MODELLING COBALT EXTRACTION WITH CYANEX 272

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ABSTRACT

A model has been developed to calculate the equilibrium constant $K$ for cobalt extraction using Cyanex 272. This involved defining the pH extraction isotherm in terms of the extractant concentration, pH, and percent extraction. Using the calculated $K$ values, it is possible to generate $pH$ extraction isotherms for various conditions and calculate change in enthalpy ($\Delta H^\circ$) for the extraction. Although relationships between temperature, ionic strength, and organic concentrations have been expressed mathematically and incorporated in the model, the present paper focuses solely on the effects of temperature.

INTRODUCTION

The development of a solvent-extraction (SX) flowsheet for cobalt extraction requires a detailed understanding of the chemistry of the system. Most new nickel-cobalt SX projects go through initial laboratory screening tests and extensive piloting [1-5] before the final flowsheet is established. The information generated in these testwork programs is then used to design the commercial plant. This is an essential but time consuming and costly requirement for developing projects.

The ultimate aim of this project is to produce an integrated solvent-extraction model of a cobalt-nickel circuit that can adjust the overall extraction extent for each stage based on the pH, temperature, ionic strength of the aqueous phase and the extractant concentration and loading capacity of the organic phase, thereby reducing test-program requirements. The first phase of this work is to develop a model based on the cobalt-Cyanex 272 system. Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) is the extractant of choice for cobalt-nickel separation due to its higher selectivity for cobalt over nickel in both sulfate and chloride media [6-8]. The chemical structure of Cyanex 272 is shown in Figure I.
Process Equilibria

The metal loading of the phosphinonic extractant, Cyanex 272 has been described by a number of researchers [9-15] and can be expressed by Equation 1 [14]:

\[ M^{n+} + \frac{n+x}{y} (RH)_y \rightleftharpoons M(RH)_x + n \cdot H^+ \]  

(1)

where RH is Cyanex 272, the superscript bar represents the organic phase, \( n \) represents the valence of the metal (\( M \)), \( x \) is the number of additional Cyanex 272 molecules required due to the co-ordination number of the complex formed, and \( y \) usually represents either a dimer in aliphatic or a monomer in aromatic diluents [14].

The equilibrium constant \( K \) for a single metal loading onto Cyanex 272 can be expressed by Equation 2, where \( \gamma \) represents the activity coefficient of each species:

\[ K = \frac{[MR_x(RH)_y][H^+]^{n-x}}{[M^{n+}][RH]^y} \frac{\gamma_{MR_x(RH)_y} \cdot \gamma_{H^+}}{\gamma_{M^{n+}} \cdot \gamma_{RH}} \]  

(2)

At low concentrations, we can assume ideal conditions whereby the activity coefficients can be assumed to be equal to 1, thereby simplifying Equation 2 to Equation 3:

\[ K = \frac{[MR_x(RH)_y][H^+]^{n-x}}{[M^{n+}][RH]^y} \]  

(3)

The nature of the extracted metal species with respect to coordination stoichiometry and geometry affects the values of \( x \) and \( y \). At low metal loadings, the structure of the metal-Cyanex complex is different for Co and Ni. Cobalt is tetrahedrally coordinated in Cyanex 272 as Co(RH)\(_3\) and nickel forms the hydrated octahedral complex Ni(RH)\(_2\)(RH)\(_2\) [10] as shown in Equations 4 and 5, respectively. These have been written assuming the Cyanex 272 is present as a dimer (\( y = 2 \)) in the diluent, although they can also be expressed as Co(RH)\(_2\) and Ni(RH)\(_2\), respectively [13].

\[ \text{Co}^{3+} + 2(RH)_2 \rightleftharpoons \text{Co}(R,H)_2 + 2H^+ \]  

(4)

\[ \text{Ni}^{3+} + 3(RH)_2 \rightleftharpoons \text{Ni}(R,H)_2(RH)_2 + 2H^+ \]  

(5)

To control the pH for maximum extraction requires the addition of a base to neutralize the acid generated. To avoid excessive dilution of the aqueous phase with base
during the reaction, a pre-equilibration step of the organic is performed using ammonia or sodium hydroxide to convert the extractant into its salt [16-17]. However, when more than 50 to 70% of the Cyanex 272 is converted to its salt, there is a tendency for third-phase formation to occur [12,17-18]. Therefore, when comparing equilibrium constants quoted by different authors, it is important to note the exact experimental conditions used.

Calculating pH-Extraction Isotherms

An equation was derived for calculating the percentage extraction versus pH isotherm for the Co-Cyanex 272 system. This was used as the basis to recalculate the mathematical pH-extraction isotherms for the experimental data. This was achieved by rearranging the equilibrium constant (Equation 6) for the cobalt-Cyanex 272 system given in Equation 4:

\[ K = \frac{[Co(R, H)_{2}][H^{+}]}{[Co^{3+}][R(H)]_{2}} \]  

(6)

from which the following equation can be derived:

\[ \frac{[Co(R, H)_{2}]}{[Co(R, H)_{2}][Co^{3+}]} = \frac{K[R(H)]_{2}}{K[R(H)]_{2}^{2} + [H^{+}]} \]  

(7)

Using the assumptions that the initial cobalt loading on the extractant prior to contact with the aqueous phase was zero, the O:A ratio was 1, and the change in volume of the two phases during the reaction is negligible, it follows that at equilibrium the final molar concentration of the cobalt Cyanex 272 complex is equal to the molar amount of cobalt extracted and the total molar amount of cobalt initially present is equal to the concentration of the cobalt Cyanex 272 complex plus the concentration of the cobalt remaining in the aqueous phase (Equation 8):

\[ \text{Extraction fraction} = \frac{[Co(R, H)_{2}]}{[Co(R, H)_{2}][Co^{3+}]} \]  

