Eco-friendly Selective Synergistic Extraction Rare-Earths from Waste CRT Phosphor Powder Sulfuric Acid Leachate with Imidazolium-Based Ionic Liquid [OMIm] [PF_6] and Extractant Cyanex272

Xiangmiao Tian, Yufeng Wu, Xiaofei Yin, Yu Gong, Kaihua Zhang and Yu Fu

Abstract Considering the benefits of resource, environment and economy, recycling secondary rare earth resources is becoming an extremely significant resource regeneration way. In this paper, we reported a novel synergistic extraction system combining ionic liquid [OMIm] [PF_6] and extractant Cyanex272 to separate and purify the REE from the leachate of waste CRT phosphor powder. Some extraction parameters were studied including extraction acidity, the ratio of organic phase to aqueous phase, the ratio of Cyanex272 and [OMIm] [PF_6], extraction time and extraction temperature. The optimal parameters of the extraction process was obtained as extraction acidity 0.2 mol/L, the ratio of organic phase to aqueous phase 1:5, the ratio of Cyanex272 and [OMIm]PF_6 $X_C = 0.4$, extraction time 10 min and extraction temperature 25 °C. Under these conditions, REE is successfully and efficiently extracted and separated with zinc and aluminum, which revealed a potential application for REE separation and purification from electronic waste.

Keywords Ionic liquid extraction · Rare earth · CRT phosphor powder

---

X. Tian · Y. Wu (✉) · X. Yin · Y. Gong · K. Zhang · Y. Fu
Institute of Circular Economy, Beijing University of Technology,
No. 100, Pingleyuan Street, Chaoyang District, Beijing 100124, China
e-mail: wuyufeng3r@126.com

X. Tian
e-mail: popcorn555@126.com

Y. Han (ed.), *Advances in Energy and Environmental Materials*,
Springer Proceedings in Energy, https://doi.org/10.1007/978-981-13-0158-2_52

Introduction

Rare earth (REE) is an important strategic resource due to its unique optical, electronic and magnetic properties which has been widely applied in the vital fields of defense industry, aerospace vehicle, photoelectric display [1]. However, as it is difficult to replace in industries, a long-term of irrational exploitation, a crisis of REE has emerged in recent years [2, 3]. However, in the other hand, with the rapid development of display technology, cathode ray tube (CRT) display has been replaced by other types of display such as LCD, LED etc. What happened in China can be a good example, more than 30 million of scrap CRTs is generated only the year of 2013 [4]. Generally speaking, waste CRT is disposed by conventional treatments such as incineration, landfill as municipal refuse, which can cause massive pollution and damage to the environment by polluting the soil, water and air, and then endangering public health [5–7].

CRT is mainly composed of panel glass, funnel glass, electron gun, deflection coil and phosphor layer, usually, about 0.15–1 g REEs contained in the phosphor layer are yttrium and europium as luminescent material [8]. Therefore, large amounts of REE resources abandoned can be recovered and reused [9]. At present, as for the recycling of REEs from the CRT phosphor powder, the general process is "acid leaching- oxalate precipitation- calcination", providing the disadvantage of complicated technology, high energy consuming and high pollution [10–12] Ionic liquid (IL) is a rising reagent has widely used the field of separation and purification is the reason that it is an efficient and green reagent [13–17]. Noticeably, it is also applied in the separation of REEs, Rout and Binnemans used Cyanex923 with ionic liquid extracted the trivalent rare-earth ions showed that the combines extraction system had the great ability of separating the rare-earth and the mechanism of trivalent rare-earth ions was ion-exchange [18]. Zhu et al. utilized the ionic liquid tricaprylmethyl-ammonium nitrate and the extractant di(2-ethylhexyl) 2-ethylhexyl phosphonate to extract REE nitrates, their research results indicated the synergistic system they developed was help for the separation of light REEs from heavy REEs [19].

In this paper, based on our previous study, a novel IL-based synergistic extraction method is proposed for the separation of REE from the waste CRT phosphor powder sulphuric leachate (WCPL) by using ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate and extractant Bis(2,4,4-trimethylpentyl) Phosphinic acid (Cyanex272) [20]. The parameters investigated are acidity, the ratio of organic phase to aqueous phase, the ratio of Cyanex272 and [OMIm] [PF_6], exaction time and extraction temperature. In conclusion, we firstly develop a novel, efficient, green IL-based REE extraction technology employed in the recycling of REEs from the waste CRT phosphor powder, and this technology is a feasible to separate and recycle REEs from WCPL directly which can avoid high energy consuming process and achieve high purity secondary REE resources.

