The Development Of Process Modeling For CYANEX® 272 Extractant

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1. Introduction

CYANEX 272 is a phosphinic acid formulation most commonly used to separate Co from Ni rich streams. It is also used commercially for impurity removal (Fe/Zn), and in rare earth separations. These metal separations are achieved through optimization of a number of parameters which have historically been determined through intensive pilot testing due to the complexity of the chemistry involved.

Cytec Industries Inc. has now developed a simulation software package to assist operators and engineering companies to optimize and design solvent extraction circuits for CYANEX 272. These new modeling capabilities are expected to significantly reduce the amount of laboratory work required while increasing confidence in the ability to achieve the desired metal separations. The new program allows one to evaluate the expected impact of various changes to the PLS metal composition, reagent concentration, O/A ratios, pH profile, and overall circuit configuration/layout.

This paper will review some of the difficulties in modeling phosphinic acid extractants and factors which must be considered. The primary challenges include predicting an accurate isotherm when multiple metals are competing to load or strip, and defining how to complete integrated circuit analysis under these competing conditions. Methodologies used in the past are compared to the current capabilities – along with how these new capabilities may be used to estimate the impact on operational and capital costs. The impact of various operation changes will be reviewed.

2. Current Methodologies For Evaluating CYANEX 272 Circuits

Scientists use different techniques (i.e. pH-loading or S Curves, log D plots, etc.) to try to simplify and understand the complex metal extraction behavior of CYANEX 272. Although helpful in explaining theory, it is difficult to directly apply the techniques to real SX plant conditions. Some of the assumptions made are not directly relevant to an operating plant. Also, the behavior of the components in these systems is not always well understood. Consequently, few techniques have been developed for how extractants will behave in multi-metal feed solutions.

2.1 S Curves

CYANEX 272 has an affinity for a number of metals. The order of metal extraction is typically depicted by generating pH loading curves or ‘S curves’ as shown in Figure 1. Copper, iron, zinc, and aluminum have been excluded from the diagram for simplicity – since these metals are typically removed prior to the Co/Ni SX separation [1].

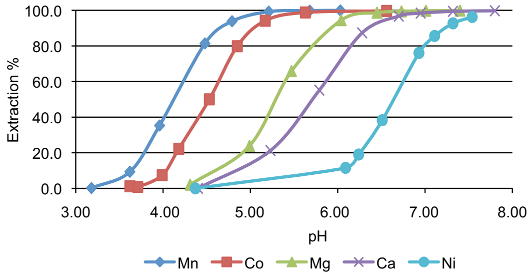

Figure 1 - CYANEX 272 Metal Extraction as a Function of pH

Solution conditions: 0.001 M Metal (as sulfates), 0.1 M CYANEX 272, O/A = 1, Temperature = 50°C

Often S curves are generated using single metal feeds where the metal concentration is significantly lower than the organic loading capacity (i.e. minimum 10:1 ligand:metal ratio). Although S curves generated under these conditions provide a relative order of metal loading, they are only indicative and specific to the conditions under which they were generated. The data is often used to estimate the metal separations achievable by calculating pH$_{50}$ values (i.e. pH$_{50}$ value is defined as the pH corresponding to 50% extraction of the metal of interest). A delta pH$_{50}$ of 2.0 between two metals is deemed sufficient for metal separation under these conditions. However, S curves for the same extractant generated with a different metal to ligand ratio, or where there are additional metals within the aqueous solution can have a significantly different appearance and delta pH$_{50}$ value. For these reasons, S-curves can be misleading and should only be used as a guide for the pH at which to complete extraction. S-curves should only be used to compare extractants under the exact same conditions of test.

2.2 Log D Evaluations

The use of single metal extraction data at high ligand to metal ratios is still useful. Data generated under these conditions, may be used to further understand the ligand behavior. Plots of log D versus pH and log D versus extractant concentration are often generated (i.e. D being the distribution coefficient of the metal between the organic and aqueous phases (D = [M]org/[M]aq)). Plots of Log D versus pH can be used to estimate the proton exchange and Log D versus Log [Extractant] can be used to estimate the likely metal to ligand ratio within the organic phase. Many authors [2-8] have studied the stoichiometry of metals such as cobalt and nickel with acidic extractants. While there is a general consensus that at low metal loadings, cobalt would prefer to adopt the tetrahedral structure and complex with 4 extractant molecules (i.e. $Co(HA_2)_2$), the number of extractant molecules attached to the metal can change as observed for example by some authors [7-8] which stated that the nickel complex was better characterized as $Ni(HA_2)_2.(H_2A_2)x.(H_2O)_{2-x}$ where x = 0, 1 or 2 depending on the extractant concentration.

Although log D plots provide a useful insight, again this data can only be applied to low metal loadings and limited to single metal feeds, these type of plots are not all that applicable to conditions in which higher organic loadings are expected (i.e. typical commercial SX plant metal loadings).

