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Extraction and Recovery of Cerium from Rare Earth Ore by Solvent Extraction

Kai Li, Ji Chen and Dan Zou

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Abstract

Rare earth elements are widely found in many minerals, some of which, such as bastnaesite, monazite, and xenotime, are of great commercial value. Cerium (Ce) is the rare earth element with the highest content in light rare earth ore. Solvent extraction is the most effective and efficient method to recover and separate Ce from other light rare earth elements. After acid leaching of rare earth minerals, leaching solution was obtained, and cerium oxide of products of high purity was obtained by extraction and stripping. It is well known that Ce(IV) can be easily separated from the other RE(III) by adopting the traditional solvent extraction. Based on this principle, the clean process of oxidation roasting and Ce(IV) separation for Sichuan bastnaesite was developed. And then, a preliminary flow sheet of two-step oxidation and extraction of Ce(IV) for Bayan Obo mixed rare earth ores was further proposed.

Keywords: cerium oxide, solvent extraction, rare earth ore, complexation

1. Introduction

Rare earth (RE) elements exist in a variety of minerals, some of which, such as bastnaesite, monazite, and Bayan Obo mixed rare earth ores, are of great significance and commercial value [1–3]. As for the rare earth resources in the world, bastnaesite deposits in China and the United States account for the largest proportion. The carbonatite-hosted bastnaesite deposits at Mountain Pass, the bastnaesite deposits in Sichuan Province, and the large deposits in Bayan Obo area are the most noteworthy deposits. Monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the United States are the second largest

deposits [4–8]. The Bayan Obo mixed rare earth ores, which is mainly composed of bastnaesite and monazite, is the largest light rare earth resource in the world [3, 9]. The Bayan Obo deposit is actually the tailings of the iron ore processing scheme of Fe-RE-Nb deposit [10, 11].

Cerium (Ce) is the RE element present in the highest concentration in light RE ores, $CeO_2/\sum REO$ reaches 50% in bastnaesite ($REFCO_3$), while $CeO_2/\sum REO$ is approximately as high as 45–50% in monazite ($REPO_4$) [12]. **Table 1** gives the chemical compositions of different light RE concentrates [12]. Cerium atoms' electronic configuration is $[Xe]4f^15d^16s^2$. Losing two 6s electrons and one 5d electron, it forms the most common Ce(III). Ce(III) has the tendency to lose electron to become $4f^0$ and forms Ce(IV) [13]. Ce(IV) can exist stably in the aqueous solution because of the lowest standard electrode potential of Ce(IV)/Ce(III) [14]. Ce(IV) exhibits a markedly different chemical behavior compared to other RE(III). The use of the variable valence properties of cerium and its stable structure is of great significance in RE separation [15]. Solvent extraction is reported to be one of the most effective techniques to extract Ce(IV) [16]. When Ce(III) was oxidized into Ce(IV), it can be easily separated from RE(III) because of high separation factor values of Ce(IV) to Th(IV) (>100) and RE(III) (>600) [17].

Compared with other rare earth elements, Ce(IV) has strong complexation and coordination ability because of its small ionic radius [18]. Ce(IV) can form stable complexes with F^-, NO_3^-, HSO_4^-, and $H_2PO_4^-$ in solution, which are easy to be extracted by organic extractants [19–21]. Utilizing complex properties of Ce(IV) with these anions, the recovery of Ce and these associated resources from rare earth ore by solvent extraction can be realized.

A number of extractants such as acidic organophosphorus extractants [22–27], neutral organophosphorus extractants [28–36], amines [37], bifunctional ionic liquid extractants (Bif-ILEs) [38–40], and others [41–48] have been used for the extraction and separation of Ce. When Ce was extracted into organic phase, pure cerium solution can be obtained by stripping, and then cerium products can be obtained by adding ammonium carbonate, oxalic acid, ammonia water, and so on. The high purity cerium oxide can be produced by calcination of these cerium products.