Experimental

Materials and Reagents. Phosphor powder was obtained from Shenzhen Green Eco-Manufacture Hi-tech Co., which was mixed with different kinds of scrap CRT phosphor powder. It was firstly sieved by 200 mesh to remove bulky solid impurity substance, and ball-milled 12 h by ball grinder under the rotation rate of 250 r/min for the purpose of well-distributed pretreatment. Afterwards, waste phosphor powder was leached by sulphuric acid according to our preliminary leaching investigations, then it was filtrated for subsequent extraction investigations.

All of other chemicals and reagents used in this research were of Analytical grade, and all of them without further purification in using process. Sulphuric acid ($\geq 95\%$) and hydrogen peroxide were purchased from Beijing Chemical Works. All of extractants used in our research were di-(2-ethylhexyl) phosphate (P204), Phosphonic acid (2-ethylhexyl)-mono (2-ethylhexyl) ester (P507), Tributyl phosphate (TBP), Tri-alkyl phosphine oxide (TRPO), Bis(2,4,4-trimethylpentyl) Phosphinic acid (Cyanex 272), 260# solvent oil, trialkyl-phosphine oxides (Cyanex 923), both of them were purchased from Shanghai Rare-earth Chemical Co. Ltd. Both of selected Ionic Liquids (ILs) were: [OMIm] [PF_6] (1-octyl-3-methylimidazolium hexafluorophosphate >99%), [BMIm] [BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate, >99%), [BMIm] [PF_6] (1-butyl-3-methylimidazolium hexafluorophosphate, >99%) were purchased from Center of Green-chemistry and Catalysis, Lanzhou Institute of Chemical Physics. Y, Eu, Zn and Al (1000 mg/L, HNO_3) standard solutions were purchased from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials, General Research Institute for Nonferrous Metals, China.

Instrumentations. HJ-6A multiposition magnetic stirrer hotplate (Guohua) applied to achieve mixing uniformly in the process of extraction. The PH measurements carried out by a PB-10 digital PH-meter (Sartorius, German). Optima 8000 inductively coupled plasma-optical emission spectrometer (ICP-AES) (PerkinElmer, USA) was performed to determine the concentration of metals in the aqueous phase before and after extraction. All extraction experiments performed by three times to ensure the reproducibility of the values, and relative standard deviations were to be within $\pm 1\%$.

Extraction Procedures. Firstly, to determine which kind of extractant and ionic liquid is efficient to extraction Y, Eu and Zn, Al from phosphor powder acid leaching solution, different organic extractants and ionic liquids were extracted selectively for 4 major metals respectively. It was performed at room temperature with a mechanical shaker at a medium speed for 10 min and employed a 20:1 of phase ratio of aqueous phase to IL phase under pH = 2.5. After the extraction process reached equilibrium, the ion concentration of four major metals in the aqueous phase were measured by ICP-AES with triplicates. After extractant and IL were determined, a series of experiments about the effect of acid concentration in leaching liquor, phase ratio, extraction temperature, the volume fraction of extractant and IL, extraction time. The extraction percentage (E%), distribution ratio (D), synergistic enhancement coefficient (R) and separation factor (α) could be written using the following equations:

$$D = \frac{[M]_{IL}}{[M]_{aq}} = \frac{[M]_i - [M]_f}{[M]_f} \times \frac{V_{aq}}{V_{IL}} \tag{1}$$

$$E\% = \frac{[M]_i - [M]_f}{[M]_i} \times 100 \tag{2}$$

$$R = \frac{D_{C+I}}{D_C + D_I} \tag{3}$$

$$\alpha = \frac{D_1}{D_2} \tag{4}$$

where $[M]_i$ and $[M]_f$ (mol/L) represents the metal concentration in the aqueous phase before and after extraction, respectively. V_{aq} and V_{IL} (mL) are the volumes of the aqueous phase and ionic liquid phase, respectively. D_{C+I}, D_C and D_I are the distribution ratios of M metal with Cyanex 923-[OMIm] [PF_6], Cyanex 923 and [OMIm] [PF_6], respectively. D_1 and D_2 are represents the distribution of metal 1 and 2.

