

Modeling and simulation of solvent extraction processes for purifying rare earth metals with PC88A

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Abstract—A new simulation logic and thermodynamic equilibrium analysis algorithm combined with a new model simplification technique was developed to simulate the solvent extraction process for purifying rare earth metals from chloride solution with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) as a solvent. The proposed model simplification method significantly reduces the number of the nonlinear equilibrium equations to be simultaneously solved to overcome the initial guess problem and obtain numerically stable convergence pattern in solving the equilibrium analysis problem and performing the rigorous simulation of the extraction process. A new equilibrium analysis algorithm on the basis of the simplified nonlinear equilibrium equations is also proposed to estimate the equilibrium concentrations by solving the rigorous first principle extraction model. Finally, a solvent extraction simulator is developed to estimate all the concentrations of all the stages of the solvent extraction process by solving the equilibrium analysis problem at each stage in a sequential way. The proposed simulator does not suffer from the initial guess problem and shows very robust convergence pattern without any numerical problems.

Key words: Solvent Extraction, PC88A, Rare Earth, Distribution Coefficient, Simulation, Equilibrium Analysis, Model Simplification

INTRODUCTION

Rare earths are extremely important materials with applications in metallurgy, electronics, nuclear energy, superconductors, hydrogen storage, optics etc. [1]. The separation of rare earths is one of the most difficult challenges because the properties of rare earths are very similar. Several processes such as solvent extraction, fractional precipitation, fractional crystallization and ion exchange can be used to separate rare earth metals. Among them, the solvent extraction process has been recognized as one of the most efficient ones in industry. Acidic organophosphorus solvents such as di-(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) for the industrial extraction process have been widely used. PC88A provides higher loading capacity and higher separation factor compared to D2EHPA.

Many researchers have focused on developing non-rigorous mathematical models for the rare earth extraction [2-9]. The non-rigorous mathematical models have various forms of power law, exponential form, artificial neural network and time-series. The models are obtained by fitting the model parameters to experimental equilibrium data. Though these simple models or black-box models have remarkable advantages in terms of simplicity and convenient application, they have inherent limitations in describing the behavior outside the range of experimental data. A rigorous first principle model approach has been also developed for the rare earth equilibrium analysis [10-14]. Though the rigorous equilibrium models successfully provide a good agreement with experimental equilibrium data, it is

difficult for the rigorous approach to completely solve the initial guess problem of the repetitive root-finding method such as the Newton-Raphson method and obtain a numerically stable convergence pattern. Also, there is no systematic study on the simulation of the solvent rare earth extraction process on the basis of rigorous complex formation reaction equations and material balance equations.

We propose a new robust simulation logic and thermodynamic equilibrium analysis algorithm to rigorously simulate the solvent extraction process for purifying rare earth metals from chloride solution with the PC88A. The number of the nonlinear equilibrium equations to be simultaneously solved is significantly reduced by the proposed model simplification technique to overcome the initial guess problem and obtain numerically stable convergence in solving the nonlinear equations, which is crucial to making the rigorous first principle simulation to be successful. Also, a new thermodynamic equilibrium analysis algorithm combined with the proposed model simplification technique is developed to estimate the equilibrium concentrations without any numerical problems. Finally, a solvent extraction simulator is proposed to estimate all the concentrations of all the stages of the solvent extraction process by solving the equilibrium analysis problem at each stage in a sequential way. The proposed simulator does not suffer from the initial guess problem and shows very stable convergence pattern without any numerical problems.

MODELING AND SIMULATION OF SOLVENT EXTRACTION PROCESS

The solvent extraction process considered in this research is to separate the two components of the light rare earth metal and the

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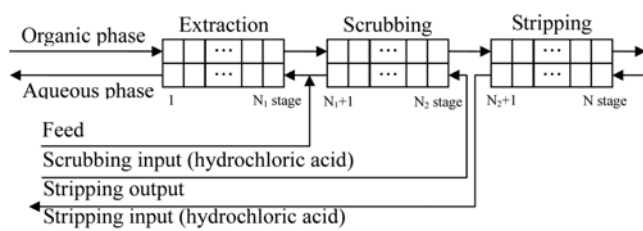


Fig. 1. Schematic diagram of the solvent extraction process for purifying rare earth metals.

heavy rare earth metal in chloride solution with PC88A as a solvent. A schematic diagram of the two component solvent extraction process is shown in Fig. 1. It consists of the extraction part, the scrubbing part and stripping part. The scrubbing input and the stripping input stream are hydrochloric acid solution. The feed stream is chloride solution containing the rare earth metals to be separated. The extraction part is to load the rare earth metals in the aqueous phase to the organic phase and the scrubbing part is to unload the light rare earth metal in the organic phase to the aqueous phase to increase the purity of the output streams. The stripping part is to recover the heavy rare earth metal from the organic phase in the form of the aqueous solution by completely unloading it.

In this section, a new model simplification technique is developed to reduce the number of nonlinear equilibrium equations to be simultaneously solved to overcome the initial guess problem and obtain numerically stable convergence pattern in solving nonlinear equilibrium equations. Next, a new equilibrium analysis algorithm is developed to solve the thermodynamic equilibrium problem, followed by a solvent extraction simulator to estimate all the concentrations of all the stages of the solvent extraction process.

1. Equilibrium Equations

Table 1 shows the typical complex formation reactions in the aqueous phase or between the two immiscible phases for the two components rare earth equilibrium process. The equilibrium equations corresponding to the reactions in Table 1 are as follows:

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

$$K_{RE1,1} = \frac{[RE1Cl^{2+}]}{[RE1^{3+}][Cl^-]}, \quad K_{RE1,2} = \frac{[RE1(OH)^{2+}]}{[RE1^{3+}][OH^-]},$$

Table 1. Complex formation reactions in the two components rare earth equilibrium process

Reactions	Equilibrium constant
$H_2O = H^+ + OH^-$	K_w
$RE1^{3+} + Cl^- = RE1Cl^{2+}$	$K_{RE1,1}$
$RE1^{3+} + OH^- = RE1(OH)^{2+}$	$K_{RE1,2}$
$RE1^{3+} + 2OH^- = RE1(OH)_2^+$	$K_{RE1,3}$
$RE1^{3+} + 3OH^- = RE1(OH)_3^0$	$K_{RE1,4}$
$RE1^{3+} + \alpha_{RE1} H_2A_2 = RE1_{org,H_2A_2} + 3H^+$	\bar{K}_{RE1,H_2A_2}
$RE2^{3+} + Cl^- = RE2Cl^{2+}$	$K_{RE2,1}$
$RE2^{3+} + OH^- = RE2(OH)^{2+}$	$K_{RE2,2}$
$RE2^{3+} + 2OH^- = RE2(OH)_2^+$	$K_{RE2,3}$
$RE2^{3+} + 3OH^- = RE2(OH)_3^0$	$K_{RE2,4}$
$RE2^{3+} + \alpha_{RE2} H_2A_2 = RE2_{org,H_2A_2} + 3H^+$	\bar{K}_{RE2,H_2A_2}

