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Enrichment of trace rare earth elements from the leaching liquor of ion-absorption minerals using a solid complex centrifugal separation process[†]

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Abstract

A novel solid complex centrifugal separation (SCCS) process has been developed to enrich trace rare earth (RE) elements from the leaching liquor of ion-absorption RE minerals. When compared to liquid–liquid centrifugal extraction (LLCE), the proposed process employed 100% extractant without a volatile diluent for the RE enrichment process, which led to a much shorter equilibrium time of 5 min. Taking into account their ability to form solid complexes with RE ions from an aqueous phase, some alkyl phenoxy carboxylic acid derivatives, including *p*-*tert*-octylphenoxy acetic acid (POAA), iso-propanoic acid (POPA) and iso-butyric acid (POBA), were synthesized and used as the solid extractants. The SCCS process included the following steps: first, the solid extractants with a saponification degree of 80% were mixed with 0.5 g L^{-1} RE solution at a liquid/solid phase ratio of 200/1 to obtain the solid RE complexes. Second, the solid RE complexes were separated from the aqueous phase using a liquid/solid centrifugal separator. Finally, a high concentration of RE solution (>200 g L^{-1}) was obtained by the stripping of solid RE complexes with concentrated HCl. In the SCCS process, a precipitation rate of more than 95.4% and a stripping rate of nearly 100% for RE could be achieved. Water solubilities of the as-prepared solid extractants in raffinate solution were tested to be lower than 32.8 ppm at 25 °C and the mass loss were determined as 0.6% for each cycle. The as-obtained high concentration RE solution with the purity of 96.9 wt% can be used directly as a feed solution for the next individual RE element separation.

1 Introduction

It is known that the RE elements (15 lanthanides plus yttrium and scandium) have been applied in many high-tech products, which rely on their unique electronic, magnetic, and optical properties.[1–3] Heavy RE elements, such as Y, Dy and Ho–Lu, are relatively scarce. However, the Dy element is indispensable for enhancing the magnetic coercivity in conventional NdFeB permanent magnets.[4,5] As for Lu, PET detector technology relies on Lu oxyorthosilicate scintillation crystals.[6,7] Ion-absorption RE minerals are the most significant primary heavy RE resource and are mainly found in South China. Due to its existence as an ion-exchangeable phase within low grade minerals (0.05–0.3 wt%), it is difficult to enrich and recover the RE elements through the conventional physical beneficiation methods, such as gravity separation, magnetic separation and flotation.[8–11] Ammonium sulphate solution has been used to leach ion-absorption type RE minerals; however, the RE ions are accompanied with non-RE metallic species, such as Al^{3+}, Fe^{3+} and Ca^{2+}, in the leaching liquor at low concentrations (0.1–5 g L^{-1}).[12] With the continuous exploitation of ion-absorption minerals, the RE grade of the minerals are significantly reduced, resulting in a decrease in the RE concentration in the leaching liquor and an increase in the concentration of the non-RE metallic species.[13]

The RE feed solution for the extraction separation in the workshop should be at a high concentration. Three major enrichment and recovery processes for trace RE elements from the leaching liquor of ion-absorption minerals have been used in the RE industry and are summarized as follows:

(1) Oxalic acid precipitation process. This is often used in industrial operations due to its simplicity and effective recovery of RE elements. RE elements in the leaching liquor can be precipitated using oxalic acid ($H_2C_2O_4$) after *in situ* leaching from the ion-absorption minerals using acidic $(NH_4)_2SO_4$. However, owing to its toxicity and water solubility (14.3 g per 100 g water at 30 °C), the regeneration of $H_2C_2O_4$ is quite difficult and does not conform to the development trend of green processes.[14–16] Recently, static magnetic field enhanced precipitation with oxalic acid has been applied to the precipitation of RE elements from the leaching liquor of ion-absorption minerals. When compared to the results obtained for the non-magnetization process, the results obtained for the magnetic process appear to be better, and its optimal precipitation conditions were obtained with a precipitation solution at pH 2, $RE_2O_3 : H_2C_2O_4$ ratio of 2.5 : 1 and a magnetic strength at 400 kA m^{-1}.[17] The $H_2C_2O_4$ precipitation reaction can be written using the following equation:

$$2RE^{3+} + 3H_2C_2O_4 \rightarrow RE_2(CO_3)_3\downarrow + 6H^+ \qquad (1)$$

(2) NH_4HCO_3 precipitation process. Because NH_4HCO_3 is a cheap, non-toxic and easily available agricultural chemical product, this method has better economic performance. However, the precipitation of low concentration RE elements with NH_4HCO_3 as a precipitant to form crystalline RE carbonate is difficult, which makes the subsequent solid/liquid phase separation difficult.[18,19] The NH_4HCO_3 precipitation reaction can be written as follows:

$$2RE^{3+} + 6NH_4HCO_3 \rightarrow RE_2(CO_3)_3\downarrow + 3CO_2\uparrow + 3H_2O + 6NH_4^+ \quad (2)$$

(3) Liquid–liquid extraction process. Traditional liquid–liquid extraction (LLE) shows excellent results for the enrichment and recovery of RE, which adopt organic phosphonic acids, alkylated carboxylic acids and phenoxy carboxylic acids as the extractants and HCl as a stripping reagent.[20–23] Very recently, a novel extraction method for the separation and enrichment of RE elements has been reported, in which a three-stage HEH(EHP) extraction at V_A/V_O = 10/1 and a three-stage HDEHP stepwise extraction at V_A/V_O = 25/1 are required to enrich the heavy and light RE elements, respectively. The total recovery for RE elements can reach 99% and the heavy and light RE elements concentrations are up to 240 and 200 g L^{-1} after stripping with 6 mol L^{-1} HCl, respectively.[24] A new bubbling organic liquid membrane extraction process has also been reported to extract and enrich RE elements with extremely low concentrations from the acidic sulphate leach solutions of ion-absorption type RE minerals.[25] Two processes *via* liquid–liquid centrifugal extraction (LLCE) have been previously reported: recovering RE from wet-process phosphoric acid (WPA) using di-(2-ethylhexyl) phosphoric acid (D_2EHPA)[26] and the enrichment of RE from ion-adsorption minerals using naphthenic acid (NA).[27] When compared to the mixer-settlers widely applied in the RE hydrometallurgical industry, the centrifugal contactor revealed advantages such as low hold-up volume, excellent phase separation and high mass transfer efficiency. Neglecting the dimerization effect of the acid extractants, the extraction reactions can be written as follows:

$$RE^{3+} + 3HL_{(org)} \rightarrow REL_{3(org)} + 3H^+ \quad (3)$$

Although the LLE and LLCE have been proven to be reliable and efficient techniques, unexpected emulsification may appear under low acidity conditions and lead to the difficulties in the liquid–liquid phase separation process. The proportion of the diluent in the organic phase is greater than 60%, resulting in fire risks and environmental hazards of volatile organic compounds (VOCs).

