

# FIRST PRINCIPLES MODELLING OF THE SOLVENT EXTRACTION AND STRIPPING OF URANIUM INCLUDING MOLYBDENUM CONTROL

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## ABSTRACT

Solvent extraction is a commonly used method in the production of uranium ore concentrate from run of mine ore. However, molybdenum commonly co-exists with uranium ores and, if not removed, can cause significant operational issues including crud formation and product contamination. Molybdenum readily co-extracts with uranium into the organic phase when commonly used ternary amine extractants, such as Alamine 336 and Armeen 380, are employed. Optimal rejection of molybdenum to the raffinate while minimizing product loss from organic regeneration requires detailed understanding of the chemistry occurring in the extraction, stripping, and regeneration circuits.

Typical approaches to understand molybdenum transport in an operational solvent extraction plant include development of plant extraction and stripping isotherms for uranium and molybdenum. These isotherms, while very useful, are specific to the operating regime from which they are obtained, and therefore, are of limited utility when ore characteristics change. In this work, we present an alternative approach to model solvent extraction based upon fundamental thermodynamic analysis. Rather than using plant isotherms, pure system (i.e. single component) isotherms available in the open literature are used to calculate fundamental thermodynamic constants of interfacial reactions. By isolating the extraction of a single component, the process can be represented exactly in a thermodynamic model and, thus, the free energy of the organic salts involved in the extraction mechanism can be calculated by data fitting. Pure system isotherm data generated by Yakabu and Dudeney<sup>1</sup> for sulphuric acid / uranyl sulphate and Coca et al.<sup>1</sup> for molybdic acid was used in this work.

Using the fitted thermodynamic model, a process model of a typical uranium solvent extraction plant, including extraction, stripping, and regeneration circuits, was developed using SysCAD. SysCAD is a highly flexible process simulation platform which is widely used in mineral processing. Recent improvements have enabled the integration of high-fidelity thermodynamic engines, such as OLI, ChemApp (FactSage), AQSol, HSC, and PHREEQC. Individual mixer-settler units were modelled using an embedded PHREEQC interface to calculate aqueous and organic chemical speciation in the mixer via free energy minimization for the extraction circuit and wash cell of the plant. The stripping circuit was modelled using a stripping isotherm, and the regeneration cell was modelled using reactions with PHREEQC calculations for aqueous pH.

*Keywords: Extraction, stripping, regeneration, uranium, molybdenum, multiphase, modelling, simulation*

## INTRODUCTION

The production of uranium ore concentrate from mined ore consists of the following process steps:

- Grinding
- Leaching
- Counter-current decantation
- Pregnant solution pretreatment
- Solvent extraction (including extraction, stripping, and organic regeneration)
- Product precipitation and drying / calcining
- Water and tailings treatment

This paper focuses on the step which arguably forms the heart of the process: solvent extraction. In this circuit, tertiary amines, such as Alamine 336 or Armeen 380, are used to selectively recover uranyl sulphate anionic complexes from pregnant solution. Typical pregnant liquors also contain molybdate and arsenate species, which are present as oxyanions under normal conditions. These species co-extract with uranium and can cause operational issues within the circuit in addition to compromising the quality of the product. This work focuses on the distribution of uranium and molybdenum in a typical solvent extraction circuit employing ammonia stripping and sodium carbonate regeneration.

Typical operating approaches to understanding uranium and molybdenum distribution in a solvent extraction circuit involve developing circuit mass balances based upon sampling campaigns to estimate the distribution coefficients and/or operating isotherms for these metals. This approach, while effective for narrow operating windows, becomes of less utility when significant ore changes require changes to upstream operating conditions. This work aims to demonstrate a method to use fundamental principles of multiphase chemical equilibrium to develop a model with a greater scope of applicability. Furthermore, the laboratory work required to obtain the required data is relatively straightforward.