$$K_{RE1,3} = \frac{[RE1(OH)_2^+]}{[RE1^{3+}][OH^-]^2}, \quad K_{RE1,4} = \frac{[RE1(OH)_3^0]}{[RE1^{3+}][OH^-]^3} \quad (2)$$

$$\bar{K}_{RE1,H_2A_2} = \frac{[RE1_{org,H_2A_2}][H^+]^3}{[RE1^{3+}][H_2A_2]_{org}^{\alpha_{RE1}}},$$

$$\bar{K}_{RE1,H_2A_2} = K_{RE1,H_2A_2}(1 + \beta_{1,RE1}I + \dots + \beta_{N_{RE1},RE1}I^{N_{RE1}}) \quad (3)$$

$$K_{RE2,1} = \frac{[RE2Cl^{2+}]}{[RE2^{3+}][Cl^-]}, \quad K_{RE2,2} = \frac{[RE2(OH)^{2+}]}{[RE2^{3+}][OH^-]},$$

$$K_{RE2,3} = \frac{[RE2(OH)_2^+]}{[RE2^{3+}][OH^-]^2}, \quad K_{RE2,4} = \frac{[RE2(OH)_3^0]}{[RE2^{3+}][OH^-]^3}, \quad (4)$$

$$\bar{K}_{RE2,H_2A_2} = \frac{[RE2_{org,H_2A_2}][H^+]^3}{[RE2^{3+}][H_2A_2]_{org}^{\alpha_{RE2}}},$$

$$\bar{K}_{RE2,H_2A_2} = K_{RE2,H_2A_2}(1 + \beta_{1,RE2}I + \dots + \beta_{N_{RE2},RE2}I^{N_{RE2}}) \quad (5)$$

where RE1 and RE2 represent the light rare earth element and the heavy rare earth element, respectively. The subscript “org” means the organic phase. H_2A_2 denotes the PC88A dimer. $[•]$ represents the molarity concentration in mol/L. K 's are the equilibrium constants. $RE1_{org,H_2A_2}$ and $RE2_{org,H_2A_2}$ are the complexes formed through the reaction between the PC88A and the rare earth element. I represents the total ion strength of the aqueous phase to incorporate the non-ideal behavior of the electrolyte solution. In this research, only H^+ , OH^- , $RE1^{3+}$, $RE2^{3+}$, $RE1Cl^{2+}$, $RE2Cl^{2+}$ are considered to calculate the total ionic strength of I because the amounts of the other ions are usually negligible. Some of the equilibrium constants and stoichiometric coefficients can be determined by thermodynamic database. The other equilibrium constants and β 's should be determined by fitting them to experimental equilibrium data.

The following material balance equations for the overall equilibrium concentrations can be easily derived:

$$[H_2A_2]_{org}^{IV} = [H_2A_2]_{org} + \alpha_{RE1}[RE1_{org,H_2A_2}] + \alpha_{RE2}[RE2_{org,H_2A_2}] \quad (6)$$

$$[RE1]^{IV} = [RE1^{3+}] + [RE1Cl^{2+}] + [RE1(OH)^{2+}] + [RE1(OH)_2^+] + [RE1(OH)_3^0] + [RE1_{org,H_2A_2}]R_{O/A} \quad (7)$$

$$[RE2]^{IV} = [RE2^{3+}] + [RE2Cl^{2+}] + [RE2(OH)^{2+}] + [RE2(OH)_2^+] + [RE2(OH)_3^0] + [RE2_{org,H_2A_2}]R_{O/A} \quad (8)$$

$$[Cl]^{IV} = [Cl^-] + [RE1Cl^{2+}] + [RE2Cl^{2+}] \quad (9)$$

where $R_{O/A} = v_{organic}/v_{aqueous}$ is the ratio of the organic volumetric flowrate ($v_{organic}$, corresponding to the organic volume in the case of batch-type experiment) to the aqueous volumetric flowrate ($v_{aqueous}$, corresponding to the aqueous volume in the case of batch-type experiment). $[H_2A_2]_{org}^{IV}$ denotes the overall concentration of the PC88A dimer in the organic phase. $[RE1]^{IV}$, $[RE2]^{IV}$ and $[Cl]^{IV}$ are the overall concentrations of the light rare earth element, the heavy rare earth element and the chloride element in the aqueous phase. Eqs. (7)-(8) are derived with the assumption that all RE1 and RE2 in the organic phase are moved to the aqueous phase before the equilibrium state is established. The assumption is valid because the equilibrium concentrations are independent of the reaction path. All $[•]^{IV}$ concentrations are invariant for the complex formation reactions.

Also, the aqueous phase should be electronically neutral. Then,

the following charge balance equation is derived.

$$\begin{aligned} &[H^+] + 3[RE1^{3+}] + 2[RE1Cl^{2+}] + 2[RE1(OH)^{2+}] \\ &+ [RE1(OH)_2^+] + 3[RE2^{3+}] + 2[RE2Cl^{2+}] \\ &+ 2[RE2(OH)^{2+}] + [RE2(OH)_2^+] = [Cl^-] + [OH^-] \end{aligned} \quad (10)$$

The total number of the equilibrium concentrations ($[RE1^{3+}]$, $[RE1Cl^{2+}]$, $[RE1(OH)^{2+}]$, $[RE1(OH)_2^+]$, $[RE1(OH)_3^0]$, $[RE1_{org,H_2A_2}]$, $[RE2^{3+}]$, $[RE2Cl^{2+}]$, $[RE2(OH)^{2+}]$, $[RE2(OH)_2^+]$, $[RE2(OH)_3^0]$, $[RE2_{org,H_2A_2}]$, $[H^+]$, $[OH^-]$, $[Cl^-]$, $[H_2A_2]$) of the first principle equilibrium model is 16. It is the same with the number of the equilibrium equations from Eq. (1) to Eq. (10). So, all the equilibrium concentrations can be estimated by solving the nonlinear equilibrium equations simultaneously. But, solving 16 the nonlinear equations simultaneously tends to result in serious numerical problems. It is difficult to guess such a large number of the initial estimates before solving the nonlinear equations using a nonlinear equation solver like the Newton-Raphson method. A wrong initial guess may result in poor convergence or divergence problem in solving the nonlinear equations. Also, solving all the nonlinear equations simultaneously increases the possibility of numerical divergence. To solve these numerical problems, a model simplification technique needs to be developed to significantly reduce the number of the nonlinear equations to be solved simultaneously.

