

## **An ASCEND Library for the Modeling, Simulation and Optimization of Solvent Extraction for Metal Recovery**

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### **Abstract**

A library for the study of solvent extraction (SX) phenomena in metal recovery has been developed. An interfacial reaction-with-diffusion model was constructed to simulate the transfer mechanism in a mixer-settler. To simulate phase inversion phenomena, a model was developed that treats the ambivalent region as a combination of both aqueous and organic continuous phases. An equilibrium model was also included, together with simple models for leaching and electro-winning, and models for mixers and splitters. These models allow the study of solvent extraction phenomena, such as the effect of pH or impeller rotational speed on equilibrium and pseudoequilibrium isotherms; operating conditions, such as internal recycle; and process configuration, such as comparison of a conventional SX circuit versus series-parallel SX circuits. The library can be useful for the modeling, simulation, parameter estimation, and optimization of hydrometallurgy metal recovery. Examples of potential applications are given at the end of this paper.

**Keywords:** Solvent extraction, modeling, simulation, hydrometallurgy

### **1. Introduction**

SX technology is one of the most important processes in metal recovery. In mineral processing technology, SX consists of two circuits coupled by a common solvent that contains an extractant. In the extraction circuit, the metal or metals of interest are transferred from the aqueous into the organic phase, and the phases are allowed to separate by gravity. In the stripping circuit, the metal is stripped out of the solvent by contact with a lean aqueous solution, and the solvent is returned to the extraction circuit. Process flow patterns typically range from single-solvent circulation loops to schemes employing organic and aqueous phase bypass, intermediate solvent recycle, series, parallel, and series/parallel circuits. Further, SX phenomena in hydrometallurgy involve complex multicomponent behavior in which selectivity, phase inversion, mass transfer

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rate, phase ratio, residence time, aqueous pH, organic extractant concentration, agitation speed, and other variables can affect the performance of the whole system.

For the design of these systems, El-Rifai and Ettouney (1999) and Gálvez et al. (2004) have presented graphical methods for the process design of coupled separation operations. Alonso et al. (2001) presented an MINLP optimization model to find the flowsheet configuration of SX circuits. However, these works do not address situations and phenomena such as multicomponent extraction and extraction rate. Aminian et al. (2000) presented a model for SX based on diffusion with interfacial reaction, but the model does not treat phase inversion, and different stream patterns were not included. Recently, Pinto et al. (2004) have studied the optimization of SX of Zn and Cd including chemical reaction, mass transfer, and mixer-settler hydrodynamics.

Although several works have been published on optimization, modeling, and design of these systems, the need exists for a general tool that can be used to improve our understanding of SX processes and phenomena. The objective of this work is to develop an ASCEND library (Westerberg, 1998) of models for SX that can be used for parameter estimation, process simulation, modeling, optimization, and design.

## 2. Mathematical Model

For the extraction of a metal,  $M_i$ , the stoichiometry of the overall reaction can be represented by the equation:



where  $M_i$  represents the  $i$ th extracted species,  $n_i$  the ionic balance, and  $HR$  the extractant molecule. In this work the reaction is assumed to take place at the phase boundary, which is generally accepted to be the case for several systems, such as the copper-LIX system.

For such a reversible and heterogeneous reaction to occur, the metal ions  $M_i$  and the extractant molecule  $HR$  both must first diffuse to the interface, and the products  $H^+$  and  $M_i R_{n_i}$  must diffuse away from the interface (see Figure 1).

The rate of transfer of species from and to the bulk aqueous and organic phases are modeled as follows:

$$r_i^a = m_i^a (x_i - x_i^{\text{int}}) \quad (2)$$

$$r_H^a = m_H^a (x_H - x_H^{\text{int}}) \quad (3)$$

$$r_i^o = m_H^o (y_i - y_i^{\text{int}}) \quad (4)$$

$$r_{RH}^a = m_{RH}^a (y_{RH} - y_{RH}^{\text{int}}) \quad (5)$$

where  $m_i^a$ ,  $m_H^a$ ,  $m_i^o$ ,  $m_{RH}^o$  are the mass transfer coefficient for metal  $i$ ,  $H$ , and  $RH$  in the aqueous (superscript  $a$ ) and organic (superscript  $o$ ) phases. The molar concentrations are  $x$  for the aqueous solutions and  $y$  for the organic solutions, with the  $r$  being the rate of transfer between the bulk phase and the interface.

