Flowsheet design and improvements in solvent extraction modelling using cyanex reagents

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Solvent extraction (SX) in hydrometallurgical processes is an essential technology for manufacturing high purity metals such as copper, rare earth oxides, uranium, cobalt, nickel, etc. With regard to cobalt, much experience has been gained over the last thirty years on the use of CYANEX 272 for its purification and recovery from weakly acidic nickel-rich sulfate solutions and has proven its effectiveness in the manufacture of high purity cobalt metals or salts. These successes were achieved through the optimisation of a number of parameters that were historically determined through intensive pilot testing due to the complexity of the chemistry involved. Syensqo developed solvent extraction modelling capabilities (MINCHEM) to help operators design and optimise circuits using CYANEX and DEHPA reagents. This modelling program has been available and utilised for several years now, and it has guided flowsheet design by narrowing process conditions such as reagent concentration, staging configuration, and pH profile to achieve a given separation and purity requirement. Recently, using the same methodology, improvements have been made to the functionality of the tool to evaluate full circuit models more easily. This article will describe SX applications using CYANEX reagents and highlight the improvements made to the program with specific examples.

INTRODUCTION

Solvent extraction (SX) is commonly used for the purification of critical metals and is incorporated or being evaluated in most flowsheets targeting battery metals (Rickelton, Robertson, & Burley, 1982; Rickelton, Flett, & West, 1984; Rickelton & Nucciarone, 1997). SX has applications in these flowsheets for impurity removal and purification of Cu, Mn, Co, Ni and Li. An example of the versatility of solvent extraction may be seen in potential flowsheets for spent battery processing where production of high purity cobalt, nickel and lithium are targeted (Agarwal, Khalid & Porvali, 2019). Figure 1 demonstrates the multiple steps where SX may be incorporated in the process.

First, treatment of the solution should be considered to remove iron and aluminum by precipitation or other means. Depending on the copper concentration and economics, SX using hydroxyoximes (e.g., ACORGA extractants) would allow for copper cathode production through electrowinning. Otherwise, copper cementation or precipitation should be considered to remove it from solution. Once iron, aluminum and copper are removed, manganese will be the main impurity to target next. An impurity removal circuit using Di(2-ethylhexyl) phosphoric acid (DEHPA) is effective in extracting manganese away from cobalt along with any residual iron, aluminum and copper. After the impurity circuit, a CYANEX 272 circuit can be utilised for recovery of cobalt, leaving nickel and lithium in the raffinate. Additional SX circuits can be considered using a carboxylic acid for nickel and CYANEX 936P for lithium.

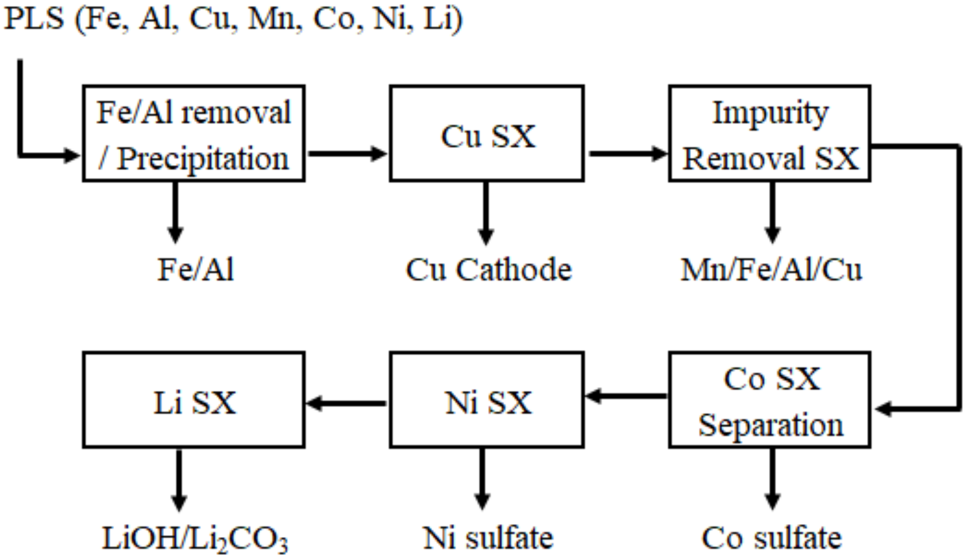

Figure 1. Example SX flow diagram for separation and purification of Co, Ni and Li.