To develop an efficient and sustainable enrichment process for trace RE ions from the leaching liquor of ion-absorption minerals, a solid complex centrifugal separation (SCCS) method was developed in the present study. It is worthwhile to mention that there was a well-established chelating method to recover trace metals in the field of analytical chemistry.[28] Similar to the chelating method, the principle of the SCCS method is that metal salt compounds can be produced when mixing complexing agents containing coordination groups with trace metal ions. The metal salts can be easily dissolved in organic solvents, but they could not be dissolved in water. However, the significant difference between the SCCS method developed in the present study and the chelating method is that the former is a solid–liquid separation without an organic solvent and the latter is a liquid–liquid separation that depends on an organic solvent diluent.

2 Experimental

2.1 Materials and reagents

The raw materials used for the syntheses of the solid extractants, including *p-tert*-octylphenol (m.p. 84 °C), chloroacetic acid, 2-chloropropionic acid and 2-bromo butyric acid, were purchased from Chendu Xiya Reagent Chemical Technology Co., Ltd, China. NaOH, aqueous ammonia, ethanol and ammonium sulphate were purchased from Sinopharm Chemical Reagent Co., Ltd. Naphthenic acid (NA) was kindly provided by Shanghai Rare Earth Chemical Co. Ltd of China.

Ion-absorption RE minerals were provided by Longyan Rare-earth Development Co., Ltd, China. RE oxides (La_2O_3–Lu_2O_3, plus Y_2O_3) were purchased from Fujian Changting Golden Dragon Rare Earth Co., Ltd, China, among which La_2O_3–Dy_2O_3, Tm_2O_3–Lu_2O_3 and Y_2O_3 were of high grade (99.99%), and the purities of Ho_2O_3 and Er_2O_3 were 99.9%. All the other chemicals were used without further purification.

Inductively coupled plasma optical emission spectroscopy (ICP-OES), recorded on a Horiba Ultima 2 instrument, was used to determine the concentrations of the RE elements in the aqueous phase. The ^{1}H and ^{13}C NMR spectra were obtained on an AV III-500 Bruker spectrometer. Scanning electron microscopy (SEM) images were collected on a Hitachi SU1510 at an accelerating voltage of 30 kV. Particle sizes were measured on a Brookhaven NanoBrook Omni, USA instrument. Fourier transform infra-red (FT-IR) spectra were recorded using a Nicolet iS50 spectrometer (Thermo Scientific) in the range 600–4000 cm^{-1}. Ultraviolet-Visible (UV-Vis) diffuse reflectance spectra were collected using an Agilent Cary 5000 UV-Vis spectrophotometer. Carbon and hydrogen content in the organic samples were analysed using a Elementar Vario micro cube, Germany.

2.2 Synthesis and characterization of the extractants

Alkyl phenoxy carboxylic acids, including *p*-*tert*-octylphenoxy acetic acid (POAA), *p*-*tert*-octylphenoxy iso-propanoic acid (POPA) and *p*-*tert*-octylphenoxy iso-butyric acid (POBA), were synthesized and their molecular structures are shown in Fig. 1.

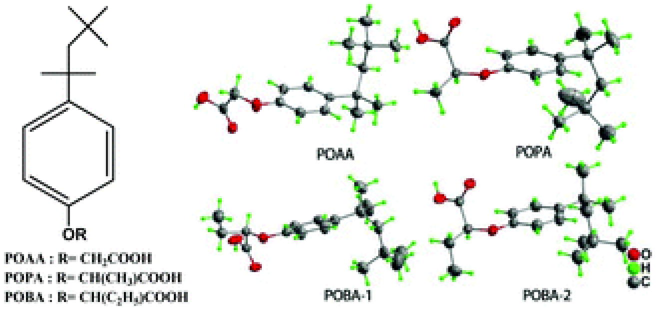

Fig. 1 Molecular structures of POAA, POPA and POBA (Ellipsoid mirror isomer at 30%).

They were prepared on a laboratory scale *via* Williamson reaction and the synthetic routes followed are relatively simple and green: (1) 0.2 mol of 4-*tert*-octylphenol, 0.21 mol of chloroacetic/propionic/butyric acid and 0.41 mol of NaOH were mixed together in alcoholic media. The mixture was stirred at 110 °C for 6 h. A certain amount of NaOH was added to control the system pH at 10–11 throughout the reaction. (2) The resultant solution was sequentially neutralized using 6 mol L^{-1} HCl, extracted with diethyl ether, washed with deionized water and evaporated on a rotary evaporator until dry. (3) The products were purified by recrystallization from *n*-hexane. As for a large-scale preparation, the reaction time of 1.5 h was considered sufficient.

***p*-*tert*-Octylphenoxy acetic acid (POAA).** Final yield 83%. Purity >99% (acid–base titration method). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.68 (s, 9H), 1.30 (s, 6H), 1.69 (s, 2H), 4.62 (s, 2H), 6.89 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 12.95 (s, 1H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 32.0, 32.1, 32.5, 38.1, 56.8, 64.9, 114.0, 127.3, 142.4, 155.8, 170.8. Melting point 124 °C. Water solubility 33.3 ppm at 25 °C (UV-Vis Spectrophotometry).

***p*-*tert*-Octylphenoxy iso-propanoic acid (POPA).** Final yield 80%. Purity >98%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.34 (s, 15H), 1.65 (d, J = 6.9 Hz, 3H), 1.69, (s, 2H), 4.78 (q, J = 6.9 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.9 Hz, 2H); ^{13}C NMR (500 MHz, CDCl$_3$) δ 13.7, 26.8, 27.6, 27.6, 33.3, 52.3, 67.6, 109.8, 122.6, 139.1, 149.9, 172.3. Melting point 109 °C. Water solubility 31.5 ppm at 25 °C.

