



Technical note

Modeling and simulation of multicomponent solvent extraction processes to purify rare earth metals



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ABSTRACT

A huge number of nonlinear equations must be solved to simulate the multicomponent solvent extraction process for purification of rare earth metals using saponified PC88A. Typical approaches to solve them have not been successful due to the large number of initial guess values and numerical problems such as poor convergence and divergence. In this paper, the number of nonlinear equations to be solved simultaneously is dramatically reduced by a proposed model simplification technique, which reduces the number of initial guess values and overcomes the numerical problems. Furthermore, a thermodynamic equilibrium analysis algorithm using the model simplification technique is proposed to calculate the equilibrium concentrations. Finally, a new multicomponent solvent extraction process simulator is developed to calculate the equilibrium concentrations for all stages of the solvent extraction process.

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1. Introduction

Rare earth metals have been widely used as important materials in various industrial electronics applications such as wind turbines, hybrid cars, displays, nuclear energy applications, and super conductors (Gupta and Krishnamurthy, 2005). The purity of rare earth metals must be more than 99% to utilize their important properties such as fluorescence and magnetism. However, separation of rare earth metals is very difficult because they have similar physicochemical properties. As technology has progressed, many kinds of separation methods have been explored and proposed for their high-purity separation, such as solvent extraction, fractional precipitation, fractional crystallization, and ion exchange. In particular, solvent extraction has been widely used in industry because of its advantages such as continuous operation, high capacity, and efficient separation performance. Acidic organophosphorus solvents of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) and di(2-ethylhexyl) phosphoric acid (D2EHPA) have been chosen as extractants in industrial solvent extraction processes. PC88A has a higher loading capacity and higher separation factor than D2EHPA. The hydrogen ion generated by the reaction between rare earth metals and PC88A reduces the pH of the aqueous phase. The high hydrogen ion concentration weakens the driving force for the forward extraction reaction. Hence, saponified PC88A is preferred to PC88A because it keeps the forward reaction from losing its driving force by maintaining a low hydrogen ion concentration.

Many researchers have developed non-rigorous mathematical models using the power law, exponential form, artificial neural network, and time-series model (Goto and Smutz, 1965; Sato, 1989; Thakur et al., 1993; Giles et al., 1996; Mishra et al., 2000; Thakur, 2000; Anitha and Singh, 2008; Yang et al., 2012). Though these models have strong points of simplicity and usability, they have structural limitations in predicting the equilibrium concentrations in the solvent extraction process lying outside the range of the experimental data. Therefore, rigorous models have been developed (Lee et al., 2005, 2008). These models successfully described the behavior of the solvent extraction of rare earth metals outside the range of the experimental data, but the numerical problems could not be solved. Recently, a rigorous model was successfully developed to simulate the multistage solvent extraction process (Ryu et al., 2013). It can be only applied, however, to the solvent extraction process of the rare earth metals with PC88A. Also, these rigorous models can incorporate only two-component solvent extraction processes. Therefore, we developed a new solvent extraction process simulator to simulate the equilibrium concentrations for all stages of the solvent extraction process for purifying multicomponent rare earth metals with saponified PC88A.

2. Equilibrium equations

The solvent extraction process shown in Fig. 1 is for separating light rare earth metals from heavy rare earth metals in a multicomponent system using saponified PC88A as the extractant. The solvent extraction process comprises three parts: extraction, scrubbing, and stripping. The feed stream combined with the scrubbing output stream flows into the