Each of these circuits requires a unique set of conditions to achieve the targeted separation and purity. Along with selecting the optimal reagent, many operational factors must be considered. Organic/aqueous ratios and extractant concentrations must match metal loading requirements. The SX configuration will depend on the target metals and impurities, concentrations and purity requirements. An appropriate pH profile in extract, scrub and strip should be determined along with the resulting need for acid and base addition. Variability of the SX feed should also be considered so that the circuit design can be flexible to maintain recovery and purity targets. Identifying these parameters is important for the economics and efficiency of a project or operation.

Circuit design and optimisation is not a simple evaluation and usually necessitates considerable prior SX experience along with laboratory and pilot-scale testing. To aid in the design, Syensqo created the modelling application MINCHEM specifically to facilitate quick evaluation of various operational factors. Recently, the modelling tool was upgraded to include fully integrated circuits, which allows easier modelling of more complex circuits. In this paper, two common extractants (DEHPA and CYANEX 272) will be reviewed and utilisation of the tool will be highlighted to reduce design time and cost associated with circuit design.

EXTRACTANTS AND METAL LOADING

DEHPA

DEHPA has many commercial SX applications which include primary Zinc (Zn) extraction, impurity removal ahead of Co/Ni circuits (primarily for removal of Ca and Mn along with residual Fe, Al, Cu, Zn, Cd), extraction of uranium (U), vanadium (V) and rare earths (CYTEC Industries Inc. (2016). DEHPA extractant. CYTEC technical brochure). Figure 2 (commonly called as S-curve) shows the extraction of the different metals using DEHPA as a function of pH.

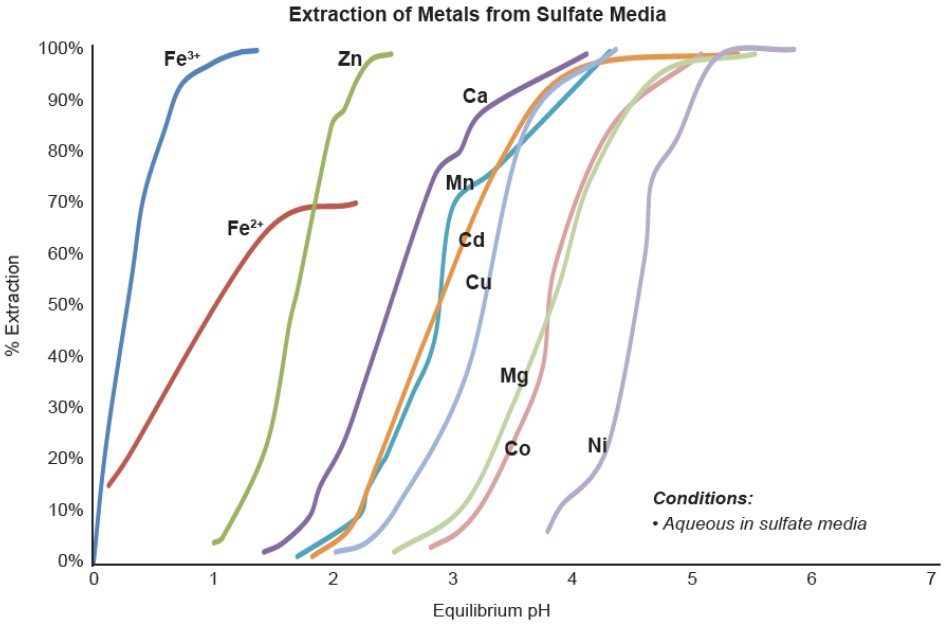

Figure 2. DEHPA S-curves.

CYANEX 272:

The active component of CYANEX 272 extractant is bis (2,4,4-trimethylpentyl) phosphinic acid. This extractant has proven to be the reagent of choice for the separation of cobalt from nickel from both sulfate and chloride media due to the high selectivity of Co over Ni (Bourget, C. & Jakovljevic, B. (2008)). It is used to produce a major portion of the world's cobalt by SX. In addition to Co/Ni separation, other CYANEX 272 applications can include Mn separation from Ca/Mg, Mg/Ni separation and rare earth separation. Figure 3 shows the relative order of metal extraction by CYANEX 272 as a function of pH.