***p*-*tert*-Octylphenoxy iso-butyric acid (POBA).** Final yield 68%. Purity >98%. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 0.74 (s, 9H), 1.13 (s, 3H), 1.37 (s, 6H), 1.72 (s, 2H), 2.08 (m, 2H), 4.62 (t, 1H), 6.86 (m, 2H), 7.31 (m, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 9.6, 26.1, 31.6, 32.4, 38.1, 57.0, 114.5, 127.3, 143.6, 155.2, 177.5. Melting point 79 °C. Water solubility 25.2 ppm at 25 °C.

2.3 Extraction procedure and data treatment

SCCS experiments were carried out by mixing the saponified extractants and RE solution to form a solid complex phase at room temperature. The mixture was centrifuged and then, the solid phase was separated from the liquid phase. The main technical parameters of the liquid/solid centrifugal separator are given as follows: effective volume of the wheel hub was 300 mL; maximum speed was 6000 rpm; separation factor (centrifugal force/gravity) was 2014; material of filter cloth was polypropylene fiber; pore of filter cloth was 300 mesh; processing capacity was 100 L h^{-1}.

To make a comparison, the LLE experiments were performed using an organic phase containing the extractants diluted with the RE aqueous solution for 30 min in a vibrating mixer at room temperature. The experiments were repeated at least twice. The extraction rate (E) for LLE, precipitation rate (P) for SCCS and the amount of RE precipitation per gram of solid extractant (Q) are defined as follows:

$$E\% = P\% = \frac{C_{\text{ini}} - C_{\text{eq}}}{C_{\text{ini}}} \times 100 \tag{4}$$

$$Q = \frac{(C_{\text{ini}} - C_{\text{eq}}) \cdot V_{\text{aq}}}{m} \tag{5}$$

where C_{ini} and C_{eq} are the initial and equilibrium concentration of RE element in the aqueous phase, respectively. V_{aq} and m represent the aqueous phase volume and the mass of extractant, respectively.

3 Results and discussion

3.1 Comparison of LLE with SCCS

LLE is a common separation method and widely used for the extraction and separation of RE elements.[29,30] The extractant for LLE should be diluted by an inert solvent, such as sulfonated kerosene, to reduce the viscosity of extractant and increase the solubility of the extraction complex in the organic phase. However, some problems gradually emerged during its industrial application, such as the emulsification of the organic phase that leads to difficulties in phase separation. The solid extracting complex formed during the LLE process needs to be avoided, or else it will continue to plug the pipe of the equipment and cause the loss of the extractant. As for the structural optimum design of the extractant, there are two methods used to ensure that the extractant remains in the liquid phase. First, increasing the degree of disorder in the extractant structure; for example, choosing a high degree of branching groups as the carbon chains of extractants. Second, mixing two, three or four extractants together to reduce the melting point of the mixture based on the principle of eutectic mixture; for example, Cyanex 923 comprises a mixture of four trialkyl phosphine oxides with the general formula R_3PO (14%), $R_2R'PO$ (42%), RR'_2PO (31%) and R'_3PO (8%), in which R denotes *n*-octyl and R′ stands for the *n*-hexyl group. When the composition reduces from 100% to 14%, the melting point correspondingly reduced from 52 °C to −5 °C.[31] As a novel extraction and separation system, the extractants were selected in a diametrically opposite manner in this study. As shown in Fig. 1, the selected alkyl phenoxy carboxylic acids including POAA, POPA and POBA are solid extractants with symmetric carbon chains, which may increase the melting points and improve the crystallization performance. The extractants were used 100% without adding a diluent like that used in LLE, such as kerosene. In addition, the formation of solid complexes was utilized to achieve the rapid separation of the solid/liquid phase.

Taking yttrium as an example, the extraction and precipitation efficiency of RE ions using the LLE (NA) and SCCS (POAA, POPA, POBA) methods were compared at room temperature, and the results are shown in Fig. 2. For the traditional LLE system, 40 min was found to be sufficient for the extraction equilibrium of the RE elements. As for the SCCS system, the equilibrium behaviour was found to be quite different from that of the traditional LLE process and less than 5 min was needed to attain the equilibrium. Without the resistance effect of the diluent, the shorter equilibrium time during SCCS can be attributed to the quick complexation reaction of the saponified extractants and RE ions in the aqueous phase. The amounts of RE precipitation per gram of solid extractants (Q) were also calculated. Due to the smallest molecular weight of POAA among the SCCS, the unit mass of POAA revealed the highest RE precipitation amount of 97.6 mg g^{-1}. Water content of the solid complexes POAA-RE, POPA-RE and POBA-RE complexes were found to be 32.7%, 77.4% and 79.4%, respectively.

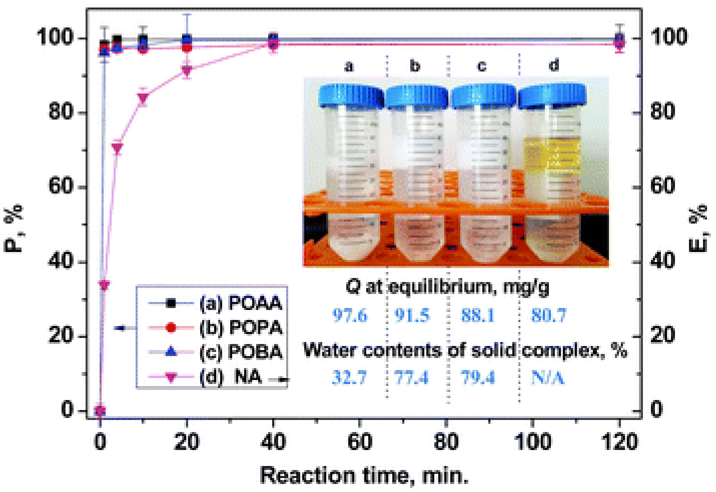

Fig. 2 Extraction and precipitation efficiency of RE with (a) POAA, (b) POPA, (c) POBA and (d) NA by LLE and SCCS methods. Aqueous phase: RE concentration = 0.969 g L^{-1}. Liquid/solid phase ratio = 200/1. C_{NA} = 0.10 mol L^{-1} in 14.5 mL kerosene, saponification degree = 80%.

