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Separation of rare earth elements from the leaching solution of waste phosphors by solvent extraction with Cyanex 272 and its mixture with Alamine 336

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Abstract: Waste phosphors contain rare earth elements (REEs) such as yttrium (Y), europium (Eu), cerium (Ce), terbium (Tb) and lanthanum (La). Separation of these REEs from the leaching solution of waste phosphors was investigated by solvent extraction with single Cyanex 272, binary mixture (mixture of Cyanex 272 and Alamine 336), ionic liquid (prepared by Cyanex 272 and Aliquat 336) in kerosene. The effect of solution pH and extractants concentration was mainly investigated. The results indicated that Y(III) was selectively extracted by single Cyanex 272 over the other four REEs from the HCl solution with initial pH range from 3 to 5. Synergistic extraction with the binary mixture was enough for the extraction of Y(III), Tb(III) and Eu(III) with a small amount of Ce(III). Scrubbing with pure Y(III) solution with intermediate acidity was effective in scrubbing Ce(III) from the loaded binary mixture organic phase. Stripping behavior of the Y(III), Tb(III) and Eu(III) by HCl solution was similar to each other. Tb(III) and Eu(III) can be separated by extraction with the binary mixture followed by scrubbing with pure Tb(III) solution. McCabe-Thiele diagrams were constructed for the extraction of Y(III) by single Cyanex 272 and that of Tb(III) by the mixture. A process was proposed for the separation of REEs from the leaching solution of waste phosphors by solvent extraction.

Keywords: phosphors, rare earth elements, HCl solution, solvent extraction, Cyanex 272

1. Introduction

Rare earth elements(REEs) are employed in the manufacture of advanced materials such as magnetic materials, lamp phosphors, batteries and ceramic technology (Binnemans, et al., 2013; Kumari, et al., 2018). It is anticipated that the annual demand for REEs would increase more than 5% until 2020 (Forte, et al., 2019). Therefore, much research is being done to recover REEs from diverse secondary resources. In several cases, some secondary resources contain hazardous components which pose danger to the environment and health. Therefore, the recovery of REEs from these secondary resources deserves research from the point of environment as well as metal demand.

Mutual separation of REEs from the diverse leaching solutions is difficult owing to their similar chemical properties. Recently, floatation (Abaka-Wood, et al., 2019) has been employed for the enrichment of rare earth oxides from the low grade mineral and the following leaching efficiency is also improved. The research on the recovery of REEs from the leaching solution of secondary resources has been investigated by numerous methods such as precipitation (Forte, Yurramendi, Aldana, Onghena and Binnemans, 2019; Ippolito, et al., 2017; Önal and Binnemans, 2019; Schaeffer, et al., 2017) and solvent extraction(Rao, et al., 2019). Generally, oxalic acid is employed as the agent for the precipitation of REEs from the leaching solution of waste phosphors (Forte, Yurramendi, Aldana, Onghena and Binnemans, 2019; Önal and Binnemans, 2019; Schaeffer, Feng, Grimes and Cheeseman, 2017). In addition, some advanced materials or technologies such as metal-organic framework (MOF) (Zhao, et al., 2019), supercritical fluid (Lin, et al., 2018), ionic liquids (Schaeffer, Feng, Grimes and Cheeseman, 2017) and

solvometallurgical process (Dewulf, 2018) show higher selectivity in the separation of REEs from several resources in the lab scale. However, higher cost and requirements on the instruments limit the practical application of these technologies to industrial scale.

Compared to precipitation, solvent extraction is more efficient in the separation of REEs because the extractants can be regenerated several times in the process (Önal and Binnemans, 2019). Some single extractants like Cyanex 272, Cyanex 572, and D2EHPA have been employed for separation of REEs from different medium. However, the low separation factor between the REEs would require the installment of lots of counter-current extraction and stripping stages (Agarwal, et al., 2018; Innocenzi, et al., 2018; Tunsu, et al., 2016; Wang, et al., 2016). In order to overcome this difficulty, synergistic extraction systems have been developed for the separation of REEs from the leaching solutions containing single or two REEs by the mixture of acidic extractants (Cyanex 272, PC886, Cyanex 301 and so on) and either neutral (TBP, TOPO) or basic extractants (Aliquat 336, Alamine 336) (Banda, et al., 2014; Devi and Sukla, 2018; Zhang, et al., 2014). Meanwhile, some novel extractants such as HEHAMP ((2-ethylhexylamino)methyl phosphonic acid mono-2-ethylhexyl ester), HEHEHP (2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester) have been employed for the mixture of REEs (Zhao, et al., 2018). Leaching of phosphors with hydrochloric acid results in an aqueous solution containing several REEs, such as Y(III), Eu(III), La(III), Ce(III) and Tb(III). Employment of single acidic extractant needs its prior treatment for the saponification in order to control the equilibrium pH of the raffinate. In contrast, the use of the mixture of acidic and basic extractant obviates the saponification step for acidic extractant, which leads to easy control of the operation and reduction in operating cost. However, few works have been reported on the separation of REEs from the leaching solutions of waste phosphors by the synergistic systems consisted of acidic and basic extractants.

