.261	5.30	99.78%	
		Extract	*2.066*	*3.368*	*2.199*			38.02%	20.22%
Scrubbing	8.63	Scub liq	31.99	0	0.002	1.086	5.04		
		Extract	2.066	3.368	2.199			38.02%	20.22%
		Scrub reflux	1.184	9.55	0.690	1.077	5.42	96.15%	
		Scr. Extract	*5.635*	*0.144*	*2.039*			97.51%	18.75%
Stripping	6.00	Scr. Extract	*5.635*	*0.144*	*2.039*				18.75%
		Rich liquor	30.33	7.137	0.019	3.269	-0.30	80.95%	
Solvent concentrations were calculated by mass balance and are given in Italics									

Conclusions

The FL model provides a powerful numerical method for the design of the extraction and scrubbing section for cases that produce extracts that do not meet the product specifications. Given the high cost of the extractants, optimizing their use is important in minimizing the economic impact of the extraction processes. It is therefore crucial that the free ligands are utilized as efficiently as possible as more extractant will be required to achieve the desired separation if they are not utilized efficiently. The model therefore helps to determine how much of the free ligands are still available for extraction as inefficient use of the ligands can result in higher production costs.

This conclusion is based on a minimum number of physical parameters: maximum loading capacity of the solvent and distribution coefficients at infinite dilution for each relevant metal.

The FL model can be used for single metal as well as multi-component and multi-species industrial solutions. In the latter, the graphical McCabe Thiele method is not applicable. While the FL model has not been verified for other metals, it can work in multi-species industrial solutions that contain Co and Ni, as the composition of the synthetic feed used in this study is as it occurs in a base metals refinery. The FL model only accounts for the interaction between free ligands and metals and cannot account for the interaction between metals where multi-metal complexes might be present in the system. Another limitation is that the model focuses only on the equilibrium conditions and does not consider the kinetics of the process.

This was demonstrated and validated for the design of a Co/Ni refinery using a 22 wt.% C272 solvent, showing that the same three FL parameters can be used for the extraction and the scrubbing section. The Co-Ni-Na ion balance was used in the method validation tests at conditions that were similar to the designed plant. In principle, the FL model is also able to design the stripping and pre-loading sections by including H-C272 exchange data.

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