Solvent Extraction Research and Development, Japan, **Vol. 14, 105 – 113 (2007)**

Separation and Recovery Process for Rare Earth Metals from Fluorescence Material Wastes Using Solvent Extraction

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The separation and recovery of rare earth metals from fluorescence material waste was investigated by using solvent extraction with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester in kerosene. Extraction equilibrium expressions were established for the trivalent metals (La, Ce, Eu, Tb, Y and Al) and divalent metals (Ca, Sr and Ba) for both single and multi components systems. The process simulation for the selective recovery of Eu, Tb and Y revealed that effective separation and recovery of Eu, Tb and Y can be achieved in two steps in a counter-current mixer-settler cascade from the alkaline earth metals (Ca, Sr and Ba) and La and Ce.

1. Introduction

Rare metals are basic materials for the production of high technology goods and systems, and their demand at high purity has therefore been increasing in recent years. The rare earth metals are also widely used as fluorescent materials for lamp, CRT and plasma displays, and for the permanent magnet motors for hybrid cars [1]. In Japan, most rare earth metals are now imported from China, and the value of these metals is rising with increasing demand [2]. As the development of effective recovery processes for rare earth metals is a quite attractive issue from the view point of resources sustainability, the recovery of these metals from increasing amounts of fluorescent wastes is worthy of study.

Solvent extraction is one of the important separation and recovery methods for valuable metals, such as vanadium [3], molybdenum [4], indium [5] and rare earth metals [6]. Although solvent extraction has been recently avoided due to the usage of organic solvents, it is still attractive from the view points of simplicity, speediness and easiness of scale-up. Kubota *et al*. investigated the recovery of rare earth metals from CRT waste from TVs by solvent extraction with calix[4]arene derivatives as extractants. They demonstrated that Y and Eu can be separated even in the presence of excess amounts of Zn and Al [7]. Takahashi *et al*. also investigated the separation and recovery of rare earth metals from fluorescence lamp waste. They demonstrated that recovery of rare earth metals of high purity, mainly Y, Eu and La, can be achieved by using ion exchange and/or solvent extraction methods [8]. However, no practical rare earth metal recycle process using solvent extraction has been commercialized due to the

issue of cost performance. The optimum conditions for solvent extraction for the separation and recovery of rare earth metals from these wastes should be therefore established.

Process simulation is well known to be effective for determining the appropriate conditions as well as for predicting the operational conditions. Several studies have been made using computer simulation of counter-current solvent extraction processes for metal separation. Tanaka *et al*. reported on the role of the extraction equilibrium constant in counter-current multistage solvent extraction-stripping processes [9]. Bagacki *et al*. has also investigated the effect of various phenomena on metal extraction with chelate type reagents in both counter-current and cross-current extraction systems [10]. Nishihama *et al*. have developed a process simulation method for a counter-current mixer-settler cascade, based on extraction equilibrium and stoichiometric relationships [11]. An effective separation and recovery process for rare earth metals could be developed by using process simulation.

In this study, a recovery process for rare earth metals from spent fluorescent material by solvent extraction was investigated, employing the common commercial extractant, PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester). Extraction equilibrium formulations for the metals, contained in the phosphor sludge, were established. On the basis of the extraction equilibrium studies, process simulations for the mutual separation of rare earth metals from an artificial leaching solution of the phosphor sludge, listed in Table 1 [12], was carried out. The present work particularly focuses on the selective recovery of Eu, Tb and Y.

Table 1 Composition of fluorescence tube material wastes†

Elements	Y	La	P	Sr	Ca	Ba	Tb	Eu	Cl	Al
Mass %	31.9	11.8	7.4	6.4	5.5	3.4	2.7	2.2	1.2	0.8

†Values are the analytical results from X-ray fluorescence measurements [12].

