Solvent extraction of cerium from various solutions by organophosphorus-based extractants: a review

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ABSTRACT

Cerium has numerous applications in the high-tech industries. In addition to the rise in demand for rare earth elements (REEs) in various end-user industries, the market for cerium is growing. It is important to recover cerium from main sources such as REEs bearing ores or relevant sources such as wastewater, spent catalysts, etc., to acquire metal concentration and preserve the environment from hazard. Solvent extraction is a substantial method for the extraction of REEs and cerium over other techniques in hydrometallurgical technologies. In this review, the solvent extraction approaches for the extraction and recovery of cerium from sulfate, the factors which affect the process of extraction. The pH, extractant, metal ion concentration, temperature, organic to aqueous (O/A) ratio, extraction, and stripping kinetics have been considered to achieve optimal conditions for the recovery process. The research findings demonstrate the potential of extraction and isolation of cerium from various solutions using organophosphorus, cationic, solvating, or mixed extractants having other metallic ions.

Keywords: Cerium; Solvent extraction; Organophosphorus extractants

1. Introduction

Rare earth elements (REEs) are comprised of yttrium (^{39}Y), lanthanum (^{57}La), scandium (^{21}Sc), and the other 14 elements after lanthanum in the periodic table of elements, i.e., from cerium (^{58}Ce) to lutetium (^{71}Lu) as scandium and yttrium are present in REEs mineral deposits as the lanthanides and exhibit similar chemical features [1].

REEs play an important role in the high-tech industries due to their outstanding optical, magnetic, acoustic, catalytic, and electrical characteristics, and due to their rapid growth demands. The separations of REEs from their primary and secondary resources become more critical and significant. On the other hand, lanthanides' biological implementations are considered to be important, relying on their similarity to calcium [2].

Cerium finds numerous applications in NiMH batteries, agents for polishing, as a glass component, coating for car, light emitting diode, liquid crystal display backlights, plasma screens, and added to aluminum to increase the corrosion resistance of aluminum. In catalytic converters and large-scale devices, cerium oxides and other cerium substances are being used to decrease sulfur oxide emissions in the petrochemical industry. They have the capability to oxidize carbon monoxide and O_3 to carbon dioxide and oxygen, which is much less expensive than Pt group metal alternatives in automotive. Cerium is a diesel fuel ingredient for encourages complete combustion of fuel for more energy performance [3–5].

Cerium (2nd element in the lanthanide group) is the most widespread in light rare earth (RE) minerals since it reflects about 50% in bastnaesite (La, Ce)FCO_3 and 45%–50% in monazite (Ce, La, Y, Th)PO_4 along with phosphate rocks and it is chemically featured by possessing two stable valence states (III and IV) [6]. Table 1 indicates the chemical compositions of various REE concentrates [7].

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Table 1
Chemical composition of various REE concentrates

Ores	REO (%)	CeO$_2$/∑REO (%)	P$_2$O$_5$ (%)	ThO$_2$ (%)
Bayan Obo mixed ores	60	50	6–7	0.2–0.3
Bastnaesite (Sichuan)	60	50	—	0.2–0.3
Monazite (Guangdong)	55–65	45–50	25–30	1–3
Xenotime (Guangdong)	50–55	—	30.6	0.4

Because of their identical chemical characteristics, the isolation of REEs is a challenging task. In this regard, separation approaches have been designed depend on solvent extraction approaches to generate high-grade solutions of single REEs or compounds [8].

In this review, the recovery of cerium from the various aquatic environments such as SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-}, and SCN^- applying various organophosphorus extractants was tested. Findings of the distribution coefficient, development of the formed complex in the organic phase, and kinetics are being characterized for insights into the mechanisms of extraction and processes development from various aqueous solutions of different resources.

1.1. Solvent extraction

Extraction using a solvent is determined by the difference in the solubility in two immiscible liquid phases between the pure elements and their compounds. Solvent extraction is usually fast, simple, less expensive, and demands only very simple equipment. It lends itself to multi-stage operation without increased consumption of heat and chemicals which make it particularly useful when either extreme purification is necessary or when the metals are so similar in their properties that a single precipitation or crystallization would not give the required degree of separation [9,10].

