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Development of an integrated model for cobalt solvent extraction using Cyanex 272

Heather A Evans^a, Linh Vu^a, Parisa A Bahri^a and Keith R. Barnard^b

^a Murdoch University – School of Engineering, South Street, Murdoch, 6150, Australia

^b CSIRO Process Science and Engineering, PO Box 7229 Karawara, WA 6152, Australia

Abstract

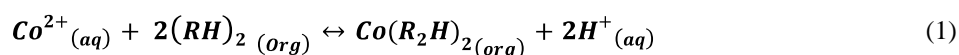
A model of metal extraction based on pH isotherms was generated and applied to a cobalt solvent extraction (SX) circuit. Cyanex 272 (*bis*-(2,4,4-trimethylpentyl) phosphinic acid) was used as the organic extractant due to its selectivity for cobalt over nickel in the extraction process. Experiments were conducted for cobalt, nickel and magnesium extraction, with the latter two representing impurity elements in Co SX. The methods for determining metal extraction incorporated the effects of temperature, solution composition and pH on the equilibrium constant k , and hence on the overall extraction extent. This information was applied to a multi-stage mixer-settler model consisting of integrated extraction units. The initial mathematical model for cobalt, which was built in Matlab can be further developed to include the impurity elements and incorporate the scrubbing and stripping units. Future work will focus on using the model for process optimisation.

Keywords: cobalt, solvent extraction, modelling, equilibrium constant, Cyanex 272

1. Solvent Extraction modelling background

1.1. Solvent extraction

Solvent Extraction (SX) is a hydrometallurgical process used to purify and concentrate metal ions of interest from an aqueous phase. It has been used on commercial scale since the 1950's (Sole et al., 2005). Selective extraction of cobalt typically from nickel-rich sulfate solutions using SX became widely possible in the 1980's with the introduction of the organic extractant Cyanex 272, which contains *bis*(2,4,4-trimethyl pentyl) phosphinic acid ('phosphinic acid') as its active component (Bourget et al., 2011). Cobalt SX using this reagent, diluted in a suitable diluent (solvent), is an equilibrium process whereby cobalt is selectively extracted from an aqueous feed solution onto the organic phase, typically by using a series of mixer-settler units. Cobalt loaded onto the organic phase is subsequently recovered by stripping with an acidic aqueous solution. The aqueous cobalt concentration can be increased by judiciously varying the aqueous to organic ratio in both the extraction and stripping stages. Cobalt extraction follows the general form of Equation 1, where RH represents the phosphinic acid.



A typical flowsheet for cobalt recovery using Cyanex 272 as the extractant is shown in Figure 1. The evaluated flowsheet consisted of three stages of counter-current extraction in mixer-settlers to effectively separate the cobalt from the pregnant leach solution (PLS). As the reaction proceeds, hydrogen ions are released from the extractant into solution, lowering the pH of the solution (Equation 1). As the reaction is highly pH dependent, alkali (base) is added to neutralise the hydrogen ions and maintain the desired pH. To minimise the risk of any entrained organic extractant being transferred to the downstream circuit, the aqueous solution leaving the last extract stage (E3) is washed with fresh diluent in the diluent wash (DW) mixer-settler. The cobalt-rich loaded organic (LO) phase leaving the first extract stage (E1) is scrubbed (Sc) to remove any co-extracted impurities such as nickel and calcium, before entering the strip circuit. Cobalt is then progressively stripped from the organic using a combination of aqueous lean electrolyte and acid to produce the loaded strip liquor (LSL) from which Co is recovered. The stripped organic is then washed with water to dilute any entrained cobalt and acid, prior to returning to the extraction circuit. For the purpose of this paper, only the extraction circuit has been modelled in detail.