2. Proposed Model Simplification Technique

A model simplification method is proposed and developed in this section to overcome the initial guess problem and poor convergence problem in solving the nonlinear equilibrium equations. First, replace $[Cl^-]$ of the first equations of Eq. (2) and Eq. (4) by $[Cl^-]$ obtained from Eq. (9). Then, the following equation is obtained.

$$\begin{aligned} \begin{bmatrix} [RE1Cl^{2+}] \\ [RE2Cl^{2+}] \end{bmatrix} &= \begin{bmatrix} 1 + K_{RE1,1}[RE1^{3+}] & K_{RE1,1}[RE1^{3+}] \\ K_{RE2,1}[RE2^{3+}] & 1 + K_{RE2,1}[RE2^{3+}] \end{bmatrix}^{-1} \\ &\quad \begin{bmatrix} K_{RE1,1}[RE1^{3+}][Cl]^I \\ K_{RE2,1}[RE2^{3+}][Cl]^I \end{bmatrix} \end{aligned} \quad (11)$$

Second, replace $[RE1(OH)^{2+}]$, $[RE1(OH)_2^+]$, $[RE1(OH)_3^0]$, $[RE2(OH)^{2+}]$, $[RE2(OH)_2^+]$, $[RE2(OH)_3^0]$ of Eq. (7) and Eq. (8) by $[RE1(OH)^{2+}]$, $[RE1(OH)_2^+]$, $[RE1(OH)_3^0]$ and $[RE2(OH)^{2+}]$, $[RE2(OH)_2^+]$, $[RE2(OH)_3^0]$ obtained from the second, third, fourth equations of Eq. (2) and Eq. (4). Then, the following equations are obtained:

$$\begin{aligned} \begin{bmatrix} [RE1_{org,H_2A_2}] \\ [RE2_{org,H_2A_2}] \end{bmatrix} &= \begin{bmatrix} \frac{[RE1]^I}{R_{O/A}} - \frac{[RE1^{3+}]}{R_{O/A}} \left(1 + \frac{K_{RE1,2}K_w}{[H^+]} + \frac{K_{RE1,3}K_w^2}{[H^+]^2} + \frac{K_{RE1,4}K_w^3}{[H^+]^3} \right) \\ - \frac{[RE1Cl^{2+}]}{R_{O/A}} \\ \frac{[RE2]^I}{R_{O/A}} - \frac{[RE2^{3+}]}{R_{O/A}} \left(1 + \frac{K_{RE2,2}K_w}{[H^+]} + \frac{K_{RE2,3}K_w^2}{[H^+]^2} + \frac{K_{RE2,4}K_w^3}{[H^+]^3} \right) \\ - \frac{[RE2Cl^{2+}]}{R_{O/A}} \end{bmatrix} \end{aligned} \quad (12)$$

Third, replace $[H_2A_2]_{org}$ of Eq. (3) and Eq. (5) by $[H_2A_2]_{org}$ obtained from Eq. (6) to derive the following equation:

$$F_1([RE1^{3+}], [RE2^{3+}]) \equiv \begin{bmatrix} [RE1^{3+}] - \frac{[RE1_{org,H_2A_2}][H^+]^3}{\bar{K}_{RE1,H_2A_2} \left([H_2A_2]^I - \alpha_{RE1}[RE1_{org,H_2A_2}] \right)^{\alpha_{RE1}}} \\ [RE2^{3+}] - \frac{[RE2_{org,H_2A_2}][H^+]^3}{\bar{K}_{RE2,H_2A_2} \left([H_2A_2]^I - \alpha_{RE2}[RE2_{org,H_2A_2}] \right)^{\alpha_{RE2}}} \end{bmatrix} = 0 \quad (13)$$

Fourth, replace $[RE1Cl^{2+}]$, $[RE1(OH)^{2+}]$, $[RE1(OH)_2^+]$, $[RE2Cl^{2+}]$, $[RE2(OH)^{2+}]$, $[RE2(OH)_2^+]$, $[OH^-]$ of Eq. (10) by $[RE1Cl^{2+}]$, $[RE1(OH)^{2+}]$, $[RE1(OH)_2^+]$, $[RE2Cl^{2+}]$, $[RE2(OH)^{2+}]$, $[RE2(OH)_2^+]$, $[OH^-]$ obtained from Eq. (2), Eq. (4) and Eq. (1) to derive the following equation:

$$\begin{aligned} F_2([H^+]) &\equiv \left([H^+] - [Cl]^I - \frac{K_w}{[H^+]} \right) + 3([RE1Cl^{2+}] + [RE2Cl^{2+}]) \\ &\quad + \left\{ [RE1^{3+}] \left(3 + 2 \frac{K_{RE1,2}K_w}{[H^+]} + \frac{K_{RE1,3}K_w^2}{[H^+]^2} \right) \right. \\ &\quad \left. + [RE2^{3+}] \left(3 + 2 \frac{K_{RE2,2}K_w}{[H^+]} + \frac{K_{RE2,3}K_w^2}{[H^+]^2} \right) \right\} = 0 \end{aligned} \quad (14)$$

Now, we are ready to solve the nonlinear equilibrium analysis prob-

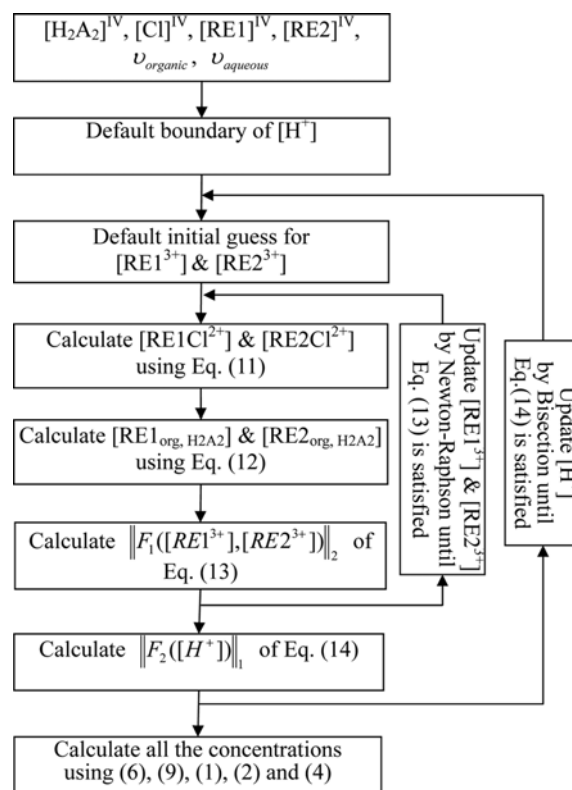


Fig. 2. Algorithm to solve the thermodynamic equilibrium analysis problem.

lem with the reduced number of the equations. Only three of the nonlinear equations of Eq. (13) and Eq. (14) combined with Eq. (11) and Eq. (12) can be solved by a repetitive nonlinear equation solver to estimate $[RE1]_{org,H_2A_2}$, $[RE1]^{3+}$, $[RE1Cl^{2+}]$, $[RE2]_{org,H_2A_2}$, $[RE2]^{3+}$, $[RE2Cl^{2+}]$, $[H^+]$ when the equilibrium constants, β , α_{RE1} , α_{RE2} and $[H_2A_2]^{IV}$, $[RE1]^{IV}$, $[RE2]^{IV}$ and $[Cl]^{IV}$ are given. All the other concentrations can be directly estimated by Eq. (6), Eq. (9), Eq. (1), Eq. (2) and Eq. (4) in the analytic way. See the next section for details.