Log D data suggests metal loading with CYANEX 272 begins with a 4:1 ligand metal stoichiometry (or higher) however it is known the ligand to metal ratio within the organic phase changes with percent metal loading. It is possible to achieve a metal loading that corresponds to a 2:1 ligand metal ratio. Exactly when and how the stoichiometry within the organic phase changes presents some complications in understanding the overall system. Figure 2 shows a significant viscosity increase when metal concentrations within the organic phase exceed 65-70% based on the expected stoichiometric load [9].

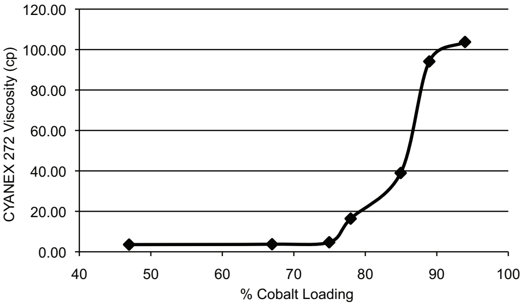

Figure 2 - CYANEX 272 Organic Phase Viscosity as a Function of Cobalt Loading

The viscosity increase is believed to be caused by a change within the ligand metal complex altering from a 4:1 or 3:1 ligand:metal stoichiometry to a 2:1. The reason for the viscosity increase is believed to be a polymerization reaction [9-10].

2.3 Additional Considerations

A basic chemical reaction for divalent metal loading with CYANEX 272 is:

$M^{2+} + 2RH \rightleftharpoons R_2M + 2H^+$

As shown the reaction is reversible and the metal may be removed from the organic phase by increasing the hydronium ion concentration in the strip solution. Due to the high pH necessary for metal extraction, a typical CYANEX 272 circuit will utilize pH control through the direct addition of caustic into the mix box (to neutralize any H^+ generated during extraction) or alternatively the ligand will be deprotonated prior to extraction through a preneutralization stage [9]. Some operations utilize a combination of both. The extraction/stripping reactions can be simply represented as shown below.

Mix box neutralization with caustic:

$M^{2+}(SO_4) + 2RH + 2NaOH \rightarrow R_2M + Na_2SO_4 + 2H_2O$

Preneutralization with caustic:

$NaOH + RH \rightarrow RNa + H_2O$

$M^{2+}(SO_4) + 2RNa \rightarrow R_2M + Na_2SO_4$

Based on relative loading of various metals as a function of pH, it is possible to complete the preneutralization of the ligand with an alternative metal, one that loads at a higher pH such as magnesium or nickel [11-12]. Under these conditions, nickel could be replaced by cobalt:

$R_2Ni + Co \rightarrow R_2Co + Ni$

Based on the multiple reactions possible and the various options for ligand neutralization, direct prediction for a multi metal feed solution is fairly complex.

3. Isotherms For Single Versus Multi Metal Solutions

3.1 Single Metal Isotherms

Using standard equilibrium data, it is fairly straight forward to estimate an equilibrium isotherm (at realistic loadings) for a single metal feed. Under these conditions, the equilibria between the metal, ligand, and acidity can be estimated, producing a relatively accurate isotherm. This remains true as long as the isotherm being generated does not exceed 65% of the stoichiometric load (where the ligand to metal ratio is believed to alter). Examples of single metal isotherms for cobalt and manganese are shown in Figures 3-4.

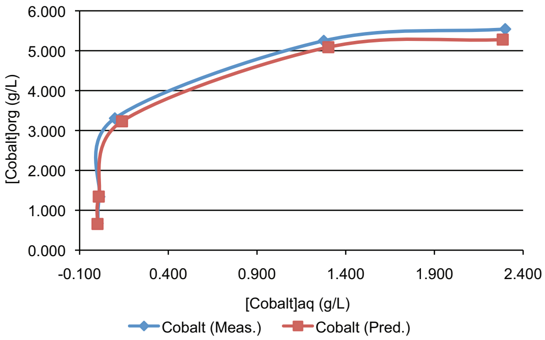

Figure 3 - Single Metal Cobalt Extraction Isotherm

Isotherm generation conditions: 3.375 g/L cobalt; 10% v/v CYANEX 272; Temperature=25°C; pH control with 100 g/L NaOH to an equilibrium pH of 5.5

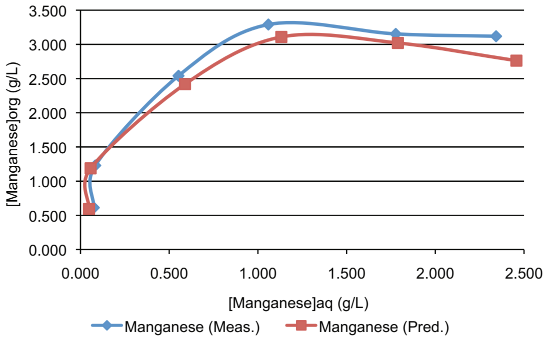

Figure 4 - Single Metal Manganese Extraction Isotherm

Isotherm generation conditions: 3.030 g/L manganese; 10% v/v CYANEX 272; Temperature=25°C, pH control with 100 g/L NaOH to an equilibrium pH of 4.5

As shown, an accurate prediction of the isotherms is possible when only one metal is present and the neutralizing agent is known. Predicting isotherms for a solution containing multiple competing metals is significantly more challenging.