Owing to lanthanide contraction, the extraction order of the REEs by organophosphorus acid extractants from the leaching solution of phosphors is Y(III)>Tb(III)>Eu(III)>Ce(III)>La(III)(Li, 2017). In present work, separation of the above-mentioned five REEs from HCl solution was investigated by solvent extraction with single Cyanex 272, binary mixture of Cyanex 272 and Alamine 336 and ionic liquid of ALiCY IL (prepared from Cyanex 272 and Aliquat 336). The extraction behavior of REEs was studied as a function of solution pH and extractants concentration. Scrubbing process was tested for separation of Y(III) over Eu(III) and Tb(III) in the loaded binary mixture by pure Y(III) solution. The loaded Y(III) in the organic phase was efficiently stripped by HCl solution. Eu(III) and Tb(III) was separated by solvent extraction with the mixture of Cyanex 272 and Alamine 336 followed by scrubbing with pure Tb(III) solution. Compared to previous works on the use of ionic liquids, the preparation of the binary mixture of Cyanex 272 and Alamine 336 is easy. Moreover, the REEs in the leaching solution of phosphors was separated in fewer stages by combined employment of single Cyanex 272 and binary mixture in this work. An integrated process was proposed for the separation of REEs from the leaching solution of waste phosphors.

2. Materials and methods

2.1. Chemicals and reagents

The synthetic leaching solution of waste phosphors, including yttrium, europium, lanthanum, cerium and terbium, was prepared by dissolving the corresponding chlorides. Among these chemicals, $YCl_3 \cdot 6H_2O$ (99.9%) was supplied by Sigma Aldrich, and $EuCl_3$ (99.9%), $LaCl_3$ (99.9%), $CeCl_3$ (99.9%) and $TbCl_3$ (99.9%) were supplied by Alfa Aesar (A Johnson Matthey Company). Table 1 lists the composition of the synthetic leaching solution of REEs. The solution pH was adjusted by adding dilute HCl or NaOH solution. All the reagents employed in the experiments were of analytical grade.

Table 1. The concentration of the rare earth elements in the synthetic HCl solution

Elements	Y	Eu	La	Ce	Tb
Concentration(mM)	56.9	2.5	0.5	0.7	0.6

The extractants used in this work were Cyanex 272 (bis(2, 4, 4-trimethylpentyl) phosphinic acid, 85%), Alamine 336 (tri-octyl/decyl amine, 95%) and Aliquat 336 (tricaprylmethylammonium chloride,

99%) which were purchased from Solvay Cytec Industries and BASF Chem. Co. Ltd. Binary mixture was prepared by mixing Cyanex 272 and Alamine 336 at equimolar concentration ratio. Ionic liquid (ALiCY IL) was prepared by mixing Cyanex 272 and Aliquat 336 on the basis of the reported method (Fortuny, et al., 2012). Kerosene was used as a diluent in all the extraction experiments.

2.2. Solvent extraction procedure

The general solvent extraction experiments were performed in a 50 mL bottle with a screwed cap. Equal volume (except otherwise stated) of organic and aqueous phase was shaken for 30 minutes by using a Burrell wrist action shaker (model 75, USA) and the mixture was separated by using separated funnel. The pH values of aqueous solution were measured with a pH meter (Orion Star A221 model). The metal concentration in aqueous phase was measured by ICP-OES (Spectro Arcos) before and after extraction. The metal concentration in organic phase was calculated by mass balance. The extraction percentage was calculated by the equation $E\% = (m_0 - m_1) / m_0 \times 100$, where m_0 and m_1 is the mass of the metal ions in the aqueous phase before and after extraction, respectively. In most cases, two replicate experiments were carried out simultaneously and the errors associated with the extraction and stripping percentages were within $\pm 5\%$.

3. Results and discussion

3.1. Changes in equilibrium pH after extraction by Cyanex 272, binary mixture and ionic liquid

In order to investigate the effect of solution pH on the extraction of REEs from the HCl solution, the initial pH of stock solution was varied from 3 to 5. The pH values before and after extraction by single Cyanex 272, binary mixture and ALiCY IL are displayed in Table 2. In these experiments, the concentration of Cyanex 272 and Alamine 336 in the mixture was fixed at 0.5 M, while 0.05 M ALiCY IL was employed. Compared to the binary mixture, the equilibrium pH values by Cyanex 272 was much lower. Although ALiCY IL concentration was much lower than that of the binary mixture, there was little difference in equilibrium pH between them. Table 2 indicates that some of hydrogen ions were extracted by the binary mixture and ALiCY IL, which agrees well with the reported results (Liu, et al., 2014; Zhang, Wang, Huang, Dong, Long and Zhang, 2014).