## CHEMISTRY MODEL THEORY

Chemical equilibrium calculations consist of the simultaneous solution of a number of equilibrium conditions of the form:

$$K_i = \prod_j a_j^{v_{ij}} \quad \text{Equation 1}$$

Here,  $K_i$  is the equilibrium constant for the  $i^{\text{th}}$  reaction, and  $a_j$  and  $v_{ij}$  are the activity and stoichiometric coefficient of the  $j^{\text{th}}$  species within the  $i^{\text{th}}$  reaction. When combined with mass balance equations for all involved chemical species, a closed form solution is obtained which can be solved by various non-linear numerical methods. The activity is defined here as the molality of a species multiplied by its activity coefficient, i.e.:

$$a_i = m_i \gamma_i \quad \text{Equation 2}$$

Various models exist for the activity coefficient and are suitable for different applications depending upon the concentration range. In uranium solvent extraction circuits, pregnant solution and raffinate are relatively dilute solutions, and thus, the Davies equation is used for calculating activity coefficients:

$$\ln \gamma = -Az_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad \text{Equation 3}$$

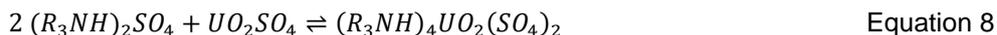
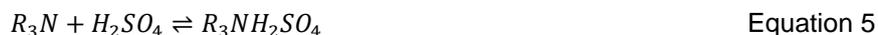
Where  $I$  is the ionic strength based upon molality:

$$I = \frac{1}{2} \sum_i z_i^2 m_i \quad \text{Equation 4}$$

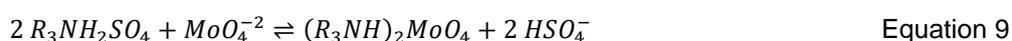
The SysCAD PHREEQC Add-On is used to calculate the aqueous and organic phase equilibrium in this work. Further information on this model, developed by the U.S. Geological Survey, is available in the PHREEQC documentation<sup>3</sup>.

In a similar manner, organic phase equilibrium is also considered. This uses the “Exchange” functionality within PHREEQC. The fundamental difference from aqueous equilibrium is that the activity of an exchange species is based upon the mole fraction of a particular exchange species relative to the total exchange sites available multiplied by an activity coefficient.

The extraction of sulphuric acid and uranyl sulphate is represented by the following reactions, as described by Yakabu and Dudeney<sup>1</sup>:



The extraction of molybdate is represented by the following reactions. This follows the form of reactions suggested by Coca et al.<sup>1</sup> but is a simplification of the actual mechanism:



The above equations were selected to represent the dominant forms of molybdate over typical extraction conditions, but neglect the extraction of polymerizations of molybdate, which are known to occur to some extent at lower pH.

## DATA FITTING

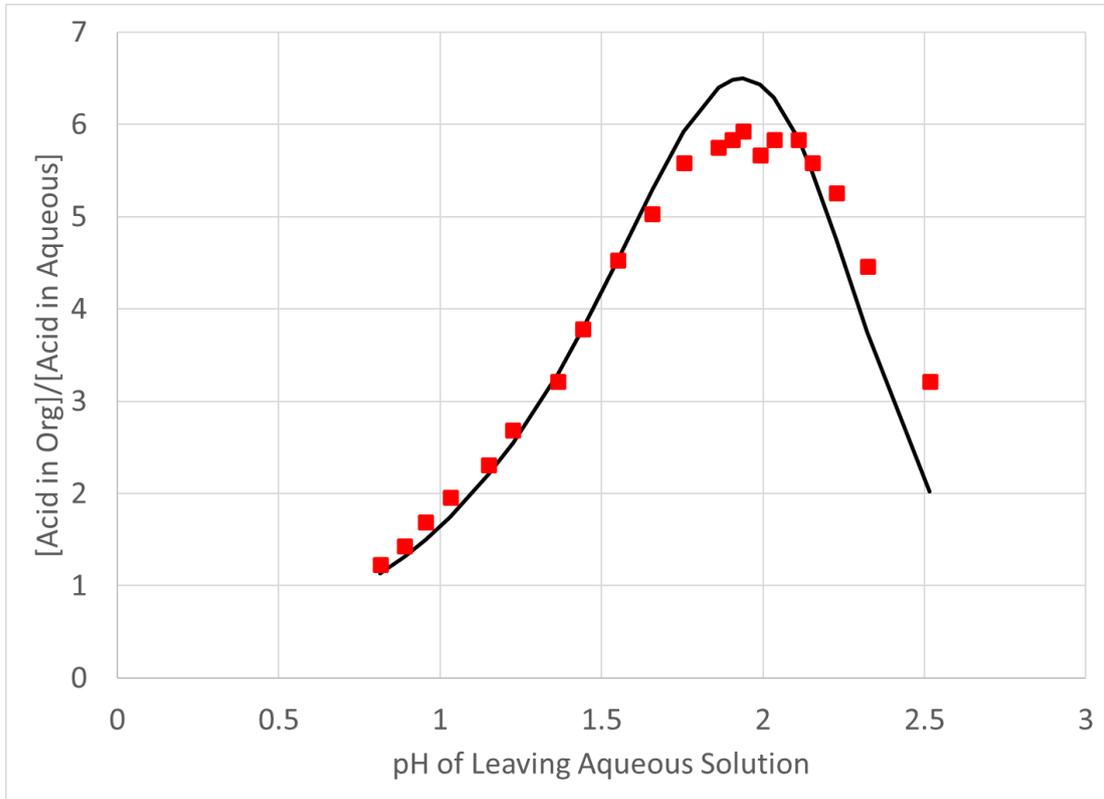
Literature data was obtained from Yakabu and Dudeney<sup>1</sup> for sulphuric acid and uranyl sulphate extraction and from Coca et al.<sup>1</sup> for molybdic acid extraction to Alamine 336 in sulphuric acid solution. The following data sets were used in the analysis:

1. Acid extraction data for 0.25 M Alamine 336 from Yakabu and Dudeney
2. Uranyl extraction data for 0.2 M Alamine 336 from Yakabu and Dudeney
3. Molybdate extraction data for 10 g/L molybdate extracted at pH 1 and 2 from Coca et al.

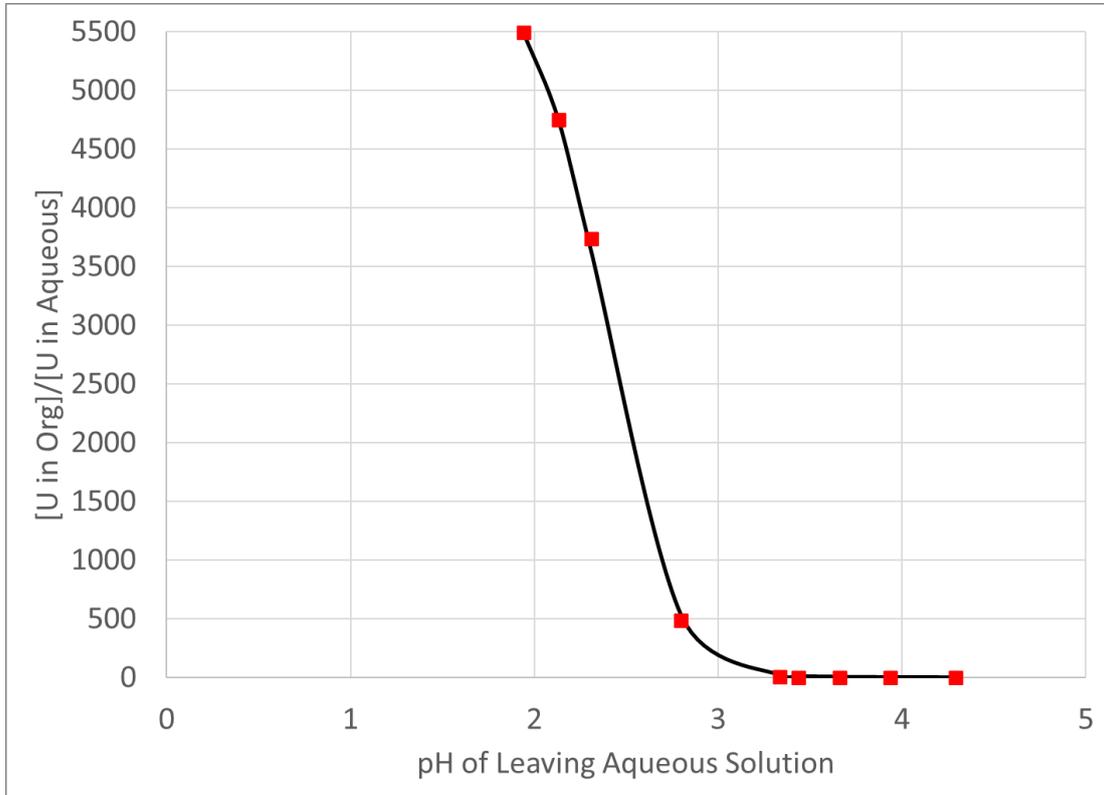
These data points were selected as they were most suited to the modelling of extraction conditions. Data fitting was done using an interface to Python. The Python SciPy optimize library was used to modify logK values used by the SysCAD model via the SysCAD PHREEQC interface.