3.2 Multi Metal Isotherms

Below are measured equilibrium isotherms based on contacting a known mixed metal feed with a given CYANEX 272 concentration. Each point on the isotherm was generated by repeatedly mixing the aqueous and organic together at a known O/A ratio – allowing the phases to separate, measuring the aqueous pH, then adding the solutions back together with additional caustic (100 gpl concentration) until the final aqueous pH met the target pH for the isotherm generation. Figures 5-7 show real mixed metal isotherms where cobalt, manganese and magnesium are present together and their extraction performance is compared with the predicted values based on their single metal curves.

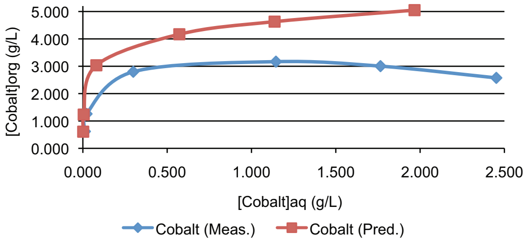

Figure 5 - Measured Mixed Metal Cobalt Isotherm vs. Predicted Single Metal Isotherm

Isotherm generation conditions: PLS (g/L): 3.100 Co; 1.130 Mn; 1.200 Mg (all as sulfates); 10% v/v CYANEX 272; Temp=25°C, pH control with 100 g/L NaOH to an equilibrium pH of 5.5

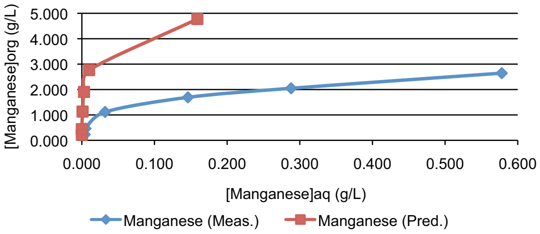

Figure 6 - Measured Mixed Metal Manganese Isotherm vs. Predicted Single Metal Isotherm

Isotherm generation conditions: PLS (g/L): 3.100 Co; 1.130 Mn; 1.200 Mg (all as sulfates); 10% v/v CYANEX 272; Temp=25°C, pH control with 100 g/L NaOH to an equilibrium pH of 5.5

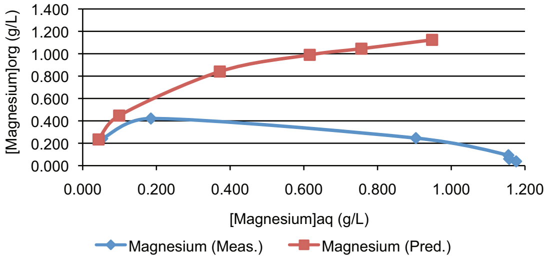

Figure 7 - Measured Mixed Metal Magnesium Isotherm vs. Predicted Single Metal Isotherm

Isotherm generation conditions: PLS (g/L): 3.100 Co; 1.130 Mn; 1.200 Mg (all as sulfates); 10% v/v CYANEX 272; Temp=25°C, pH control with 100 g/L NaOH to an equilibrium pH of 5.5

As shown, the direct prediction of a multi metal feed solution is not well represented by utilizing single metal based equilibrium data.

As shown the isotherms generated using a mixed metal feed do not match the isotherms predicted using single metal based equilibrium data. There are a number of complicating factors to be considered in order to accurately predict a mixed metal isotherm.

For any one metal loading, the amount of acid generated is dependent on the atomic weight of that metal. Example: Loading 1 gpl of cobalt on to protonated ligand will generate 1.66 gpl H_2SO_4 equivalent (98/58.93) while loading 1 gpl magnesium will generate 4.03 gpl H_2SO_4 equivalent (98/24.31). In order to maintain a constant pH (to generate a fixed pH isotherm) the amount of base required will vary dependant on what is loading. The amount of base added impacts the overall aqueous metal concentrations.

The possibility of metal/metal exchange (example magnesium for cobalt); metal/base exchange with altering dilution effects; ligand availability; and altering metal/ligand stoichiometry are all factors which need to be considered to estimate the mixed metal equilibria.

4. Historical McCabe Thiele Estimates For Cobalt Staging

Historically, in order to have a first approximation of the extract staging and O/A ratio required for a given Co recovery, a reagent concentration would be chosen, and an isotherm would be generated for a given pH. The Cobalt isotherm could then be graphed and the staging estimated via McCabe Thiele analysis. Figures 8-10 show McCabe Thiele diagrams for a feed solution initially containing 2.5 g/L cobalt, 0.1 g/L manganese, 5 g/L magnesium, 0.2 g/L calcium and 10.0 g/L nickel. For simplicity purposes, the calcium and nickel extraction isotherms are not shown. The isotherms were generated using 10% v/v CYANEX 272 at 50°C and an equilibrium pH of 6-6.2.