2. Experimental

Extraction tests were carried out by the conventional batchwise method. The commercial extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (marketed as PC-88A by Daihachi Chemical Industry Co. Ltd.), was used as received. Organic solutions were prepared by dissolving PC-88A in kerosene. Aqueous metal solutions were prepared by dissolving metal nitrate salts in deionized water. In single component systems, concentrations for divalent and trivalent metals were set at 5.0×10^{-3} and 1.0×10^{-3} mol/L, respectively. In multi component systems, mixed solutions of La (8.5×10^{-3} mol/L), Ce (4.3×10^{-4} mol/L), Eu (1.5×10^{-3} mol/L), Tb (1.7×10^{-3} mol/L), Y (3.6×10^{-2} mol/L), Al (3.0×10^{-3} mol/L), Ca (1.4×10^{-2} mol/L), Sr (7.3×10^{-3} mol/L) and Ba (7.3×10^{-3} mol/L) were used, based on the metals listed in Table 1. The concentration of PC-88A was set at 1.0 mol/L ($[\overline{(RH)_2}] = 0.5\,\text{mol/L}$) for the divalent metals and 0.2 mol/L ($[\overline{(RH)_2}] = 0.1\,\text{mol/L}$) for the trivalent metals for the single component systems, and was set at 0.5 mol/L ($[\overline{(RH)_2}] = 0.25\,\text{mol/L}$) for the multi component systems. The pH was adjusted by adding the appropriate amount of nitric acid or sodium hydroxide to the aqueous metal solution. Equal volumes (10 mL) of the aqueous and organic solutions were shaken vigorously at 298 K for more than 3 h to attain equilibrium. After phase separation, the equilibrium pH value was measured by a pH meter (HORIBA, F-23). The metal concentrations in the

aqueous solutions were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES, SHIMADZU, ICPS-7500), and those in the organic solutions were calculated from the material balance.

3. Results and Discussion

3.1 Extraction Equilibrium Formulation

The extraction equilibrium expressions for PC-88A with trivalent metals (rare earth metals and Al) and divalent alkaline earth metals have been reported [13]. Fig. 1 shows the effect of the equilibrium pH on the distribution ratio (*D*) of the metals. Straight lines with slopes of 3 and 2 for trivalent and divalent metals were obtained, respectively. The extraction equilibria of these metals are defined in Eqs. (1) and (2), respectively [13].

$$M^{3+} + 3\overline{(RH)_2} \Leftrightarrow \overline{MR_3(RH)_3} + 3H^+ ;\ K_{ex,RE,Al} \quad (1)$$

$$AE^{2+} + 3\overline{(RH)_2} \Leftrightarrow \overline{AER_2(RH)_4} + 2H^+ ;\ K_{ex,AE} \quad (2)$$

where, RE, AE and $(RH)_2$ represent rare earth, alkaline earth metals and the dimeric species of PC-88A, respectively. The extraction equilibrium constants are therefore defined as Eqs. (3) and (4).

$$K_{ex,RE,Al} = \frac{[\overline{MR_3(RH)_3}][H^+]^3}{[M^{3+}][\overline{(RH)_2}]^3} \quad (3)$$

$$K_{ex,AE} = \frac{[\overline{AER_2(RH)_4}][H^+]^2}{[M^{2+}][\overline{(RH)_2}]^3} \quad (4)$$

The extraction equilibrium constants, determined using the above equations, are summarized in Table 2. The lines in Fig. 1 are the calculated values of the distribution ratios with the obtained extraction equilibrium constants. The experimental data are seen to cluster on the lines drawn with the calculated values.