Results and Discussion

The Determination of Extraction System. Firstly, we investigated the effect of different ionic liquids [OMIm] [PF_6] and [BMIm] [PF_6], different extractants P204, P507, Cyanex272, Cyanex923, TBP, TRPO and solvent soil extraction on the valuable metals from the leachate in a single system. As shown in Fig. 1, as for ionic liquid, whether [OMIm] [PF_6] or [BMIm] [PF_6], the extraction rate both less than 20%, and the extraction performance of [BMIm] [PF_6] was better than [OMIm] [PF_6]; However, besides TBP, TPRO and solvent soil, other extractants particularly P507 and Cyanex272 has a superior extraction ability. An important phenomenon was showed that both ionic liquid and extractant has not extraction ability to Al element. Next, we combined different ionic liquids with extractants for common extraction for valuable metals, from Fig. 2, we can see that P507, Cyanex272, Cyanex923, TRPO in two ionic liquids has not shown obvious difference for 4 elements, for P204 has little extraction ability on Zn, however, TBP has any extraction effect on any element. Considering the purpose of excellent extraction on Y and Eu, but has a little extraction effect on Zn, [OMIm] [PF_6] and Cyanex272 were determined as our extraction system for further research.

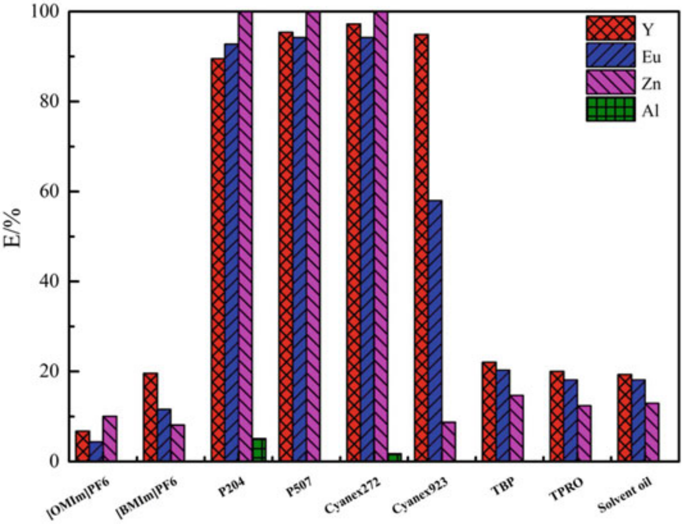

Fig. 1 Effect of extraction of different ion liquids and extractants extraction on the major metal elements of REEs from the leachate of waste CRT phosphor

The Effect of Balanced Acidity. The concentration of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1, 1.5, 2, 2.5, 3 mol/L leaching liquor were prepared, and then 10 ml leachate was taken, 1 ml [OMIm] [PF_6] and 1 ml Cyanex272 was added for extraction experiments. From Fig. 3a, it is clearly shows that acidity has a notable influence on extraction rate, as acidity increases from 0.1 up to 0.2 mol/L, except Al element, the extraction ratio of Y, Eu, Zn increase sharply from 4, 50, 0 to 96, 92, 37%, and then decrease rapidly with acidity increasing, Fig. 3b shows the relationship of distribution ratio between acidity concentration, which indicates same trend with extraction ratio. The determined system has initially realized the separation of REE elements with Zn and Al elements, therefore, the optimal acidity was selected at 0.2 mol/L.

The Effect of the Ratio of Organic Phase to Aqueous Phase. Another important factor has great influence on extraction is the ratio of organic phase to aqueous phase. As shown in Fig. 4, when the phase ratio is of 1:1, the extraction ratio of Y, Eu and Zn is 100, 97 and 65%, separately. Y element is almost not affected by phase ratio increasing to 1:50, the extraction ratio is still as high as 98%, however, the extraction of Eu and Zn elements both reduce with dwindling phase ratio levels, but the degree of decline in the Zn than Eu, thus, improving phase ratio to some extent can achieve preferable separating effect REE elements with Zn, notably particularly the decided phase ratio can’ t be too high as a result of recovering Eu to an extreme. As a result, the best phase ratio is decided at 1:5.