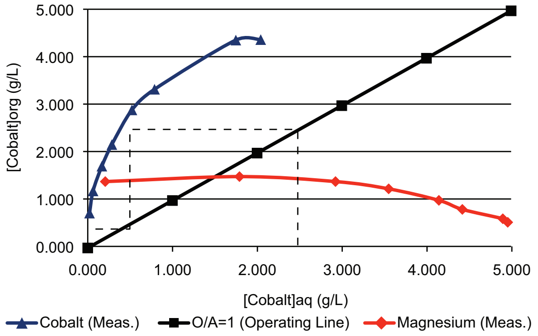

Figure 8 - Cobalt Extraction Isotherm and McCabe Thiele Diagram

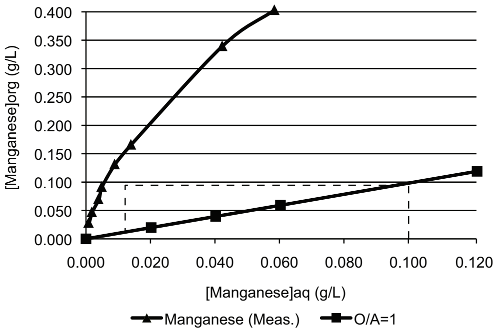

Figure 9 - Manganese Extraction Isotherm and McCabe Thiele Diagram

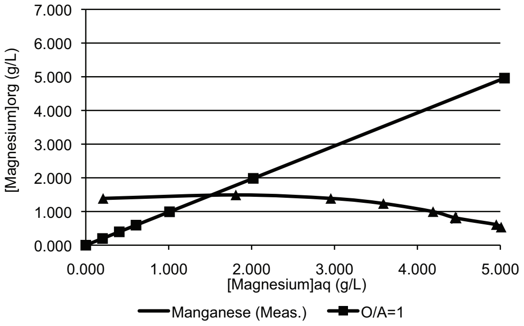

Figure 10 - Magnesium Extraction Isotherm

As shown, the McCabe Thiele analysis indicates cobalt and manganese could be efficiently extracted from the PLS using 2 stages in extract and an O/A ratio of 1.00. McCabe Thiele techniques do not however give a good indication of the impurity transfer due to the shape and positioning of some of the isotherms (especially Mg). In addition, for a typical application, a different pH would be utilized in each stage (typically higher pH in the raffinate stage, with a decreasing pH profile towards the loaded organic or E1 stage), therefore requiring multiple fixed pH isotherms for varying aqueous feeds to more accurately predict the staging requirements.

For these reasons, CYANEX 272 circuits are typically piloted under a number of conditions: pH, O/A ratios, staging (extract, scrub, and strip), scrub solution compositions, etc. to estimate the impurity transfer and expected recovery for given feed conditions.

5. Modeling Program

5.1 Description

Cytec industries Inc.'s new modeling software has been designed to significantly simplify the overall design process. The simulation software does not rely upon McCabe Thiele techniques but the simultaneous solution of multiple equilibrium calculations based on pre-generated equilibrium curves. The pre-generated equilibrium data covers various metals, metal concentrations, acidities, ligand concentrations, and temperatures.

Given a known feed composition, O/A ratio, targeted equilibrium pH, expected stage efficiency, and ligand concentration, the program will calculate the aqueous and organic mixer outlet composition. The equilibrium calculations take into account experimentally determined organic phase interactions as well as alterations in the metal/ligand complex with loading.

Based on standard chemical engineering techniques, the equilibrium calculations can be used to obtain an iterative solution to the expected overall plant (extract, scrub and strip staging) performance.

5.2 Simulation For The Overall Configuration Of A Solvent Extraction Plant

Figures 11-13 show the simulated output for the extraction, scrubbing and stripping sections of a solvent extraction plant treating a feed solution with the following conditions for the extraction section: PLS (g/L): 2.5 Co; 10.0 Mg; 50.0 Ni; 10% v/v CYANEX 272, O/A=1, Temperature = 25°C, 3 extraction stages, pH: 5.0 (E1), 5.2 (E2) and 5.4 (E3).

The loaded organic composition from the extraction circuit is then fed to the scrubbing circuit to estimate the scrub organic and scrub aqueous compositions. The conditions for the scrubbing circuit were the following for the simulation input: Loaded Organic (g/L): 2.498 Co; 0.446 Mg; 0.118 Ni; 10% v/v CYANEX 272, Scrub Liquor (g/L): 40.0 Co; O/A = 20; Temperature= 25°C; 2 scrub stages, pH: 4.20 (Sc1) and 4.50 (Sc2).