Batchwise extractions from the artificial leaching solution with PC-88A were also carried out. Fig. 2 shows the effect of the pH value on the distribution ratio of each metal in the multi

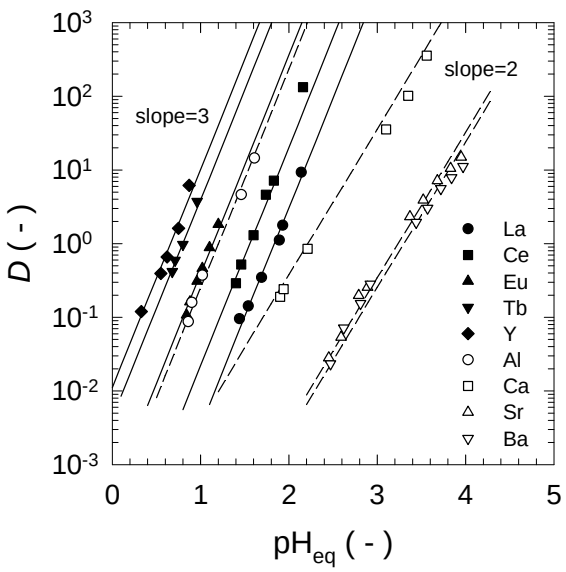

Figure 1 Effect of the equilibrium pH on the distribution ratios in single metal systems; comparison of observed data with prediction shown by the lines

Table 2 Extraction equilibrium constants for PC-88A/kerosene

Metal	La	Ce	Eu	Tb	Y	Al
K_{ex} (–)	3.29×10^{-3}	2.23×10^{-2}	4.02×10^{-1}	4.26	1.11×10	2.56×10^{-1}
Metal	Ca	Sr	Ba			
K_{ex} (L/mol)	3.12×10^{-4}	2.81×10^{-6}	2.08×10^{-6}			

components system. Since Sr and Ba are hardly extracted at all, the data for these two metals are omitted from Fig. 2. Since the distribution ratios calculated by assuming no interaction among the metals are also shown by the lines, the experimental data are seen to almost scatter around the calculated lines. This indicates that the extraction equilibrium expressions obtained in single metal systems can be applied to multi component system. In the multi component system, extraction of the divalent metals is suppressed compared with the extraction in the single metal systems. Since this is due to the competition in the extraction of coexisting metals in the multi component system, separation from the divalent alkaline metals is easily achieved.

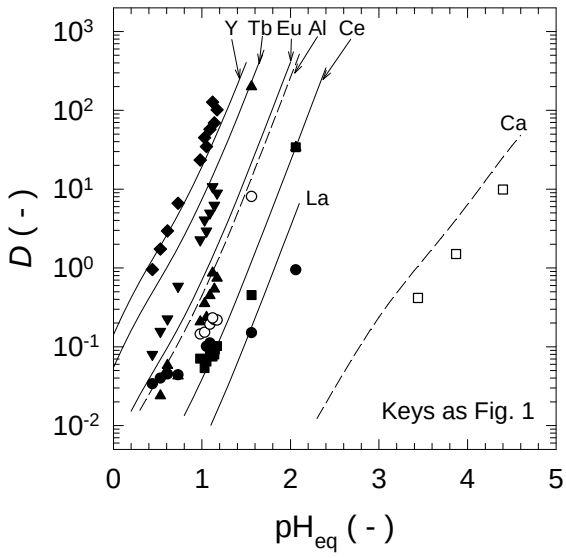

Figure 2 Effect of equilibrium pH on the distribution ratios in a multi metal system; comparison of observed data with prediction shown by the lines