The Effect of the Ratio of Cyanex272 and [OMIm] [PF_6]. Based on the different affinity of Cyanex272 and [OMIm] [PF_6] to each element in extraction process,

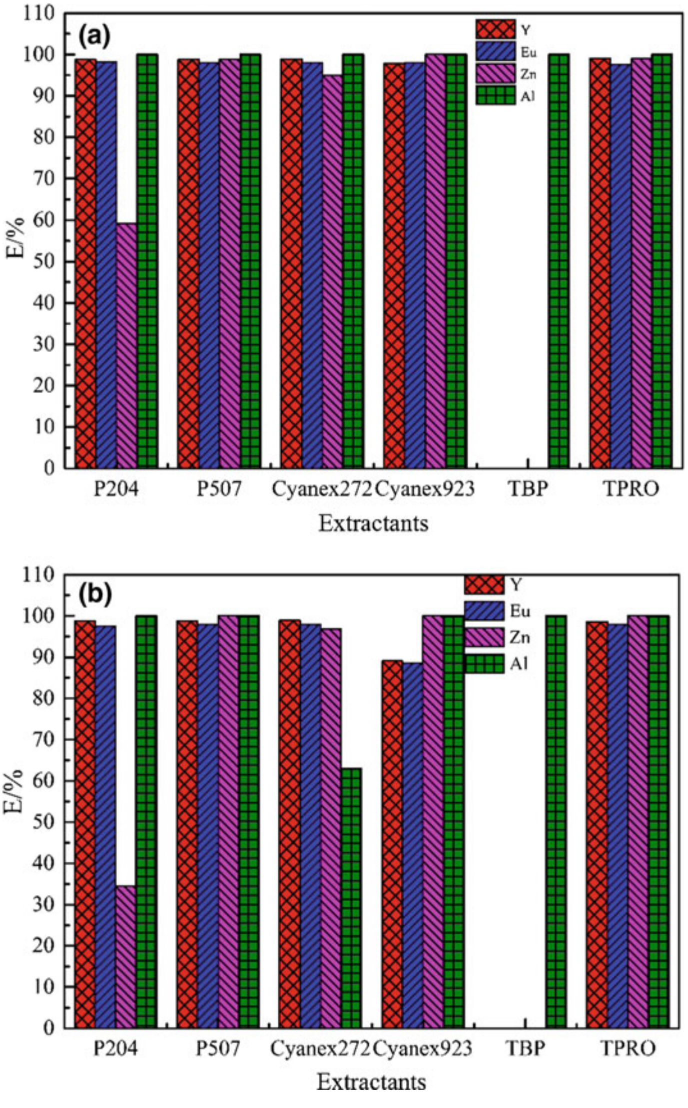

Fig. 2 Effect of extraction of ion liquids of [OMIm] [PF_6] and [BMIm] [PF_6] synergistic extraction on the major metal elements of REEs et al. from the leachate of waste CRT phosphor with different extractants, **a** ion liquid of [OMIm] [PF_6], **b** ion liquid of [BMIm] [PF_6]

consequently, it is necessary to investigate the effect of the ratio of them (the volume of Cyanex272 and [OMIm] [PF_6] to total volume are expressed as X_C and X_O independently). The analysis is demonstrating in Fig. 5, a very clearly tendency is suggested that Y, Eu, Zn has shown a different speed increase trend with the increase of the addition volume of Cyanex272, while [OMIm] [PF_6] exhibits the reverse result. When X_C increased from 0 to 0.3, the extraction rate of Y and Eu rise