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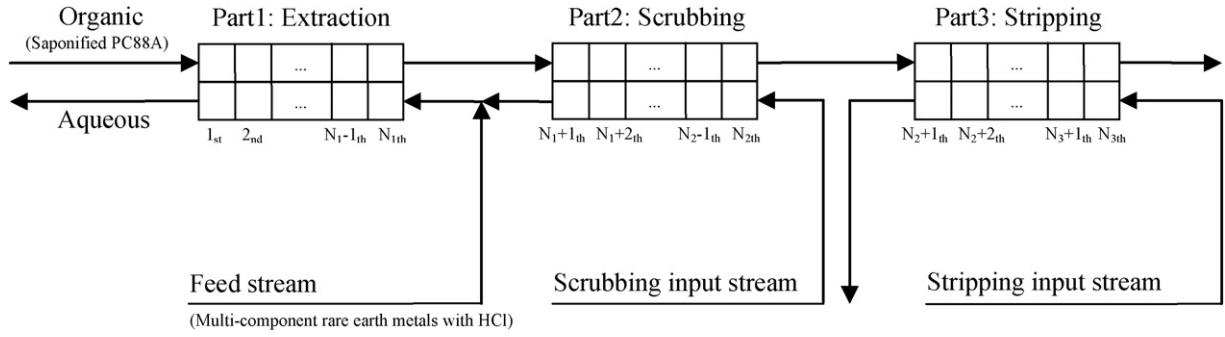


Fig. 1. Schematic diagram of the solvent extraction process for purification of rare earth metals.

aqueous phase of the last stage of the extraction part. The organic phase flows in the opposite direction of the aqueous phase. The role of each part is as follows. In the extraction part, transfer of the rare earth metals from the aqueous phase to the organic phase occurs. The scrubbing part is the transfer of the light rare earth metals in the organic phase to the aqueous phase. The stripping part is recovery of the heavy rare earth metals in the organic phase by transferring them to the aqueous phase using strong hydrochloric acid.

The equilibrium equations in the multicomponent solvent extraction process to purify rare earth metals consist of the equilibrium constant equations, the material balance equations, and the charge balance equations. The equilibrium constant equations are presented as Eqs. (1)–(4).

$$K_w = [\text{H}^+][\text{OH}^-] \quad (1)$$

$$K_{RE(i),1} = \frac{[\text{RE}(i)\text{Cl}^{2+}]}{[\text{RE}(i)^{3+}][\text{Cl}^-]}; \quad K_{RE(i),l} = \frac{[\text{RE}(i)(\text{OH})^{(4-l)+}]}{[\text{RE}(i)^{3+}][\text{OH}^-]^{(l-1)}}, \quad (2)$$

$$i = 1, 2, \dots, n, \quad l = 2, 3, 4$$

$$\bar{K}_{RE(i),H_2A_2} = \frac{[\text{RE}(i)_{H_2A_2}]_{org} [\text{H}^+]^3}{[\text{RE}(i)^{3+}] [\text{H}_2\text{A}_2]_{org}^{\alpha_{RE(i)}}}, \quad (3)$$

$$\bar{K}_{RE(i),H_2A_2} = K_{RE(i),H_2A_2} (1 + \beta_{1,RE(i),H_2A_2} I + \dots + \beta_{N_\beta,RE(i),H_2A_2} I^{N_\beta}),$$

$$i = 1, 2, \dots, n$$

$$\bar{K}_{RE(i),NaA} = \frac{[\text{RE}(i)_{NaA}]_{org} [\text{Na}^+]^3}{[\text{RE}(i)^{3+}] [\text{NaA}]_{org}^3}, \quad (4)$$

$$\bar{K}_{RE(i),NaA} = K_{RE(i),NaA} (1 + \beta_{1,RE(i),NaA} I + \dots + \beta_{N_\beta,RE(i),NaA} I^{N_\beta}),$$

$$i = 1, 2, \dots, n.$$

The K_s are defined as the equilibrium constants. $RE(i)$ means the i -th rare earth metal and n is the number of components in the rare earth metal solution. As i increases, the property of $RE(i)$ moves to the heavy rare earth metal side. H_2A_2 means the dimer of PC88A and NaA means saponified PC88A. The subscript “org” represents the organic phase, and $[]$ means molarity concentration with units of (mol solute)/(L solution). The equilibrium constants in Eqs. (3) and (4) describe the non-ideality of the electrolyte solution. Theoretically, the nonlinear functions for correction of the ideal equilibrium constant equations to describe the non-ideal behavior of the solution more accurately are