Table 3 Simulation of batchwise extraction and scrubbing†

Section		La	Ce	Eu	Tb	Y	Al
Ex #1 (pH_{eq}=2)	$[M]_{feed}$ (mol/L)	8.50×10^{-3}	4.28×10^{-4}	1.45×10^{-3}	1.70×10^{-3}	3.59×10^{-2}	2.96×10^{-3}
	$[\overline{M}]$ (mol/L)	6.64×10^{-3}	4.11×10^{-4}	1.45×10^{-3}	1.70×10^{-3}	3.59×10^{-2}	2.96×10^{-3}
	Purity (%)	13.52	0.84	2.95	3.46	73.11	6.03
Sc #1‡ (pH_{eq}=1.1)	[M] (mol/L)	6.54×10^{-3}	3.73×10^{-4}	5.12×10^{-4}	8.35×10^{-5}	6.98×10^{-4}	1.37×10^{-3}
	$[\overline{M}]$ (mol/L)	9.77×10^{-5}	3.78×10^{-5}	9.35×10^{-4}	1.62×10^{-3}	3.52×10^{-2}	1.59×10^{-3}
	Purity (%)	0.25	0.10	2.37	4.09	89.16	4.03
Sc #2§ (pH_{eq}=1.4)	[M] (mol/L)	8.71×10^{-5}	2.07×10^{-5}	5.87×10^{-5}	1.02×10^{-5}	8.52×10^{-5}	1.52×10^{-4}
	$[\overline{M}]$ (mol/L)	1.06×10^{-5}	1.71×10^{-5}	8.76×10^{-4}	1.61×10^{-3}	3.51×10^{-2}	1.44×10^{-3}
	Purity (%)	0.03	0.04	2.24	4.11	89.89	3.69

† $[\overline{(RH)_2}] = 0.25$ mol/L .

‡Organic feed of Sc #1 was organic phase of Ex #1.

§Organic feed of Sc #2 was organic phase of Sc #1.

3.2 Simulation for Separation and Recovery of Rare Earth Metals

On the basis of these results, process simulation for separation and recovery of rare earth metals from the fluorescence material wastes was carried out. From the experimental results in Fig. 2, batchwise extraction from the leaching solution is effective for separation from co-existing alkaline earth metals.

Figure 3 shows the calculated results for the batchwise extraction of rare earth metals from the artificial leaching solution. This demonstrates that trivalent metals are easily extracted, while divalent alkaline earth metals are poorly extracted, as expected from the experimental results. When the extraction is carried out at an equilibrium pH = 2, most of the trivalent metals are quantitatively extracted into the organic phase, while most of the alkaline earth metals remain in the aqueous phase.

The effect of the equilibrium pH on the percentage scrubbing and purity in the organic phase is shown in Fig. 4. At pH = 1.1, most of La and Ce can be scrubbed off into the aqueous phase, while most of the other metals remain in the organic phase. To improve the removal of La and Ce, additional scrubbing may be carried out at pH = 1.4. Overall results of the simulation for batch extraction and scrubbing are also summarized in Table 3**.**

The process simulation for the separation of Eu/Tb/Y/Al was then investigated in a counter-current mixer-settler cascade. Figure 5 shows the schematic flowsheet of the cascade. Detailed information on the calculation method for the counter-current mixer-settler cascade has been provided previously [11].