To reveal the precipitation abilities and selectivities of SCCS methods using POAA, POPA and POBA, their precipitation rates for different RE ions were compared. As shown in Fig. 3, POAA indicates better precipitation abilities for the RE ions before Y, POPA and POBA show better precipitation abilities for the RE ions after Y. Generally, the extractants reveal better precipitation abilities for light RE ions than heavy RE ions. For example, the extraction order of POAA follows the approximate reverse sequence, *i.e.*, Sm > Pr > Nd > Ce > Eu > La > Gd > Tb > Dy > Ho > Tm > Er > Yb > Lu > Y.

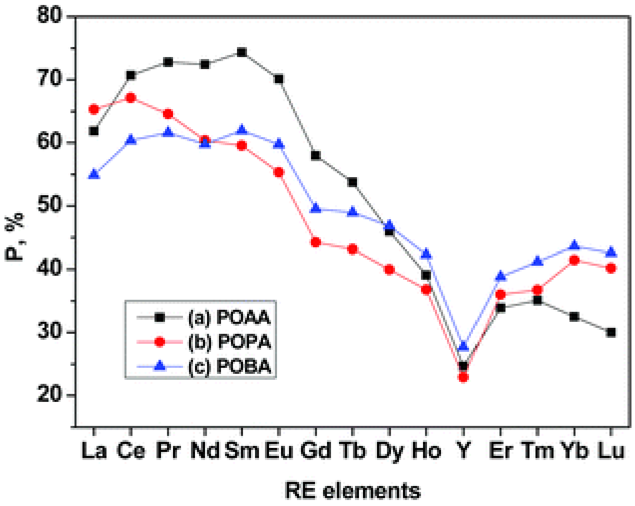

Fig. 3 Precipitation efficiency of mixed RE ions with (a) POAA, (b) POPA and (c) POBA. Aqueous phase: $\sum RE = 23.4$ g L^{-1} (8.8×10^{-3} mol L^{-1} each RE ion). Liquid/solid phase ratio = 9.5/1, saponification degree = 75%.

3.2 The formation mechanism of solid complexes

The extraction of trivalent RE elements with carboxylic acid or phosphonic acid was commonly known as the mechanism of cation exchange reaction.[32] As a weak acid, the acidic extractant itself extracts only a very small amount of RE ions. To extract the RE elements quantitatively in the aqueous phase, saponification using acid–base neutralization reactions are necessary to break the dimer of the acidic extractants. The effects of the degree of saponification on the precipitation of RE elements by POAA, POPA and POBA were investigated and the results are shown in Fig. 4. The precipitation rates of the RE elements with POAA, POPA and POBA quantitatively increase upon increasing the saponification degree over the range of 0–80%. The value of the slope follows the sequence POAA > POPA > POBA, which coincides with the pK_a sequences of POAA (pK_a = 4.88), POPA (pK_a = 5.19) and POPA (pK_a = 5.68). In addition, the formation of the solid complex, ΔRE^{3+}, and the reduction of H^+ in the solid extractants, ΔH^+, were calculated, and the results are summarized in Table 1. The ratios of $\Delta H^+/\Delta RE^{3+}$ remain at about 3 under different saponification degrees, which indicates that the precipitation rates of the RE elements are quantitative under the current saponification conditions. The water solubility of POAA, POPA and POBA were found to be 33.3, 31.5 and 25.2 ppm at 25 °C, respectively. With the increase in the saponification degrees during the precipitation processes, the water solubilities of POAA, POPA and POBA slightly increased. The saponification and precipitation reaction can be written using the following equations:

$$OH^- + HL \rightarrow L^- + H_2O \quad (6)$$

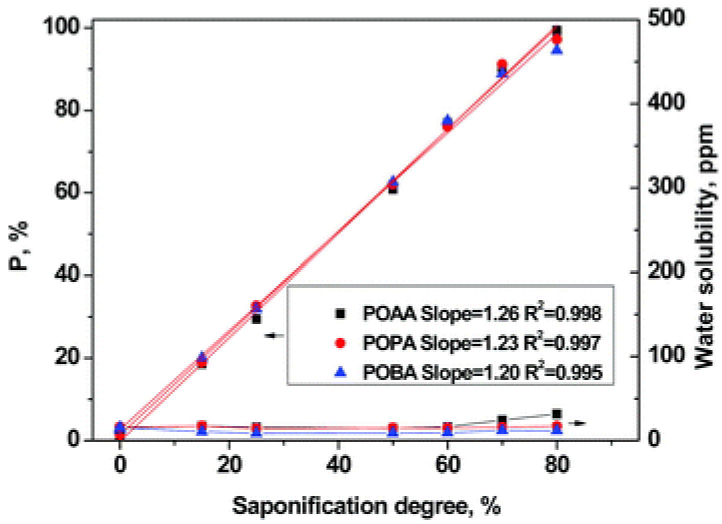

Fig. 4 The effect of saponification degree on the precipitation of RE by POAA, POPA and POBA. Aqueous phase: RE concentration = 1.11 g L^{-1}, liquid/solid phase ratio = 200/1. Saponification degree = 0–80%.

Table 1 The relationship between the formation of solid complex, ΔRE^{3+}, and the reduction of H^+ in the solid extractants, ΔH^+

Sap. rate, %	$\Delta H^+ \times 10^{-4}$ mole	$\Delta RE^{3+} \times 10^{-4}$ mol			$\Delta H^+/\Delta RE^{3+}$		
		POAA	POPA	POBA	POAA	POPA	POBA
15	2.25	0.731	0.746	0.790	3.1	3.0	2.9
25	3.75	1.16	1.28	1.25	3.2	2.9	3.0
50	7.50	2.39	2.44	2.46	3.1	3.1	3.1
60	9.00	3.02	2.98	3.04	3.0	3.0	3.0
65	9.75	3.21	3.22	3.15	3.0	3.0	3.1
70	10.5	3.54	3.57	3.49	3.0	2.9	3.0
80	12.0	3.90	3.81	3.71	3.1	3.1	3.2

3.3 Characterization of the POAA-RE, POPA-RE and POBA-RE complexes

The FT-IR spectra of POAA, POPA and POBA before and after the precipitation reaction in the range of 750–3600 cm^{-1} are depicted in Fig. 5(a–c) and (d–f), respectively. The IR spectra obtained from POAA, POPA and POBA clearly demonstrate that they are typical carboxylic acids.