The scrubbed loaded organic composition is then fed to the stripping section to simulate the barren

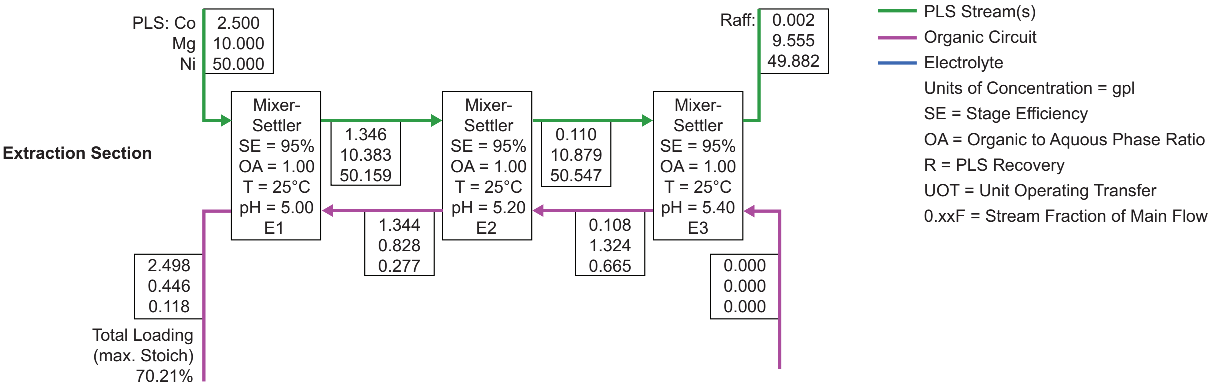

Figure 11 - Process Flow Diagram (Extraction Section)

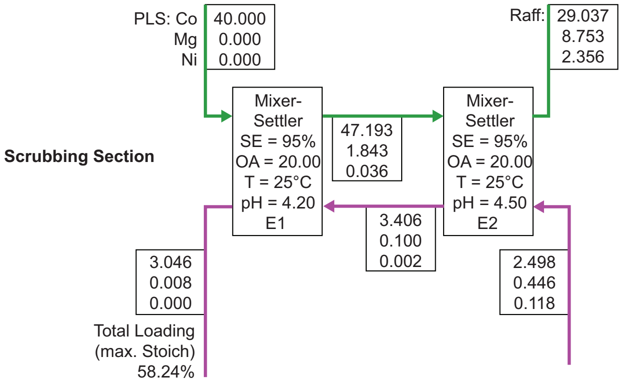

Figure 12 - Process Flow Diagram (Scrubbing Section)

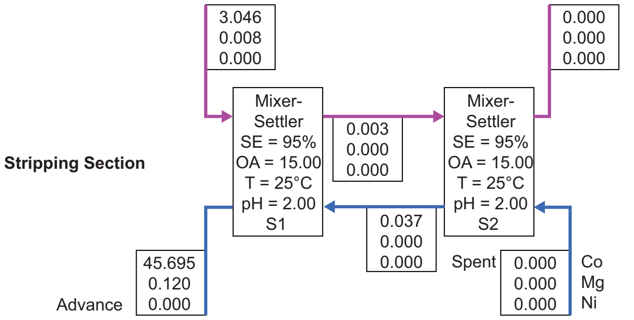

Figure 13 - Process Flow Diagram (Stripping Section)

organic and rich electrolyte compositions. The conditions for the stripping circuit were the following for the simulation input: Loaded Organic (g/L): 3.046 (Co) + 0.008 (Mg) + 0.000 (Ni), 10% v/v CYANEX 272, Strip Liquor: Sulfuric acid, O/A=15, Temperature = 25°C, 2 strip stages, pH: 2.0 (S1) and 2.0 (S2).

The program allows alteration of the feed, scrub, or electrolyte compositions, O/A ratios, pH profiles, or reagent concentration to allow a quick assessment of the expected circuit performance.

5.3 Example On The Performance Of A Scrub Operation

The program was used to evaluate the recovery of cobalt from a scrub liquor in comparison to the efficiency of the scrub stage in removing impurities. The intention was to define the optimum pH in which to run the scrub minimizing impurity transfer as well as reducing the amount of cobalt that would need to be recycled to the feed solution. The conditions for the scrubbing circuit were the following for the simulation input: Loaded Organic (g/L): 3.0 Co; 1.0 gpl metal impurity; 10% v/v CYANEX 272; Scrub Liquor (g/L): 40.0 Co, O/A=20; Temperature=25°C; 1 scrub stage. Figures 14 -16 show the rejection ratio (RR) of Cobalt to Metal impurities (Manganese, Magnesium, Nickel respectively) where the rejection ratio is defined as the organic cobalt concentration divided by the organic metal impurity concentration.

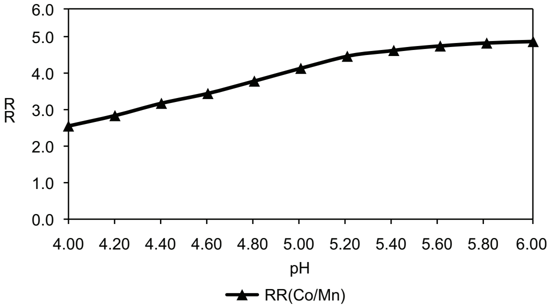

Figure 14 - Rejection Ratio (Co/Mn) and Cobalt Scrub Recovery as a Function of pH

As shown the optimum pH to maximize Co recovery (reducing that which needs to be re-circulated) and minimize impurity transfer is different for each impurity. The graphs are specific for the loaded organic conditions chosen – but give an indication of how the program may be used to optimize a specific unit operation.