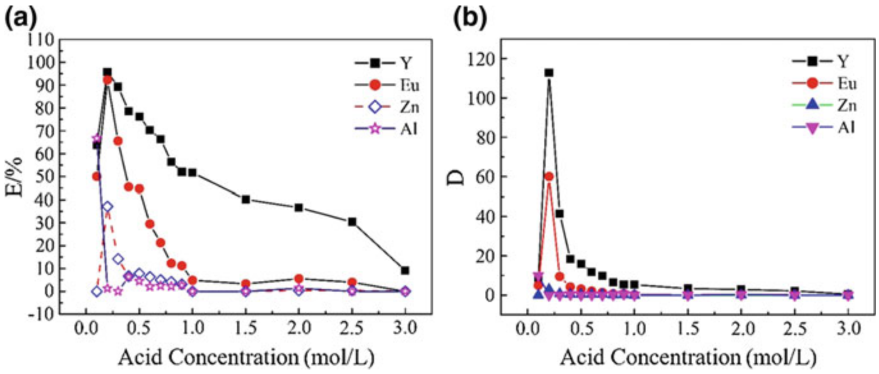

Fig. 3 Variation of the extraction rate and the distribution ratio of the major metal elements for synergistic extraction with [OMIm] [PF_6] and Cyanex272 as a function of the sulphuric acid concentration in the aqueous phase, **a** extraction rate, **b** distribution ratio

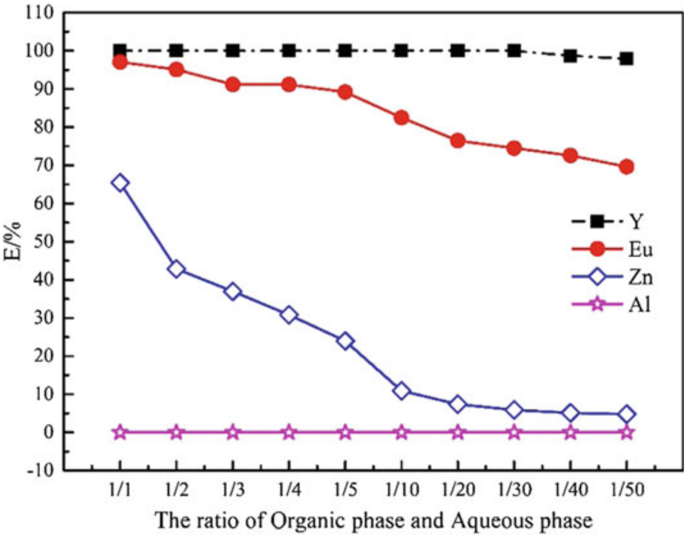

Fig. 4 Variation of the extraction rate of the major metal elements for synergistic extraction with [OMIm] [PF_6] and Cyanex272 as a function of the ratio of organic phase to aqueous phase

quickly to 100 and 94% respectively, however, Zn only increases up to 19%, Al rate reduces from 20 up to 13%; as the X_C increases, Y can be extracted completely, a little increase to Eu and a fast increase to Zn at nearly 40% extraction rate under the X_C is 1; as far as Al is concerned, it cannot be extracted entirely with the X_C up to 0.4. Further analysis found that Cyanex272 plays a dominant role in the extraction process with affinity order is Y < Eu < Zn < Al, while [OMIm] [PF_6] exhibits a strong selective effect which can reduce Cyanex272 affinity to zinc.

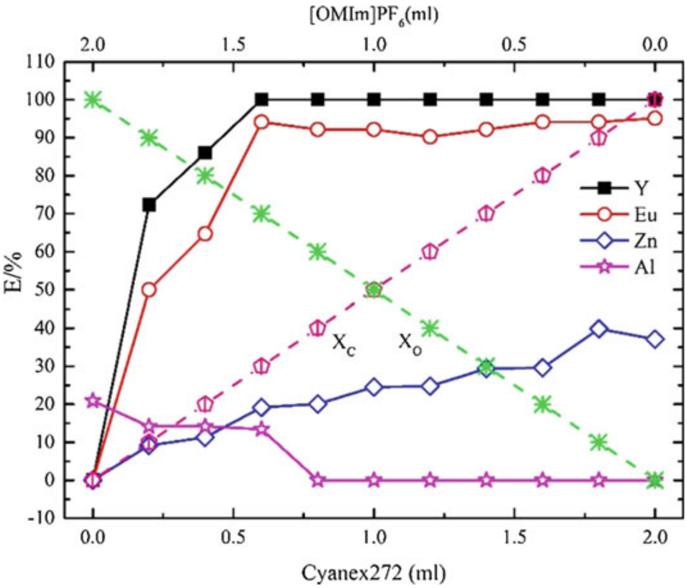

Fig. 5 Variation of the extraction rate of the major metal elements for synergistic extraction with [OMIm] [PF_6] and Cyanex272 as a function of the volume ratio of [OMIm] [PF_6] and Cyanex272

Considering a good extraction effect for Y and Eu and repellency for Zn and Al, the final phase ratio is selected at $X_C = 0.4$ and $X_O = 0.6$.