In China, there are three main RE ores, about 80% mixed RE ores in Bayan Obo, 10% bastnaesite in Sichuan and Shandong, and 2.9% ion adsorption ores in South of China. Bayan Obo ores, the largest light rare earth sources in the world, are known as the most refractory rare earth minerals for processing due to the complicated mineral structures and compositions [49]. There are 7–8% fluorine element (F) and 4–6% phosphorus element (P) in Bayan Obo mixed RE ore [15]. The classical process of decomposing mixed RE concentrate by roasting with concentrated sulfuric acid at a high temperature cannot recover F and P, which could cause environmental pollution and waste of resources [50]. Our group proposed a process for Bayan Obo mixed RE

	REO	$CeO_2/\sum REO$	F	P_2O_5
Bayan Obo mixed ore	60%	50%	7–8%	6–7%
Bastnaesite (Sichuan)	60%	50%	8–10%	
Monazite (Guangdong)	55–65%	45–50%		25–30%

Table 1. Chemical compositions of different light RE concentrates.
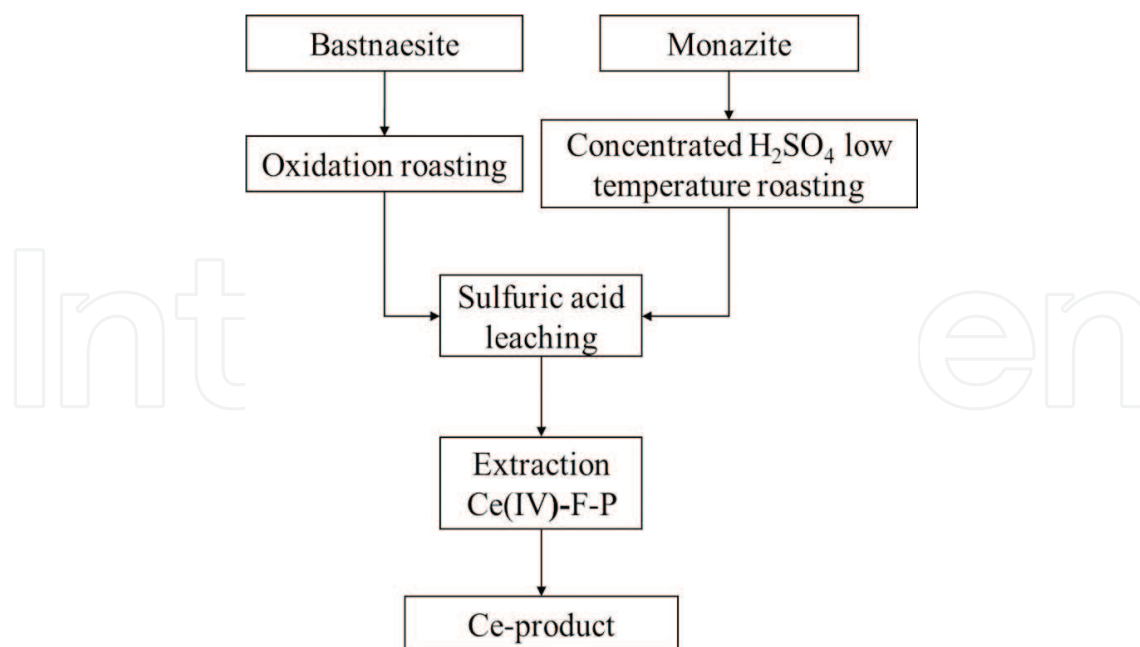
Figure 1. Oxidation and separation of Ce(IV) [18].

ore by utilizing the property of valence change of cerium. The diagram of this process is shown in **Figure 1**. When Ce(III) was oxidized to Ce(IV), F(I) and P can be easily recovered from leaching liquor by solvent extraction in virtue of the complex properties of Ce(IV) with F(I) and P [18]. After extraction, Ce products can be obtained by reductive stripping.