The bands at 1743, 1720 and 1717 cm^{-1} are assigned to the stretching vibrations of C=O of COOH in the molecules of POAA, POPA and POBA, respectively, which are consistent with the single crystal structures (Fig. S1†). It can be explained that for the stretching vibration, the stronger the hydrogen bonding, the wider is the band and greater is the displacement in the direction of low wavenumber due to the hydrogen bonding effect between the molecules.[33] The C=O asymmetric stretching vibrations occur at 1610, 1612 and 1614 cm^{-1} indicating the presence of carboxylate groups in the structures of POAA-RE, POPA-RE and POBA-RE, respectively.

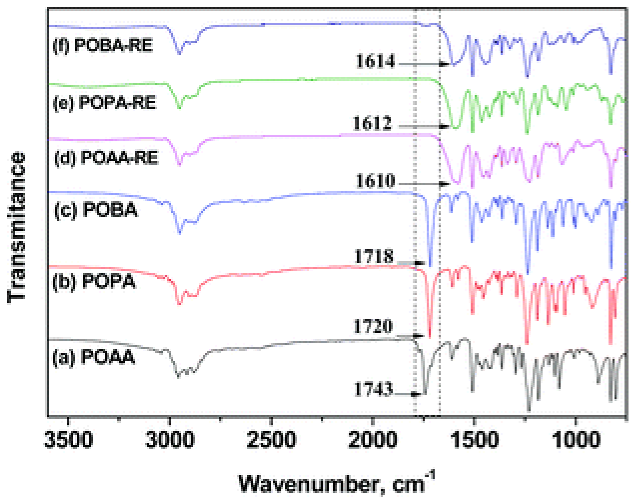

Fig. 5 IR spectra of (a) POAA, (b)POPA, (c) POBA, (d) POAA-RE, (e) POPA-RE and (f) POBA-RE.

^{1}H NMR spectroscopy was also employed to characterize POAA, POPA, POBA and their corresponding complexes with the RE ions before and after the precipitation reactions. As shown in Fig. 6, the ^{1}H NMR characteristic peaks for one $-CH_2$ group and two $-CH$ groups in the molecules of POAA, POPA and POBA are at 4.62, 4.75/4.77 and 4.58, while the peaks are shifted to 4.04, 4.46 and 4.39 after SCCS, respectively. Such changes can be ascribed to the coordination interactions between the acid molecules and RE ions.

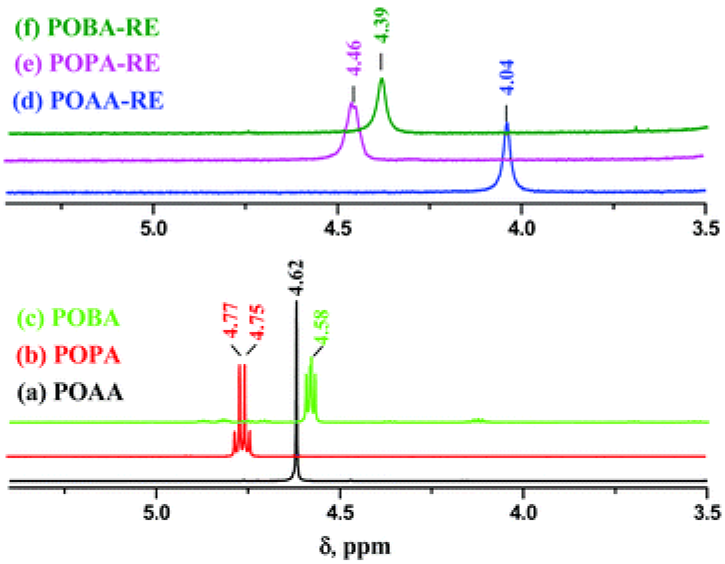

Fig. 6 ^1H NMR spectra for one $-CH_2$ and two $-CH$ groups in (a) POAA, (b) POPA and (c) POBA, and their corresponding RE complexes (d) POAA-RE, (e) POPA-RE and (f) POBA-RE.

The surface morphologies of POAA-RE, POPA-RE and POBA-RE complexes were probed using scanning electron microscopy (SEM). As shown in Fig. 7(a–c), the POAA-RE, POPA-RE and POBA-RE complexes were presented as layered structure when adding 1.5×10^{-3} mole of saponified POAA/POPA/POBA into 8.85×10^{-3} mol L^{-1} $RECl_3$ solution. If the RE concentration further decreases, as shown in Fig. 7(d–f), the POAA-RE, POPA-RE and POBA-RE complexes appear as rod-like structures.