functions of the ionic strength. So, in this research, two polynomials are used as shown in Eqs. (3) and (4). The polynomials can describe the non-ideality with better accuracy as increasing N_β and β_{N_β} . I denotes the total ionic strength of the aqueous phase. The β_s are the correction parameters to help describe the real electrolyte solution more accurately. They can be estimated by fitting the parameters to the experimental values.

The material balance equations presented as Eqs. (5) and (6) are based on the stoichiometry of the reactions.

$$[\text{Na}^+] = 3 \sum_{i=1}^n [\text{RE}(i)_{NaA}]_{org}; \quad [\text{NaA}]_{org}^{IV} = [\text{NaA}]_{org} + 3 \sum_{i=1}^n [\text{RE}(i)_{NaA}]_{org};$$

$$[\text{H}_2\text{A}_2]_{org}^{IV} = [\text{H}_2\text{A}_2]_{org} + \sum_{i=1}^n \alpha_{RE(i)} [\text{RE}(i)_{H_2A_2}]_{org}; \quad [\text{Cl}^-]^{IV} = [\text{Cl}^-] + \sum_{i=1}^n [\text{RE}(i)\text{Cl}^{2+}] \quad (5)$$

$$[\text{RE}(i)]^{IV} = [\text{RE}(i)^{3+}] + [\text{RE}(i)\text{Cl}^{2+}] + [\text{RE}(i)(\text{OH})^{2+}] + [\text{RE}(i)(\text{OH})_2^+] + [\text{RE}(i)(\text{OH})_3^0] + R_{O/A} \left([\text{RE}(i)_{H_2A_2}]_{org} + [\text{RE}(i)_{NaA}]_{org} \right), \quad i = 1, 2, \dots, n \quad (6)$$

$[\text{H}_2\text{A}_2]_{org}^{IV}$ and $[\text{NaA}]_{org}^{IV}$ denote the overall concentrations of the PC88A dimer and the saponified PC88A in the organic phase, respectively. $[\text{RE}(i)]^{IV}$ and $[\text{Cl}^-]^{IV}$ are the overall concentrations of the rare earth element and the chloride element in the aqueous phase, respectively. It can be assumed that all $RE(i)$ in the organic phase are transferred to the aqueous phase before the two phases reach equilibrium, because the equilibrium concentrations are independent of the reaction path. Eq. (6) is then easily derived. All $[\bullet]^{IV}$ concentrations are invariant for complex formation reactions. $R_{O/A} = v_{organic}/v_{aqueous}$ is defined as the ratio of the organic volumetric flowrate to the aqueous volumetric flowrate.

The charge balance equation is derived from the assumption that the aqueous phase is electrically neutral. The charge balance equation is shown in Eq. (7).

$$[\text{H}^+] + [\text{Na}^+] + \sum_{i=1}^n (3[\text{RE}(i)^{3+}] + 2[\text{RE}(i)\text{Cl}^{2+}] + 2[\text{RE}(i)(\text{OH})^{2+}] + [\text{RE}(i)(\text{OH})_2^+]) = [\text{Cl}^-] + [\text{OH}^-]. \quad (7)$$

Note that the number of the equilibrium concentrations is $7n + 6$. It is the same as the number of the equations in Eqs. (1)–(7). Therefore, it is possible to estimate all the equilibrium concentrations by solving $7n + 6$ nonlinear equations.

3. Equilibrium equation solver and thermodynamic equilibrium analysis algorithm

There are a lot of equilibrium equations that must be solved to simulate the multicomponent solvent extraction process. But, it is not easy to solve them simultaneously because they need numerous initial guess values. Solving the nonlinear equations by improper initial guess values could result

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