3. Proposed Algorithm for Thermodynamic Equilibrium Analysis

The proposed algorithm to estimate all the equilibrium concentrations for the solvent extraction process with the PC88A is shown in Fig. 2. $\|\bullet\|_2$ and $\|\bullet\|_1$ represent the 2-norm and 1-norm, respectively. The outer loop is to update the equilibrium concentration of $[H^+]$ using the bisection root-finding method to solve the nonlinear equation of Eq. (14). The boundary of $[H^+]$ for the bisection method can be clearly determined because the range of the pH value is known. For example, the default setting, $[H^+]_{min} = 10^{-0.1}$ corresponding to pH=0.1 and $[H^+]_{max} = 10^{-5.0}$ corresponding to pH=5.0 can cover most extraction cases. The inner loop is to update $[RE1]^{3+}$ and $[RE2]^{3+}$ to solve the nonlinear equation of Eq. (13) using the Newton-Raphson root-finding method. Extensive simulation confirmed that the default initial guess of $[RE1]^{3+} = [RE1]^{IV}/10$ and $[RE2]^{3+} = [RE2]^{IV}/10$ can be applied to most extraction cases. As a result, the user does not need to determine any initial values additionally.

4. Proposed Algorithm to Simulate Solvent Extraction Process

The proposed algorithm to estimate all the equilibrium concen-

trations at all the stages of the solvent extraction process is shown in Fig. 3. It sequentially solves the thermodynamic equilibrium analysis problem with considering the material balance equations at each stage of the solvent extraction process until all the equilibrium concentrations converge.

To perform the thermodynamic equilibrium analysis at the i -th stage, the overall concentration of $[H_2A_2]_{org,i}^{IV}$, $[RE1]_i^{IV}$, $[RE2]_i^{IV}$ and $[Cl]_i^{IV}$ of the i -th stage should be known. The overall concentration of $[H_2A_2]_{org,i}^{IV}$ of the i -th stage is the same as that of the organic output of the $(i-1)$ -th stage because H_2A_2 exists only in the organic phase. Similarly, the overall concentration of $[Cl]_i^{IV}$ of the i -th stage is the same as that of the aqueous output of the $(i+1)$ -th stage because Cl exists only in the aqueous phase. The overall concentrations of $[RE1]_i^{IV}$ and $[RE2]_i^{IV}$ should be the same as the total amounts of the corresponding elements included in the aqueous output of the $(i+1)$ -th stage and in the organic phase output of the $(i-1)$ -th stage. That is, it is assumed that the elements of RE1 and RE2 included in the organic phase move to the aqueous phase before the thermodynamic equilibrium reaction is established. This assumption is valid because the equilibrium is not affected by the reaction path. Then, the material balance equations of the solvent extraction process can be summarized as follows:

$$\begin{aligned} & [[H_2A_2]_{org,1}^{IV} \quad [H_2A_2]_{org,2}^{IV} \quad \cdots \quad [H_2A_2]_{org,N}^{IV}] \\ & = [[H_2A_2]_{org,0}^{IV} \quad [H_2A_2]_{org,1}^{IV} \quad \cdots \quad [H_2A_2]_{org,N-1}^{IV}], \\ & [H_2A_2]_{org,0}^{IV} = [H_2A_2]_{org}^{IV} \end{aligned} \quad (15)$$

$$[[Cl]_1^{IV} \quad [Cl]_2^{IV} \quad \cdots \quad [Cl]_{N-1}^{IV}] = [[Cl]_2^{IV} \quad [Cl]_3^{IV} \quad \cdots \quad [Cl]_{N-1}^{IV}] \quad (16)$$

$$\begin{aligned} & [[Cl]_{N+1}^{IV} \quad [Cl]_{N+2}^{IV} \quad \cdots \quad [Cl]_{N-1}^{IV}] \\ & = [[Cl]_{N+2}^{IV} \quad [Cl]_{N+3}^{IV} \quad \cdots \quad [Cl]_{N-1}^{IV}] \end{aligned} \quad (17)$$

$$\begin{aligned} & [[Cl]_{N+1}^{IV} \quad [Cl]_{N+2}^{IV} \quad \cdots \quad [Cl]_{N-1}^{IV}] \\ & = [[Cl]_{N+2}^{IV} \quad [Cl]_{N+3}^{IV} \quad \cdots \quad [Cl]_{N-1}^{IV}] \end{aligned} \quad (18)$$

$$\begin{aligned} & [Cl]_{N+1}^{IV} = ([Cl]_{feed}^{IV} v_{feed} + [Cl]_{N+1}^{IV} v_{scrubbing}) / (v_{feed} + v_{scrubbing}), \\ & [Cl]_{N+2}^{IV} = [Cl]_{scrubbing\ input}^{IV}, \quad [Cl]_N^{IV} = [Cl]_{scrubbing\ input}^{IV} \end{aligned} \quad (19)$$

$$\begin{aligned} & [[RE]_1^{IV} \quad [RE]_2^{IV} \quad \cdots \quad [RE]_{N-1}^{IV}] = [[RE]_2^{IV} \quad [RE]_3^{IV} \quad \cdots \quad [RE]_{N-1}^{IV}] \\ & + [[RE]_{org,H_2A_2,0}^{IV} \quad [RE]_{org,H_2A_2,1}^{IV} \quad \cdots \quad [RE]_{org,H_2A_2,N-2}^{IV}] \\ & \left\{ \frac{v_{organic}}{v_{feed} + v_{scrubbing\ input}} \right\} \end{aligned} \quad (20)$$

$$\begin{aligned} & [[RE]_{N+1}^{IV} \quad [RE]_{N+2}^{IV} \quad \cdots \quad [RE]_{N-1}^{IV}] \\ & = [[RE]_{N+1}^{IV} \quad [RE]_{N+2}^{IV} \quad \cdots \quad [RE]_{N-1}^{IV}] \\ & + [[RE]_{org,H_2A_2,N+1}^{IV} \quad [RE]_{org,H_2A_2,N+1}^{IV} \quad \cdots \quad [RE]_{org,H_2A_2,N-2}^{IV}] \\ & \left\{ \frac{v_{organic}}{v_{scrubbing\ input}} \right\} \end{aligned} \quad (21)$$

$$\begin{aligned} & [[RE]_{N+1}^{IV} \quad [RE]_{N+2}^{IV} \quad \cdots \quad [RE]_{N-1}^{IV}] \\ & = [[RE]_{N+1}^{IV} \quad [RE]_{N+2}^{IV} \quad \cdots \quad [RE]_{N-1}^{IV}] \\ & + [[RE]_{org,H_2A_2,N+1}^{IV} \quad [RE]_{org,H_2A_2,N+1}^{IV} \quad \cdots \quad [RE]_{org,H_2A_2,N-2}^{IV}] \end{aligned}$$