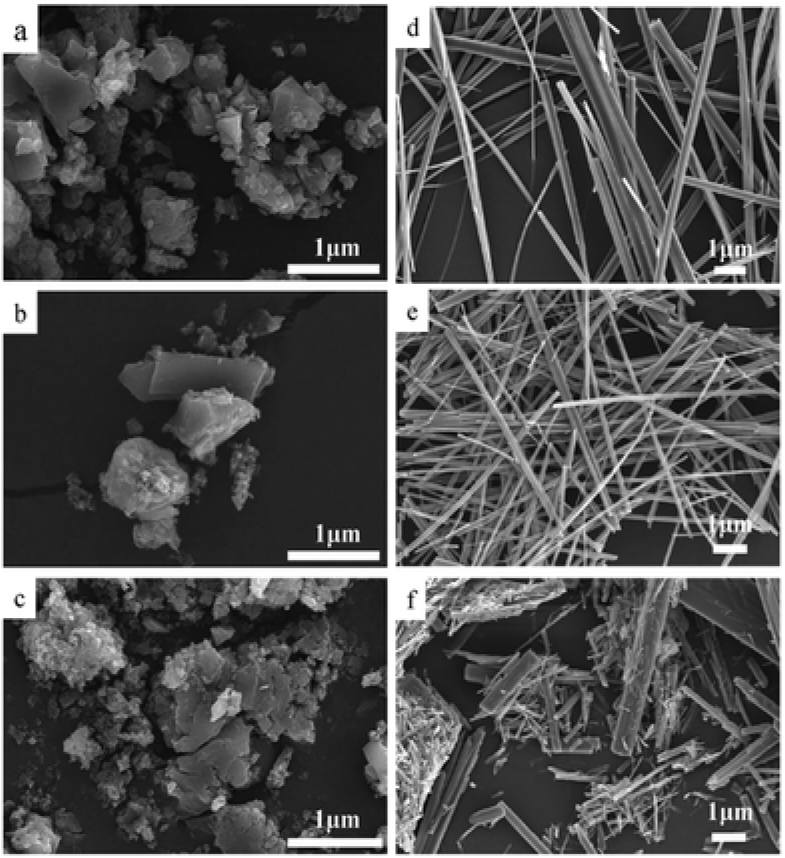

Fig. 7 SEM photographs of the POAA-RE, POPA-RE and POBA-RE complexes. (a–c) Aqueous phase: RE concentration = 1.40 g L^{-1}, V_{aq} = 40 mL. Liquid/solid phase ratio = 100/1. (d–f) Aqueous phase: RE concentration = 0.140 g L^{-1}, V_{aq} = 40 mL. Liquid/solid phase ratio = 1000/1.

3.4 Pilot test

Pilot tests were carried out to verify the current method for the enrichment of trace RE elements in the leaching liquor from ion-absorption RE minerals and a schematic description of the SCCS procedure is shown in Fig. 8. First, the solid extractants were prepared and saponified into anionic surfactants with alkali, such as sodium hydroxide and ammonia, which could fully break the dimers of the acidic extractants and allow contact with the aqueous phase. Second, insoluble solid complexes were formed by adding the saponified extractants into low concentration RE solution. Therefore, the RE elements were transferred from the aqueous phase into the solid phase. The solid complexes could be easily separated from a raffinate solution containing non-RE impurities using a liquid/solid centrifugal separator. Finally, a high concentration RE solution was obtained by the stripping of solid complexes with concentrated HCl. The extractant and $(NH_4)_2SO_4$ in the raffinate solution were designed to be recycled. Considering the excellent amount of RE precipitation per gram (*Q*) and water contents of solid complexes, POAA was selected as the extractant in the pilot test.

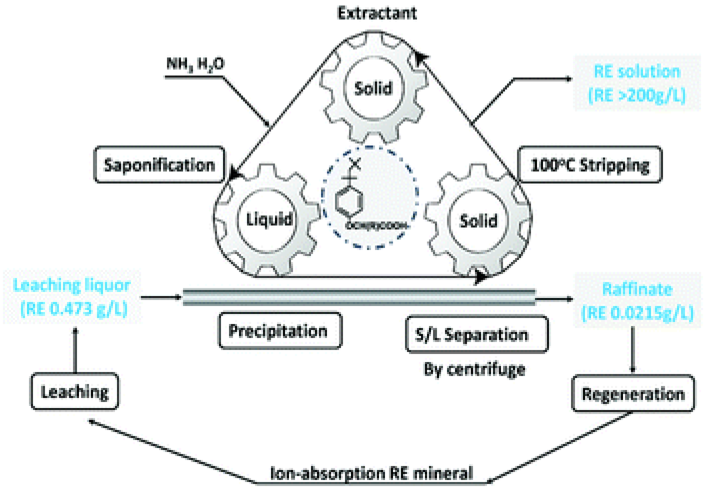

Fig. 8 Schematic description of the SCCS process used for the enrichment of RE elements from the leaching liquor of ion-absorption minerals.

The ion-absorption RE minerals were collected at Longyan of Fujian Province, China, and the partitioning of the ion-exchange phase from the minerals was determined to be 0.114%. The compositions of the ion-absorption RE minerals are shown in Table 2. The proportion of heavy RE elements containing Gd–Lu in the ion-adsorption RE mineral accounts for 14.2%, which is much higher than other types of RE minerals, such as bastnaesite and monazite.

Table 2 Compositions of the ion-absorption RE minerals and products

		RE products, %	
Ingredients	RE mineral, %	Process-I	Process-II
Y_2O_3/REO	25.17	25.3	23.4
La_2O_3/REO	24.70	23.3	23.9
CeO_2/REO	4.54	3.77	4.16
Pr_6O_{11}/REO	5.91	5.87	6.38
Nd_2O_3/REO	20.50	20.6	21.6
Sm_2O_3/REO	4.44	4.83	5.05

[a] Unit: g L^{-1}.

		RE products, %	
Ingredients	RE mineral, %	Process-I	Process-II
Eu_2O_3/REO	0.50	0.576	0.587
Gd_2O_3/REO	4.60	4.71	4.62
Tb_4O_7/REO	0.72	0.790	0.763
Dy_2O_3/REO	4.05	4.51	4.26
Ho_2O_3/REO	0.79	0.854	0.795
Er_2O_3/REO	2.05	2.28	2.09
Tm_2O_3/REO	0.25	0.300	0.258
Yb_2O_3/REO	1.57	1.96	1.76
Lu_2O_3/REO	0.21	0.319	0.279
∑REO	0.114	213.0[a]	201.7[a]
Al_2O_3	13.0	6.29[a]	7.00[a]
Fe_2O_3	<0.20	0.028[a]	0.026[a]
CaO	11.7	0.59[a]	0.50[a]

[a] Unit: g L^{-1}.

Leaching test was carried out to obtain the RE leaching liquor of ion-absorption minerals. Nowadays, the RE concentrate is recovered *via* an *in situ* leaching process using 1–4 wt% $(NH_4)_2SO_4$ solution in the industry. The leaching process of minerals is a type of ion-exchangeable process between the positive ions in the solution and the clay minerals. The linear relationship between $1-2/3\alpha-(1-\alpha)^{2/3}$ and leaching time, as shown in Fig. 9(a), suggests that the leaching kinetics abide by the inner-diffusion-controlled process of the spherical particles;[34,35] the kinetics of the process is given by the following equation:

$$1-2\alpha/3-(1-\alpha)^{2/3}=K\cdot t \qquad (7)$$

where α is the leachability at a given time and K is the rate constant.