Results of the data fitting are provided in Figure 1 - Figure 3. Based upon the fitting exercise, the following was noted:

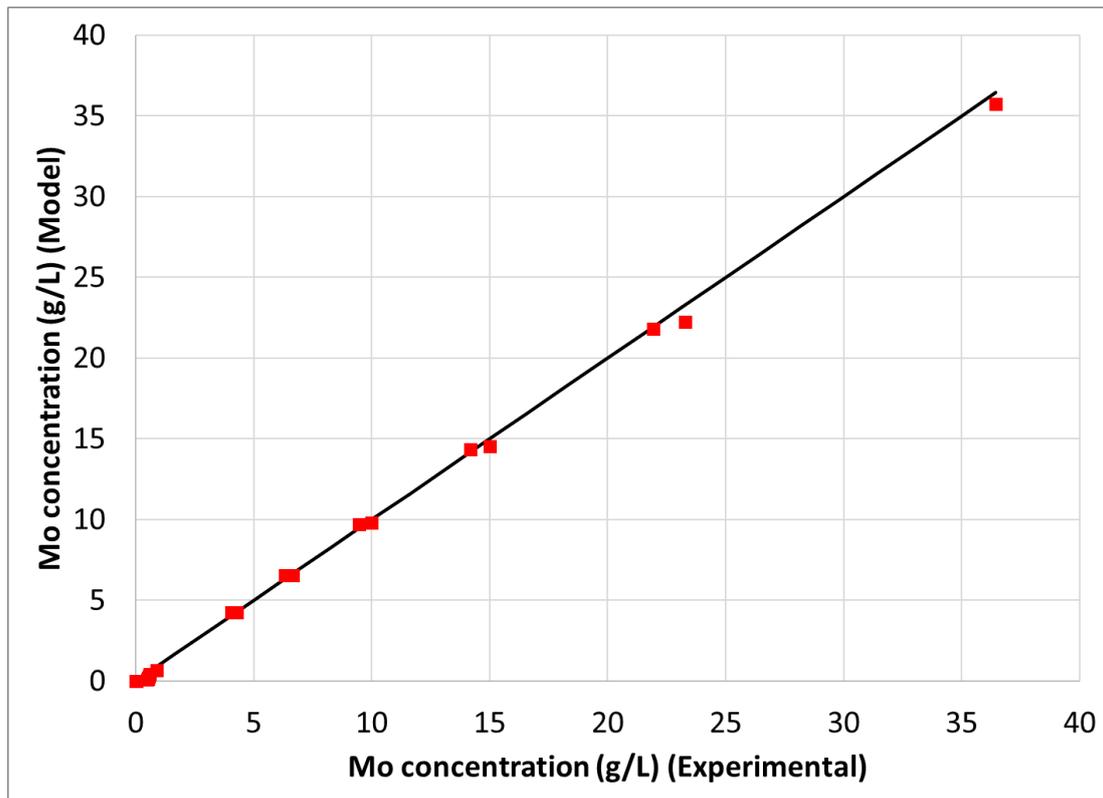
1. The simplified molybdate extraction mechanism suggested by Coca et al.<sup>1</sup> was sufficient to adequately model the extraction behaviour of molybdate and bimolybdate anions to Alamine 336.
2. Both acid and uranium extraction to Alamine 336 was adequately modelled using data and mechanisms reported in Yakabu and Dudeney<sup>1</sup>.