Table 2. Variation of the equilibrium pH of the aqueous solution after extraction with different extractants

Extractant	Equilibrium pH				
	3.01	3.5	4.01	4.51	5.0
0.5 M Cyanex 272	1.12	1.10	1.16	1.34	1.16
0.5 M Cy272+0.5 M Alamine 336	3.15	3.09	3.01	2.88	3.08
0.05 M ALiCy	3.07	3.11	3.14	3.16	3.25

(3.01, 3.5, 4.01, 4.51 and 5.0 represent the initial pH of the aqueous solution)

3.2. Extraction by single Cyanex 272

Fig. 1 shows the extraction of REEs from the HCl solution by Cyanex 272 as a function of initial pH from 3 to 5. Around 30% of Y(III) was extracted into the organic phase by 0.5 M Cyanex 272 and this value remained constant with regard to the variation of initial pH. The extraction of other four rare earth elements was negligible in these experiments. These results indicated that Y(III) can be selectively extracted over other REEs by single Cyanex 272, and the initial pH has little influence on the extraction of REEs. The results agreed with the extraction order of REEs by organophosphorus acidic extractants, namely $Y(III) > Tb(III) > Eu(III) > Ce(III) > La(III)$ (Li, 2017).

Only Y(III) could be selectively extracted over the other four REEs. In order to obtain optimum conditions for the separation of Y(III), the effect of Cyanex 272 concentration on the extraction of REEs from HCl solution was investigated at the initial pH of 4. Fig. 2 shows that the extraction percentage of Y(III) increased from 30% to 54% as Cyanex 272 concentration increased from 0.1 to 0.9 M. In these experiments, the extraction of the other four REEs except Y(III) was negligible in each condition,

indicating that it would be possible to separate Y(III) by multiple counter-current extraction with Cyanex 272.

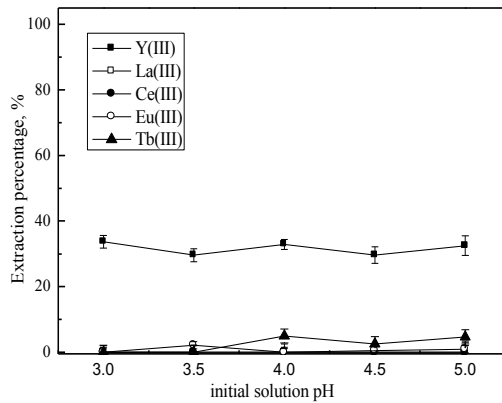


Fig. 1. Effect of initial pH on the extraction of REEs by 0.5 M Cyanex 272

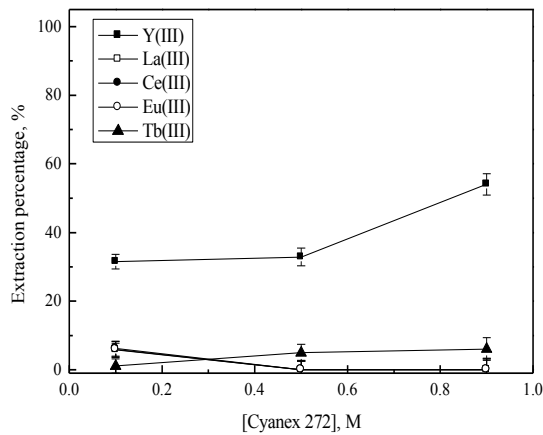


Fig. 2. Effect of Cyanex 272 concentration on the extraction of REEs from the solution with initial pH of 4

In order to obtain the extraction isotherm of Y(III) by single Cyanex 272, the volume ratio of the two phases was varied from 1/5 to 5/1. In these experiments, the concentration of Cyanex 272 and initial pH were fixed at 1 M and 4, respectively. The resulting McCabe-Thiele diagram is shown in Fig. 3. At least 5 stages are needed for the complete extraction of Y(III) at an O/A ratio of 0.3. The concentration of the other four REEs in the organic phase at the different O/A ratios is shown in Table 3. The results show that only a small amount of Tb(III) was co-extracted into the organic phase, and the extraction percentage of Tb(III) decreased a little with the increase of O/A ratio. However, other REEs (La(III), Ce(III) and Eu(III)) are remained in the aqueous phase irrespective of the volume ratio of organic to aqueous phase. This data indicates the feasibility of the separation of Y(III) by single Cyanex 272 from the HCl solution.