The ratio of distribution (D) was evaluated from the following Eq. (1):

$$D = \frac{(C_0 - C_e)V_a}{C_e V_0} \qquad (1)$$

where C_0 and C_e are the original and equilibrium concentration of metal (mg/L), respectively. V_0 and V_a are the volume of organic and aqueous phase, where the separation factor is given by Eq. (2):

$$\beta = \frac{D_1}{D_2} \qquad (2)$$

Solvent extraction is stated to be among the most successful approach to recovery cerium(IV), which make it facile from other REEs. Hence, the recovery of Ce(IV) is thoroughly studied to adjust the processes of solvent extraction.

2. Organophosphorus-based extractants

The extractants containing organophosphorus are normally applied for the solvent recovery of cerium as di-(2-ethyl-hexyl)phosphoric acid (DEHPA or D2EHPA), PC 88A, a purified 2-ethyl-hexyl hydrogen 2-ethyl-hexyl phosphonate, HEH(EHP), and di-2,4,4-tri-methyl-pentyl-phosphinic acid (Cyanex 272), tri-butyl-phosphate (TBP), tri-*n*-octyl-phosphine oxide (TOPO or Cyanex 921), bis(2-ethylhexyl) ((2-ethylhexylamino)methyl) phosphine oxide (DEHAPO), Cyanex 923 [a mixture containing four tri-alkyl-phosphine oxides namely di-octyl-hexyl-phosphine oxide (≈42%), di-hexyl-octyl-phosphine oxide (≈32%), tri-hexyl-phosphine oxide (≈8%), and tri-octyl-phosphine oxide (≈14%)], Cyanex 925 (bis-(2,4,4-tri-methyl-pentyl) octyl-phosphine oxide), bis(2-ethyl-hexyl)phosphinic acid (PIA8), ethyl-hexyl-phosphonic-acid mono-2-ethyl-hexyl-ester (P$_5$O$_7$), di-(2-ethyl-hexyl)[*N*-(2-ethyl-hexyl)amino methyl]phosphonate (Cextrant-230), and tris-(2-ethyl-hexyl) phosphine oxide (TEHPO) are perhaps the most popular extractants for cerium and other REEs. Also for ionic liquids (ILs)/organophosphorus-based extractants [11].

2.1. Extraction of cerium from sulfate solution

Sulfuric acid is normally applied for leaching and disintegration of ores and concentrates as monazite, xenotime, and bastnaesite. For this purpose, the solvent extraction of many rare-earth ions from SO_4^{2-} liquors is extensively investigated. In this concern, the recovery of Ce(IV), F, and CeF_2^{2+} with di-2-ethyl-hexyl phosphoric acid (D2EHPA) + Cyanex 923 from medium containing H$_2$SO$_4$ is investigated by Zhang et al. [12]. The authors found that extracted species were found to be $Ce(HSO_4)_2 \cdot A_2 \cdot 1.5B$, HF·B, and $CeF_2(HSO_4) \cdot A \cdot 2B$, respectively; where A is D2EHPA and B is Cyanex 923, while Ce(III) is not isolated by Cyanex 923, D2EHPA or their blend under the experimental parameters, the separation factors of Ce^{4+}/Ce^{3+} amount to 1321.18, CeF_2^{2+}/Ce^{3+} amount to 36.35 was exhibited by the extractant mixture that enhances the separation processes.

Cyanex 923 was applied for the Ce(IV) and F(I) recovery from H$_2$SO$_4$ leaching of bastnaesite ore. The mechanism of the recovery Ce(IV) along with F(I) can be connected to the $Ce(HF)(HSO_4)_2(SO_4) \cdot 2$ C923 development. It is worth to mention that boric acid enhances the recovery of HF and participates in the organic layer in the form of $(HF)(H_3BO_3) \cdot C923$ whilst it has little impact on the Ce(IV) extraction [13].

The SO_4^{2-} ion can hinder the recovery of Ce(IV) remarkably during the extraction using DEHPA due to its complexation with Ce^{4+} while the existence of (F$^-$) can improve the recovery of Ce^{4+} by the production of CeF_2^{2+} and CeF^{3+} which can almost be fully recovered. It is worth to mention that if the molar ratio of F/Ce in the beginning of

the aqueous layer is approximately greater than 1.5, and the precipitation which was noted cannot efficiently progress the extraction process [14]. Isolation of the actinides from the lanthanides at an industrial level was continuous to be an important technological problem. Lu et al. reported the recovery of Ce(IV) and Th(IV) from sulfate solution, the recovery of Ce(IV) was insensitive to the solution acidity whilst the recovery of Th(IV) enhanced with the acidity of the aqueous medium using Cyanex 923 in benzene as a diluent that favored a separation between Ce(IV) and Th(IV) depending on the impact of sulfuric acid concentration. The isolation of Ce(IV) and Th(IV) from aqueous medium containing SO_4^{2-} using Cyanex 923 can be described by the following Eq. (3):