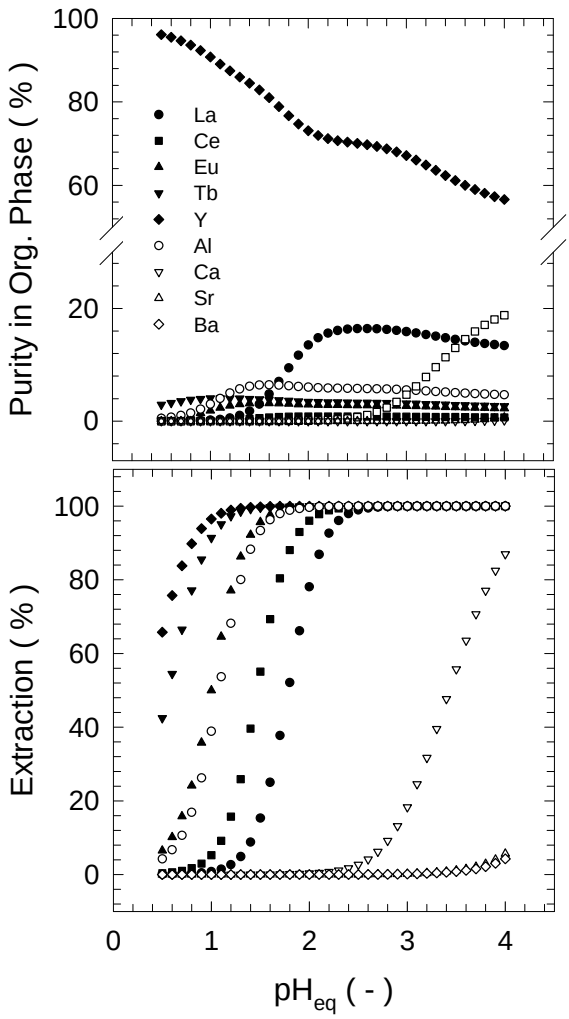

Figure 3 Calculation results of the effect of pH on percentage extraction and purity of metals in the organic phase. $[\overline{(RH)_2}] = 0.25$mol/L

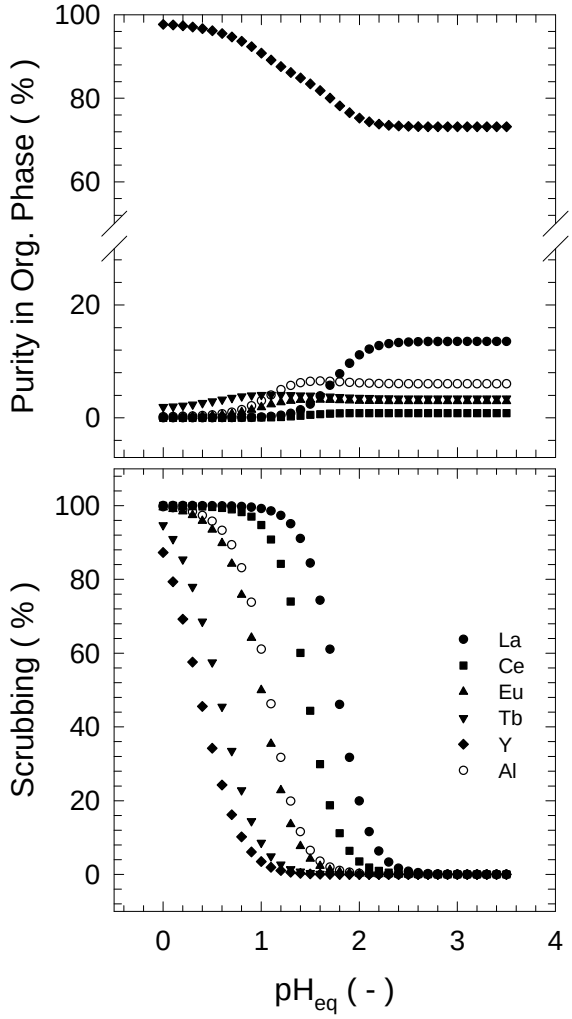

Figure 4 Calculation results of the effect of pH on percentage scrubbing and purity of metals. $[\overline{(RH)_2}] = 0.25$mol/L

