

# Steady State Modelling, Simulation and Optimisation of a Multi Stage Cobalt Solvent Extraction Circuit

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## Abstract

The cobalt solvent extraction (CoSX) system using Cyanex 272 as the organic extractant, has been modelled for single, two and three stage extraction circuits using MATLAB and Aspen Custom Modeler (ACM) mathematical modelling software. Steady state simulations and optimisations have been conducted on the developed models.

An initial sensitivity analysis has shown that increasing pH or the organic to aqueous (O:A) ratio significantly increases individual metal extraction efficiencies. However to achieve the ultimate aim of maximising cobalt extraction while minimising magnesium and nickel co-extraction and reagent consumption, an economic objective function has been formulated within the optimisation problem to solve for the optimum pH setpoint and O:A ratio. For this case study a two stage Co SX circuit with the (O:A) ratio at 0.162 and pH at 4.64 was found to be optimal. This set of conditions would achieve 99% cobalt extraction, while limiting magnesium co-extraction to 9% and nickel co-extraction to <0.5%.

*Keywords: Cobalt solvent extraction, Cyanex 272, ACM modelling, Solvent extraction optimisation.*

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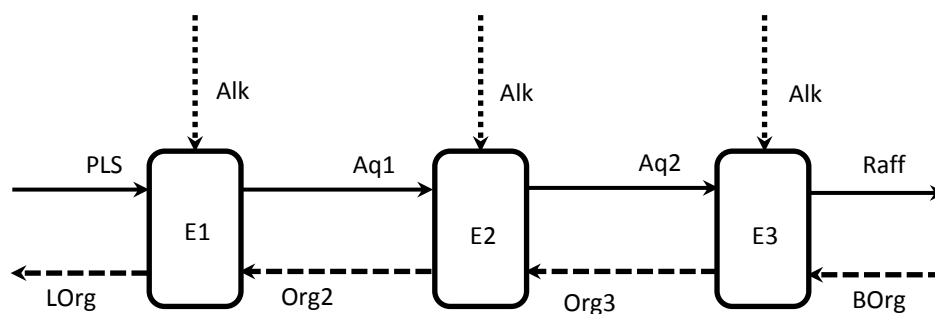
## Introduction

Hydrometallurgical solvent extraction (SX) has long been a useful and economic process to purify and concentrate metal ions of interest from an aqueous phase. The process generally consists of a single or multiple extraction stages followed by a stripping stage. Several mixer-settler units are used to model the mass transfer of metals from the aqueous to the organic phases in the extraction stages; and then the stripping of these metals from the organic phase to the electrolyte in the stripping stage. Over the last five decades significant work has been done on SX modelling of selected metals with a specific organic extractant, as well as on process modelling of mixer-settlers or extraction columns. The majority of this work has focussed on copper extraction using salicylaldoxime or ketoxime extractants, with proprietary modelling packages MEUM<sup>®</sup> and Isocalc<sup>®</sup> being developed by reagent suppliers Cytec and BASF respectively. This paper presents the steady state modelling, simulation and optimisation of a cobalt-magnesium-nickel SX circuit, focusing on a multi stage extraction circuit.

## Cobalt Solvent Extraction Process Description

The aim of the cobalt (Co) SX process is to maximise the extraction efficiency of Co while keeping the extraction efficiencies of two impurities magnesium (Mg) and nickel (Ni) at minimum levels. During the extraction stage of the SX continuous process, Co transfer between the aqueous and organic phases takes place in the mixers and the phases are separated in the settlers. In this case study Cyanex 272 containing the active component bis(2,4,4 trimethylpentyl)phosphinic acid, was used as

the organic extractant. For a mixer-settler arrangement, the mixer was modelled as a single Continuous-Stirred Tank Reactor (CSTR) also referred to as an extractor (E). The current Co SX process modelling used three mixer-settler units arranged in series (Figure 1). The two main inlet streams, an aqueous solution and the organic solvent, flow counter-currently through each mixer. The aqueous feed also known as the pregnant leach solution (PLS) enters the first CSTR (E1), progressing down the circuit with a gradually decreasing metal tenor to produce the raffinate (Raff) leaving the final CSTR which in the case of Figure 1 is E3. The organic solution entering E3 is referred to as the barren organic (BOrg) and progressively loads with metal to produce the loaded organic (LOrg) leaving E1. An additional inlet stream of alkali (Alk) or acid was added to each mixer for pH control. It is also possible to recycle a part of the organic solution ( $LO_n$ ) to each mixer to reduce entrainment and maximise mass transfer efficiencies or direct part of the BOrg stream to multiple mixers to increase the Co extraction efficiency.