**Figure 1: Comparison of Measured points to Predicted Sulphuric Acid Extraction to 0.25 M Alamine 336 in kerosene**



**Figure 2: Comparison of Measured points to Predicted Uranyl Sulphate Extraction to 0.2 M Alamine 336 in kerosene**



**Figure 3: Comparison of Measured points to Predicted molybdenum concentration in organic and aqueous for 10% by volume Alamine 336 in kerosene (10 g/L Mo in aqueous head solution)**

### Solvent Extraction Model

The SysCAD model of the Solvent Extraction circuit consists of a series of interconnected Mixer Settler unit models with PHREEQC calculations embedded to calculate the composition exiting from the mixer. Settler performance is modelled by user-inputted values describing phase separation. Organic in aqueous, and aqueous in organic entrainment is incorporated. SysCAD performs a complete mass and energy balance on the flowsheet.

A solvent extraction flowsheet is particularly difficult to converge due to the organic flowing in a closed loop. Typically, modelling of a pure closed loop flow requires complex control methods to achieve the required recirculation flow. The “Composition Fetch” feature within SysCAD allows direct specification of the organic loop flowrate by creating an open tear.

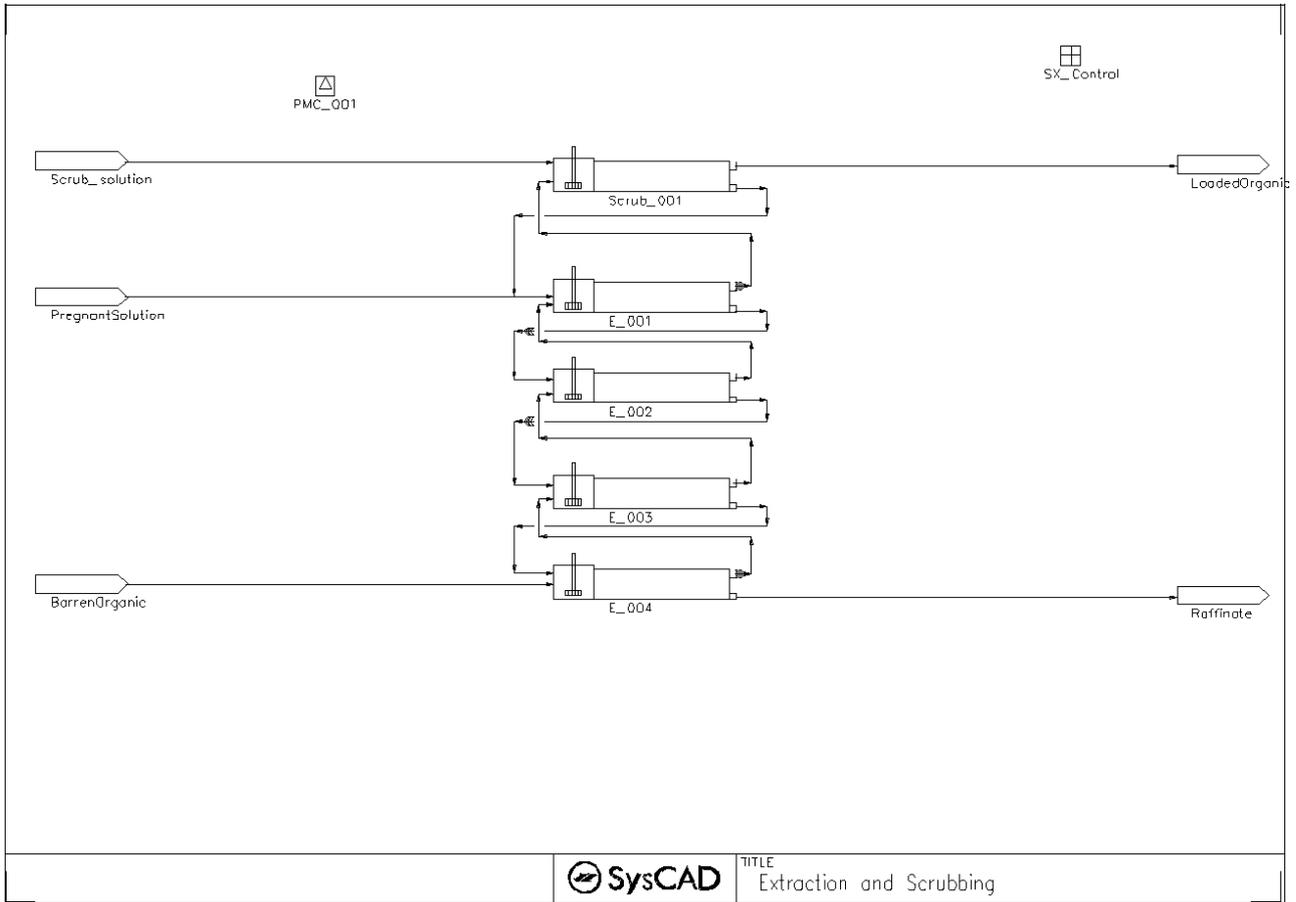


Figure 4: SysCAD flowsheet for Extraction and Scrubbing circuit

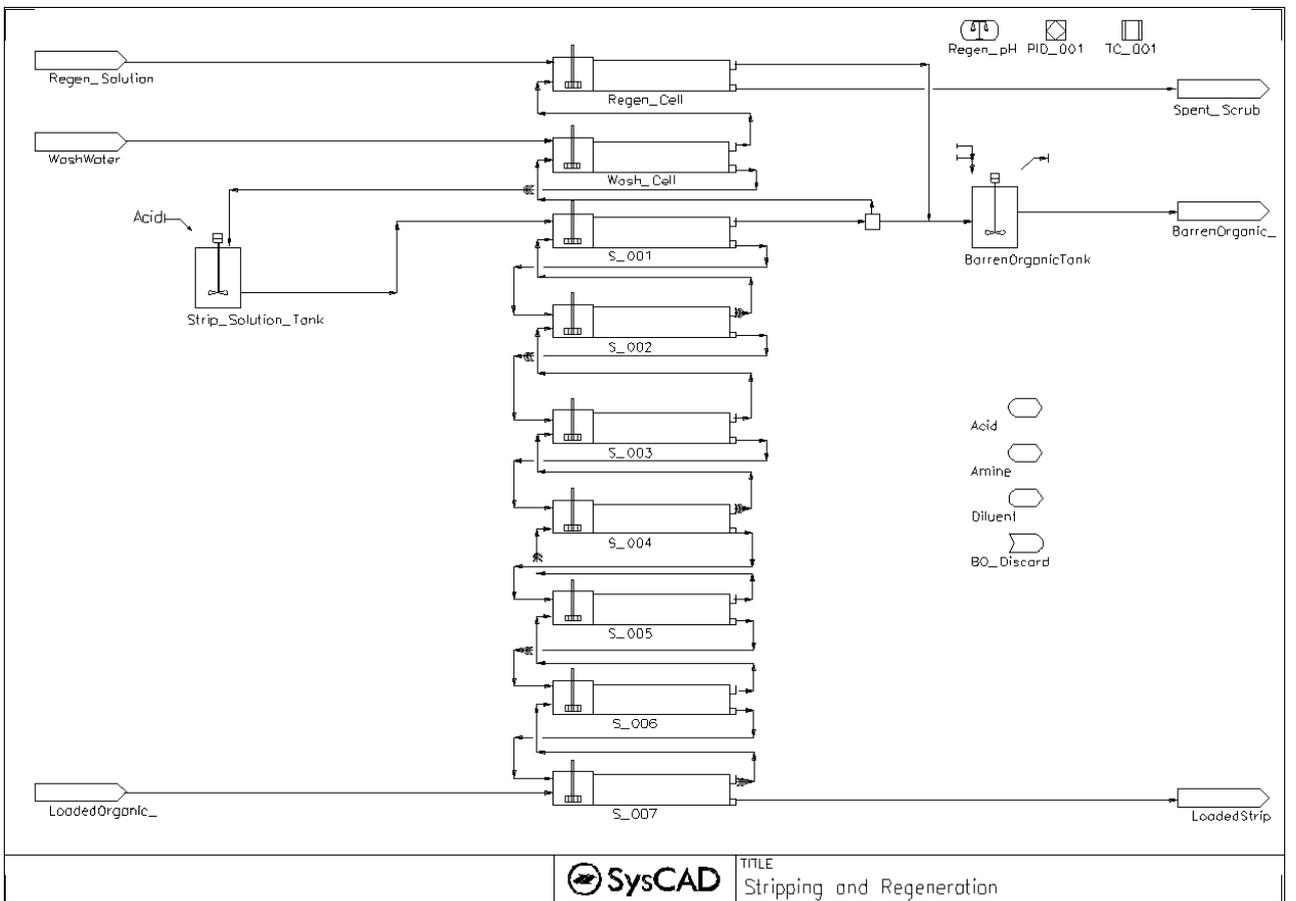
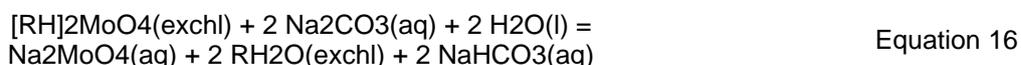
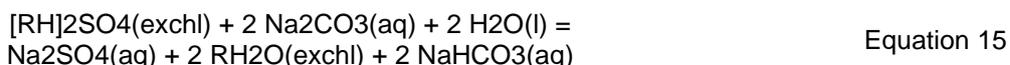
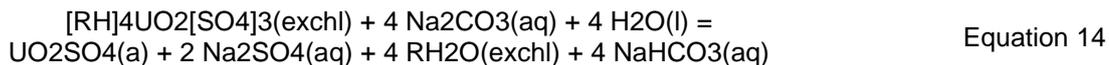
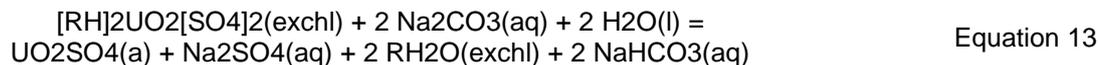
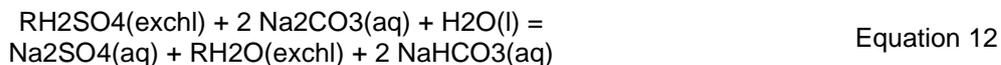
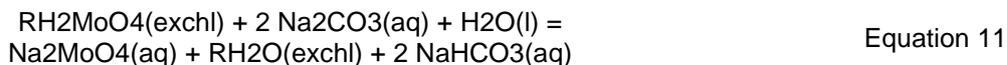