The Effect of Extraction Time. The effect of extraction time on four valuable elements are displayed in Fig. 6, it can be seen that extraction time plays a minor effect on extraction ratio, the extraction rate of Y and Eu rises with the increase of extraction time, when the extraction time increased from 1 min to 60 min, the extraction rate of Y and Eu only increased by 17 and 17% respectively, but Zn appears to be opposite trend that when the extraction time increased from 1 min to 30 min, the extraction rate of Zn only declines 4%, while the extraction time becomes 60 min, the extraction rate of Zn turns into 0. Al never extracted no matter how extraction time changes. As a consequence, the extraction Y and Eu is greatly influenced by extraction time, however, Zn is slightly affected by extraction time. When the time reaches a certain limit, a small amount of Zn is also released under the equilibrium move. Sufficient REE extraction rate, reduction extraction of Zn and time-saving are taken into comprehensive consideration, the optimum extraction is suggested to be 10 min.

The Effect of Extraction Temperature. Figure 7 is a description of the relationship of different elements extraction rate between extraction temperature. From the graph, it is concluded that extraction temperature has a little influence on Y extraction with only 3% increase when the extraction temperature changed from 25 to 55 °C, a greater effect on Eu and Zn with an increase of 22 and 27%,

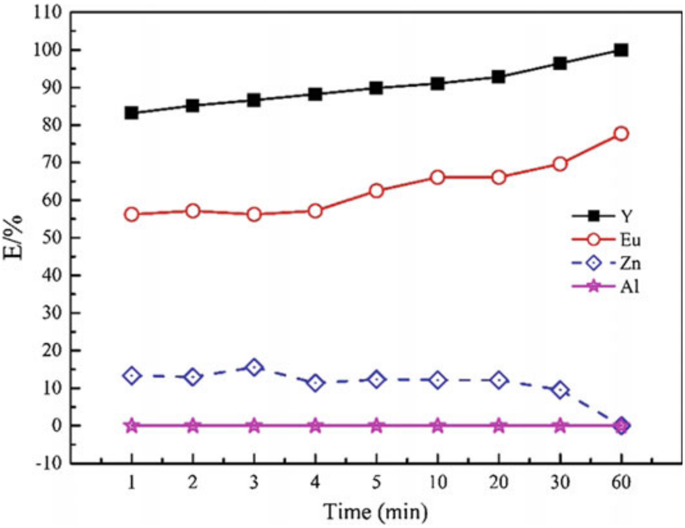

Fig. 6 Variation of the extraction rate of the major metal elements for synergistic extraction with [OMIm] [PF_6] and Cyanex272 as a function of the volume ratio of [OMIm] [PF_6] and Cyanex272

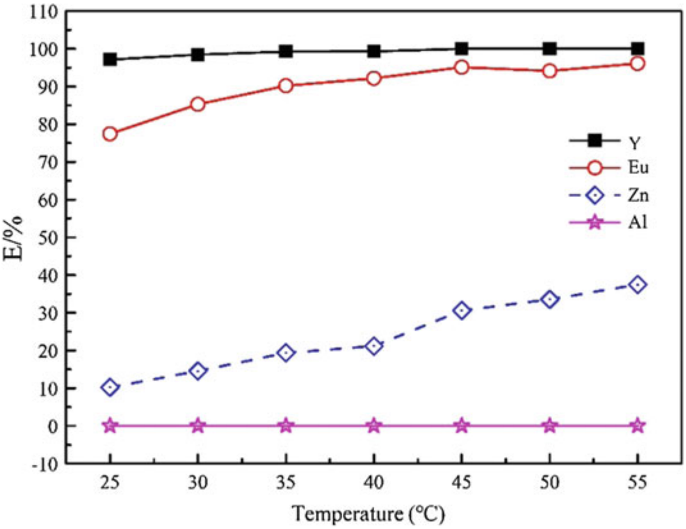

Fig. 7 Variation of the extraction rate of the major metal elements for synergistic extraction with [OMIm] [PF_6] and Cyanex272 as a function of the extraction time