2. Aqueous chemistry of Ce(IV)

2.1. Ce(IV) in aqueous solution

Ce is the only lanthanide element that can form stable molecular complexes in the +4 oxidation state. The stability of the +4 state of cerium is attributed to the $4f^0$ electron configuration [51]. However, much less is known about the properties of Ce(IV) aqueous species than those of Ce(III). For example, the hydration structure of Ce(II) has been extensively studied by many methods [52–58]. In most cases, it is a part of the systematic study of the trivalent rare earth series. In contrast, even for the simplest aqua species of purely hydrated complex, there is little success in the identification of Ce(IV) aqua complexes in solution. In fact, in the scientific literature, Ce(IV) aqua species are often described only as "Ce(IV)" or "Ce(IV) complex," without specifying their chemical species or composition, simply because of a lack of information [59]. Moreover, because of their high electric charge, Ce(IV) has a strong tendency toward hydrolysis in aqueous solution and undergoes polynucleation or further, leading to colloid formation [60]. Several precedent studies have also implied the formation of soluble polymeric species with oxo- and/or OH-bridging [61]. Based on an extended X-ray absorption fine structure (EXAFS) study and density functional theory (DFT) calculations, Ikeda-Ohno et al. have demonstrated that the Ce(IV) ion in perchloric acid exists in the form of oxo-bridged dimer (**Figure 2**) [59].
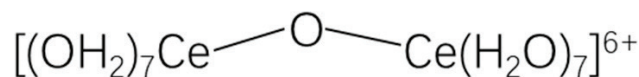
Figure 2. A proposed structure of the cationic dinuclear Ce(IV) species present in perchloric acid.

Using synchrotron X-ray and Raman spectroscopies and EXAFS, Ellis et al. also found that in strong acidic nitrate solution, ammonium ceric nitrate is a dinuclear Ce(IV) complex with a bridging oxo ligand, formulated as $[(H_2O)_x Ce^{IV}-O-Ce^{IV}(OH_2)_x]^{6+}$ (x = 6 or 7) [62]. On the contrary, the present quantum chemical calculations confirm that the Ce^{4+} coordination number is 9 and the relative free energies of Ce^{4+} is the 10- and 8-coordinate isomers in aqueous solutions.

2.2. Ce(IV) complexes with anions in aqueous solution

Ce(IV) is unstable in perchloric acid aqueous solution because its standard electrode potential in perchloric acid aqueous solution is 1.61 V [19]. Therefore, when water decomposes and releases oxygen, Ce(IV) would be slowly reduced to Ce(III). In addition, Ce(IV) is very easy to hydrolyze and polymerize like other tetravalent cations. It is necessary to maintain high acidity in the medium to avoid it. Due to these difficulties, the data of the stability constants of Ce(IV) complexes are very scarce.

Although the studies on nitrato-cerium complexes started earlier, there is contradictory information about these complexes in the relevant literature [63–66]. It was found by potentiometric method that when $[NO_3^-] < 3.2$ mol/L, there was only one complex in the form of $Ce(NO_3)^{3+}$ in nitric acid aqueous solution [67]. The other two methods, the spectrophotometry and the extraction method, indicate that the ligand number of nitrato-cerium complexes may vary from 1 to 6. The distribution of Ce(IV) species in aqueous media was studied by measuring the total optical absorbance of Ce(IV) species in different nitric acid-perchloric acid mixture solutions. The stability constants of the nitrato-cerium complexes were determined spectrophotometrically [67].

There are considerable evidences of complex formation between ceric ions and sulfate ions in aqueous solution. Jones et al. have measured the migration in high sulfur concentration solutions and found that the color migrated to the anode. Some researchers [68–70] have measured the electromotive force of the cerium sulfuric acid solution; the results show that a complex is certainly formed, but its nature cannot be determined clearly. Besides, evidence for complexing has been found by Moore et al. [71] from kinetic studies on the reaction of Ce(IV) with arsenite ions. The first complex of Ce(IV) and sulfate in perchloric acid solution was studied by spectroscopic method [72]. The results show that the instability constant of the first complex varies with the concentration of total Ce(IV) ion plus sulfate and a higher complex was also found in this system. Hardwick et al. [73] made a spectral study on the association of Ce(IV) with sulfate. The results show that Ce(IV) interacts with one, two, and three sulfate ions in turn to form complexes. As is expected, as the number of sulfate ions in the complexes increases, the trend of association becomes smaller. Nevertheless, there were no higher complexes of more than three sulfate complexes with Ce(IV).