Table 3. Effect of volume ratio of organic to aqueous on the extraction of La(III), Ce(III), Eu(III) and Tb(III) by 1 M Cyanex 272

Phase ratio (O/A)		La	Ce	Eu	Tb
1:5	Loaded organic, mM	0	0	0	0.08
	Extraction, %	0	0	0	14
1:1	Loaded organic, mM	0	0	0	0.01
	Extraction, %	0	0	0	3
5:1	Loaded organic, mM	0	0	0	0.03
	Extraction, %	0	0	0	5

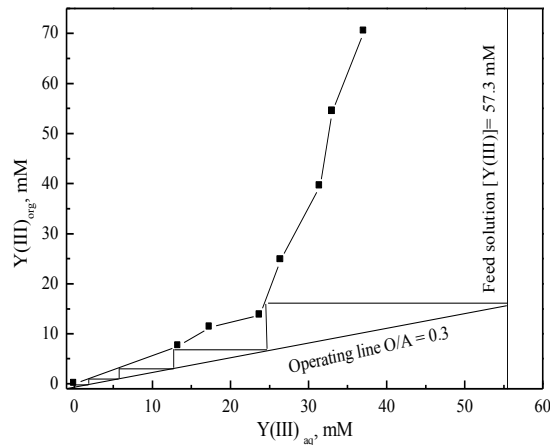


Fig. 3. McCabe-Thiele diagram for the extraction of Y(III) by 1.0 M Cyanex 272 from solution with initial pH of 4

3.3. Synergistic extraction by binary mixture and ionic liquid ALiCY IL

3.3.1. Effect of solution pH

Synergistic extraction of REEs from the HCl solution was investigated by the binary mixture and the ionic liquid ALiCY IL. For this purpose, a binary mixture consisting of 0.5 M Cyanex 272 and 0.5 M Alamine 336 was employed in the initial solution pH range from 3 to 5. The effect of solution pH on the extraction of REEs is shown in Fig. 4. The extraction of Tb(III) increased a little as solution pH increased from 3 to 4 and then remained a constant value of 95%. In the meantime, more than 95% of Y(III) and 82% of Eu(III) were extracted into the binary mixture and solution pH affected little the extraction of these two metal ions. Only 12% of Ce(III) was extracted in each condition, while no La(III) was extracted in each condition.

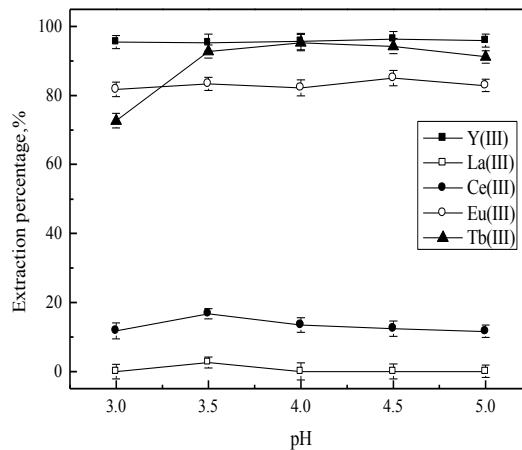


Fig. 4. Effect of initial pH on the extraction of REEs by the binary mixture of 0.5 M Cyanex 272 and 0.5 M Alamine 336

Compared to the results obtained by single Cyanex 272 in Fig. 1, the presence of Alamine 336 showed synergism for the extraction of Y(III), Eu(III), Tb(III) and Ce(III). The extraction percentage of Ce(III) is much lower, indicating that scrubbing of Ce(III) from the loaded binary mixture would result in the loaded organic containing only Y(III), Eu(III), and Tb(III). Most of REEs exist as REE^{3+} and REECl_2^+ in the HCl solution whose pH ranges from 3 to 5. Therefore, the extraction of REEs by Alamine 336 and Aliquat 336 would be negligible (Agarwal, Safarzadeh and Bendler, 2018; Li, 2017). The extraction of REEs by the binary mixture of Cyanex 272 and Alamine 336 can occur step by step (Liu, Jeon and Lee, 2014). Namely, Y(III) is extracted by Cyanex 272 as represented in Eq.(1)(Zhang, Wang, Huang, Dong, Long and Zhang, 2014) and the hydrogen ions are extracted into organic by protonation of Alamine 336

(R₃N) during the extraction(Liu, Jeon and Lee, 2014). The protonated Alamine 336 could react with Cyanex 272 as represented in Eq. (3)(Liu and Lee, 2016).

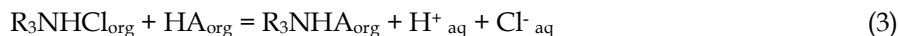
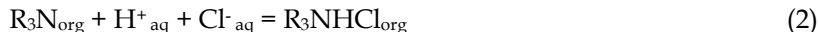
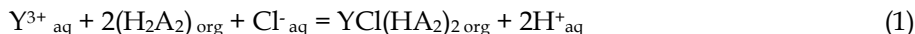


Fig. 5 shows the extraction of REEs by the ionic liquid ALiCY IL as a function of aqueous solution pH. Around 30% of Y(III), Eu(III) and Tb(III) were extracted into the ionic liquid and solution pH did not affect the extraction of REEs in the experimental ranges. About 5% of Ce(III) came into the organic phase with the above 3 REEs but no La(III) was extracted. In these experiments, the concentration of ALiCY IL was 0.05 M, which was much smaller than that of single Cyanex 272 and the binary mixture. Compared to the extraction results by single Cyanex 272 and the binary mixture of Cyanex 272 and Alamine 336, solution pH showed negligible effect on the extraction of REEs by ALiCY IL. This can become advantageous in the continuous operation because either control of solution pH or saponification of the acidic extractant is not necessary.