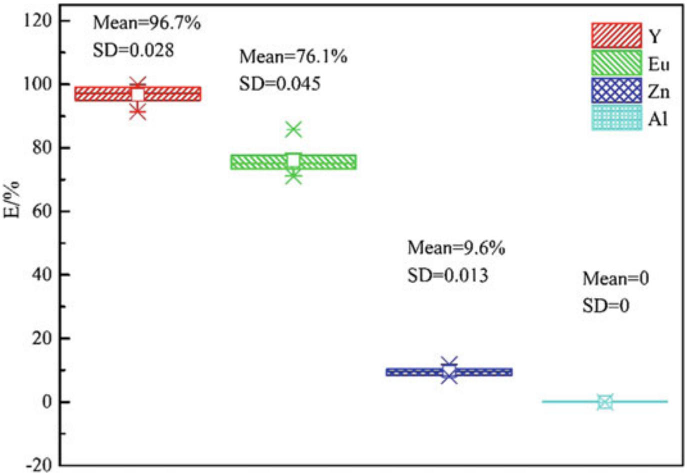

Fig. 8 Variation of the extraction rate of the major metal elements for synergistic extraction with [OMIm] [PF_6] and Cyanex272 under optimal parameters

Table 1 Distribution coefficients of REEs to Zn and synergistic extraction coefficients of Y, Eu, and Zn under the extraction system of [OMIm] [PF_6] and Cyanex272

Separation factor (β)	Synergistic extraction	[OMIm] [PF_6]	Cyanex272
$\beta_{Y/Zn}$	265.84	2.77	0.17
$\beta_{Eu/Zn}$	17.95	1.50	0.08
$\beta_{(Y+Eu)/Zn}$	141.90	2.14	0.13
elements	Y	Eu	Zn
R	4.74	1.35	0.003

respectively. Given that decreasing interference from impurities and reducing energy consumption, the extraction temperature is set as 25 °C (room temperature).

Extraction Experiments under the Optimal Extraction Parameters. The results of parallel experiments under optimal extraction parameters are expressed in Fig. 8 has indicated that the average extraction rate of Y, Eu, Zn is 96.7, 76.1, 9.6%, separately, and Al not be extracted completely. By calculating separation factor REE with Zn under single Cyanex272 system, single [OMIm] [PF_6] system and synergistic extraction system, conclusion can be made that the separation factor in dual extraction system heavily higher than single extraction system, which illustrates that selected extraction system has higher extraction selectivity to Y and Eu compared with Zn and Al. Simultaneously, calculating synergistic enhance factor is listed in Table 1 has indicated that the synergistic enhance factor of Y and Eu is 4.74 and 1.35 which is extremely greater than 1 suggesting synergistic extraction existed in the extraction process of Y and Eu, while for Zn, the factor 0.003 is far less than 1 which is demonstrating there is no synergistic extraction existed in the extraction process of Zn. Although the extraction rate of Eu is not very high and about 9.6% Zn is still extracted after extraction once, the Y and Eu can be thoroughly extracted with the purity is as high as 99.99% and no any phenomenon of co-extraction generated.

Conclusions

The extraction behavior of Y, Eu, Zn, Al with a novel ionic liquid, [OMIm] [PF_6], and extractant Cyanex272 was investigated. Cyanex272 exhibited a higher affinity to Zn and Al than Y and Eu, while [OMIm] [PF_6] exhibited a higher selectivity to REE than Zn and Al. the optimal extraction parameters for the [OMIm] [PF_6] and Cyanex272 extraction system, were obtained as extraction acidity of 0.2 mol/L, extraction phase 1:5, the addition volume ratio of ionic liquid and extractant 0.6, extraction time 10 min, extraction temperature 25 °C. Under these conditions, REE is separated fully with Zn and Al after 3 times extraction. The whole process is a green, efficient and energy-saving method for separation and recycling REEs, which can be applied in the REE recycling field of waste CRT electrical and electronic equipment.

Acknowledgements This work was financially supported by Beijing Nova Program (Z1511000003150141), National Natural Science Foundation of China (2174068), Academician Workstation in Yunnan Province and Key Discipline for Resource, Environment & Circular Economy of Beijing (Q5104001201503).