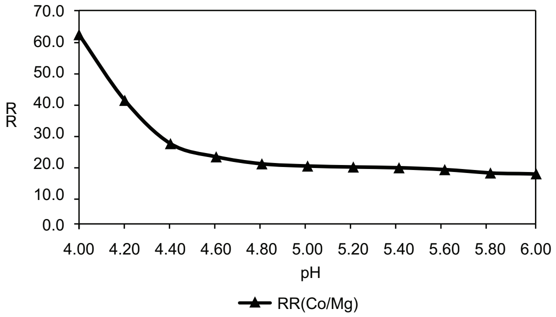

Figure 15 - Rejection Ratio (Co/Mg) and Cobalt Scrub Recovery as a Function of pH

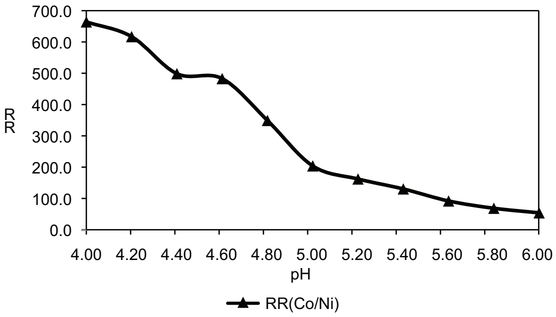

Figure 16 - Rejection Ratio (Co/Ni) and Cobalt Scrub Recovery as a Function of pH

6. Current Status

Since the program capabilities are dependent on experimentally generated equilibrium data, work continues to generate data for various CYANEX 272 concentrations and temperatures.

A recent piloting was completed to allow comparison of expected and measured results under various conditions. In this case the pilot plant utilized 10vol% CYANEX 272 to treat a feed containing 2.97 gpl cobalt and 4.99 gpl nickel in two separate configurations. For pH control, the barren organic from the strip circuit was preneutralized with 10 M NaOH (i.e. 400 g/L) to achieve a preneutralization of 15% of the ligand (for Figure 17) and 34% (for Figure 18).

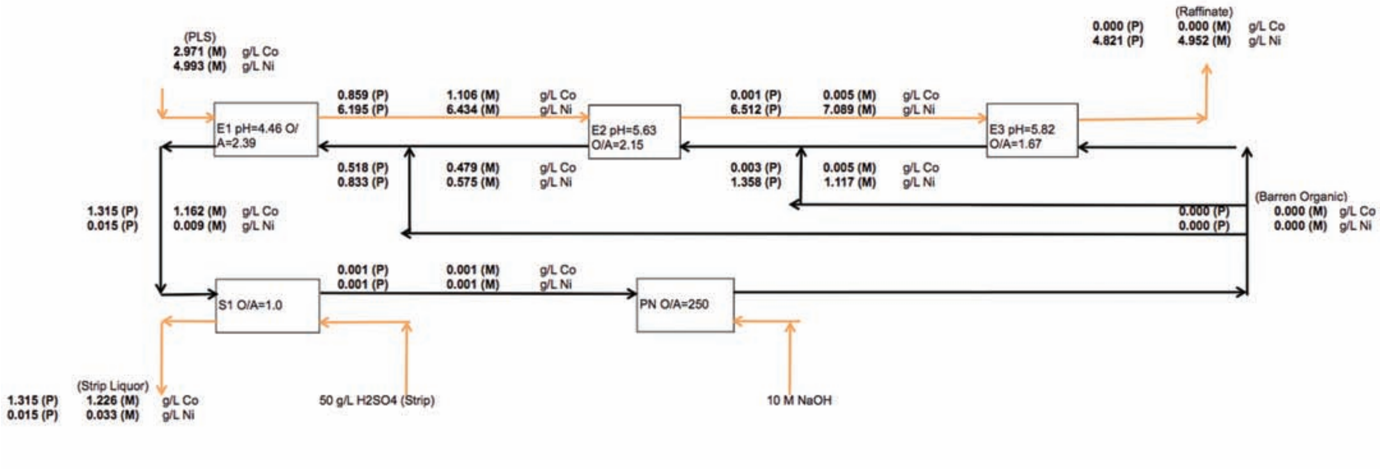

Figure 17 - Predicted (denoted as "P") vs. Measured (denoted as "M") Pilot Plant Performance (Organic in both Series and Parallel)