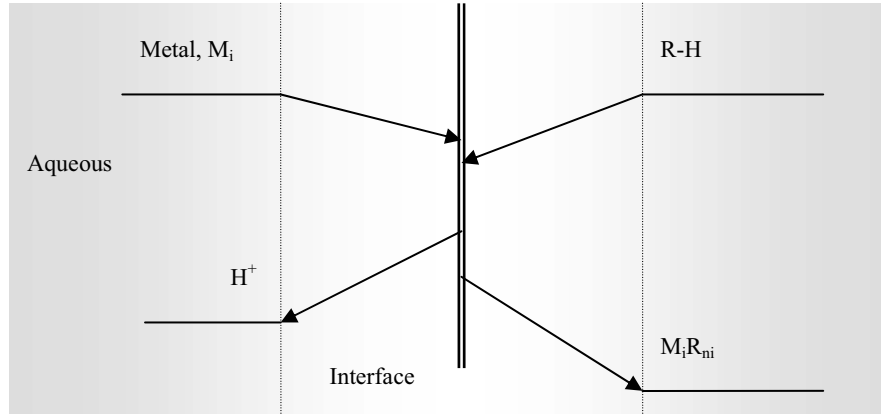


Figure 1- A schematic diagram for the extraction process.

The reaction rate equation per unit interfacial area is

$$\lambda_i = k_{ri} \left[ K_i \frac{(x_i^{\text{int}})^m (y_{RH}^{\text{int}})^n}{(x_H^{\text{int}})^p} - \frac{(x_H^{\text{int}})^{ni-p} (y_i^{\text{int}})}{(y_{RH}^{\text{int}})^{ni-n} (x_i^{\text{int}})^{1-m}} \right] \quad (6)$$

where  $K_i$  is the equilibrium constant for the reaction

$$(K_i)^z = \frac{k_{fi}}{k_{ri}} = \left[ \frac{y_i^{\text{int}} (x_H^{\text{int}})^{ni}}{x_i^{\text{int}} (y_{RH}^{\text{int}})^{ni}} \right]^z \quad (7)$$

$m$ ,  $n$  and  $p$  are the partial reaction orders for the forward reaction.

The mass balance equations for metal  $i$  are as follows:

$$\begin{aligned} Q_a^{\text{in}} x_i^{\text{in}} - Q_a^{\text{out}} x_i^{\text{out}} + A f_i &= 0 \\ Q_a^{\text{in}} y_i^{\text{in}} - Q_a^{\text{out}} y_i^{\text{out}} - A f_i &= 0 \end{aligned} \quad (8)$$

$Q_a$  and  $Q_o$  are the volumetric flow rates of the aqueous and organic phases under continuous operation.  $f_i$  is the rate of transfer of metal  $i$  per unit area.  $A$  is the total interfacial area. Analogous mass balance equations for  $H$  and  $RH$  are also written. At steady state, the rate of diffusion of the metal ion through the concentration boundary layer must equal the rate of reaction at the interface, therefore

$$r_i^a = -r_i^o = \lambda_i = f_i \quad (9)$$

Modeling of the interfacial area  $A$  is a challenging problem because the phenomenology of phase inversion is still poorly understood. Experimental studies have consistently shown that in stirred vessels the phase that is present at less than about 0.3 volume

fraction will usually be the dispersed phase. However, this leave a large volume fraction range called the ambivalent region, and it is in this region that industrial separations usually operate. In this work, the ambivalent region is modeled by considering one phase to be continuous in a certain fraction of the mixer volume with the other phase continuous in the remaining fraction (see Figure 2). Then the interfacial area can be estimated with the following equation:

$$A = 6 V_o \alpha / d_{bo} + 6(V_m - V_o) (1 - \alpha) / d_{ba} \quad (10)$$

Here  $V_o$  is the volume of organic phase and  $V_m$  is the volume of the mixer. The value of  $\alpha$  is 1 for aqueous continuity and 0 for organic continuity. For the ambivalent region, the value of  $\alpha$  is a function of the organic holdup. The values of  $d_{bo}$  and  $d_{ba}$ , the mean diameter of the spherical organic and aqueous droplets, can be estimated as a function of impeller diameter and velocity, holdup and density of the dispersed phase, viscosity of both phases, and interfacial tension (Godfrey et al., 1989).

### 3. Applications

The model may be applied in various ways; two examples are given here. The first example studies the effect of aqueous pH and organic extractant concentration on the equilibrium isotherm of a Cu/Fe system. The second example analyzes the consequences of internal recycle on the interface area, including phase inversion.

#### 3.1 Equilibrium behavior of simultaneous Cu/Fe extraction

Although several mathematical models have been proposed to simulate SX operation, little has been done to simultaneously analyze the behavior of several elements. In copper recover operations, the presence of iron in the leached solution influences the behavior of the system. Figures 3 and 4 show both copper and iron equilibrium isotherms computed for a copper-iron solution. Figure 3 shows the effect of extractant concentration, while Figure 4 shows the effect of the aqueous solution pH. These results agree with the behavior observed experimentally.

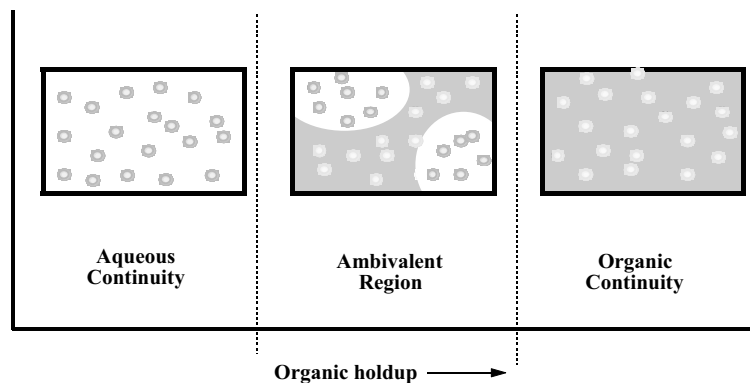


Figure 2. Effect of organic hold up on phase inversion.