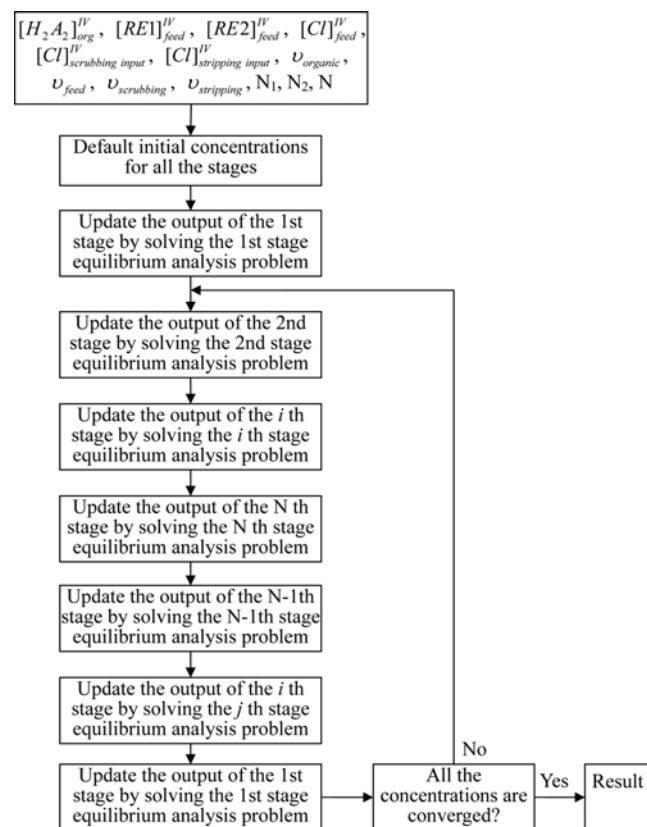


Fig. 3. Algorithm for the simulation of the solvent extraction process.

$$\left\{ \frac{v_{\text{organic}}}{v_{\text{scrubbing input}}} \right\} \quad (22)$$

$$[\text{RE}]_{N_1}^{\text{IV}} = \frac{[\text{RE}]_{\text{feed}}^{\text{IV}} v_{\text{feed}} + [\text{RE}_{\text{org}, \text{H}_2\text{A}_2}]_{N_1-1} v_{\text{organic}}}{v_{\text{feed}} + v_{\text{scrubbing input}}} \quad (23)$$

$$[\text{RE}]_{N_2}^{\text{IV}} = [\text{RE}]_{\text{scrubbing input}}^{\text{IV}} + \frac{[\text{RE}_{\text{org}, \text{H}_2\text{A}_2}]_{N_2-1} v_{\text{organic}}}{v_{\text{scrubbing input}}} \quad (24)$$

where $[\text{RE}]_i^{\text{IV}} = [[\text{RE}1]_i^{\text{IV}} \text{ } [\text{RE}2]_i^{\text{IV}}]^T$, $[\text{RE}]_i = [[\text{RE}1]_i \text{ } [\text{RE}2]_i]^T$, $[\text{RE}_{\text{org}, \text{H}_2\text{A}_2}]_i = [[\text{RE}1_{\text{org}, \text{H}_2\text{A}_2}]_i \text{ } [\text{RE}2_{\text{org}, \text{H}_2\text{A}_2}]_i]^T$ and v_{feed} , $v_{\text{scrubbing}}$ and $v_{\text{stripping}}$ are the volumetric flowrates of the feed, scrubbing and stripping stream, respectively. N_1 , $N_2 - N_1$ and $N - N_2$ are the number of stages of the extraction, scrubbing and stripping part as shown in Fig. 1. $[\bullet]_{\text{feed}}^{\text{IV}}$, $[\bullet]_{\text{scrubbing input}}^{\text{IV}}$, $[\bullet]_{\text{stripping input}}^{\text{IV}}$ and $[\bullet]_{\text{org}}^{\text{IV}}$ denote the overall concentrations in the feed, scrubbing, stripping and organic input stream, respectively. $[\text{RE}1]_i$ and $[\text{RE}2]_i$ denote the summation of all the concentrations in the aqueous phase for the light and the heavy rare earth element as follows:

$$[\text{RE}1]_i = [\text{RE}1^{3+}]_i + [\text{RE}1\text{Cl}^{2+}]_i + [\text{RE}1(\text{OH})^{2+}]_i + [\text{RE}1(\text{OH})_2^+]_i + [\text{RE}1(\text{OH})_3^0]_i, \quad i=1, 2, \dots, N \quad (25)$$

$$[\text{RE}2]_i = [\text{RE}2^{3+}]_i + [\text{RE}2\text{Cl}^{2+}]_i + [\text{RE}2(\text{OH})^{2+}]_i + [\text{RE}2(\text{OH})_2^+]_i + [\text{RE}2(\text{OH})_3^0]_i, \quad i=1, 2, \dots, N \quad (26)$$

Once the overall concentrations at the i -th stage are obtained by Eqs. (15)–(26), all the equilibrium concentrations at the i -th stage can be estimated by the proposed equilibrium equation solver.

The initial concentrations for the 0-th iteration of the proposed simulator are determined as follows: All the initial aqueous overall concentrations of the scrubbing part are determined to be the same as those of the scrubbing input stream. And, all the initial aqueous overall concentrations of the extraction part are set by the summation of the overall concentrations of the feed stream and the scrubbing input stream. Then, the initial overall concentrations for the 0-th iteration are summarized as follows:

$$[\text{Cl}]_i^{\text{IV}} = ([\text{Cl}]_{\text{feed}}^{\text{IV}} v_{\text{feed}} + [\text{Cl}]_{\text{scrubbing input}}^{\text{IV}} v_{\text{scrubbing}}) / (v_{\text{feed}} + v_{\text{scrubbing}}), \quad i=1, 2, \dots, N_1 \quad (27)$$

$$[\text{Cl}]_i^{\text{IV}} = [\text{Cl}]_{\text{scrubbing input}}^{\text{IV}}, \quad i=N_1+1, N_1+2, \dots, N_2 \quad (28)$$

$$[\text{Cl}]_i^{\text{IV}} = [\text{Cl}]_{\text{scrubbing input}}^{\text{IV}}, \quad i=N_2+1, N_2+2, \dots, N \quad (29)$$

$$[\text{RE}]_i^{\text{IV}} = [\text{RE}]_{\text{feed}}^{\text{IV}} v_{\text{feed}} / (v_{\text{feed}} + v_{\text{scrubbing}}), \quad i=1, 2, \dots, N_1 \quad (30)$$

where $[\text{RE}]_i^{\text{IV}} = [[\text{RE}1]_i^{\text{IV}} \text{ } [\text{RE}2]_i^{\text{IV}}]^T$ and $[\text{RE}]_{\text{feed}}^{\text{IV}} = [[\text{RE}1]_{\text{feed}}^{\text{IV}} \text{ } [\text{RE}2]_{\text{feed}}^{\text{IV}}]^T$.