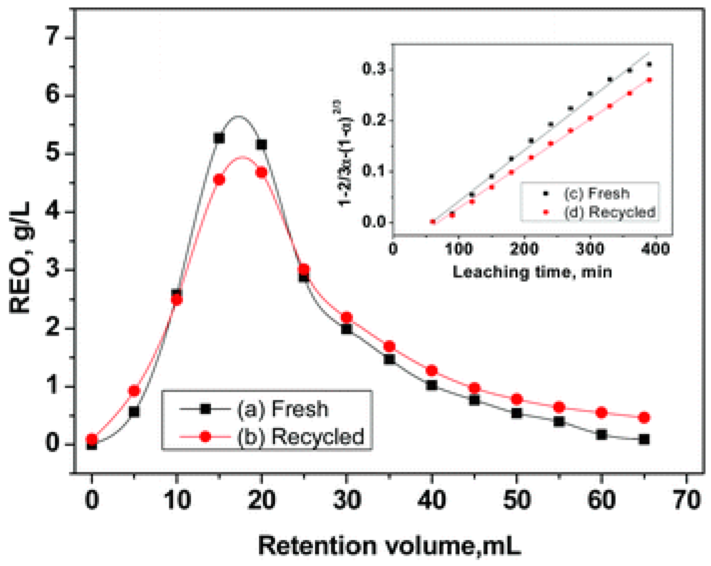

Fig. 9 Leaching test for ion-absorption RE minerals using (a) fresh $(NH_4)_2SO_4$, 20.0 g L^{-1} and (b) recycled $(NH_4)_2SO_4$, 20.2 g L^{-1}. The leaching kinetics tests were carried out in a PMMA column with an inner diameter of 3.2 cm at room temperature, filling amount of ion-absorption RE ore of 100 g and filling height of 9 cm. The linear relationship between $1-2/3\alpha-(1-\alpha)^{2/3}$ and leaching time using (c) fresh $(NH_4)_2SO_4$ with a slope of 9.76×10^{-4} and R^2 of 0.987, and (d) recycled $(NH_4)_2SO_4$ with a slope of 8.36×10^{-4} and R^2 of 0.991 were also determined.

In the precipitation section using a large liquid/solid phase ratio of 200/1, 2000 mL of the RE leaching liquor were prepared as the feed solution and the RE concentration was diluted at 0.473 g L^{-1}. Two samples of 10 g POAA were selected and saponified with NaOH (Process-I) and $NH_3·H_2O$ (Process-II). The solid complexes were formed by adding the saponified extractants into the RE feed solutions. After removing the raffinate solution using the liquid/solid centrifugal separator, 14.7 g and 14.8 g of the solid RE complexes were obtained and the precipitation rates were determined to be 95.6% and 95.5% in Process-I and II, respectively.

The particle morphologies and sizes of the solid complexes were measured and the results are shown in Fig. 10. As a comparison, the precipitate powders of $RE_2(C_2O_4)_3$ and $RE_2(CO_3)_3$ using $H_2C_2O_4$ and NH_4HCO_3 as the precipitants were also prepared under the same conditions. The extractant POAA was saponified using NaOH and $NH_3·H_2O$ in Process-I and II, respectively. This revealed that the surface morphologies of POAA-RE with particle sizes of 40–50 μm were quite similar. The particle sizes of $RE_2(C_2O_4)_3$ and $RE_2(CO_3)_3$ were found to be 6 and 2 μm, respectively. The superior particle size of POAA-RE makes a significant contribution to the separation of the solid phase and liquid phase.

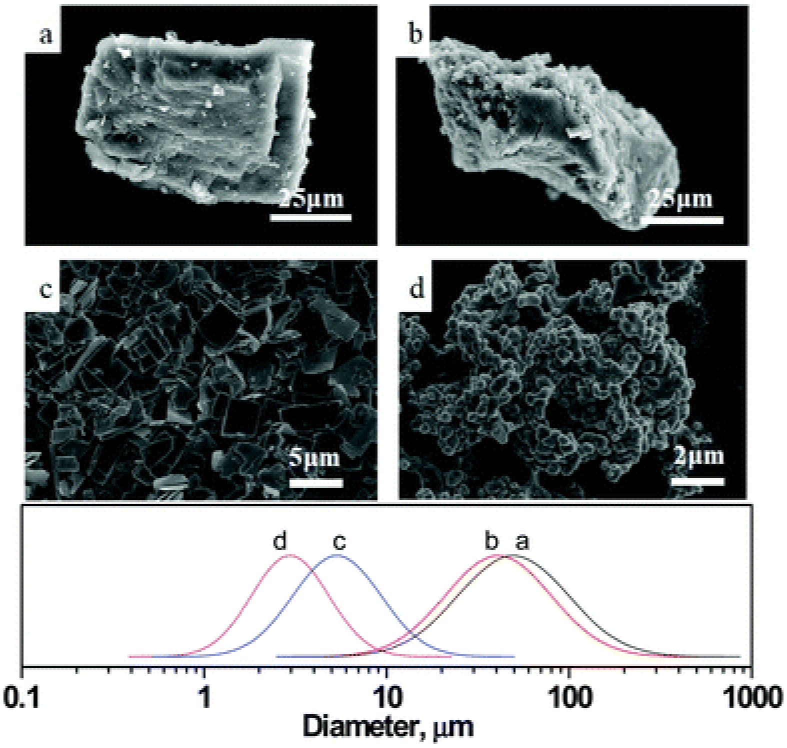

Fig. 10 Particle morphologies and sizes of the solid precipitates. (a) POAA-RE: POAA was saponified with NaOH. (b) POAA-RE: POAA was saponified with NH_3 H_2O. (c) $RE_2(C_2O_4)_3$: $H_2C_2O_4$ was used as precipitant. (d) $RE_2(CO_3)_3$: NH_4HCO_3 was used as precipitant.

In view of the convenience of separation, the liquid/solid centrifugal separator was employed, which contributed to improving the production efficiency. A larger scale liquid/solid centrifugal separator with a wheel hub volume of 150 L is recommended to be installed in the RE mining area, which has a processing capacity of 1200 m^3 leaching liquor of the ion-absorption RE minerals per day. For a lower occupied area of the equipment, it may be installed on a removable mining truck to reduce the construction cost of the mining enterprise.