(8)

Therefore, Equations 7 and 8 can be combined to express the extraction fraction for cobalt by Cyanex 272 by using Equation 9:

\[ \text{Extraction fraction} = \frac{K[R(H)]_{2}^{2}}{K[R(H)]_{2}^{2} + [H^{+}]} \]  

(9)

EXPERIMENTAL

The aqueous phases consisted of 0.5 g/L of cobalt added as CoSO₄·H₂O, dissolved in deionized water. Sodium sulfate (0.2 M) was added to the aqueous phase to increase the ionic strength and enhance phase separation. An 12.5% NH₃ solution was used for pH adjustment. Sulfuric acid was diluted to 100 g/L with deionized water and
used for stripping the organic samples. The organic phase was prepared by diluting as-received Cyanex 272 with Shellisol 2046 to make 20 % v/v Cyanex 272. Assuming a purity of 88%, density of 0.92 g/L, and molecular weight of 290, the molar concentration of RH = 0.558 M.

Each experiment involved placing a predetermined volume of aqueous solution in a stainless steel square mixing box with a pH probe and overhead stirrer in a water bath set to the desired temperature. The starting pH of the aqueous phase was adjusted to between 3.0 and 4.0. A Metrohm 776 Dosimat auto titrator and DSO datataker logger were set up to accurately control and record the amount of alkali (NH₄OH) added. A set volume of organic phase to meet the desired organic-to-aqueous ratio (O:A of 1:1) was allowed to reach temperature before being added to the mixing box. After 5 minutes of aqueous-continuous mixing at constant pH, it was assumed that equilibrium had been reached, and a sample was taken. The pH of the mixture was increased to the next set point by the addition of a small volume of ammonia solution via the auto titrator. Once the pH had stabilized, a further 5 minutes mixing was allowed before the next sample was taken. This process was repeated until the final pH setpoint.

The organic samples were stripped (100 g/L sulphuric acid, A:O 2:1) prior to assay. The aqueous raffinate and aqueous strip solutions were submitted for assay by ICP-OES.

RESULTS AND DISCUSSION

The baseline temperature for the experiments was 35 °C, and this test was repeated in triplicate to verify the reproducibility of the pH isotherms and calculated K values produced. Keeping all other factors constant, increasing the temperature from 25 °C to 55 °C caused the extraction isotherms to shift to lower pH values (Figure 2).

![Figure 2. Effect of temperature on cobalt extraction using Cyanex 272.](image)

Using the extractant concentration (RH), pH, and calculated percentage extraction (extraction fraction) for each data set and a least-squares approximation of the
equilibrium constant \( K \) for this system, it was possible to recreate the pH isotherms and calculate the equilibrium constant for each system using Equation 9. An example of the close fit between the experimentally determined pH isotherm and the calculated pH isotherm for the baseline conditions is shown in Figure 3. The variation of \( K \) and \( \ln K \) with temperature results are shown in Table 1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( K \times 10^4 )</th>
<th>( \ln K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.54</td>
<td>-17.49</td>
</tr>
<tr>
<td>35</td>
<td>6.23, 6.14, 7.60</td>
<td>-16.59, -16.60, -16.39</td>
</tr>
<tr>
<td>45</td>
<td>16.7</td>
<td>-15.60</td>
</tr>
<tr>
<td>55</td>
<td>32.3</td>
<td>-14.95</td>
</tr>
</tbody>
</table>

The change in enthalpy \( \Delta H^\circ \) for cobalt extraction with Cyanex 272 was then determined by substituting the Gibbs relationship \( \Delta G^\circ = -RT \ln K \) into \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \) and differentiating with respect to temperature at constant pressure \( (p) \) (Equation 10) to get a plot of \( \ln K \) versus \( 1/T \), a straight line with a gradient equal to \( -\Delta H^\circ / R \) [19]. A plot of the current data (Figure 4) gave a \( \Delta H^\circ \) value of 69.3 kJ/M. Previous work at 8-32% v/v Cyanex 272 reported a \( \Delta H^\circ \) of 51.18 kJ/M [20].

\[
\left( \frac{\partial \ln K}{\partial (1/T)} \right)_p = -T \left( \frac{\partial \ln K}{\partial T} \right)_p = -\frac{\Delta H^\circ}{RT} = -\frac{\Delta H^\circ}{R} \tag{10}
\]

\( K = \text{Equilibrium constant at constant temperature} \quad T = \text{Temperature in Kelvin} \quad \Delta H^\circ = \text{Change in Enthalpy} \quad R = \text{Ideal Gas Constant (8.314 J.K}^{-1}.\text{Mol)}\]

Figure 3. Comparison between experimental and calculated pH isotherm.

Figure 4. Arrhenius plot for Co-Cyanex 272 extraction.
Further work has been conducted to determine the effect of nickel and magnesium, ionic strength, organic concentration, and O:A ratio on the equilibrium constant $K$ for Co-Cyanex 272 extraction and will be reported separately.

CONCLUSIONS

The first step in building versatile functionality into a commercial flowsheeting package was to define the pH extraction isotherm mathematically. The resulting equation defines an S-shaped curve characteristic of pH extraction isotherms and allows determination of $K$, the equilibrium constant. Operation at several different temperatures allowed the $\Delta F^*$ of the system to be determined.

Future work will aim to incorporate the effect of multiple metals and activity coefficients into the model. This will lead to a better understanding of the system. The model will then be incorporated into a commercially available flowsheeting package to give improved modelling capabilities for SX circuits.

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