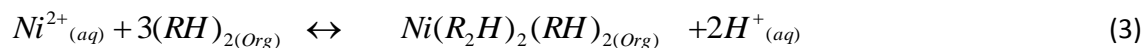
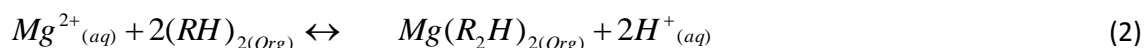
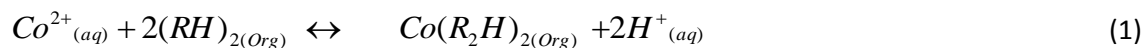


**Figure 1.** Schematic of a Co SX process with three mixer-settler units.

## Cobalt Solvent Extraction Process Model

### Solvent Extraction Process Reactions

The extraction equations for Co and the impurities Mg and Ni with phosphinic acid are given in Equations from (1) to (3), assuming a tetrahedral co-ordination for cobalt and magnesium and an octahedral co-ordination for nickel (Sole and Hiskey, 1992; Islam et al. 2007).



In the above reactions the subscripts (*aq*) and (*Org*) stand for aqueous and organic phases, respectively; [RH] is the available extractant concentration, which in this case study is the phosphinic acid contained in Cyanex 272. More importantly each individual metal extraction efficiency is dependent on [RH] as shown in Equations (4) and (6).

$$X_{eff(M)} = \frac{k_M [RH]^z}{k_M [RH]^z [H]^2} \quad \text{where } M = Co, Mg, \text{ or } Ni, z = 2 \text{ for } Co, Mg \text{ and } z = 3 \text{ for } Ni \quad (4)$$

In Equation (4),  $k_M$  is the equilibrium constant determined for each individual metal: Co, Mg and Ni. These equilibrium constants are temperature (T) dependent as shown in the Arrhenius relationship in Equation 5, where the constants A and B for each metal along with the equilibrium constants were

determined from single metal experimental data in the temperature range 298 to 328 K (Evans et al. 2012).

$$\ln(k_M) = \frac{A}{T} + B \quad (5)$$

$$[RH] = [RH]_{in} - \frac{n(RH)_{Co} + n(RH)_{Mg} + n(RH)_{Ni}}{F_{Org}} \quad (6)$$

In Equation (6),  $n(RH)_M$  is the amount of RH consumed in kmol/h during the extraction reaction for each metal,  $F_{Org}$  is the organic flowrate in  $m^3/h$  and  $[RH]_{in}$  is the initial concentration in  $kmol/m^3$  of extractant entering the extractors E1, E2 and E3. This together with the value of pH setpoint in each extractor allows the calculation of the available RH, followed by the extraction efficiencies for each metal and finally the metal content of each stream leaving each extractor.

### Solvent Extraction Steady State Model

The simulation of a mixer-settler unit requires known inlet conditions such as feed aqueous composition, organic composition and organic solvent flowrate, which is commonly expressed as organic to aqueous ratio (O:A). Other information is usually given or set such as temperature and pH setpoints in the extractors. One challenge to be faced in the simulation of the multi stage Co SX is the requirement of known stage extraction efficiencies to solve the mass balance and extraction equations. However the stage extraction efficiencies are dependent on the available extractant concentration  $[RH]$  as shown in Equations (4) and (6), which can only be calculated after the mass balance and extraction equations are solved. One possibility is conducting an iterative process with initial guesses of the stage extraction efficiencies. The results found in each iteration are used to back-calculate the stage extraction efficiencies, which will be used in the following iteration until convergence is obtained for the process. This procedure is very tedious and time consuming while yielding less accurate results. However, the use of a mathematical modelling software such as MATLAB (R2013a) or Aspen Customer Modeler (ACM, V8.4 2013) would overcome these mentioned disadvantages.