5. Estimating the Overall Chloride Concentration in the Feed Stream

Note that $[\text{H}_2\text{A}_2]_{\text{feed}}^{\text{IV}}$, $[\text{Cl}]_{\text{feed}}^{\text{IV}}$, $[\text{RE}1]_{\text{feed}}^{\text{IV}}$ and $[\text{RE}2]_{\text{feed}}^{\text{IV}}$ in the feed stream should be known before starting the solvent extraction process simulation. Usually, pH, $[\text{RE}1]_{\text{feed}}^{\text{IV}}$, $[\text{RE}2]_{\text{feed}}^{\text{IV}}$ in the feed stream of the solvent extraction process are measurable. But, it is nearly impossible to measure or guess the overall concentration of $[\text{Cl}]_{\text{feed}}^{\text{IV}}$ in the feed stream with acceptable accuracy because there are unmeasurable uncertainties in preparing the feed stream in the form of the chloride solution. So, $[\text{Cl}]_{\text{feed}}^{\text{IV}}$ in the feed stream should be estimated

by solving the equilibrium equations in the aqueous phase before starting the solvent extraction process simulation.

The feed has only the aqueous phase (no organic phase exists). Then, the equilibrium equations in the feed stream can be expressed as follows:

$$K_w = [\text{H}^+][\text{OH}^-] \quad (31)$$

$$K_{\text{RE}1,1} = \frac{[\text{RE}1\text{Cl}^{2+}]}{[\text{RE}1^{3+}][\text{Cl}^-]}, \quad K_{\text{RE}1,2} = \frac{[\text{RE}1(\text{OH})^{2+}]}{[\text{RE}1^{3+}][\text{OH}^-]}, \quad K_{\text{RE}1,3} = \frac{[\text{RE}1(\text{OH})_2^+]}{[\text{RE}1^{3+}][\text{OH}^-]^2}, \quad K_{\text{RE}1,4} = \frac{[\text{RE}1(\text{OH})_3^0]}{[\text{RE}1^{3+}][\text{OH}^-]^3}, \quad (32)$$

$$K_{\text{RE}2,1} = \frac{[\text{RE}2\text{Cl}^{2+}]}{[\text{RE}2^{3+}][\text{Cl}^-]}, \quad K_{\text{RE}2,2} = \frac{[\text{RE}2(\text{OH})^{2+}]}{[\text{RE}2^{3+}][\text{OH}^-]}, \quad K_{\text{RE}2,3} = \frac{[\text{RE}2(\text{OH})_2^+]}{[\text{RE}2^{3+}][\text{OH}^-]^2}, \quad K_{\text{RE}2,4} = \frac{[\text{RE}2(\text{OH})_3^0]}{[\text{RE}2^{3+}][\text{OH}^-]^3}, \quad (33)$$

$$[\text{RE}1]_{\text{feed}}^{\text{IV}} = [\text{RE}1^{3+}] + [\text{RE}1\text{Cl}^{2+}] + [\text{RE}1(\text{OH})^{2+}] + [\text{RE}1(\text{OH})_2^+] + [\text{RE}1(\text{OH})_3^0] \quad (34)$$

$$[\text{RE}2]_{\text{feed}}^{\text{IV}} = [\text{RE}2^{3+}] + [\text{RE}2\text{Cl}^{2+}] + [\text{RE}2(\text{OH})^{2+}] + [\text{RE}2(\text{OH})_2^+] + [\text{RE}2(\text{OH})_3^0] \quad (35)$$

$$[\text{Cl}]_{\text{feed}}^{\text{IV}} = [\text{Cl}^-] + [\text{RE}1\text{Cl}^{2+}] + [\text{RE}2\text{Cl}^{2+}] \quad (36)$$

$$[\text{H}^+] + 3[\text{RE}1^{3+}] + 2[\text{RE}1\text{Cl}^{2+}] + 2[\text{RE}1(\text{OH})^{2+}] + 3[\text{RE}2^{3+}] + 2[\text{RE}2\text{Cl}^{2+}] + 2[\text{RE}2(\text{OH})^{2+}] + [\text{RE}2(\text{OH})_2^+] = [\text{Cl}^-] + [\text{OH}^-] \quad (37)$$

Eqs. (31)–(37) should be solved to estimate $[\text{Cl}]_{\text{feed}}^{\text{IV}}$ in the feed stream for the given measurements of pH (equivalently, $[\text{H}^+]$), $[\text{RE}1]_{\text{feed}}^{\text{IV}}$, $[\text{RE}2]_{\text{feed}}^{\text{IV}}$ and the equilibrium constants.

These equations can be simplified as follows:

First, replace $[\text{RE}1\text{Cl}^{2+}]$, $[\text{RE}1(\text{OH})^{2+}]$, $[\text{RE}1(\text{OH})_2^+]$, $[\text{RE}2\text{Cl}^{2+}]$, $[\text{RE}2(\text{OH})^{2+}]$, $[\text{RE}2(\text{OH})_2^+]$ of Eqs. (34)–(35) by $[\text{RE}1\text{Cl}^{2+}]$, $[\text{RE}1(\text{OH})^{2+}]$, $[\text{RE}1(\text{OH})_2^+]$, $[\text{RE}2\text{Cl}^{2+}]$, $[\text{RE}2(\text{OH})^{2+}]$, $[\text{RE}2(\text{OH})_2^+]$ obtained from Eqs. (32)–(33) to derive the following equations of Eqs. (38)–(39).

$$[\text{RE}1^{3+}] = \frac{[\text{RE}1]_{\text{feed}}^{\text{IV}}}{1 + K_{\text{RE}1,1}[\text{Cl}^-] + \frac{K_{\text{RE}2,2}K_w}{[\text{H}^+]} + \frac{K_{\text{RE}2,3}K_w^2}{[\text{H}^+]^2} + \frac{K_{\text{RE}2,4}K_w^3}{[\text{H}^+]^3}} \quad (38)$$

$$[\text{RE}2^{3+}] = \frac{[\text{RE}2]_{\text{feed}}^{\text{IV}}}{1 + K_{\text{RE}2,1}[\text{Cl}^-] + \frac{K_{\text{RE}2,2}K_w}{[\text{H}^+]} + \frac{K_{\text{RE}2,3}K_w^2}{[\text{H}^+]^2} + \frac{K_{\text{RE}2,4}K_w^3}{[\text{H}^+]^3}} \quad (39)$$

The following Eq. (40) is obtained from Eqs. (32)–(33). Also, Eq. (37) can be rewritten to Eq. (41).

$$[\text{RE}1\text{Cl}^{2+}] = K_{\text{RE}1,1}[\text{RE}1^{3+}][\text{Cl}^-], \quad [\text{RE}1(\text{OH})^{2+}] = K_{\text{RE}1,2}[\text{RE}1^{3+}]K_w/[\text{H}^+], \quad [\text{RE}1(\text{OH})_2^+] = K_{\text{RE}1,3}[\text{RE}1^{3+}]K_w^2/[\text{H}^+]^2, \quad [\text{RE}2\text{Cl}^{2+}] = K_{\text{RE}2,1}[\text{RE}2^{3+}][\text{Cl}^-], \quad [\text{RE}2(\text{OH})^{2+}] = K_{\text{RE}2,2}[\text{RE}2^{3+}]K_w/[\text{H}^+], \quad [\text{RE}2(\text{OH})_2^+] = K_{\text{RE}2,3}[\text{RE}2^{3+}]K_w^2/[\text{H}^+]^2 \quad (40)$$

$$f([\text{Cl}^-]) = [\text{H}^+] + 3[\text{RE}1^{3+}] + 2[\text{RE}1\text{Cl}^{2+}] + 2[\text{RE}1(\text{OH})^{2+}]$$