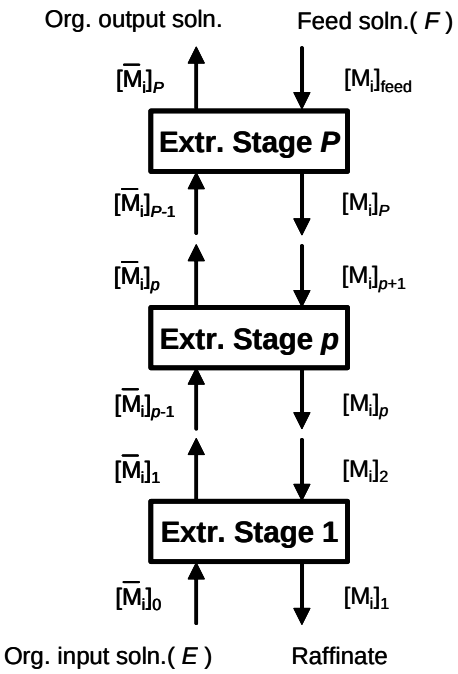

Figure 5 Schematic flowsheet for the counter-current mixer-settler cascade

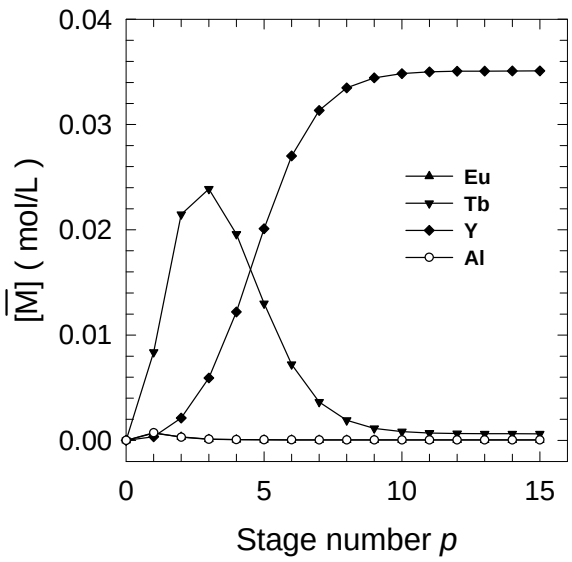

Figure 6 Simulation of the separation of Y from a Eu/Tb/Y/Al mixture in a counter-current mixer-settler cascade with 15 extraction stages at F/E = 1. $[\overline{(RH)_2}] = 0.15$mol/L and pH_{eq} = 1.02

The distribution ratios for the metals (Eu, Tb, Y and Al) in stage p are expressed by Eq. (5) as this can be calculated with the extraction equilibrium formulations.

$$[\overline{M_i}]_p = [M_i]_p \cdot D_{i,p} \quad (\text{i = Eu, Tb, Y and Al}) \tag{5}$$

The mass balance of each metal in stage p is expressed by Eq. (6).

$$F \cdot [M_i]_{p+1} = F \cdot [M_i]_p + E \cdot [\overline{M_i}]_p - E \cdot [\overline{M_i}]_{p-1} \tag{6}$$

The overall mass balance of the each metal is shown in Eq. (7).

$$F \cdot [M_i]_{feed} + E \cdot [\overline{M_i}]_0 = F \cdot [M_i]_1 + E \cdot [\overline{M_i}]_p \tag{7}$$

In this simulation, the input values for the flow ratio (F/E = 1), $[\overline{(RH)_2}]_{feed} (= 0.15\,\text{mol/L})$, and a 15 stage cascade were applied. The equilibrium pH values of each stage are fixed to obtain effective extraction.

The calculation results are showed in Fig. 6. Although co-extraction of Tb together with Y took place in the early stages, the ion exchange reaction between extracted Tb and Y in the aqueous phase progresses from the middle of the cascade, to achieve the effective separation of Y without the need for a scrubbing section. The detailed results are summarized in Table 4. Although 36.3 % of the Tb, against leaching solution, was contained in the organic phase, this was ignored to permit construction of a simple process in the present work. If the recovery of Tb in the organic solution is to be considered, the organic phase should be scrubbed to remove co-extracted Tb.

The separation of Tb from the raffinate using a 10 stage counter-current mixer-settler cascade

was then investigated. The input flow ratio values (F/E = 1) and $[\overline{(RH)_2}]_{feed}$ (=0.005 mol/L) were used. The calculation results are shown and listed in Fig. 7 and Table 4, respectively. Although the percentage recovery of Tb was 58.1 % from the leaching solution, a purity of 85.7% Tb was obtained.

After this extraction step, the mixture of Eu and Al still remained in the raffinate. Since the separation factor of Eu from Al is extremely small, precipitative separation of Eu with oxalic acid is considered to be an effective separation method [14]. When over three equivalent amounts of oxalic acid (6.8×10^{-3} mol/L) was added to an actual aqueous solution of an Eu/Al mixture ([Eu] = 8.4×10^{-4} mol/L and [Al] = 1.1×10^{-3} mol/L), a white precipitate was rapidly obtained. When the composition of the precipitate was analyzed after dissolution with nitric acid, no Al was detected. The separation of Eu/Al is therefore easily achieved by this precipitation method. The overall flow chart for the present proposed separation process is shown in Fig. 8.