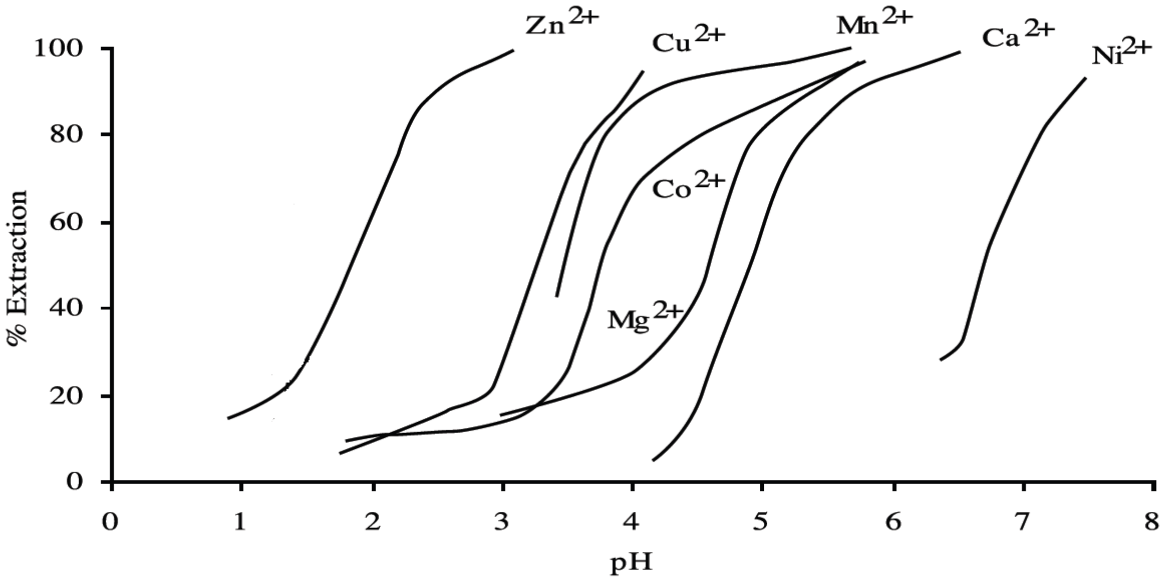

Figure 3. CYANEX 272 S-curves.

METAL LOADING

The extraction reaction for both DEHPA and CYANEX 272 is shown below for divalent metals (Rickelton, Robertson, & Burley, 1982; Rickelton, Flett, & West, 1984; Rickelton & Nucciarone, 1997)):

$$2\ RH + M^{2+} \rightarrow R_2M + 2\ H^+ \qquad [1]$$

As metal loads (i.e. cobalt), acid is generated and prevents further metal from loading due to the pH requirement to drive extraction. Therefore, the addition of a base is required to control pH. The specific based utilised can vary based on economic factors, logistics, availability, and byproduct recovery/regeneration. The following bases are commonly used: ammonium hydroxide, sodium hydroxide, or sodium carbonate may be used.

To neutralise the acid generated during loading, base can be introduced into the circuit via two possible methods: direct addition of base into the mixers or pre-neutralisation of the organic.

Direct Mixbox pH Control
A predefined target pH can be achieved for each stage when base is introduced directly to the mixbox. A pH target is usually chosen for each step in pilot-scale testing to generate a multi-stage pH profile that maximises the recovery of the target metal or metals while rejecting contaminants. To achieve sufficient circuit performance during commercial operation, the necessary pH profile needs to be carefully regulated, necessitating quick and accurate pH measurement.

To measure the pH a portion of the aqueous phase can be removed from the mixbox emulsion or a pH electrode introduced into the aqueous of the settler or weir. In order to avoid organic fouling and scale buildup, which could compromise the electrode's ability to monitor pH accurately, routine maintenance and calibration are also necessary. Metal hydroxide precipitates may occur as a result of localised high pH areas, or 'hot spots', caused by base addition straight into the mixbox. According to Bourget and Jakovljevic (2008), hotspot occurrence can be reduced by using relatively diluted base solutions (100 gpl NaOH), although the effect on the water balance must be taken into account.