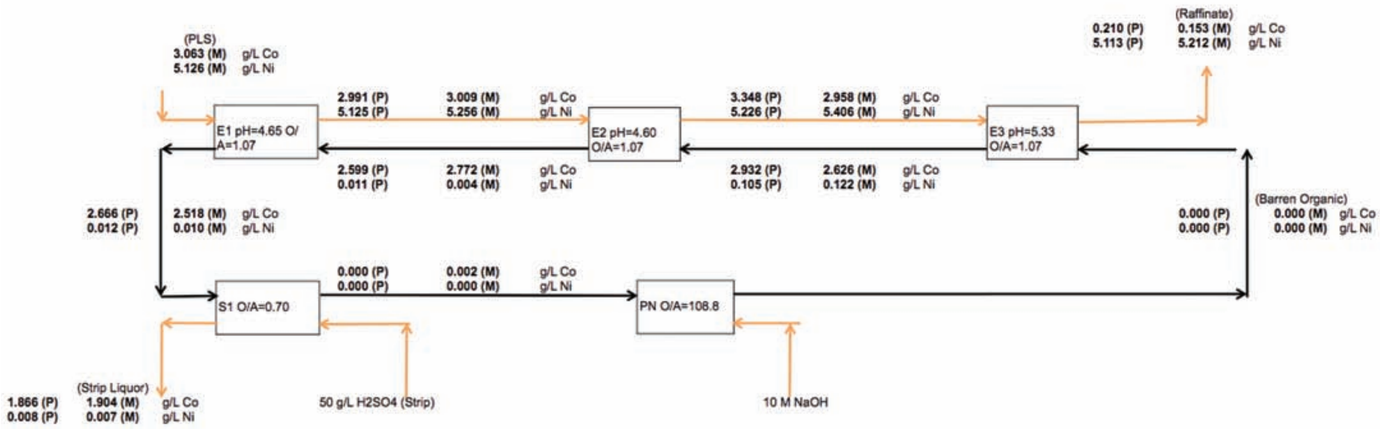

Figure 18 - Predicted (denoted as "P") vs. Measured (denoted as "M") Pilot Plant Performance (Organic in both Series and Parallel)

As shown the program provides a reasonable prediction. Variations between measured and predicted data are attributed to minor variation in recorded pH, as well as variations in stage efficiency.

The accuracy of the model is highly dependent on the solutions reaching equilibrium and accurate pH and flow control.

7. Plant Design / Operational Improvement Possibilities

The program in its current state, has been used to evaluate existing operational parameters at a few existing operations as well as multiple design scenarios. It is believed the program will aid in the design of plants by potentially minimizing the overall staging requirements, and can be used to help optimize existing operations by providing quick and relatively accurate guidance on the optimum O/A ratio, pH profile or reagent concentration required to maximize desired metal transfer and minimize impurities.

Figures 19 and 20 show the simulated output for 2 different extraction configurations based on the same feed composition (i.e. 4 g/L cobalt and 80 g/L nickel). The primary difference between the two circuits is the number of extract stages and the pH profile utilized. As shown, by optimizing/adjusting the pH profile (2nd configuration in Figure 20) it is possible to reduce the overall staging requirements. In these examples, a reduction in the overall staging requirements (from 4 to 3) and operating O/A ratio (from 1.3 to 1.2) should be possible while still achieving the same (or higher) cobalt recovery (from 0.035 to 0.014 g/L cobalt left in the raffinate) and delivering essentially the same organic impurity profile to the scrub circuit (from 35.5 to 38.3 in terms of Cobalt/Nickel rejection ratio in the loaded organic).

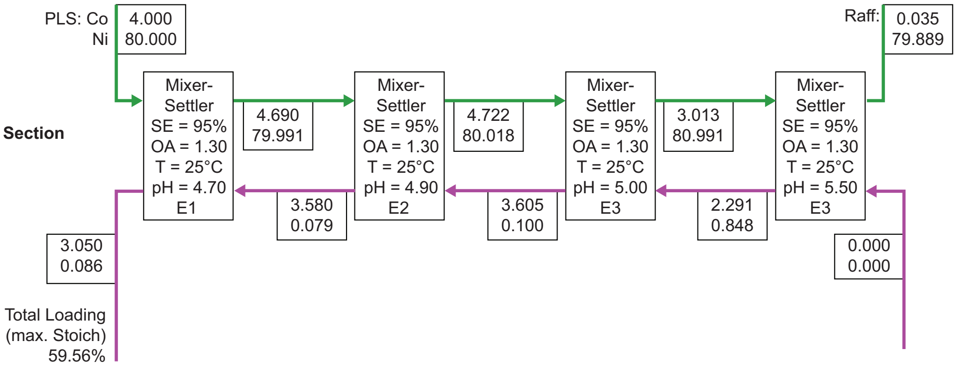

Figure 19 - Simulation with Non Optimized pH Profile (4.7 (E1), 4.9 (E2), 5.0 (E3), 5.50 (E4))