The stability constants of the fluoride complexes of cerium(IV) in 1 M (HClO$_4$, NaClO$_4$) medium have been measured potentiometrically using a fluoride ion-selective electrode. This procedure ensures the stability of the oxidation state and prevents hydrolysis and polymerization of Ce(IV). Logarithms of the average values of ß$_1$, ß$_2$, ß$_3$, and ß$_4$ were estimated to be 7.57 ± 0.04, 14.50 ± 0.03,

20.13 ± 0.37, and 24.14 ± 0.10, respectively [19]. Besides, in sulfuric acid medium, Qiao studied the complexation behavior of fluorine (I) with Ce(IV). The results show that Ce(IV) and F(I) could form a stable complex in the form of $[CeF_2^{2+}]$ and logarithm of the average values of ß was 10.67 [20].

3. Solvent extraction of Ce(IV)

Many extractants have been reported and applied in nitric acid and sulfuric acid for Ce(IV) extraction, for example, acidic organophosphorus extractants [22–27], neutral organophosphorus extractants [28–36], amines [37], and bifunctional ionic liquid extractants (Bif-ILEs) [38–40]. Among them, tributyl phosphate (TBP), di-(2-ethylhexyl) 2-ethylhexyl phosphate (DEHEHP), di-(2-ethylhexyl) phosphate (P204), 2-ethylhexylphosphoric acid mono 2-ethylhexylester (P507), and Cyanex 923 are the most commonly used extractants for Ce(IV) extraction (listed in **Table 2**). Synergistic extraction [26, 35] is also an important method to enhance the extraction efficiency. It was reported that P204 + P507 and P204 + Cyanex 923 had synergistic extraction effects for Ce(IV) extraction from sulfuric acid medium.
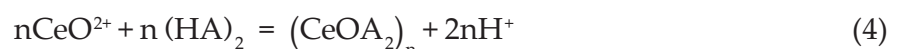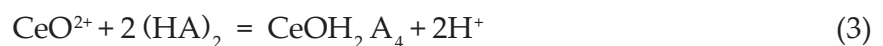
3.1. Acidic organophosphorus extractants

Several acidic organophosphorus extractants [22–27] were used to extract cerium(IV); among these extractants, P204 or P507 is a great extractant for Ce(IV) with a high capacity, extraction efficiency, and selectivity. Peppard et al. studied the extraction of Ce(IV) from HNO_3 solution with P204 in 1957. Tedesco et al. studied the extraction of cerium in kerosene from sulfuric acid solution by di(2-ethylhexyl) phosphate (P204, HA). The effects of DEHPA concentration and pH on the extraction of cerium were determined. However, the mechanism of extraction of Ce(IV) by P204 is not clear. Tedesco et al. considered that the possible extraction mechanism is as follows [22]:

When pH < 1.0

$$Ce^{4+} + 4\,(HA)_2 = CeH_4A_8 + 4H^+ \tag{1}$$

$$nCe^{4+} + 2\,(HA)_2 = (CeA_4)_n + 2nH^+ \tag{2}$$

when pH = 1.7–2.0

$$CeO^{2+} + 2\,(HA)_2 = CeOH_2A_4 + 2H^+ \tag{3}$$

$$nCeO^{2+} + n\,(HA)_2 = (CeOA_2)_n + 2nH^+ \tag{4}$$

When the R-O group in dialkyl phosphoric acid molecule is replaced by R group, such as P507, its pKa value increases and its acidity increases. The distribution ratio of rare earth elements extracted by P507 is lower than that of P204. Li et al. [24] have studied the separation of Ce(IV) with P507 in nitric acid system and sulfuric acid system. The mechanism of extraction of Ce(IV) in sulfuric acid system by P507 is as follows:
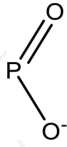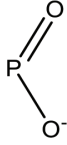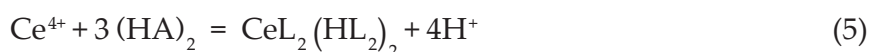
	Extractants	Functional group	Ref.
Neutral organophosphorus	TBP	P=O	[15]
	DEHEHP		[28, 29]
	Cyanex 923		[30–34]
Acidic organophosphorus	P507		[25, 26]
	P204		[23, 24]
Amines	N1923	RNH$_2$	[37]
Bif-ILs	[A336][P507]		[39]
	[A336][P204]		[38]