$$M^{4+} + SO_4^{2-} + 2HSO_4^{2-} + 2B^- = \overline{M(SO_4)(HSO_4)_2 \cdot 2B} \qquad (3)$$
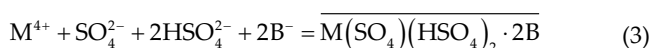
where M^{4+} assigned to Ce(IV) or Th(IV) and B referred to Cyanex 923 [15]. Khaironie et al. stated the isolation of Ce(IV), Nd(III), and La(III) using D2EHPA steaming from sulfuric acid solution. The extraction ability of the reported lanthanides by D2EHPA was reduced in the rank of La(III) < Nd(III) < Ce(IV). It is worth mentioning that the recovery of REEs by extractants containing organophosphorus improves with the increase in atomic number. While for the extractants containing amine compounds, that reduces with the increase in atomic number, i.e., the extractants containing organophosphorus and amines possess two reverse behavior patterns [16]. In this respect, the extractant combining the two moieties in one extractant will give new behavior during the extraction process of RE. In this respect, α-amino-phosphonate extractant (Cextrant-230) was reported for cerium isolation from the medium containing sulfate. The result indicate that around (92%) Ce is recovered applying 0.1 mol/L Cextrant-230 in heptane in four extraction steps, two steps of washing (I) and two steps of Ce(IV) reductive stripping [17].

Aminophosphine substance, bis(2-ethyl-hexyl) ((2-ethyl-hexyl-amino)methyl) phosphine oxide (DEHAPO), was used for the recovery of Ce(IV) from the media containing sulfuric acid. The recovery performance of Ce(IV) with DEHAPO was compared with other extractants such as P507, Cyanex 923, and Cextrant-230. The results suggest that DEHAPO displays greater recovery performance for Ce(IV) than Cextrant-230, Cyanex 923, and P507 when H_2SO_4 acid concentration is lesser than 1.0 mol/L, the recovery performance of Ce(IV), Th(IV), and REs(III) as Gd, La, Yb.

Di(2-ethylhexyl) (2-((2-ethyl-hexyl)amino)propan-2-yl) phosphonate (DEHAPP, abbreviated as B) was fabricated for the selective Ce(IV) recovery from sulfate media that possess a good recovery performance towards Ce(IV) in comparison to other neutral extractants containing organophosphorus such as Cyanex 923, DEHEHP, and Cyanex 925. The equilibrium constants and thermodynamic variables of the extraction processes were estimated. The complexes extracted were evaluated to be $H_2SO_4 \cdot B_{(org)}$ and $Ce(HSO_4)2SO_4 \cdot 2B_{(org)}$. A recovery approach was applied facially for the Ce(IV) selective recovery from bastnaesite leaching, in which the quality of cerium product attained 99.5% with a yield of 90.7% [18].

The bastnaesite leach contains 64 g/L Ce(IV), 65 g/L ΣCe, 128 g/L ΣRE, 270 ppm Th, and 0.89 ppm H_2SO_4. By five-step extraction applying DEHAPP 30% (v/v) as organic phase in normal heptane and one-step stripping applying the solution of hydrogen peroxide, the CeO_2 material with a quality of 99.5% was developed with a product of 90.7% yield where thorium amount is 0.063%. Obviously, DEHAPP would be used for the selective recovery and effective isolation of Ce(IV) from bastnaesite [19].

Di(2-ethylhexyl)-*N*-heptylaminomethylphosphonate (DEHAMP) was used for the isolation of Ce(IV), Th(IV), and RE(III) from the media containing sulfate. DEHAMP has strong extraction performance for Ce(IV) and Th(IV) due to the little steric hindrance steaming from the amino group in the form of a straight chain than that of a branched chain in Cextrant 230. The great extractability of Ce(IV) with DEHAMP remains almost constant with the increased acidity till the aqueous concentration of H_2SO_4 seems to be 4.0 ppm while the isolation of Th(IV) reduces with the increasing aqueous acidity [20]. The authors investigated the extraction of Ce(IV) and phosphorus from the sulfuric acid liquor of Bayan Obo REO minerals, using Cyanex 923 diluted in *n*-heptane. They stated that the recovery performance of Ce(IV) increases from (77%) at 0.01 ppm to (>85%) at 0.03 ppm of P where the extracted species was proved by IR and NMR studies [21].