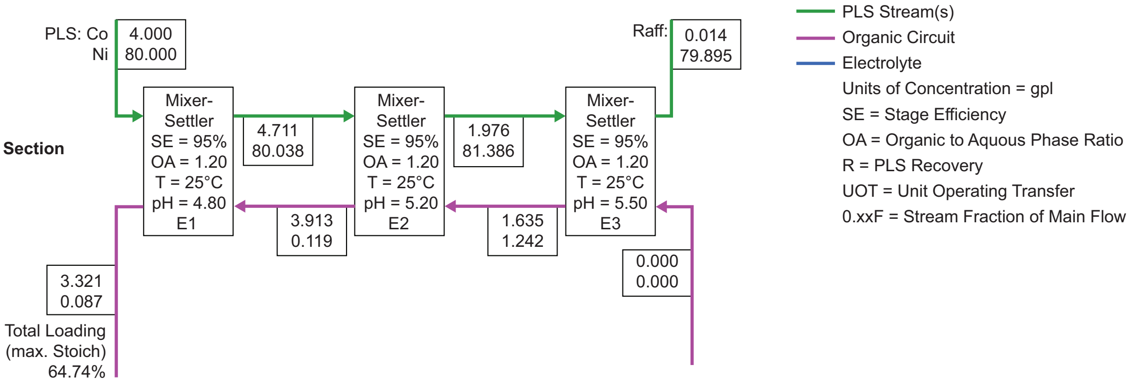

Figure 20 - Simulation with Improved pH Profile (pH: 4.8 (E1), 5.20 (E2) and 5.50 (E3))

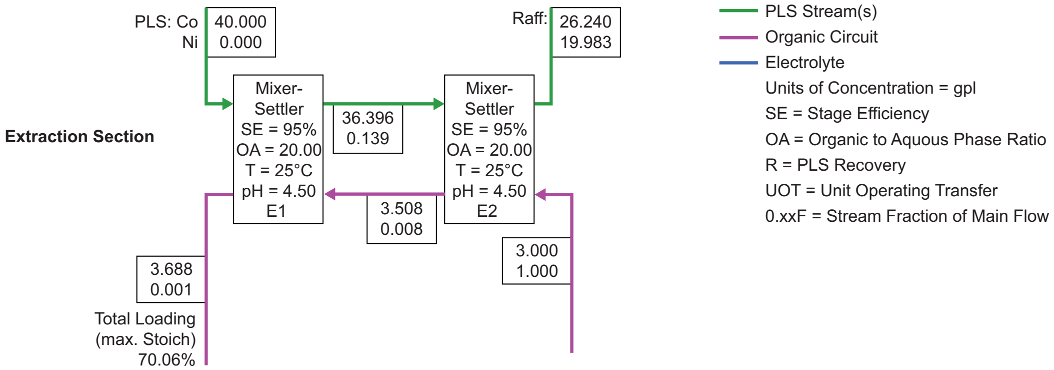

Figure 21 - Simulated Scrub Operation (Non Optimized)

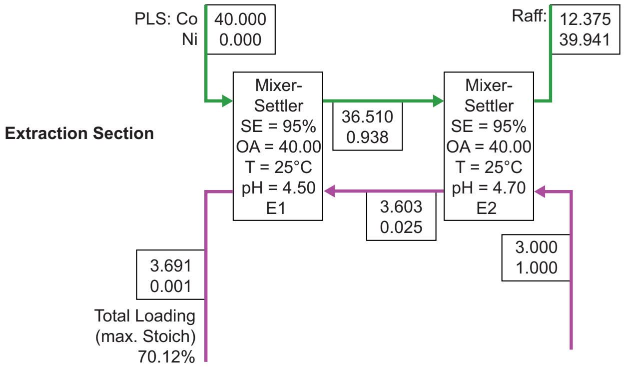

Figure 22 - Simulated Scrub Operation (Improved pH Profile / O/A Ratio)

The same principle can be applied to optimize the conditions of the scrub circuit. Figures 21 and 22 show the simulated output for 2 different scrub configurations based on the same loaded organic composition and the same cobalt scrub solution but different operating O/A ratios and pH values. As shown, while the 2 configurations achieved the same organic impurity profile (i.e. 1 ppm nickel left and a final Cobalt/Nickel rejection ratio of 3688 and 3691 for each configuration), the 2nd configuration (Figure 22) should allow a reduction in the scrub liquor flow (operating O/A ratio from 20 to 40) and a higher cobalt scrub recovery (i.e. from 34.4% to 69.1%). Optimization of the conditions would result in a reduced cobalt recycle (requiring re-extraction, additional acid/base, and reagent).

8. Conclusions

The current methods of estimating stage requirements are time consuming, not very accurate due to pH variations, and impurity profiles are nearly impossible to obtain under these methods and only an extended pilot plant trial would give this information. A simulation software package has been developed by Cytec Industries Inc. that can quickly predict any circuit (i.e. multi-stage configurations, pH profiles, O/A ratios, reagent concentrations, etc.) and give a relatively accurate prediction of metal loading, recovery, and all relevant impurity profiles with the ultimate objectives of maximizing reagent/plant performance as well as assisting operators and engineering companies design and optimize plants using CYANEX 272. It is believed the program can be used to help existing operations improve their overall performance by showing what is actually happening within each stage. For green field projects, the work required for designing a new operation should be significantly reduced while improving confidence in the solvent extraction flowsheet. This program should allow improvements in both circuit design and circuit optimization. Identification of potential cost savings (by improved impurity profiles) or production increases can be quickly calculated and compared based on changes to the operating parameters.

9. References

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