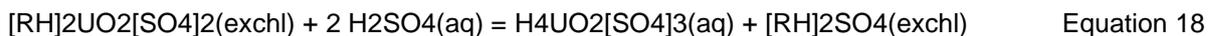
Figure 5: SysCAD flowsheet for Stripping and Regeneration circuit

The extraction circuit, as well as the scrub cell and wash cell, were modelled using the first principles thermodynamic model from fitting done in the previous section.

Regeneration was modelled using the following reactions in SysCAD:



Stripping was modelled using the following reactions in SysCAD:



The extent of reaction was calculated using the stripping isotherm developed by Morais et al.<sup>4</sup>.

## Simulation Results

Baseline input parameters used in the model are provided in Table 1.

**Table 1: Summary of baseline input parameters used in uranium solvent extraction circuit**

Pregnant Aqueous Flow (m <sup>3</sup> /h)	100
OA Ratio Scrub (m <sup>3</sup> /m <sup>3</sup> )	5
OA Ratio Strip (m <sup>3</sup> /m <sup>3</sup> )	20
Barren Organic Flow (m <sup>3</sup> /h)	65
Barren Organic to Regen (%)	10
Pregnant Aqueous U <sub>3</sub> O <sub>8</sub> (g/L)	5
Pregnant Aqueous Mo (mg/L)	50
Pregnant Aqueous Free Acid (g/L)	10
Scrub Free Acid (g/L)	80
Strip Free Acid (g/L)	450
Regen Na <sub>2</sub> CO <sub>3</sub> (%)	2
Barren Organic Amine Conc (%)	3
Regen pH	9
Number of Strip Cells	7

Key results of the simulation are presented in Table 2:

**Table 2: Summary of key simulation results**

Barren Organic Mo (g/L)	0.69
Barren Organic U <sub>3</sub> O <sub>8</sub> (g/L)	0.34
Loaded Strip U <sub>3</sub> O <sub>8</sub> (g/L)	132
Loaded Strip Flow (m <sup>3</sup> /h)	3.8
Loaded Strip Free Acid (g/L)	394
Na <sub>2</sub> CO <sub>3</sub> Usage (kg/kg)	0.70
Acid Usage (kg/kg)	2.99
U <sub>3</sub> O <sub>8</sub> Recovery (%)	99.5
Regeneration U <sub>3</sub> O <sub>8</sub> Losses (kg/d)	58
Raffinate U <sub>3</sub> O <sub>8</sub> Losses (kg/d)	0.6

The molybdenum balance for the circuit is presented in Table 3.