Table 2. Equilibrium constants and stoichiometric coefficients

Parameters	Data
K_w	10^{-14}
$K_{RE1,1}$	$10^{-2.03}$
$K_{RE1,2}$	$10^{6.16}$
$K_{RE1,3}$	$10^{13.92}$
$K_{RE1,4}$	$10^{20.22}$
$K_{RE2,1}$	$10^{-0.22}$
$K_{RE2,2}$	$10^{6.17}$
$K_{RE2,3}$	$10^{12.57}$
$K_{RE2,4}$	0
α_{RE1}	1.5
α_{RE2}	2.0

$$+[\text{RE1}(\text{OH})_2^{2+}] + 3[\text{RE2}^{3+}] + 2[\text{RE2C}^{2+}] + 2[\text{RE2}(\text{OH})_2^{2+}] + [\text{RE2}(\text{OH})_2^{2+}] - [\text{Cl}^-] - K_w/[\text{H}^+] = 0 \quad (41)$$

Note that $[\text{H}^+]$, $[\text{RE1}]_{\text{feed}}^{IV}$ and $[\text{RE2}]_{\text{feed}}^{IV}$ are measurable. And, assume that the equilibrium constants are known. Then, $f(\bullet)$ in Eq. (41) combined with Eqs. (38)-(40) is the function of $[\text{Cl}^-]$. $f([\text{Cl}^-])=0$ can be solved by the bisection method. Then, it is straightforward to estimate the overall chloride concentration of $[\text{Cl}]_{\text{feed}}^{IV} = [\text{Cl}^-] + [\text{RE1Cl}^{2+}] + [\text{RE2Cl}^{2+}]$ in the feed stream.

SIMULATION STUDY

The proposed equilibrium analysis solver and solvent extraction process simulator for Sm-Gd-PC88A extraction case is demonstrated to evaluate the proposed methods.

Table 2 shows the equilibrium constants of Sm and Gd in the aqueous phase and the stoichiometric coefficients [10]. The equilibrium constants for the reactions between the aqueous phase and the organic phase (K_{RE1, H_2A_2} and K_{RE2, H_2A_2}) and the model parameters ($\beta_{1, RE1}$ and $\beta_{1, RE2}$) to incorporate non-ideal behavior are estimated by solving the following optimization problem with the Levenberg-Marquardt method to fit the experimental equilibrium data. For detailed experimental equilibrium data, refer to [10].

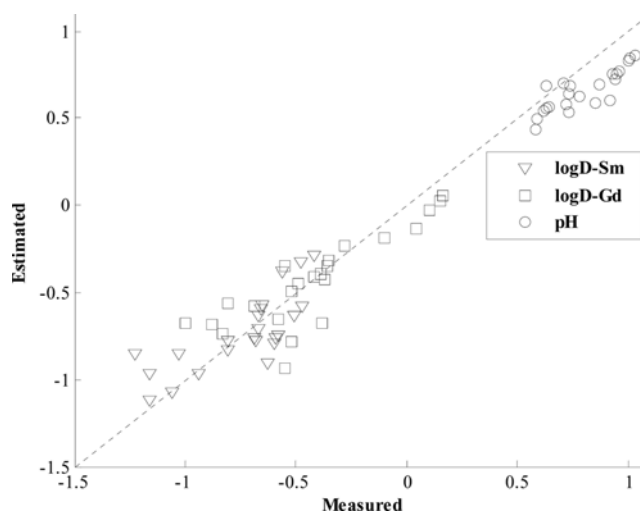
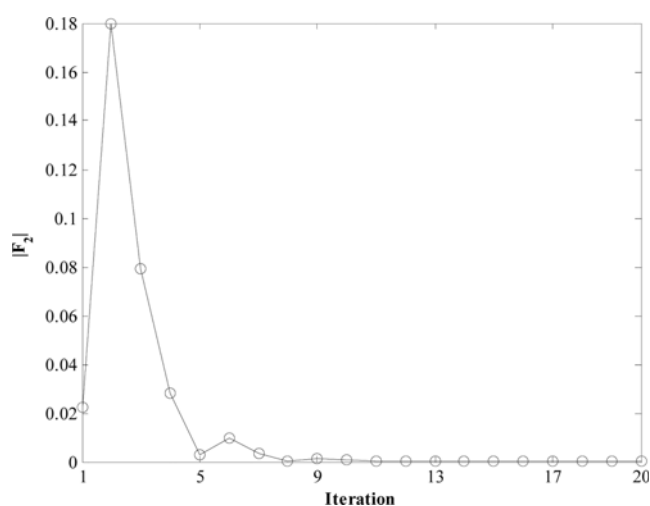
$$\min_{K_{RE1, H_2A_2}, K_{RE2, H_2A_2}, \beta_{1, RE1}, \beta_{1, RE2}} \sum_{i=1}^{N_{exp}} \{ (\log D_{RE1, i}^{\text{measured}} - \log D_{RE1, i}^{\text{estimated}})^2 + (\log D_{RE2, i}^{\text{measured}} - \log D_{RE2, i}^{\text{estimated}})^2 \} \quad (42)$$

where $D_{RE1, i}^{\text{measured}}$ and $D_{RE1, i}^{\text{estimated}}$ are the i -th measurement and the i -th estimate of the proposed method for the distribution coefficient of the light rare earth. $D_{RE2, i}^{\text{measured}}$ and $D_{RE2, i}^{\text{estimated}}$ are the i -th measurement and the i -th estimate of the proposed method for the distribution coefficient of the heavy rare earth. N_{exp} is the number of the measurements.

Table 3 shows the estimates obtained by solving the nonlinear optimization problem of Eq. (42) and Fig. 4 compares the distribution coefficients and pH values estimated by the proposed equilibrium model with the experimental equilibrium data. For all the cases, the default settings are used for the boundary of the bisection method and the initial guess of the Newton-Raphson method. Fig. 5 shows the typical convergence pattern of the objective function ($\|F_2([\text{H}^+])\|_1$, the absolute value of $F_2([\text{H}^+])$ of Eq. (14)) of the bisection method

Table 3. Model parameters estimated from the experimental data

Parameters	Estimates
K_{RE1, org, H_2A_2}	0.003161
K_{RE2, org, H_2A_2}	0.013305
$\beta_{Np, RE1}$	-0.446343
$\beta_{Np, RE2}$	0.184405