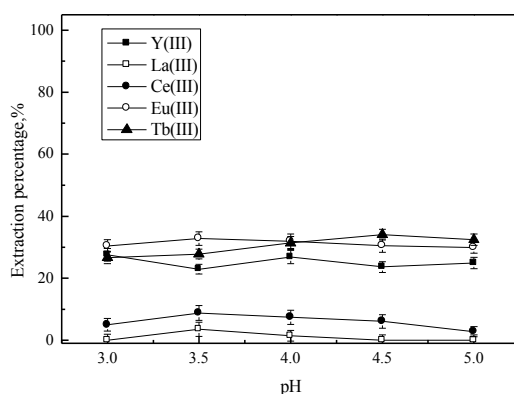


Fig. 5. Effect of initial pH on the extraction of REEs by 0.05 M ALiCY IL.

3.3.2. Effect of extractant concentration

The extraction behavior of the REEs between the binary mixture and ALiCY IL was similar to each other. Namely, Y(III), Eu(III) and Tb(III) together with a small amount of Ce(III) were extracted into the organic phase, while La(III) remained in the raffinate. The difference in the extraction percentage of the REEs resulted from the difference in the concentration of the binary mixture and ALiCY IL employed in the previous experiments. Compared to the synthesis of ALiCY IL, the binary mixture can be easily prepared and be regenerated(Liu and Lee, 2016). Therefore, the binary mixture was selected for further experiments and the concentration of each extractant in the binary mixture was varied from 0.1 to 0.5 M, while keeping the concentration ratio of the two components at unity. Fig. 6 shows that the extraction percentage of Y(III) increased from 20% to 95% as the concentration of Cyanex 272 in the binary mixture increased from 0.1 M to 0.5 M. Meanwhile, the extraction of Eu(III) and Tb(III) followed the similar increasing trend from 1% and 7% to above 82% and 95%, respectively. However, the extraction percentage of Ce(III) began to increase a little when Cyanex 272 concentration became 0.3 M and no La(III) was extracted at all conditions.

3.4. Scrubbing of Ce(III) by pure Y(III) solution

Extraction of the REEs in the synthetic solution with the binary mixture would result in loaded organic which contains most of Y(III), Eu(III) and Tb(III) together with a small amount of Ce(III). Since there was a large difference in the extraction percentage between Y(III) and Ce(III) by the binary mixture, scrubbing of Ce(III) from the loaded organic by aqueous Y(III) solution was tested. First, the loaded organic was prepared by contacting 0.5 M binary mixture with the synthetic aqueous solution with initial pH of 4. The concentration of the metals in the loaded binary mixture was 54.5 mM of Y(III), 1.6 mM of Eu(III), 0.8 mM of Tb(III), 0.08 mM of Ce(III).

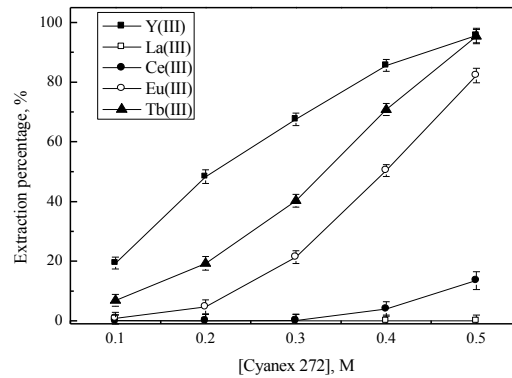


Fig. 6. Effect of Cyanex 272 concentration in the mixture with Alamine 336 on the extraction of REEs from the solutions with initial pH of 4. (The concentration ratio of Cyanex 272 to Alamine 336 was unity)

In scrubbing experiments, the concentration of Y(III) was varied from 5.3 mM to 20.5 mM in the scrubbing solution, while the initial solution pH was fixed at 4. According to Table 4, the scrubbing percentage of Ce(III) was constant at 10% in the experimental ranges, while that of Eu(III) and Tb(III) was negligible. As the concentration of Y(III) in the scrubbing solution increased, the concentration of Y(III) in the loaded organic increased from 53.5 mM to 60.1 mM, indicating that 0.5 M concentration of binary mixture does not reach its loading capacity. Since scrubbing is the most effective in its loading capacity condition, another scrubbing experiments were done by decreasing the initial pH of the scrubbing solution. In these experiments, the concentration of Y(III) and initial pH of the scrubbing solution were controlled to 11.2 mM and 0.6, respectively. Table 4 clearly indicates that the scrubbing percentage of Ce(III) increased from 10% to 51% as initial pH decreased from 4 to 0.6, while there was little difference in the scrubbing percentage of Eu(III) and Tb(III). Therefore, it might be said that solution pH is much more important than the concentration of Y(III) in the scrubbing of Ce(III) from the loaded binary mixture. These results indicate that the Ce(III) could be scrubbed by multiple counter-current scrubbing.