Synergistic extraction is broadly applied to isolate and purify both lanthanides(III) and actinides [22,23]. Luo et al. reported the isolation of cerium(IV) from sulfuric acid applying a synergistic extractant composed of 2-ethyl-hexyl phosphonic acid mono-2-ethyl-hexyl ester (HEH/EHP, HL) and HDEHP (HA). The findings demonstrated that at the mole fraction of HEH/EHP = 0.6, the greatest synergistic variables were acquired, and the extracted species was determined as $Ce(SO_4)0.5HL2A2$. A cation exchange mechanism was suggested for the isolation, which was reported to be exothermic [24].

Different basic and acid extractants have been used to examine the solvent extraction of Ce(III), Th(IV), Zr(IV), and Fe(III) from the medium containing sulfate results from the leached monazite. Initially, Th(IV) was isolated with Cyanex 272 at pH = 1 followed by the separation of Fe(III) with *N*-methylaniline, finally, Zr(IV) was settled at pH = 2.5 (84%) while Ce(III) retains in the final aqueous phase [25].

ILs are known as sustainable solvents due to various unique features, such as good low flammability, thermal stability, and low vapor pressure. Still, few implementations are successful in industrial uses due to the challenging removal of metal ions or the loss of IL components. Further research to develop the extraction performance of IL-based extraction methods needs to be implemented. ILs were used in the mining, smelting, separation, and extraction of REs as eco-friendly solvents and extractors [26].

In this respect, the recovery of Ce(IV) in H_2SO_4/H_3PO_4 was evaluated by Zhang et al. [12] applying quaternary ammonium ILs such as [trialkylmethylammonium] [di-(2-ethyl-hexyl)orthophosphinate] ([A336][P507][tri-alkyl-methyl-ammonium][di-2-ethylhexylphosphinate]) ([A336][P204]), and [tri-alkyl-methyl-ammonium][bis-2,4,4-tri-methyl-pentylpho-sphinate] ([A336][C272]) in addition

to bifunctional IL extractors (Bif-ILES) [A336][P507], [A336][P204], and [A336][C272] in *n*-heptane.

The recovery performance of Ce(IV) decreases in the rank of [A336][C272] > [A336][P507] > [A336][P204]. In comparison to Bif-ILEs, the capacity of recovery with Cyanex 923 is somewhat higher than using [A336][C272], tri-*n*-butyl phosphate seems to have the least effective capacity of extracting Ce(IV). Also, they examine the recovery performance of Ce(IV), Th(IV), and trivalent RE with DEHEHP in the IL, 1-methyl-3-octylimidazolium hexafluorophosphate ([C8mim]PF6) was investigated and compared with that in the *n*-heptane system. The results show that the extraction was in the following rank Ce(IV) > Th(IV) > RE(III) in both IL and *n*-heptane [27].

Under suitable conditions the recovery of Ce(NO$_3$)$_4$ containing F(I) by DEHEHP in both *n*-heptane and IL was accomplished. The Ce(IV) may be obtained quantitatively back in the IL system and extracted as part of high quality CeF$_3$ and cerium sulfate. High grade cerium as CeF$_3$ nanoparticles or Ce(III) sulfate solution is generated using DEHEHP/IL as the extracting phase that allows recovering Ce(IV) and F(I) from bastnaesite [28].

2.2. Extraction of cerium from nitrate solution

Many authors briefly examined the recovery of cerium from the medium containing nitrate. Zhao et al. studied the isolation of Ce(IV), Th(IV), and REE(III) with DEHEHP in heptane from the solution obtained after roasting bastnaesite with Na$_2$CO$_3$ and subsequent leaching with nitric acid. The extraction percent changes in the rank Ce(IV) > Th(IV) >> REE(III). Ce(IV) was stripped using dilute H$_2$SO$_4$ containing H$_2$O$_2$. Therefore, Ce(IV) can be efficiently isolated from Th(IV) and REE(III) under the appropriate conditions [11].