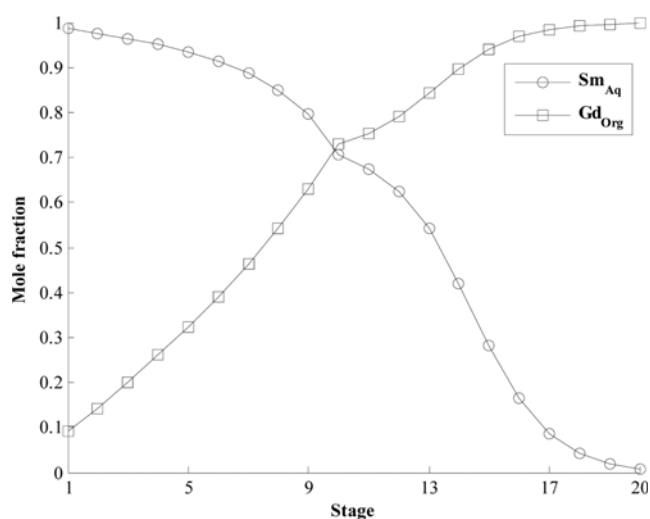
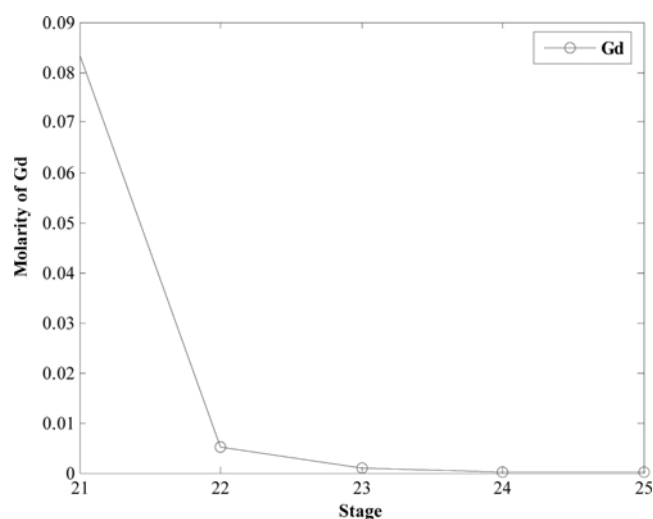
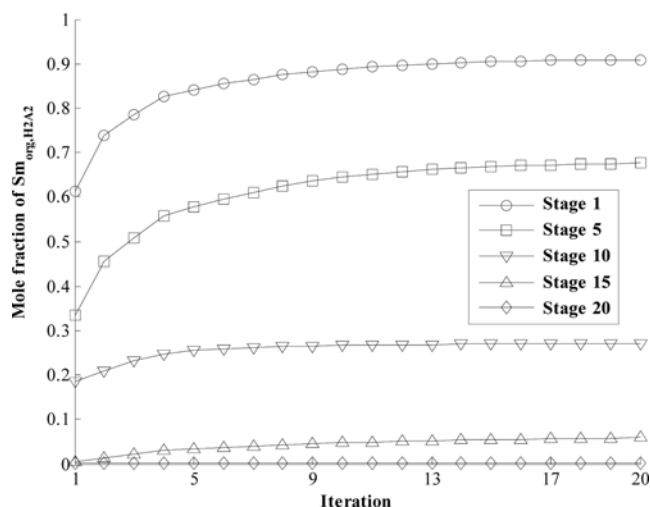
**Fig. 4. Comparison of the experimental equilibrium data with the estimates by the proposed equilibrium analysis method.****Fig. 5. Typical convergence pattern of the bisection method in the proposed equilibrium analysis algorithm with respect to iteration.**

in the proposed equilibrium analysis algorithm. It confirms that the proposed method provides stable convergence and does not suffer any numerical problems because the proposed method needs only two initial guesses rather than 16 initial guesses; moreover, the default setting for two the initial guesses can cover most solvent extraction cases.

The two component solvent extraction process with the equilibrium constants in Table 2, the estimated model parameters in Table 3 and the design variables in Table 4 is simulated to estimate all the

Table 4. Variables for the simulation of the solvent extraction process

Variables	Description	Data
N_1	The number of the extraction stage	10 Stages
$N_2 - N_1$	The number of the scrubbing stage	10 Stages
$N - N_2$	The number of the stripping stage	5 Stages
ν_{organic}	Volumetric flowrate of the organic stream	70 cc/min
ν_{feed}	Volumetric flowrate of the feed stream	50 cc/min
$\nu_{\text{scrubbing}}$	Volumetric flowrate of the scrubbing stream	20 cc/min
$\nu_{\text{stripping}}$	Volumetric flowrate of the stripping stream	30 cc/min
$[\text{H}_2\text{A}_2]_{\text{org}}^{\text{IV}}$	Molarity of H_2A_2 in the organic stream	0.5 M
$[\text{RE1}]_{\text{feed}}^{\text{IV}}$	Molarity of RE1 in the feed stream	0.05 M
$[\text{RE2}]_{\text{feed}}^{\text{IV}}$	Molarity of RE2 in the feed stream	0.05 M
$[\text{Cl}]_{\text{feed}}^{\text{IV}}$	Molarity of HCl in the feed stream	0.1 M
$[\text{Cl}]_{\text{scrubbing input}}^{\text{IV}}$	Molarity of HCl in the scrubbing input stream	0.5 M
$[\text{Cl}]_{\text{stripping input}}^{\text{IV}}$	Molarity of HCl in the stripping input stream	2.0 M

**Fig. 6. Mole fractions of Sm in the aqueous phase and Gd in the organic phase of the extraction/scrubbing part simulated by the proposed method.****Fig. 8. Molarity of Gd in the aqueous phase of the stripping part simulated by the proposed method.****Fig. 7. Typical convergence pattern in the proposed solvent extraction simulator with respect to iteration.**

equilibrium concentrations at all the stages of the solvent extraction process. Fig. 6 shows the simulation results, the mole fraction of Sm and Gd at each stage in the extraction and scrubbing part. As expected, high purity-heavy rare earth and high purity-light rare earth are obtained in the output streams of the extraction part and the scrubbing part, respectively. Fig. 7 shows the typical convergence pattern with respect to the iteration in the proposed solvent extraction simulator. The default setting for the boundary of the bisection method and the initial guess of the Newton-Raphson method are used in solving all the equilibrium analysis problems at all the stages. It successfully obtains the estimates without any numerical problems for all the cases. Consider the concentration of Gd in the aqueous phase in the stripping part in Fig. 8. Most of Gd in the organic phase is unloaded and moved to the aqueous phase by the strong hydrochloric acid as expected.

CONCLUSIONS

A new model simplification technique, equilibrium analysis algo-

rithm and simulation logic for the solvent rare earth extraction process are proposed. The proposed simulator solves the equilibrium analysis problem at all the stages of the solvent extraction process in a sequential way until the estimates converge. It shows remarkably stable convergence pattern and does not suffer from any numerical problems in calculating all the equilibrium concentrations at all the stages due to the model simplification and the enhanced equilibrium analysis solver. The proposed model simplification technique can significantly reduce the number of the nonlinear equations to be simultaneously solved. A new equilibrium analysis solver combined with the model simplification method uses only two initial guesses rather than sixteen initial guesses, resulting in extremely stable convergence. The default settings for the initial boundary of the bisection method and the initial guess for the Newton-Raphson method in the equilibrium analysis solver can cover most solvent extraction cases. Simulation results demonstrate that the proposed approaches can provide very stable convergence without any numerical problems.

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