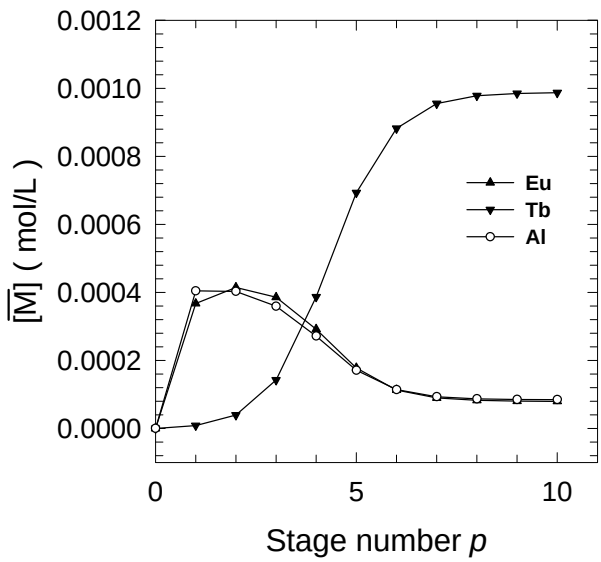

Figure 7 Simulation for the separation of Tb from a Eu/Tb/Al mixture in a counter-current mixer-settler cascade with 10 extraction stages at F/E = 1. $[\overline{(RH)_2}] = 0.005$mol/L and pH_{eq} =2.60

Table 4 Simulation of a counter-current mixer-settler cascade for the separation of Eu/Tb/Y/Al

Section		F/E	Stage number	$[\overline{(RH)_2}]_{feed}$ (mol/L)	pH_{eq}	[Eu] (mol/L)	[Tb] (mol/L)	[Y] (mol/L)	[Al] (mol/L)	$[\overline{Eu}]$ (mol/L)	$[\overline{Tb}]$ (mol/L)	$[\overline{Y}]$ (mol/L)	$[\overline{Al}]$ (mol/L)
MS #1	input	1	15	1.5×10^{-1}		8.76×10^{-4}	1.61×10^{-3}	3.51×10^{-2}	1.44×10^{-3}	0	0	0	0
	output				1.022	8.44×10^{-4}	9.89×10^{-4}	1.54×10^{-5}	1.41×10^{-3}	3.17×10^{-5}	6.17×10^{-4}	3.51×10^{-2}	3.32×10^{-5}
MS #2	input	1	10	5.0×10^{-3}		8.44×10^{-4}	9.89×10^{-4}	0	1.41×10^{-3}	0	0	0	0
	output				2.601	7.65×10^{-4}	1.67×10^{-6}	0	1.32×10^{-3}	7.98×10^{-5}	9.87×10^{-4}	0	8.46×10^{-5}

4. Conclusion

The separation and recovery of rare earth metals from fluorescent material wastes by using solvent extraction with PC-88A in kerosene was investigated as follows:

(1) Extraction equilibrium expressions for the trivalent (La, Ce, Eu, Tb, Y and Al) and divalent metals (Ca, Sr and Ba) were established, and these equilibrium expressions can be applied to the multi component system.

(2) Using process simulation, the effective separation and recovery of Eu, Tb and Y can be achieved by

two steps in a counter-current mixer-settler cascade, together with precipitation with oxalic acid, followed by batchwise extraction-scrubbing processes.

(3) The separation and recovery process developed in the present work is based on solvent extraction and precipitation, which is feasible for the recovery of valuable resources at industrial scale.