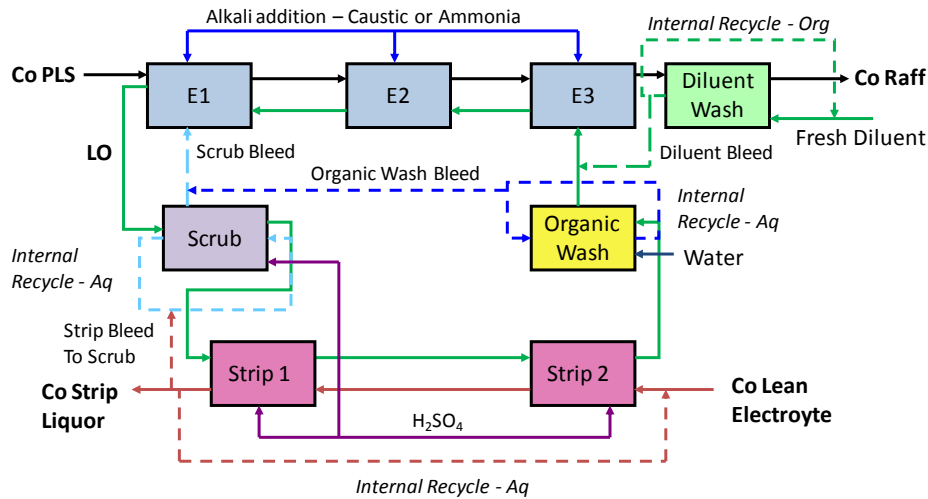


Figure 1: Flowsheet for cobalt solvent extraction using Cyanex 272

1.2. Modelling

Flowsheet modelling is an important area in the metallurgy/chemical engineering disciplines due to the high cost of new metallurgical plants and more complex processing routes being used. Engineers designing new plants and optimising existing circuits need to have a good understanding of the process and what is likely to happen if any of the input variables change during operation. While initial bench scale and pilot scale testwork can provide valuable information regarding the chemistry of the system, the long term testing required is very expensive. Therefore the use of flowsheet modelling to assist in project evaluation is becoming more widespread. The commercial modelling packages are continually being updated as new computational techniques are developed and more is known about the unit operations being modelled.

From the SX perspective, the most developed models are the proprietary modelling packages owned and operated by the reagent suppliers, the most common of which are the Isocalc™ (total metallurgy) and MINCHEM® computer simulation packages developed by Cognis (formally Henkel) and Zeneca (now Cytec) respectively, as tools to assist in simulating copper solvent extraction (CuSX) processes involving sulfuric acid leaching followed by copper extraction using a phenolic oxime extractants. These modelling packages are used to develop circuit layouts, flow options, recovery options, reagent inventory and make-up requirements. Both packages rely on extensive isotherm libraries developed over a number of years covering an extremely wide range of feed and reagent combinations. Outputs from these models include McCabe-Thiele plots, calculations of stage efficiencies and final rich electrolyte and raffinate copper concentrations. These can be used to model alternate plant configurations. Inputs required are stripped organic copper concentration, feed rate and concentration and reagent concentration. However these can be varied to achieve a desired output concentration. These programs are helped by the high selectivity these phenolic oximes show for copper over other metal ions. In recent years Cytec has been adapting the MINCHEM® software for use in cobalt solvent extraction using Cyanex 272 (Bourget et al., 2011). However, this is a challenging task as this reagent can extract multiple cations besides cobalt, and exhibits variable complex stoichiometry.

2. Experimental

To generate the data required for model construction, some experimental work was undertaken. This involved the construction of pH-extraction isotherms for cobalt, nickel and magnesium extraction with Cyanex 272 under various operating conditions (refer Figure 2). The experimental procedure has been discussed elsewhere (Evans et al., 2008), and only the key results will be included here.

2.1. Relationship between $\log k$ and extraction extent for cobalt, nickel and magnesium

It is known that cobalt and magnesium tend to form tetrahedrally co-ordinated complex with phosphinic acid and nickel forms a hydrated octahedral complex (Tati, 1993; Badrul et al., 2007). As shown elsewhere (Evans et al., 2008) for the purpose of this work, we can express the extraction extent ($\epsilon\%$) for each metal, which can be readily measured directly, in terms of its equilibrium constant (k) and the free or available phosphinic acid (RH). Based on the resulting coordination complexes for cobalt and magnesium we use Equation 2 and for nickel we use Equation 3.

$$\epsilon\% = \frac{k[(RH)_2]^2}{k[(RH)_2]^2 + [H^+]^2} \quad (2)$$

$$\epsilon\% = \frac{k[(RH)_2]^3}{k[(RH)_2]^3 + [H^+]^2} \quad (3)$$

The equilibrium constant was determined for each metal using the experimental data and using least squares regression techniques to solve for $\log k$. Examples of the experimental and calculated isotherms for the three metals are shown in Figure 2.