### Steady State Model Using MATLAB and Aspen Customer Modeler

The available input data together with the model equations were used to develop in MATLAB steady state models for a single mixer-settler unit and several interconnected mixer-settler units. As MATLAB solvers sequentially solve the model equations, "fsolve" could be used to solve systems of nonlinear equations of several variables. One main disadvantage of using "fsolve" was that process constraints could not be included in the code. An alternative option was formulating the SX process model as an optimisation problem and using the solver "fmincon". In this manner the solver could solve the nonlinear equations with respect to all process constraints while searching for the unknown extraction efficiencies and the outlet conditions of the aqueous and organic solutions leaving each extractor.

On the other hand the solver in ACM could simultaneously solve the model equations. In other words the equations describing the process could be written in any particular order. As long as the number of equations and the numbers of unknowns were the same or the Degree of Freedom was equal to zero, the problem could be solved for the unknown extraction efficiencies and the outlet conditions of the aqueous and organic solutions leaving each extractor as mentioned in the above sections.

## Solvent Extraction Optimisation Model

Since the (O:A) ratio and pH setpoints in each extractor can be varied to improve the extraction efficiency of Co while reducing the co-extraction of impurities Mg and Ni, an optimisation problem can be formulated. The main aim is to maximise Co mass transfer from aqueous to organic phases while minimising the mass transfer of impurities such as Mg and Ni.

In MATLAB a double loop optimisation framework was written, in which the inner loop solved the nonlinear equations for the unknown extraction efficiencies and outlet conditions. Meanwhile the outer loop searched for the optimum pH setpoint and the organic to aqueous (O:A) ratio.

Given the solver in ACM could solve the system of nonlinear equations simultaneously, only a single optimisation model was required to solve for the optimum pH setpoint and the organic to aqueous (O:A) ratio.

## Results and Discussion

The mathematical models of Co SX were developed for one, two and three extraction stages in both MATLAB and ACM. These models can be used for steady state simulations and optimisation purposes. Programming the Co SX process in MATLAB, especially optimisation programming, is more difficult for other users to understand and thus share. However the steady state Co SX model in MATLAB can be easily modified to be used in dynamic simulations for control purposes in the future.

Programming the same process in ACM is more straightforward, easier to understand and hence easier to share among users. One of the best features of modelling in ACM is that only some different mathematical models need to be initially developed. For example to obtain a mathematical model of a multi stage Co SX circuit, the first and the last extractors should be modelled first because for a counter-current flow arrangement, the fresh aqueous feed only enters the first extractor; and the fresh organic solvent only enters the last extractor. All other extractors between these two specific first and last ones share the same model. Consequently only one middle extractor requires a mathematical model. This developed model can be copied, pasted and connected with streams in the flowsheet to form a 4- or more than 4 stages Co SX circuit.

Some results obtained from steady state simulations and optimisations of a one, two and three extraction stage Co SX model using MATLAB and ACM are shown in the following tables for comparison.

### Co SX Process Simulations and Optimisations

Steady state problems were set up for one, two and three stage extraction models using a baseline set of conditions, namely 20 %v/v Cyanex 272 in kerosene as the organic extractant and a PLS with flowrate of 300 m<sup>3</sup>/h containing 0.5 g/L cobalt, 5.0 g/L magnesium and 4.0 g/L nickel in a sulfate system at 35 °C and at an O:A ratio of 1. The pH of the aqueous fresh feed was fixed at 4.9 and the pH setpoints were set at 5.5 for a single stage; 5.0 and 5.3, respectively for a two stage; and 5.0, 5.1 and 5.3, respectively for a three stage Co SX circuit.

The extraction efficiencies given by MATLAB and ACM are almost equivalent. Differences can be reduced by setting the same tolerance values for both MATLAB and ACM when executing the programs. The results in Table 1 show that if the O:A ratio is set at 1, the Co extraction efficiency does not improve significantly regardless of the number of extractors used. Almost all Co mass transfer from aqueous to organic phase has taken place in the first extractor. Similarly, increasing the number of extractors does not help to decrease the concentrations of impurities Mg and Ni in

the loaded organic phase. Individual optimisations therefore should be set up and performed for each of the single, two and three extraction stage circuits.