Table 2. The commonly used extractants for Ce(IV) extraction.

Low acidity:

$$Ce^{4+} + 3\,(HA)_2 \;=\; CeL_2\,(HL_2)_2 + 4H^+ \tag{5}$$

High acidity:

$$Ce^{4+} + 2HSO_4^- + SO_4^{2-} + (HL)_2 \;=\; H_2Ce\,(SO_4)_3 \bullet 2HL \tag{6}$$

However, it is difficult to extract F$^-$ from sulfuric acid solution by P204 and P507 [30]. The addition of boric acid and other masking agents eliminates the effect of F$^-$ [74], which would introduce impurities and increase cost.

### 3.2. Neutral organophosphorus extractants

Neutral organophosphorus extractants were applied widely in recently years for Ce(IV) extraction. Tri-butyl-phosphate (TBP) was used to recover Ce(IV) from high acidic HNO$_3$ solutions by adding an appropriate quantity of H$_3$BO$_3$, and high-purity CeO$_2$ was recovered [75]. However, high extraction acidity and severe co-extraction of mineral acids make TBP extraction of Ce(IV) not superior. Besides, a low extraction efficiency was also a serious problem for Ce(IV) extraction compared with others. Therefore, a new extractant named di-(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP) was used to extract and recover Ce(IV) from HNO$_3$ solution by Li's group [28, 29]. However, a low extractability and a low loading capacity limit the application of this extractant. In addition, the problem of reduction of cerium(IV) in DEHEHP extraction was also a challenge. Because of its low solubility in aqueous phase, liable hydroxylation, high miscibility with ordinary organic diluents, and low extraction acidities compared to other neutral organophosphorus extractants,

Cyanex 923 (a mixture of straight-chain alkylated phosphine oxides) is considered to be the most used extractant in Ce(IV) extraction [76].

In recent years, our group has used extractant Cyanex 923 to extract and separate Ce(IV) from nitric acid system and sulfuric acid system. Lu et al. [30, 31] studied the extraction and separation of Ce(IV), Th(IV), RE(III), and Fe(III) from sulfuric acid system by Cyanex 923. The experimental results show that the order of extracting metal ions in H_2SO_4 media was Ce(IV) > Th(IV) > RE(III) > Fe(III).

Liao et al. had studied the thermodynamics and kinetics of Cyanex 923 extraction of Ce(IV) from the liquor of bastnaesite in detail. The results showed that Cyanex 923 could effectively extract Ce(IV) from sulfuric acid system. The extraction mechanism was as follows:

Cyanex 923 extracts Ce(IV) from a sulfuric acid solution without fluorine:

$$Ce^{4+} + SO_4^{2-} + 2HSO_4^- + 2Cyanex\ 923 = Ce(SO_4)(HSO_4)_2 \bullet 2Cyanex\ 923 \qquad (7)$$
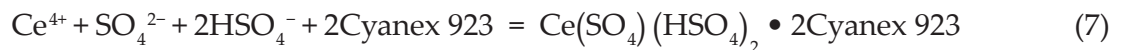
Cyanex 923 extracts Ce(IV) from a sulfuric acid solution with fluorine:

$$Ce^{4+} + HF + SO_4^{2-} + 2HSO_4^- + 2Cyanex\ 923 = Ce(HF)(SO_4)(HSO_4)_2 \bullet 2Cyanex\ 923 \qquad (8)$$
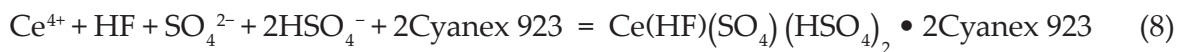
Li et al. studied the extraction and recovery Ce(IV) from nitrate solutions by Cyanex 923. The extraction mechanism was as follows:

Without fluorine:

$$Ce^{4+} + 4NO_3^- + 2Cyanex\ 923 \rightarrow Ce(NO_3)_4 \bullet 2Cyanex\ 923 \qquad (9)$$

With fluorine:

$$Ce^{4+} + 4NO_3^- + F^- + H^+ + Cyanex\ 923 \rightarrow Ce(HF)(NO_3)_4 \bullet Cyanex\ 923 \qquad (10)$$
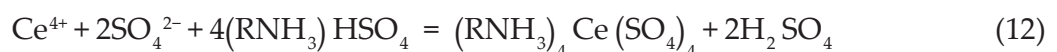
3.3. Amines extractants

The mechanism of extracting Ce(IV) from sulfuric acid solution with primary amine extractant N1923 was studied by Li et al. It was found that the mechanism of extraction of Ce(IV) by N1923 had a great relationship with acidity.

Low acidity:

$$Ce^{4+} + 2SO_4^{2-} + 2(RNH_3)_2 SO_4 = (RNH_3)_4 Ce(SO_4)_4 \qquad (11)$$

High acidity:

$$Ce^{4+} + 2SO_4^{2-} + 4(RNH_3)HSO_4 = (RNH_3)_4 Ce(SO_4)_4 + 2H_2SO_4 \qquad (12)$$
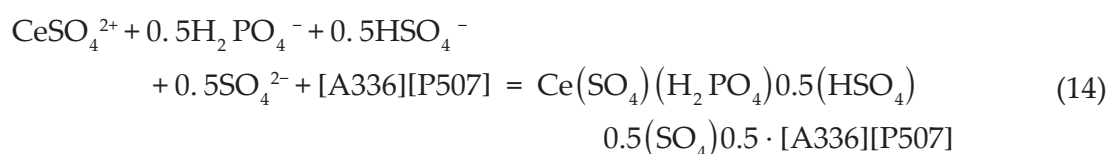
3.4. Bifunctional ionic liquid extractants

In recent years, quaternary ammonium salts have been widely used in ionic liquids, including surfactants, extractants, catalysis and biodegradation, and many other fields [77–79]. Common ionic liquids are divided into four categories, including imidazole, pyridines, quaternary ammonium salts, and quaternary phosphine salts [80]. Among them, ammonium and phosphorus ionic liquid extractants were investigated in REs separation because of this low price and little toxicity [81]. The neutral complexation mechanism of Bif-IlEs has higher extractability and selectivity, and lower acid and base consumption and no emission of ammonia, nitrogen, Na^+ or Ca^{2+} wastewater.

A series of high purity quaternary ammonium salt ionic liquids ([A336][P507], [A336][P204], [A336][C272]) have been synthesized by Chen's team using the simple and efficient acid-base neutralization method. The synthetic route is given in **Figure 3** [82].

[A336][P507] as shown in **Figure 4** can be used for the separation of Ce(IV) from sulfuric acid solution [39]. Zhang has studied the extraction equilibrium of Ce(IV) from sulfuric acid by using [A336][P507], the extraction mechanism was as follows [39]:

$$Ce^{4+} + SO_4^{2-} + 2HSO_4^- + 2[A336][P507] = Ce(SO_4)(HSO_4)_2 \bullet 2[A336][P507] \tag{13}$$

Zhang [21] has investigated the extraction of Ce(IV) in H_2SO_4/H_3PO_4 system [42]. The possible extraction equilibrium is shown in Eq. (5):

$$\begin{aligned} CeSO_4^{2+} + 0.5H_2PO_4^- + 0.5HSO_4^- \\ + 0.5SO_4^{2-} + [A336][P507] = Ce(SO_4)(H_2PO_4)0.5(HSO_4) \\ 0.5(SO_4)0.5 \cdot [A336][P507] \end{aligned} \tag{14}$$