Pre-Neutralisation
It is possible to pre-neutralise CYANEX 272 with enough base to load the desired metal(s) before extraction, as an alternative to directly controlling the pH of the mixbox. Below is an illustration of a sodium hydroxide pre-neutralisation reaction.

$$RH + NaOH \rightarrow NaR + H2O \qquad [2]$$

As sodium (or ammonium) on the organic exchanges with the metal in the feed, extraction takes place. pH is not altered throughout the metal extraction process.

$$2\ NaR + M^{2+} \rightarrow MR_2 + 2\ Na+ \qquad [3]$$

Operating guidelines indicate pre-neutralisation should not exceed 50–55% of the ligand to prevent problems such as third phase formation. Higher concentrations of base (28% w/w NH_4OH or 400 gpl NaOH) may be used relative to mixbox pH control, reducing water addition to the circuit (Bourget & Jakovljevic, 2008).

Understanding metal loading, selectivity and an appropriate pH profile and control are required to start evaluating circuit conditions for a given separation. Extensive benchtop and pilot test work are typically required to confirm the design conditions. To reduce the uncertainty of circuit design and time requirements for laboratory testing, circuit modelling can be a helpful approach.

MINCHEM PROCESS MODELING - INITIAL DESIGN

Syensqo previously developed CYANEX 272-specific solvent extraction modelling software to assist operators in the design and optimisation of their circuits. The tool supports optimising reagent/plant performance by determining the process conditions desired for optimal selectivity against impurity metals and allowing study of a wide-range of circuit configurations prior to pilot-scale testing.

SX flowsheet development and optimisation requires significant laboratory and pilot scale testing, which is time-consuming and costly. Syensqo's MINCHEM modelling software allows for an accelerated assessment of the SX configuration and operational parameters to assist in the design and optimisation (Bourget, Soderstrom & Donegan, 2011).

Presently MINCHEM modelling capabilities include applications using CYANEX 272 for cobalt and related metals, CYANEX 572 and CYANEX 801 for rare earth elements and DEHPA for Zn and common impurity metals.

MINCHEM METHODS AND INPUTS

The MINCHEM modelling software utilises lab generated equilibrium data for multiple metals and extractants to determine resulting metal concentrations and pH; by using the equilibrium calculations, the software takes into account metal exchange and selectivity achievable for a given circuit design, and by using standard chemical engineering calculations the program follows an iterative process to determine the circuit performance (Soderstrom 2010).

The process is repeated for each section of the SX plant. For example, multiple iterations are completed across extract to obtain a first estimate of the loaded organic and raffinate composition. Iterations are then completed across scrub using the first loaded organic and an assumed scrub feed to obtain a first approximation of the scrubbed loaded organic composition and a spent scrub composition. Iterations are then completed across strip using the scrubbed loaded organic and an assumed strip liquor composition to obtain a new barren organic and rich liquor composition.

The iterative process is completed around each extract, scrub, and strip cascades and then around the full process until an overall mass balance is achieved. Figure 4 graphically shows the iterative process utilised by the program.

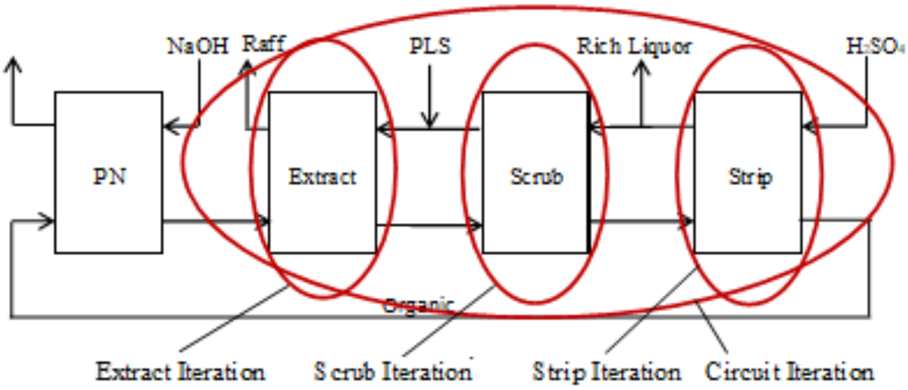

Figure 4. Circuit iterative process.