**Table 3: Overall circuit molybdenum balance for baseline conditions**

<b>Inputs</b>	
Molybdenum in Feed (kg/d)	120
<b>Outputs</b>	
Molybdenum in Raffinate (kg/d)	0.22
Molybdenum in Spent Scrub Solution (kg/d)	119.77
Molybdenum in Loaded Strip (kg/d)	0.01

Due to limitations in the stripping model, the stripping of molybdenum from the loaded organic to the strip solution was not considered. Thus, the molybdenum concentration in the loaded strip was due to organic entrainment only. Future work to improve this model should use high accuracy thermodynamic packages for aqueous systems, such as OLI or AQSol, to more accurately characterize the stripping process for uranium and molybdenum.

## Sensitivity Analysis

The utility of a good process model is its ability to evaluate the effect of process changes. In other words, the predicted change in results from a process change is generally more accurate than actual model predictions for a baseline condition.

In this analysis, we look at the following scenarios to evaluate their impact:

1. Reduction of the U<sub>3</sub>O<sub>8</sub> head grade in the pregnant solution from 5 g/L to 4 g/L
2. Reduction of the number of stripping cells from 7 to 6
3. Increase in the strip solution flow from O/A ratio (organic : aqueous) of 20 to O/A ratio of 15
4. Increase in the pregnant solution molybdenum concentration from 50 mg/L to 100 mg/L and resultant doubling of the regeneration of organic

By reviewing the response of the model to these changes in operating and design conditions, as summarized in Table 4, it is seen that model responses are in line with expected trends. For example, increasing the strip solution flowrate (Scenario 3) decreases the uranium in the pregnant strip solution, but correspondingly decreases the uranium losses in regeneration. It is also notable that the level of molybdenum in the feed has a significant effect on circuit recovery, due to the need to increase regeneration.

**Table 4: Sensitivity analysis results**

	<b>Baseline</b>	<b>Scenario 1</b>	<b>Scenario 2</b>	<b>Scenario 3</b>	<b>Scenario 4</b>
Barren Organic Mo (g/L)	0.69	0.69	0.69	0.69	0.61
Barren Organic U <sub>3</sub> O <sub>8</sub> (g/L)	0.34	0.25	0.46	0.07	0.31
Loaded Strip U <sub>3</sub> O <sub>8</sub> (g/L)	132	110	132	104	132
Loaded Strip flow (m <sup>3</sup> /h)	3.8	3.6	3.8	4.8	3.7
Loaded Strip Free Acid (g/L)	394	408	394	411	396
Na <sub>2</sub> CO <sub>3</sub> usage (kg/kg)	0.70	0.88	0.70	0.67	1.47
Acid usage (kg/kg)	2.99	3.73	2.99	3.99	2.99
U <sub>3</sub> O <sub>8</sub> recovery (%)	99.5	99.5	99.3	99.9	99.0
Regeneration U <sub>3</sub> O <sub>8</sub> Losses (kg/d)	58	44	79	12	119
Raffinate U <sub>3</sub> O <sub>8</sub> Losses (kg/d)	0.6	0.5	0.9	0.1	0.5

## **CONCLUSIONS**

Based upon this work, the following conclusions can be made:

1. A first principles model of extraction combined with practical engineering models of regeneration and stripping were combined to develop a realistic model of the extraction and strong acid stripping process of uranium.
2. Sensitivity analysis shows expected trends for changes in operating and design parameters.
3. Stripping of molybdenum from the loaded organic to the strip solution was not considered in this model. Thus, the model will underpredict the co-stripping of molybdenum into the product. Future work on this model should incorporate a thermodynamics package for calculation of uranium and molybdenum distribution in the strong acid stripping circuit.
4. The level of molybdenum in the ore can impact circuit design considerably due to the need to regenerate the organic while maintaining high uranium recovery.

## **ACKNOWLEDGEMENTS**

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