The stripping experiments were carried out in flasks at a liquid/solid phase ratio of about 1/2.7. After heating a mixture of the solid RE complexes and 5.5 mL of concentrated HCl up to 100 °C, high concentration of 213.0 and 201.7 g L^{-1} RE solutions were obtained. Then, the extractants were washed using 10 mL of deionized water to remove the entrained RE ions. The total stripping rates were calculated as 100.0% and 99.2% in Process-I and II, respectively. Water solubilities of the solid extractants in the raffinate solutions were tested to be lower than 32.8 ppm at 25 °C and their mass losses were calculated to be 0.6% during the SCCS processes. Enrichment factors of the RE elements were calculated to be 450 and 426 times through process I and II, respectively. Detailed material balance calculations of the RE elements are shown in Table 3. The high concentration RE solution with the purity of 96.9 wt% can be directly used as the feed solution for the workshop of individual RE separation. To avoid the diffusion of volatile hydrochloric acid into the atmosphere, an absorption device is urgently needed in the stripping section when the mixture is heated to 100 °C. Acid mist absorbers made of glass fiber reinforced plastics (FRP) are recommended to ensure the waste gas after purification to meet the requirements of the Rare Earth Industrial Pollutant Discharge Standard of China (GB26451-2011, HCl < 60 mg m^{-3}).

Table 3 Material balance calculation of RE during the SCCS process

	Procedure	C_{RE}, g L^{-1}	m, g/or V, mL	m_{RE}, g	Material balance, %	Precipitation rate/stripping rate, %
Process-I						
Extraction section	Feed	0.473	2000	0.946	(100)	95.6
	Raffinates	0.0209	2000	0.0418	4.42	
Stripping section	Solid complex	0.0615	14.7	0.904	(100)	101.4
	Stripping solution	213.0	4.2	0.895	99.0	
	Washing solution	2.16	10	0.0216	2.39	
Process-II						
Extraction section	Feed	0.473	2000	0.946	(100)	95.5
	Raffinates	0.0215	2000	0.0430	4.50	
Stripping section	Solid complex	0.061	14.8	0.903	(100)	99.1
	Stripping solution	201.7	4.2	0.847	93.8	
	Washing solution	4.82	10	0.0482	5.34	

The extractant can be regenerated and the raffinate solution containing 7.23 and 8.26 g L^{-1} $(NH_4)_2SO_4$ can be recycled by adding 20 g L^{-1} $(NH_4)_2SO_4$; the leaching test with the recycled $(NH_4)_2SO_4$ is also shown in Fig. 9(b). The leaching of the RE elements from the ion-absorption RE minerals using the regenerated raffinate solution containing $(NH_4)_2SO_4$ also abides by the inner-diffusion-controlled law and shows a linear relationship between $1-2/3\alpha-(1-\alpha)\ 2/3$ and the leaching time. The regenerated POAA was characterized by IR spectrocopy and elemental analysis. As shown in Fig. 11, the characteristic peak at 1743 cm^{-1}, which was assigned to the stretching vibration of C=O in COOH, is consistent with the molecular structure before and after the SCCS process. Elemental analysis was also conducted and the results indicate that there was no evident change in the carbon and hydrogen contents when the POAA was regenerated. When compared to the commonly used RE precipitation processes using $H_2C_2O_4$ and NH_4HCO_3, the reuse of the extractant also reveals the potential to reduce production costs.

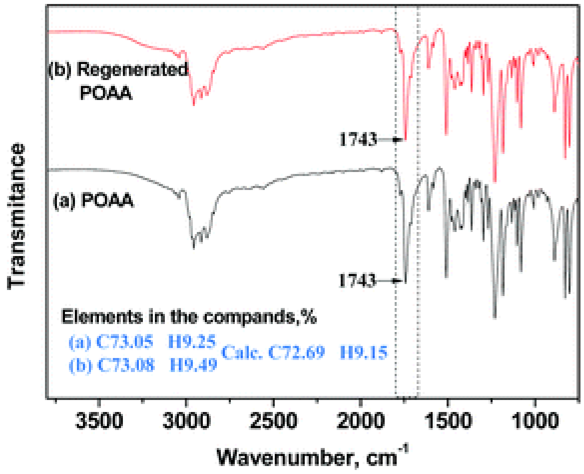

Fig. 11 IR spectra of (a) POAA before SCCS and (b) regenerated POAA.

4 Conclusions

This article presents an efficient and sustainable procedure for the enrichment of trace RE elements from the leaching liquor of ion-absorption minerals *via* a solid complex centrifugal separation (SCCS) process using *p*-*tert*-octyl phenoxy carboxylic acid derivatives as the solid extractants. Because of the higher symmetry of their alkyl chains, the developed extractants easily formed solid complexes with the RE ions, resulting in the excellent separation performance of the solid phase and aqueous phase. When compared to the time required for attaining extraction equilibrium through the liquid–liquid centrifugal extraction (LLCE) method, the extraction equilibrium through SCCS method was achieved 8 times faster. Furthermore, pilot tests were carried out to verify the SCCS method for the enrichment of trace RE elements in the leaching liquor from ion-absorption RE minerals. In the precipitation and stripping sections, the precipitation rate and stripping rate reached more than 95.5% and nearly 100% at a liquid/solid phase ratio of 200/1 and 1/2.7, respectively. Enrichment factors of the RE elements reached 450 and 426 times when the solid extractants were saponified using NaOH and $NH_3 \cdot H_2O$, respectively. Residual RE and extractant concentrations of the final raffinates decreased to less than 0.021 g L^{-1} and 32.8 ppm, respectively. A high concentration of RE solution (>200 g L^{-1}) was obtained with a purity of 96.9 wt%, which can be used as feed solution for the individual RE separation. Both the extractant and raffinate solution can be regenerated for recycling RE enrichment and leaching, which conform to the trends of green processes. No volatile diluent, rapid equilibrium, non-emulsifying, larger liquid/solid phase ratio and larger sizes of RE precipitates are advantages of the proposed SCCS process. This process combined with centrifugal equipment can greatly improve the production efficiency and reduce the cost for the ion-absorption RE minerals separation industry. Moreover, the extractants POAA, POPA and POBA revealed better precipitation abilities for light RE (*i.e.*, Pr, Nd, Sm), which indicate the promising applications of SCCS for the recovery of Sm from waste Sm-Co permanent magnet or Nd, Pr and Dy from end-of-life NdFeB magnet. More investigations on the developed SCCS processes for RE mining and secondary resource recycling are underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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