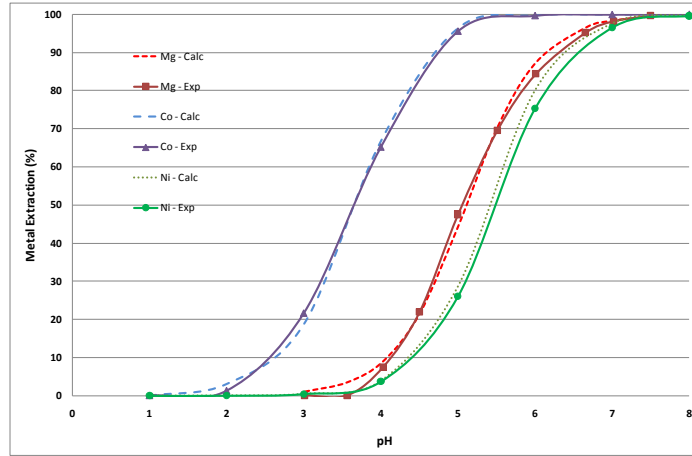


Figure 2: Experimental and calculated isotherms for cobalt, nickel and magnesium as extracted from single metal systems with 20% v/v Cyanex 272 at 35 °C.

3. Model Construction

The steady state model developed for the 3-integrated extraction units is based on the total and component mass balances around the whole system and each unit. For the purpose of the extraction model, each unit has three inlet streams: aqueous phase (A), organic phase (O) and ammonia hydroxide solution (B) used for pH neutralisation. It is assumed that B is soluble in the aqueous phase and no tertiary phases are generated, so that there are only two outlet streams A and O.

Inputs to the model are the feed composition of the aqueous phase (pH, Co, Mg and Ni concentrations), the composition of the barren organic (available RH, any residual loaded metal values Co, Mg and Ni), extraction unit pH, the temperature of the system (in K) and organic and aqueous flow rates (m^3/h). For the purpose of the initial model it is assumed that the mass flowrate of the organic phase does not change throughout the extraction stage. For the three metals studied, it was found that the Arrhenius relationship (Equation 4) could be used to determine the effect of temperature (T) on the equilibrium constant (k).

$$\ln k = \frac{A}{T} + B \quad (4)$$

The two constants A and B were determined for each metal individually and the results are shown in Table 1. The high correlation (R^2) for cobalt and magnesium show that the equilibrium constants for these metals does indeed follow the Arrhenius relationship. However, the R^2 for nickel was significantly lower, indicating that nickel extraction with Cyanex 272 was relatively independent of temperature.

The model also calculates the mass of ammonia hydroxide solution to be added to each unit to maintain the pH of the reaction at a desired set-point, e.g. pH 5.5. If ammonia is not added to the mixer, the pH will drop during the extraction reaction, which lowers the overall metal extraction for the process. If too much ammonia is added, then more impurity metals will be co-extracted, and the risk of metal precipitation also increases.

Table 1: Values for constants A and B determined as a function of operating temperature

Metal	A	B	R ²
Cobalt	-8330.5	10.509	0.9892
Magnesium	-9670.9	9.252	0.9677
Nickel	-2233.4	-18.115	0.6632

The available information and the model equations were applied to develop a steady state model in Matlab code. Using the constants A and B with the temperature of the system allows the determination of the equilibrium constant for each metal. This together with the input values previously mentioned, eg pH, allows the calculation of the available RH and metal content of each stream leaving the extraction unit. As the Matlab solver can only sequentially solve the model equations, the extraction efficiency for units E1, E2 and E3 must be known to recalculate the concentration of RH in the organic phase leaving each unit. The initial model focused only on cobalt extraction using the assumption that $\epsilon_1 = \epsilon_2 = \epsilon_3$. The value of ϵ_3 can be calculated directly from the pH, initial RH concentration and k as per Equation 2. After the first simulation is performed, ϵ_1 , ϵ_2 and ϵ_3 must be back-calculated. If their values are significantly different from ϵ_3 , the second simulation with updated values for ϵ_1 , ϵ_2 and ϵ_3 must be performed and back-calculated until insignificant change in values of ϵ is achieved.

The initial cobalt only model assumed a feed of 0.5 g/L cobalt at pH of 5.5 with a flow rate of 300 m³/h, at an O:A ratio of 1. At the high extraction efficiency of 95%, only 2 stages were required to extract the cobalt producing a raffinate of 0.01 g/L Co.

4. Future work

The Matlab model will be updated to include nickel and magnesium. The mathematical model will be transferred to Aspen Custom Modeller (ACM), which with its object oriented features will provide the ability to build a more efficient flowsheet incorporating recycle streams to more accurately reflect a commercial operation. This will then be used for trialling different process configurations and operating parameters leading to the optimisation of the process.

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