Table 4. Scrubbing of Ce(III), Eu(III) and Tb(III) from the loaded binary mixture by using pure Y(III) solution

Scrub feed (mM)	pH	Scrub solution (mM)				Scrubbed LO (mM)				Scrubbing %		
		Y	Ce	Eu	Tb	Y	Ce	Eu	Tb	Ce	Eu	Tb
5.3	4	6.3	0.01	0.01	0	53.5	0.04	2.0	0.5	10	1	0
10.4	4	9.8	0.01	0.01	0	55.1	0.04	2.0	0.5	11	1	0
15.5	4	13.1	0.01	0.01	0	56.9	0.04	2.0	0.5	10	1	0
20.5	4	14.8	0.01	0.01	0	60.1	0.04	2.0	0.5	10	1	0
11.2	0.6	14.2	0.01	0.01	0	52.5	0.04	1.9	0.5	51	1	0

LO= loaded organic. Binary mixture of 0.5 M Cyanex 272 and 0.5 M Alamine 336, O/A = 1

3.5. Stripping of metals from loaded organic

Once the Ce(III) in the loaded binary mixture can be scrubbed by scrubbing with Y(III) aqueous solution, it is necessary to separate the 3 REEs (Y(III), Eu(III) and Tb(III)) from the loaded binary mixture. Since stripping is the reverse reaction of the extraction, HCl solution was selected as a stripping solution. In these experiments, the concentration of HCl in the stripping solution was varied from 0.5 M to 2.0 M. Fig. 7 shows that the stripping percentage of the 3 REEs (Y(III), Eu(III) and Tb(III)) increased from zero to completeness as HCl concentration increased from 0.5 M to 2 M, indicating that it is difficult to separate the 3 REEs by stripping with HCl solution.

3.6. Separation of Eu(III) and Tb(III)

3.6.1. Extraction of Eu(III) and Tb(III)

Although Y(III) was selectively extracted by single Cyanex 272 over Tb(III) and Eu(III), these three metal

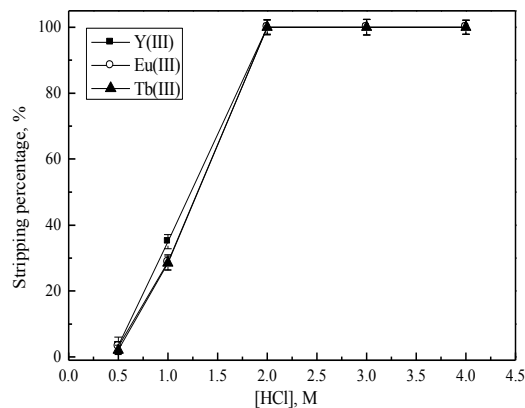


Fig. 7. Effect of HCl concentration on the stripping percentage of Y(III), Tb(III) and Eu(III) from the loaded binary mixture. (Concentration of Y(III), Eu(III) and Tb(III) in the loaded organic phase was 1.6, and 0.5 mM, respectively)

ions were extracted by the mixture of Cyanex 272 and Alamine 336. Our stripping results indicate that it is difficult to separate Y(III), Tb(III) and Eu(III) by stripping with HCl solution. In terms of separation efficiency, it is better to selectively extract Y(III) by using single Cyanex 272. Since the extraction behavior of Tb(III) and Eu(III) by single Cyanex 272 as well as the mixture of Cyanex 272 and Alamine 336 was similar, extraction of both Tb(III) and Eu(III) followed by scrubbing was tried in this work. For this purpose, the mixture of Cyanex 272 and Alamine 336 was employed for the extraction of both metal ions. A synthetic aqueous solution where the concentration of Eu(III) and Tb(III) was 2.5 mM and 0.6 mM was employed. In these experiments, the concentration ratio of Cyanex 272 to Alamine 336 in the mixture was fixed at unity. Fig. 8 shows the effect of Cyanex 272 concentration in the mixture on the extraction of Eu(III) and Tb(III). The extraction percentage of Tb(III) increased from 45% to 85%, while that of Eu(III) rose from 10% to 40% as the concentration of Cyanex 272 in the mixture increased from 0.05 M to 0.2 M.