Extract circuit analysis
Model Inputs: Number of stages, metals concentration of feeds, initial pH / pre-neutralisation of organic, extractant type and concentration, organic to aqueous ratio.

Model Outputs: loaded organic and raffinate composition, pH profile for each stage.

In the case where the circuit uses a direct mixbox base addition, the pH can be fixed across the circuit and the number of stages can be varied to determine the right combination (Figure 5A). For a circuit using pre-neutralised organic, it will require to vary the pre-neutralisation percentage until the desired recovery is achieved (Figure 5B).

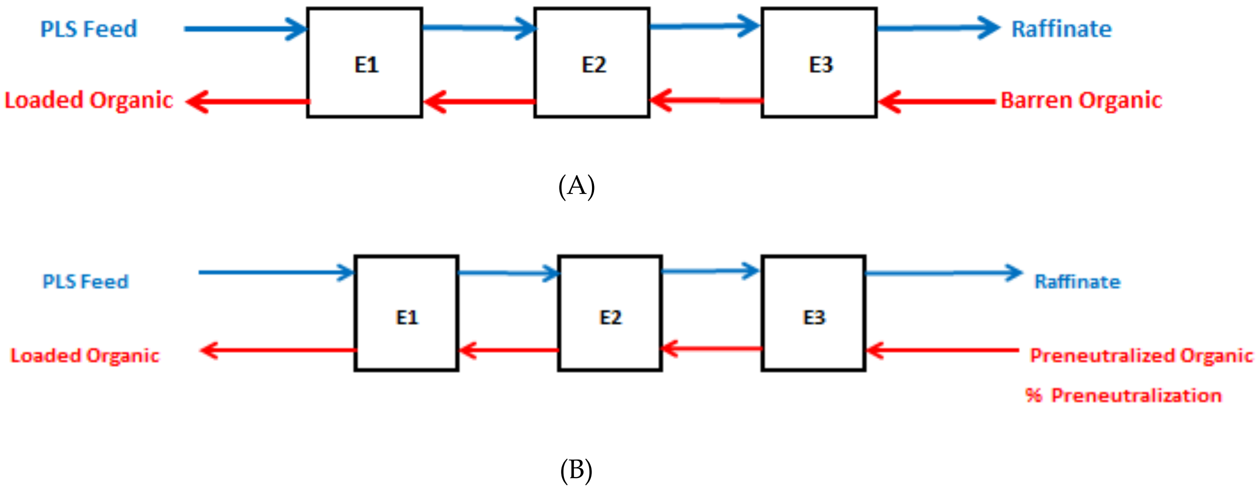

Figure 5. Extraction profile for a direct mixbox base addition and for a pre-neutralised organic.

- Typical optimised pH profile in mixbox pH control: A higher pH in E3 is recommended to achieve high recovery of the metal of interest, while lowering pH in E1 to minimise impurity co-extraction;
- A similar pH profile is obtained naturally using pre-neutralised organic.

Scrub/Strip circuit analysis

Similar to the use of pre-neutralised organic in extraction circuits, acidified water or a fraction of the rich liquor may be used in scrubbing and stripping without the need for pH control (by acid addition to the mixbox). When sufficient acid (or metal from the rich liquor) is present in the scrub or strip liquor, the pH will drift naturally to form a pH profile that favours impurity scrubbing. A lower pH at the scrubbed organic exit promotes impurity removal and higher pH where the spent scrub exits minimises scrubbing of the metal(s) of interest (Figure 6).

Model Inputs: Scrub feed composition (acid and/or metal), organic to aqueous ratio, reagent concentration, number of stages, loaded organic composition.

Model Outputs: Scrubbed organic composition, spent scrub composition, interstage pH.