**Table 1.** Steady State Simulation of Multi Stage Co SX.

		Single	Two Stage		Three Stage		
	Metal	E1	E1	E2	E1	E2	E3
<b>pH setpoint</b>		5.50	5.00	5.30	5.00	5.10	5.30
<b>Extraction</b>	Co	0.998	0.982	0.997	0.975	0.990	0.998
<b>Efficiency (ACM)</b>	Mg	0.660	0.169	0.579	0.126	0.270	0.621
	Ni	0.071	0.001	0.052	0.001	0.014	0.061
<b>C<sub>out</sub> in LOrg (g/L)</b>	Co	0.500	0.497		0.497		
	Mg	3.285	3.252		3.774		
	Ni	0.284	0.237		0.265		
<b>C<sub>out</sub> in Raff (g/L)</b>	Co	0.001		0.000			0.000
	Mg	1.706		1.749			1.215
	Ni	3.729		3.763			3.692
<b>Extraction</b>	Co	0.998	0.985	0.999	0.980	0.994	0.999
<b>Efficiency (Matlab)</b>	Mg	0.670	0.196	0.769	0.149	0.390	0.769
	Ni	0.023	0.000	0.071	0.002	0.010	0.072

The above baseline set of conditions was used except that in this case the optimisation variables are the O:A ratio and the pH setpoint. The objective function was formulated using an economic model, Equation (7), which was based on the selling price (SP) of cobalt and an assumed penalty price (PP) for co-extracted magnesium and nickel, where  $m$  represents the mass of metal extracted and (RC) the cost of reagents (extractant, kerosene, alkali, acid).

$$\text{Maximise Profit} = SP_{Co} m_{Co} - PP_{Mg} m_{Mg} - PP_{Ni} m_{Ni} - RC \quad (7)$$

Subject to:

- The set of equality constraints represented by Equations (4) and (6);
- The set of inequality constraints including:
  - ✓  $0 \leq X_{effM} \leq 1$ ;
  - ✓  $4 \leq \text{pH setpoint} \leq 5.5$ ;
  - ✓  $0 \leq [RH]$ ; and
  - ✓  $0.1 \leq O:A \leq 1.1$

Since the O:A ratio is adjusted for optimisation, the mass flowrates of Co and impurities Mg and Ni in the loaded organic phase are used instead of mass concentration for comparison purposes. The results in Table 2 show that the best scenario is the two stage SX with the (O:A) ratio at 0.162 and pH at 4.64. Compared to the fresh aqueous feed containing 150 kg/h of Co, 1500 kg/h of Mg and 1200 kg/h of Ni, the loaded organic phase is much more purified containing 149 kg/h of Co, 139 kg/h of Mg and 4.7 kg/h of Ni. This loaded organic phase is more concentrated in Co, which makes it easier to strip Co from the organic phase to the electrolyte in the stripping stage.

Some additional optimisations have been set and conducted for two and three extraction stages. In these problems the pH setpoint of each of the two or three extractors are optimised. The optimum pH profiles have been found, but these changes did not give any significant improvement in the

extraction and purification of Co within the constraints modelled here. As a result the case highlighted in Table 2 is still the best scenario.

**Table 2.** Optimisation of Multi Stage Co SX.

	Metal	Single	Two Stage		Three Stage		
		E1	E1	E2	E1	E2	E3
<b>Optimum pH</b>		5.00	4.64	4.64	4.54	4.54	4.54
<b>Extraction Efficiency</b>	Co	0.984	0.879	0.952	0.851	0.920	0.947
	Mg	0.187	0.026	0.068	0.021	0.041	0.061
	Ni	0.003	0.001	0.003	0.001	0.002	0.003
<b>Mass<sub>out</sub> in LOrg (kg/h)</b>	Co	147.6	149.1		149.9		
	Mg	280.9	139.0		176.6		
	Ni	3.3	4.7		6.1		
<b>Mass<sub>out</sub> in Raff (kg/h)</b>	Co	2.4		0.9			0.0
	Mg	1219.0		1361.0			1318.8
	Ni	1196.6		1195.2			1193.7

## Conclusions

The mathematical models of Co SX have been developed for one, two and three extraction stages in both MATLAB and ACM. These models have been used for steady state simulations and optimisation purposes. It was found that increasing pH or the O:A ratio significantly increases individual metal extraction efficiencies. However using an excessive O:A ratio or pH would also increase the effects of impurities in extracting more valuable Co economically. Therefore an economic objective function or cost function based on the cobalt price and penalty rates for impurities was developed for comparative use. The optimum operating conditions were determined to be a double stage Co SX with the (O:A) ratio at 0.162 and pH at 4.64. This condition would achieve 99% cobalt extraction, while limiting magnesium co-extraction to 9% and nickel co-extraction to <0.5%.

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