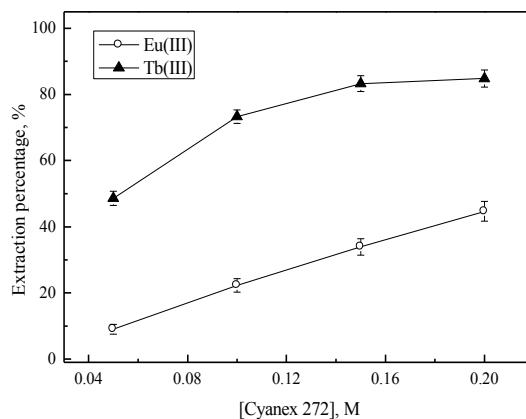


Fig. 8. Effect of the concentration of Cyanex 272 in the mixture with Alamine 336 on the extraction of Tb(III) and Eu(III). (Extraction conditions: [Cyanex 272] = [Alamine 336], initial pH = 4, [Tb(III)]_{initial} = 0.6 mM, [Eu(III)]_{initial} = 2.5 mM)

3.6.2. Scrubbing of Eu(III)

Since there is some difference in the extraction percentage of Tb(III) and Eu(III), it might be possible to separate these two metal ions by counter-current extraction. In this work, scrubbing was tested to separate Tb(III) and Eu(III). The synthetic solution of Tb(III) and Eu(III) with initial pH of 4 was extracted by the mixture of 0.2 M Cyanex 272 and 0.2 M Alamine 336. The concentration of Tb(III) and Eu(III) in the loaded organic was 0.5 mM and 0.3 mM, respectively. The scrubbing solution was prepared by varying the concentration of Tb(III) from 3.6 mM to 16.6 mM. In these experiments, the initial pH of the scrubbing solution was fixed at 4. Table 5 lists the effect of Tb(III) concentration on the

scrubbing of Eu(III) and the purity of Tb(III) in the loaded organic. As the concentration of Tb(III) in the scrubbing solution increased to 16.6 mM, the concentration of Tb(III) in organic phase increased from 3.7 mM to 13.4 mM, while the scrubbing percentage of Eu(III) increased from 32.4 to 67.3% and the purity of Tb(III) in the loaded organic increase to 99.3%. Our data indicates that it is possible to separate Tb(III) and Eu(III) by solvent extraction followed by scrubbing with pure Tb(III) solution.

Table. 5. Effect of Tb(III) concentration in the scrubbing solution on the scrubbing of Eu(III) from the loaded mixture of Cyanex 272 and Alamine 336

Scrubbing solution [Tb(III)] _{aq} , mM	[Tb(III)] _{org} , mM	[Eu(III)] _{org} , mM	Scrubbing % of Eu(III)	Purity of Tb(III), %
0	0.5	0.3	0	65.5
3.6	3.7	0.2	32.4	95.1
7.8	7.2	0.1	50.1	98.1
16.6	13.4	0.1	67.3	99.3

Binary mixture of 0.2 M Cyanex 272 and 0.2 M Alamine 336

In organic phase before scrubbing: [Tb(III)] = 0.5 mM, [Eu(III)] = 0.3 mM

3.6.3. McCabe-Thiele diagram of Tb(III)

In order to obtain the number of stages required for the complete extraction of Tb(III), McCabe-Thiele diagram for the extraction of Tb(III) by the mixture was constructed by varying the O/A ratio from 1/5 to 5. In these experiments, the mixture of 0.05 M Cyanex 272 and 0.05 M Alamine 336 was employed to reduce the extraction of Eu(III). Fig. 9 shows that two stages of counter-current extraction would lead to complete extraction of Tb(III) at a phase ratio of unity.

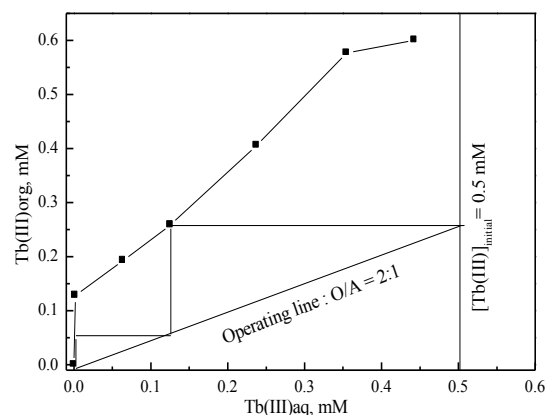


Fig. 9. McCabe-Thiele diagram for the extraction of Tb(III) with the mixture of 0.05 M Cyanex 272 and 0.05 M Alamine 336 from the solution with initial pH of 4