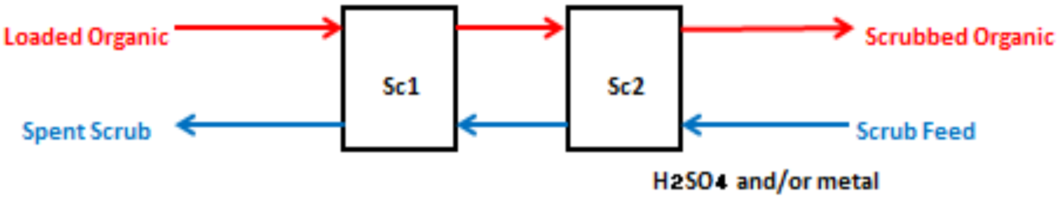

Figure 6. Scrub circuit profile.

The variation of scrub feed acid or metal concentration until the desired organic selectivity is a common practice.

For a pH profile using mixbox pH control, it is recommended to lower pH in Sc2 to achieve high scrub efficiency of impurity elements and increase pH in Sc1 to minimise impurity co-scrubbing of the metal of interest.

MINCHEM PROCESS MODELING - UPGRADED VERSION

Syensqo has built on the previous version of the modelling tool, which has proved its effectiveness in the design of solvent extraction circuit. An upgraded version was released in 2024, improving the functionality/integration and user interface to allow more efficient modelling of complex circuits.

Two main objectives were pursued for the upgrade:

1. Full integration of an SX circuit including extract, scrub and strip
2. Update user interface.

In the initial design, each part or stage (extract/scrub/strip) is iterated separately until a mass balance is achieved, then the next stage is performed. However, in the upgraded version, the model runs until a mass balance is achieved over the entire process, including extraction, scrubbing, and stripping, before proceeding further. This likely improves efficiency by considering the entire process as a whole rather than individual stages.

A more user-friendly interface improves the overall user experience, making interaction with the program easier. Faster execution is another aspect which means quicker results, which can be crucial in time-sensitive situations or when dealing with large datasets. Overall, these improvements contribute to a more efficient and effective workflow, leading to faster model development.

PROCESS MODELLING EXAMPLE

As an example, a fully integrated circuit simulation with pre-neutralisation was run to assess the metal concentrations of outlet solutions and operating conditions for a plant treating a PLS containing 7.00 g/L Co, 8.00 g/L Mg and 47.00 g/L Ni at pH -2.3 using 25% v/v CYANEX 272 in diluent at 50°C with 5E + 6Sc + 3S circuit configuration. The objective is to produce a high purity cobalt stream. Some additional parameters are shown below.

Extraction:

➔ Pre-neutralisation: 35%
➔ O/A ratio: 1.15

Scrub:

➔ Scrub feed: 55 gpl H_2SO4 (no metal)
➔ O/A= 15

Strip:

➔ Strip feed: 200 gpl H_2SO4 (no metal)
➔ O/A= 25

The complete steady state circuit is displayed in Figure 7. All metal concentrations are listed in grams per litre.