### 3.2 Effect of Internal Recycle

Internal recycle is often practiced in SX, wherein one phase is recycled from the settler back to the mixer. For example, in hydrometallurgical SX systems, a concentrating of the metal between the feed and stripping aqueous streams is usually necessary. This means that the feed to stripping aqueous flow rate ratio is usually large, in turn meaning large phase ratios in either or both of the extraction and stripping stages. In such cases the resulting mixtures in a mixer-settler will tend to emulsify and be difficult to separate. One approach to overcome the problem is to use internal recycle.

Another example is the use of internal recycle to reduce the entrainment of the organic phase in the aqueous stream or vice versa. A mixer settler with organic phase internal recycle was simulated and the effect of phase inversion on total interfacial area was studied. Results as given in Figure 5 can be obtained. The interfacial area depends on the phase inversion, with discontinuity between regions and with a maximum value. These profiles agree with experimental observations (Hoh et al., 1989).

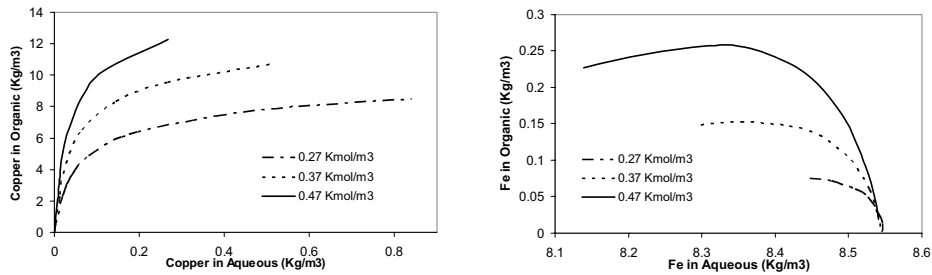


Figure 3 Effect of extract concentration on equilibrium isotherms in Cu/Fe system

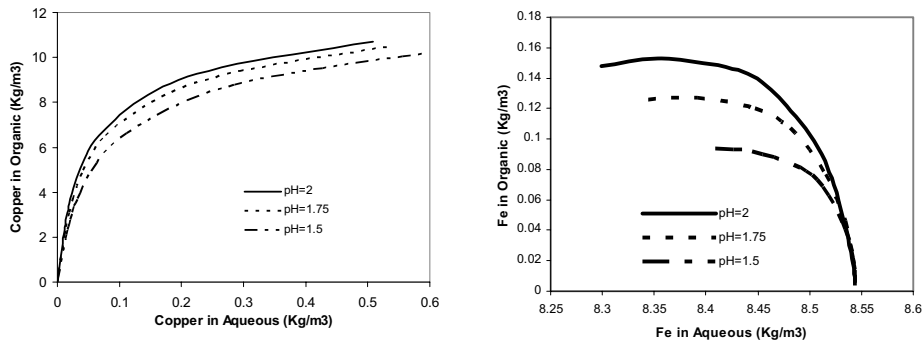


Figure 4. Effect of aqueous pH on equilibrium isotherms in Cu/Fe system

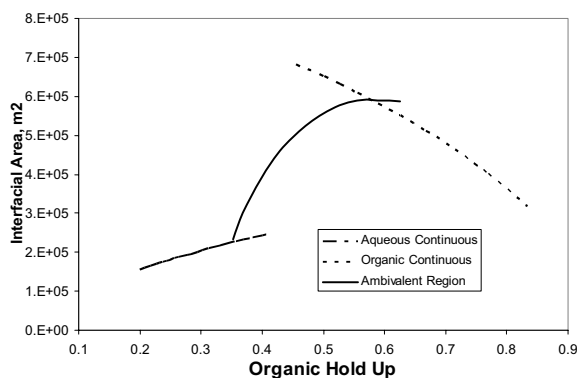


Figure 5. effect of organic phase holdup on interfacial area.

#### 4. Conclusions

A library for the modeling, simulation and optimization of SX for metal recovery had been developed in ASCEND. The library contains several models, including a model of diffusion with interfacial reaction to simulate the transfer mechanism in a mixer-settler. A model for phase inversion phenomena was developed and integrated into the SX model. The simulated results agree well with the observed behavior of SX phenomena and processes. By utilizing the capabilities of ASCEND, the library can be used to estimate unknown parameters using an optimization routine. Once the model is calibrated, the library can be used for process simulation, modeling, optimization, and design, or in research to improve our understanding of the SX process and associated phenomena.

Although the present library has simple models for leaching and electrowinning, future work includes the development of rigorous models for these operations.

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