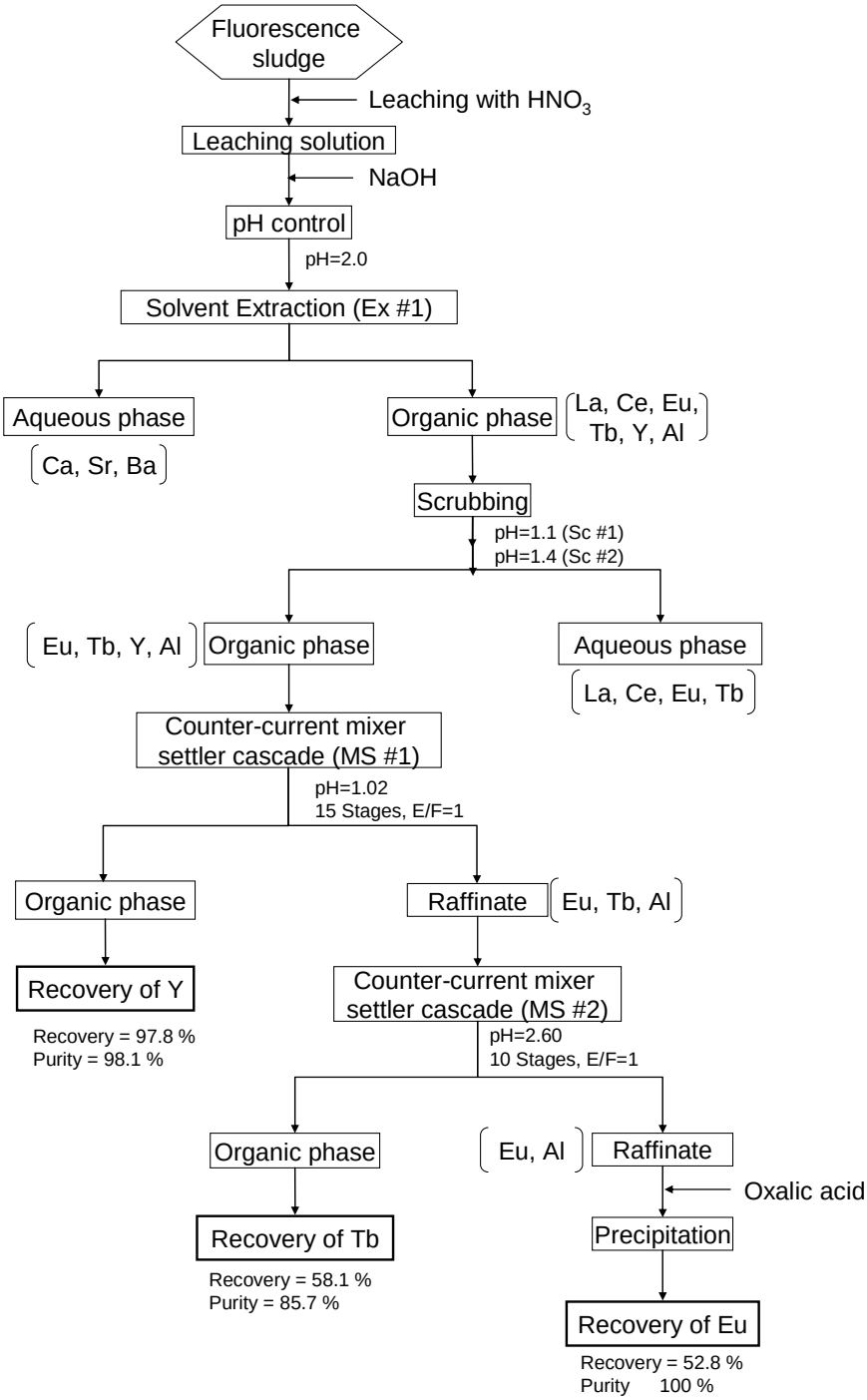

Figure 8 The overall flow chart of the present separation process. The recovery is calculated against the leaching solution compositions

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