References

1. K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, Recycling of rare earths: a critical review. J. Clean. Prod. **51**, 1–22 (2013)
2. S. Massari, M. Ruberti, Rare earth elements as critical raw materials: focus on international markets and future strategies. Resour.Policy **38**, 36–43 (2013)
3. X.J. Yang, A. Lin, X. Li, Y. Wu, W. Zhou, Z. Chen, China's ion-adsorption rare earth resources, mining consequences and preservation. Environ. Dev. **8**, 131–136 (2013)
4. Q. Xu, G. Li, W. He, J. Huang, X. Shi, Cathode ray tube (CRT) recycling: current capabilities in China and research progress. Waste Manage. **32**, 1566–1574 (2012)
5. I.C. Nnorom, O. Osibanjo, M.O.C. Ogwuegbu, Global disposal strategies for waste cathode ray tubes. Resour. Conserv. Recycl. **55**, 275–290 (2011)
6. Q. Song, J. Li, A systematic review of the human body burden of e-waste exposure in China. Environ. Int. **68**, 82–93 (2014)
7. S. Sthiannopkao, M.H. Wong, Handling e-waste in developed and developing countries: initiatives, practices, and consequences. Sci. Total Environ. **463–464**, 1147–1153 (2013)
8. X.T. Yu-Gong, Y. Wu, L.L. Zhe-Tan, Recent development of recycling lead from scrap CRTs: A technological review. Waste Manage. **57**, 176–186 (2016)

9. F. Ardente, F. Mathieux, M. Recchioni, Recycling of electronic displays: analysis of pre-processing and potential ecodesign improvements. Resour. Conserv. Recycl. **92**, 158–171 (2014)
10. L.V. Resende, C.A. Morais, Process development for the recovery of europium and yttrium from computer monitor screens. Miner. Eng. **70**, 217–221 (2015)
11. V. Innocenzi, I. De Michelis, F. Ferella, F. Beolchini, B. Kopacek, F. Vegliò, Recovery of yttrium from fluorescent powder of cathode ray tube, CRT: Zn removal by sulphide precipitation. Waste Manage. **33**, 2364–2371 (2013)
12. V. Innocenzi, I. De Michelis, F. Ferella, F. Vegliò, Recovery of yttrium from cathode ray tubes and lamps' fluorescent powders: experimental results and economic simulation. Waste Manage. **33**, 2390–2396 (2013)
13. A. Rout, S. Wellens, K. Binnemans, Separation of rare earths and nickel by solvent extraction with two mutually immiscible ionic liquids. RSC Adv. **4**, 5753–5758 (2014)
14. A. Rout, K. Binnemans, Separation of rare earths from transition metals by liquid-liquid extraction from a molten salt hydrate to an ionic liquid phase. Dalton Trans. **43**, 3186–3195 (2014)
15. R. Martínez-Palou, R. Luque, Applications of ionic liquids in the removal of contaminants from refinery feedstocks: an industrial perspective. Energ. Environ. Sci. **7**, 2414 (2014)
16. X. Sun, Y. Dong, Y. Wang, Y. Chai, The synergistic extraction of heavy rare earth elements using EHEHP-type and BTMPP-type functional ionic liquids. RSC Adv. **5**, 49500–49507 (2015)
17. Y. Shen, W. Li, J. Wu, S. Li, H. Luo, Solvent extraction of lanthanides and yttrium from aqueous solution with methylimidazole in an ionic liquid. Dalton Trans. **43**, 10023–10032 (2014)
18. A. Rout, K. Binnemans, Influence of the ionic liquid cation on the solvent extraction of trivalent rare-earth ions by mixtures of Cyanex 923 and ionic liquids. Dalton Trans. **44**, 1379–1387 (2015)
19. M. Zhu, J. Zhao, Y. Li, N. Mehio, Y. Qi, An ionic liquid-based synergistic extraction strategy for rare earths. Green Chem. **17**, 2981–2993 (2015)
20. X. Tian, X. Yin, Y. Gong, Y. Wu, Z. Tan, P. Xu, Characterization, recovery potentiality, and evaluation on recycling major metals from waste cathode-ray tube phosphor powder by using sulphuric acid leaching. J. Clean. Prod. **135**, 1210–1217 (2016)