The isolation of La and Ce using PC 88A from the medium containing nitrate was conducted by applying a multi-steps counter-current mixer-settler extraction column in seven steps; La was scrubbed at pH = 2.7 using nitric acid. Stripping of Ce was achieved by using 1.0 M nitric acid. The organic phase was reused without influence on the extraction performance Habibpour et al. [30] reported the recovery of Ce(III) and La(III) from the solution containing HNO$_3$ applying P204 and Cyanex 272 in the presence of kerosene. The optimal parameters for the solvent extraction of cerium from the nitrate solution using 30 mM Cyanex 272 within 20 min at pH = 6. The results demonstrate that the recovery of Ce(III) is remarkable with Cyanex 272 as compared with La(III). The extraction of Ce(III) from HNO$_3$ (10^{-3} M) using a synergistic mixture of PC 88A and Cyanex 921 in kerosene was studied. The study stated that two molecules of PC 88A and one molecule of Cyanex 921 shares in the extracted species and the recovery of cerium based on the acid concentration and existence of nitrate species in the aqueous phase. Using 0.6 M HCl or 1.2 M H$_2$SO$_4$, the Ce(III) was successfully stripped. The negative change in entropy assigned to the mixed complex formed by the binary extractant mixture with Ce(III) [31]. Ce(IV) and Th(IV) solvent extraction in kerosene from 8.0 M HNO$_3$ has been explored with a neutral extractant as TBP. The extraction performance attains 99.3% and 97.7% for cerium and thorium, respectively, applying 5% TBP in kerosene, 1:1 O/A phase ratio within 5 min. The stripping of Ce(III) and Th(IV) selectively from the loaded organic phase was attained at 1.1 M H$_2$O$_2$ [32].

The process is reported to separate the cerium from a lanthanide powder utilizing ILs.In the beginning from the Ce(III), Nd(III), La(III), and Pr(III) mixture. Initially, in alkaline conditions, Ce(III) was effectively oxidized to cerium(IV) while all other lanthanide ions existed in their third state of oxidation. The lanthanide hydroxide salts are also soluble in nitric acid solution. Productive and selective extraction of Ce(IV) from tri-hexyl-tetra-decyl-phosphonium bis(tri-fluoro-methane-sulfonyl)imide [P66614][NTf2] or 1-methyl-1-butyl-pyrrolidinum bis(tri-fluoro-methane-sulfonyl)imide [C1C4Pyrr][NTf2] was accomplished. The pyrrolidinium cation was identified to be more powerful applying [C$_1$C$_4$Pyrr][NTf$_2$] than [P$_{66614}$][NTf$_2$]. Cerium was stripped using low nitric acid concentration. Recycling of the IL was attained as the extraction of Ce(IV) was about 97% and decreased to 88% after 10 extraction stages followed by one stripping stage [33].

Zuo et al. [34] stated the recovery performance of Ce(IV) along with Th(IV) and Ln(III) (Ln = Ce, Gd, Yb) nitrate by pure IL, [C8mim]PF6, was examined. [C8mim]PF6 alone displayed superior extraction performance for Ce(IV). The Th(IV) extraction was very impoverished and Ln(III) insignificant. Particularly explored was the extraction performance of Ce(IV) by [C8mim]PF6 and suggested separation mechanism was the mechanism for anion exchange. The loaded Ce(IV) was further stripped by water. The results show that pure [C8mim]PF6 can serve as a step of extraction to isolate Ce(IV) from solutions containing HNO$_3$ and comprising Th(IV) and other lanthanides(III).

Jorjani and Shahbazi [35] investigated the recovery of Y, La, Ce, and Nd using TBP in kerosene from the nitrate leaching solution of apatite concentrate. The results show that about 95%, 90%, 87%, and 80% of Nd, Ce, La, and Y, respectively. Hot, deionized water was used for scrubbing the impurities. Stripping precipitation was achieved using 10% oxalic acid. After calcination at 800°C, mixed REE oxide with an assay of around 90% was accomplished.

The recovery of Ce(IV) was investigated from HNO$_3$ by TEHPO. The complexes that extracted were recognized to be HNO$_3$·TEHPO and Ce(NO$_3$)$_4$·2TEHPO, the nitric acid was coextracted. The loaded Ce(IV) was stripped using hydrogen peroxide solution. TEHPO displays a good interfacial phenomenon and greater loading capacity than those of Cyanex 923 [36]. The recovery of Ce(IV), Y(III), and Yb(III) from nitric acid medium was conducted using Cyanex 923 in kerosene. The recovered metallic species were identified to be Ce(NO$_3$)$_3$(OH)·2Cyanex 923, Y(NO$_3$)$_2$(OH)·2Cyanex 923·H$_2$O, and Yb(NO$_3$)$_2$(OH)·2Cyanex 923·H$_2$O. The stripping of Ce(IV) was, respectively, 89.7% and 77.5% with 1.0 M HCl and 1.0 M Na$_2$CO$_3$ [37].