3.5. Synergistic extraction system

Synergistic extraction is an important method to enhance the extraction efficiency [26, 35] and has been applied for the extraction and separation of rare earths [83]. Recently, Li et al. have reported the synergistic extraction of lanthanum and Y using a mixture of Cyanex 272(BTMPPA) and 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) [84]. Sun et al.
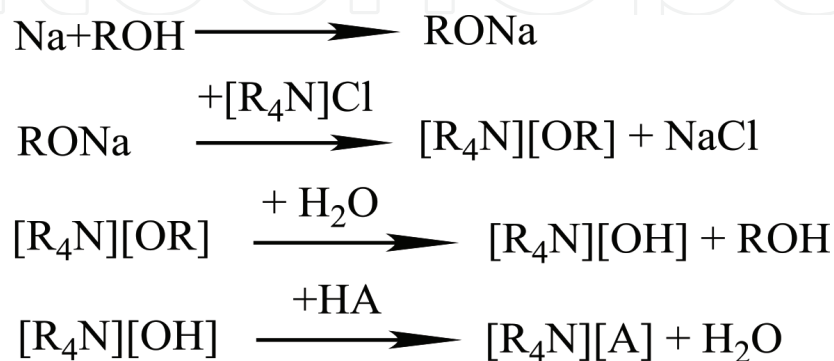
$$Na + ROH \longrightarrow RONa$$

$$RONa \xrightarrow{+[R_4N]Cl} [R_4N][OR] + NaCl$$

$$[R_4N][OR] \xrightarrow{+H_2O} [R_4N][OH] + ROH$$

$$[R_4N][OH] \xrightarrow{+HA} [R_4N][A] + H_2O$$

Figure 3. Synthesis route of quaternary ammonium salt bifunctional ionic liquid extractant [82].
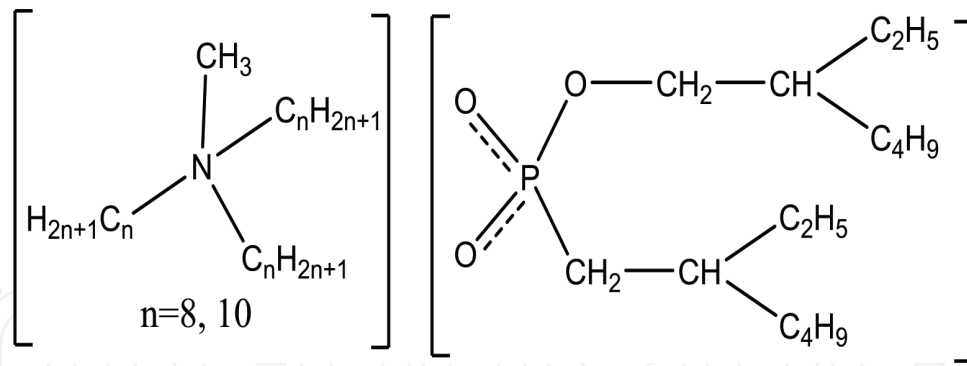
Figure 4. Chemical structures of [A336][P507].

have found the enhanced extraction and separation of yttrium from heavy rare earth using BTMPPA (Cyanex 272) and bis(2,4,4- three methyl amyl) phosphoric acid (CA-12) [85]. In addition, Reddy et al. have studied the synergistic extraction of rare earth elements by Cyanex 923 and Cyanex 301 [86]. These findings have contributed to the study of a new mixed system using Cyanex 923 as an extractant to recover Ce(IV).