3.7. Integrated process

Solvent extraction of REEs (Y(III), Eu(III), Tb(III), Ce(III) and La(III)) from the leaching solution of waste phosphors was investigated by Cyanex 272 and its mixture with Alamine 336. According to our extraction data, there is a possibility that only Y(III) can be extracted by single Cyanex 272. After selective extraction of Y(III) by single Cyanex 272, Tb(III) and a small amount of Eu(III) are extracted by the mixture of Cyanex 272 and Alamine 336. The co-extracted Eu(III) can be separated from the loaded organic by scrubbing with pure Tb(III) solution. The detailed separation of REEs from the leaching solution of waste phosphors is shown in Fig. 10. After the extraction of Y(III) by single Cyanex 272 and that of Tb(III) and Eu(III) by the mixture of Cyanex 272 and Alamine 336, La(III) and Ce(III) would remain in the raffinate. The Ce(III) can be separated by oxidative precipitation with some oxidizing agent like NaClO and then pure La(III) solution would be obtained (Banda, et al., 2014). Further experiments with real HCl leaching solutions of waste phosphors are necessary to obtain the optimum conditions.

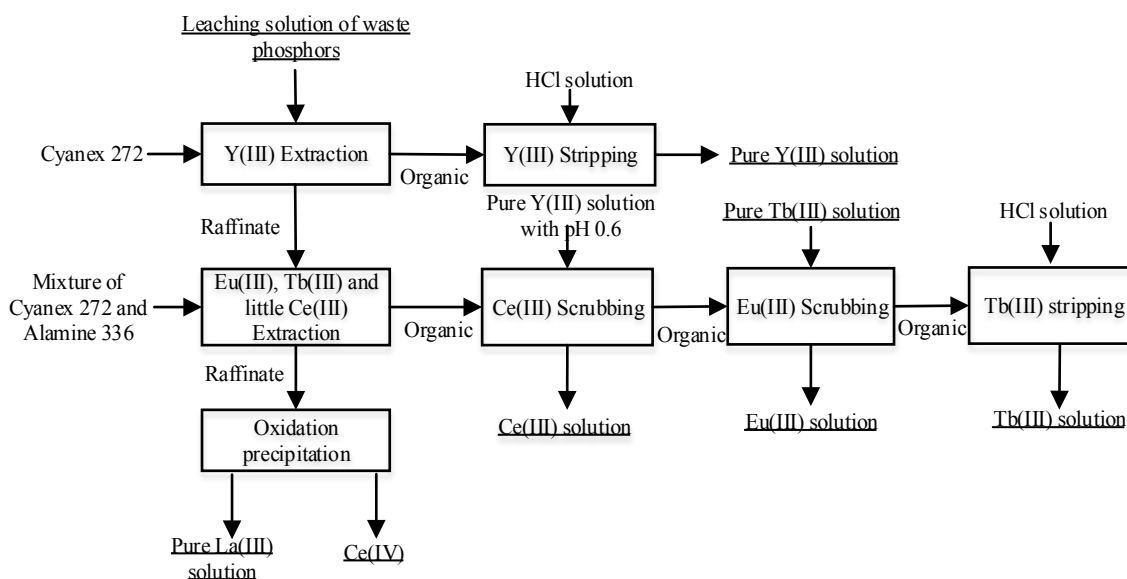


Fig. 10 The proposed process for the separation of REEs from the leaching solution of waste phosphors by Cyanex 272 and binary mixture of Cyanex 272 and Alamine 336

4. Conclusions

Separation of REEs from the chloride solution of waste phosphors containing Y(III), Eu(III), Ce(III), La(III) and Tb(III) was investigated by employing single Cyanex 272, binary mixture with Alamine 336 and the ionic liquid ALiCY IL. The effect of solution pH and extractant concentration was investigated. In the initial solution pH range from 3 to 5, single Cyanex 272 showed good potential for selective separation of Y(III) over other four REEs, and McCabe-Thiele plot indicated that 5 stages were enough for complete extraction of Y(III) from the HCl solution at the O/A ratio of 0.3. Employment of binary mixture resulted in the simultaneous extraction of Y(III), Eu(III) and Tb(III) together with Ce(III). Extraction percentage of Y(III), Tb(III), Eu(III) and Ce(III) was 95%, 95%, 82% and 12% under the condition of 0.5 M binary mixture at the initial pH of 4. By scrubbing with pure Y(III) solution with initial pH of 0.6, about half of the Ce(III) in the loaded binary mixture was scrubbed, while there was no change in the scrubbing of Tb(III) and Eu(III). The stripping behavior of the 3 REEs (Y(III), Tb(III) and Eu(III)) in the loaded binary mixture by HCl solution was similar to each other, indicating that it would be difficult to separate the 3 REEs by stripping. There was some difference in the extraction percentage of Tb(III) and Eu(III) by the mixture of Cyanex 272 and Alamine 336, indicating that counter-current extraction would lead to the separation of these metal ions. In this work, the separation of Tb(III) and Eu(III) was accomplished by extraction with the binary mixture followed by scrubbing with pure Tb(III) solution. A process was proposed for the recovery of the 5 REEs from the leaching solution of waste phosphors by utilizing our extraction data.

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