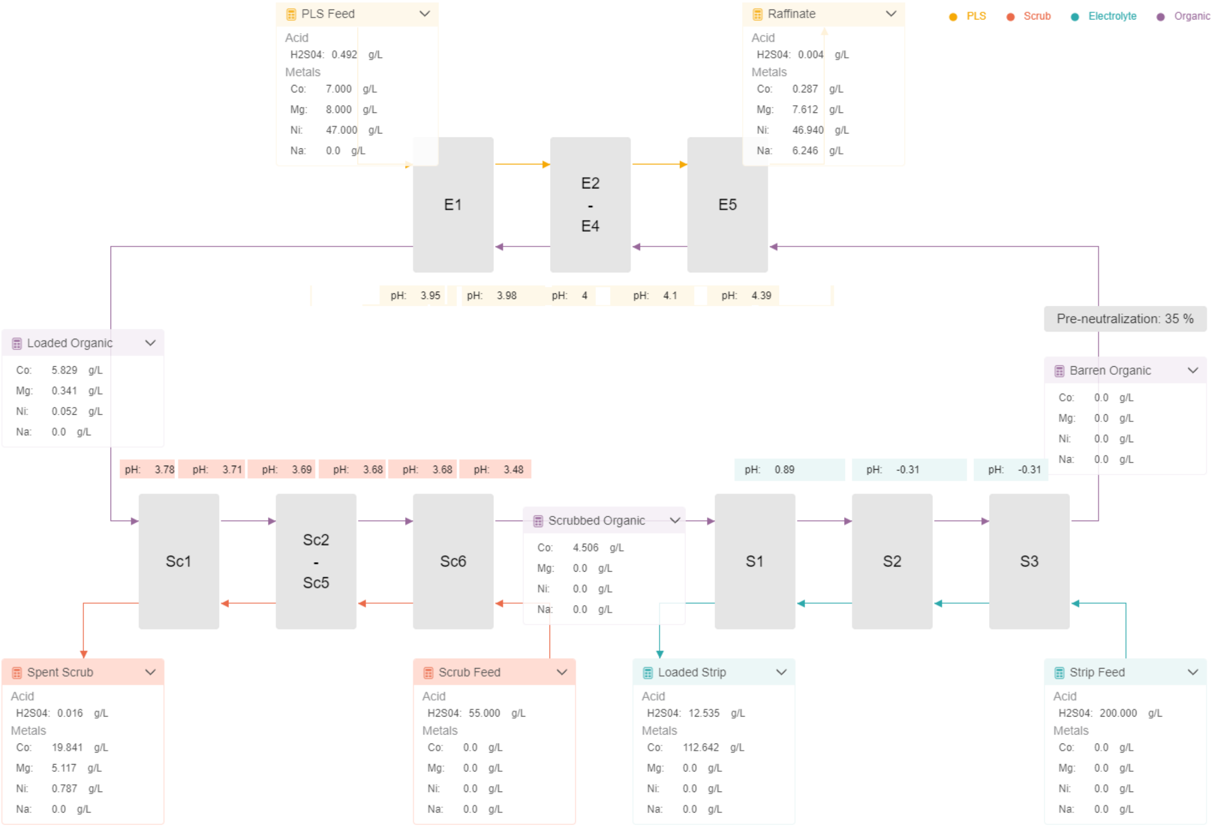

Figure 7. Prediction model for a 5E+6Sc+3S circuit configuration with CYANEX 272.

Figure 7 shows a relatively complicated circuit which was predicted as a full process in a short time by using an upgraded MINCHEM application. In the extraction part, as seen from the model, the raffinate still contains some Co, and there is a possibility to optimise the circuit by increasing the organic pre-neutralisation level or increasing extract stages number. The necessity of six scrub stages is dictated by a very strict limit on Mg content in scrubbed organic. Three stages of strip stages were enough to strip all the metals and have barren organic with no metals in.

Output of the predicted model is given in Table 1 with an indication of metal concentrations of obtained solutions and efficiencies of each section.

Table I. Metallurgical profile for the predicted model

Extraction					
pH Profile	Metals	Concentrations, g/l			Extraction efficiency, %
		E1 Aqueous Feed	Loaded Organic	Aqueous Raffinate	
3.95/3.98/4.00/4.10/4.39	Co	7.000	5.829	0.287	95.9
	Mg	8.000	0.341	7.612	4.85
	Ni	47.000	0.052	46.94	0.13
Scrub					
pH Profile	Metals	Concentrations, g/l			Scrub efficiency, %
		Scrub Liquor	Scrubbed Organic	Spent Scrub Liquor	
3.78/3.71/3.69/3.68/3.68/3.48	Co	0.000	4.506	19.841	22.70
	Mg	0.000	0.000	5.117	100
	Ni	0.000	0.000	0.787	100
Strip					
pH Profile	Metals	Concentrations, g/l			Strip efficiency, %
		Strip Liquor	Stripped Organic	Loaded Strip Liquor	
0.89/-0.31/-0.31	Co	0.000	0.000	112.642	100

The given examples clearly indicate that the objective was achieved and a pure cobalt loaded strip solution can be produced with mentioned inlet parameters of the plant.

CONCLUSION

Syensqo has enhanced its CYANEX MINCHEM software to allow the simulation of circuits. An old version has been updated, improving on time saving when it comes to the model, and a more user-friendly interface.

Modelling capabilities significantly help to expedite the development of flow sheets and support the production operations, improving the chance of successful commercialisation to make products of the desired purity.

The updated program offers significant advantages for customers of Syensqo, engineering houses and laboratories. Its enhancements, including interface and improved efficiency, enable these entities to operate more effectively. It represents a substantial step forward in optimising operations and delivering superior outcomes for customers.

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