Li et al. [35, 36] reported the extraction of Cyanex 923 + P204 for Ce(IV) in sulfuric acid system. The experimental results show that Cyanex 923 + P204 has a positive correlation with the extraction of Ce(IV) solution. The largest synergistic coefficient of Ce(IV) is obtained at the mole fraction $X_{Cyanex\ 923} = 0.8$. The synergistic enhancement coefficients (R_{max}) obtained for Ce(IV) are 23.12 in Ce(IV) solution. The synergistic extraction can be expressed as

$$Ce\left(HSO_4\right)_4 + (HA)_2 + 1.5B = Ce\left(HSO_4\right)_2 A_2 \cdot 1.5B + 2H^+ + 2HSO_4^- \tag{15}$$
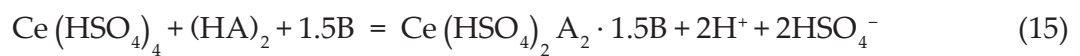
The synergistic extraction of cerium(IV) from sulfuric acid medium using a mixture of 2-ethylhexyl phosphoric acid mono 2-ethylhexyl ester (HEH/EHP, HL) and Di-(2-ethyl hexyl) phosphoric acid (HDEHP, HA) as extractants was studied [26]. The results showed that HEH/EHP = 0.6 was extracted as an organic phase in the form of $Ce(SO_4)0.5HL_2A_2$. The synergistic extraction reaction is as follows:

$$Ce^{4+} + 0.5SO_4^{2-} + H_2L_2 + H_2A_2 = Ce\left(SO_4\right)_{0.5} HL_2 A_2 + 3H^+ \tag{16}$$

4. Preparation of Ce product

Cerium and its compounds are widely used in many fields. For example, monocrystalline CeO_2 due to its excellent redox ability has an important application value in the fields of CO catalytic oxidation, organic synthesis catalysis, photocatalysis, biological oxidation resistance, and so on. Generally speaking, the preparation of Ce products can be divided into two main methods: one is the sulfuric acid double salt precipitation method and the other is the method of solvent extraction. The process of sulfuric acid double salt precipitation is as follows:

Sulfuric acid rare earth solution containing Ce(IV) → reduces Ce^{4+} to form Ce^{3+} → NaOH base decomposition → HCl solubilization → Oxalic acid precipitation → Calcination.

However, the process of this method is long; there are many steps of solid-liquid separation, the yield of rare earth is low (65–67%) and the purity of CeO_2 product is low (95–99%). In addition, the associated resources such as F, P, and Th in sulfuric acid leach liquor were not recovered effectively, resulting in waste of resources and radioactive pollution. In contrast, however, solvent extraction has many advantages. The loaded organic phases could be used to prepare nano-size CeF_3 and $CePO_4$ by reductive stripping.

Our group developed a method to prepare high-purity CeF_3 nano-powder. This method was to extract from the sulfuric acid liquor of bastnaesite to obtain the loaded organic phase firstly, and then the CeF_3 can be obtained by reduction stripping used H_2O_2. The purity of CeO_2 can be reached to 99.99% [87]. The preparation of $CePO_4$ nanoparticle was also invented by our group. This method was to extract Ce(IV) by [A336][P507] in H_2SO_4/H_3PO_4 system, and then the $CePO_4$ can be obtained by reduction stripping also using H_2O_2 [26].

5. Conclusions and outlook

Based on the introduction of solution chemistry and extraction chemistry of cerium(IV) and preparation of cerium products, the mechanism, methods, and objectives of extraction and recovery of cerium from rare earth ore are described in detail in this chapter. It is of great significance to make use of the changeable valence properties and the strong complexation and coordination ability of Ce^{4+} in REs separation. The cerium in rare earth ores can be efficiently oxidized to Ce(IV) and can be separated and recovered by solvent extraction easily. According to these studies, Li and our group established an important process to recover Ce(IV) by Cyanex 923 from rare earth ore. The Ce(III) in rare earth ore can be effectively oxidized into Ce(IV) by oxidizing roasting Baotou mixed rare earth ore. The complexation property between Ce(IV) with F and/or P in acidic solution can help to separate and recover Ce(IV), F, and P by solvent extraction. This invention can realize the comprehensive utilization of resources and avoid resource waste and environmental pollution by utilizing the associated resources of the Baotou rare earth ore to recover the Ce. It also provides a convenient condition for the subsequent separation of Th and other RE(III). More efforts on the studies of mechanism, process intensification, and equipment will be needed in the future.

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