REEs may result from secondary resources such as spent fluorescent lamps, permanent magnets, and NiMH batteries that have relatively high rare-earth content or in low concentrations in industrial wastes, such as phosphogypsum that most of the REEs are concentrated in it during the phosphoric acid wet process, the composition of REEs was found to be 53, 36, 26, 6, 27, 4.44 × 10^5, 22, 1, 17, 5, 1,

3.09×10^5, 3, 1, 3, 1, and 1.96×10^4 for Y, La, Ce, Pr, Nd, S, Sm, Eu, Gd, Dy, Ho, Ca, Er, Tm, Yb, Lu, and P, respectively [38]. Bauxite residue (red mud) as the content of REEs reaches around 0.1%, metallurgical slags, mine tailings, incinerator ash, coal ash, and wastewater streams that make the extraction of REEs and cerium from these items is of major significance [39,40]. The catalytic fluid cracking catalyst (FCC) plays a crucial role in the petrochemical industry. In this regard, for the recovery of La and Ce from FCC catalysts, a two-stage process comprising of leaching with HNO_3 followed by solvent extraction applying TBP, and P204. The extraction attains 93% and 42% for La and Ce, respectively. Aluminum was leached at 80°C utilizing 2.0 M HNO_3. The synergistic mixture 1:1 of TBP (25%) and P204 (25%) in a solution of normal decane gives a recovery of about 60% and 74% of La and Ce, respectively, in one stage [41,42].

Cerium and other REEs can be isolated from a waste comprising of a glass polishing using acid leaching approaches, that is, nitric and hydrochloric acid followed by solvent extraction. Earlier studies reported that the direct acid leaching of CeO_2 was difficult, while the use of a reductant as KI + H_2O_2 decreased the required acid concentration and leaching temperature. Ce was preferentially extracted over La using D2EHPA and PC 88A reagents through solvent extraction [5,43]. Fluorescent lamp residues are significant source for REEs. Cyanex 923 and Cyanex 572 in kerosene were utilized to recover Ce along with other REEs. A counter-current mixer-settler system at 20°C including three recovery steps, using (2:1) O/A ratio. Ce stripping and other REEs were performed using HCl (4.0 M and 6.0 M). Nevertheless, high acid content and/or temperatures or expensive materials (reductants) are needed from the key problems facing the recovery of these elements during leaching [44].

2.3. Extraction of cerium from chloride solution

The extraction performance of Ce(III) and Pr(III) from medium containing chloride using P204 in the existence of two-complexing substances lactic acid (LA) and citric acid (H_3cit) was confirmed. The extraction improves under some circumstances with the rise of the pH at equilibrium and the ratio of [H3cit]:[LA]. The isolation factors of Ce(III) and Pr(III) increase with the ratio of [H3cit]:[LA] at fixed pH, and this complexing method reached 5.78. The maximum performance was 27.08 g/L near that in the current saponified P507 extraction method. The complexing approach of extraction was seen as an efficient method for REs separating [45].

The solvent extraction experiments of La and Ce, by using partly (EHEHPA, HL) from solutions containing HCl have been conducted [46]. The extraction process the pure extractant can be described as in Eq. (4):

$$RE^{3+} + \overline{3H_2L_2} = \overline{RE(HL)_3 L_3} + 3H^+ \qquad (4)$$
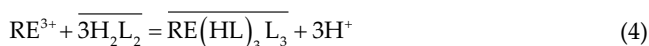
where H_2L_2 is the dimmer of the EHEHPA; $RE(HL)_3L_3$ is the extracted species. While the extraction using the saponified extractant may be illustrated as in Eq. (5):

$$2RE^{3+} + \overline{6NH_4L} + \overline{3H_2L_2} = \overline{3RE(HL)_3 L_3} + 6NH_4^+ \qquad (5)$$
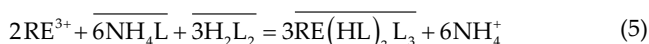
Also, HEHEHP has been conducted in the recovery of REs and shows greater separation factors for REs, and a lower acid concentration for stripping compared with the commonly used D2EHPA. However, the extraction efficiency decreases as the viscosity of the organic phase increases. In this respect, a synergistic blend of HEHEHP and sec-nonylphenoxy acetic acid CA100 was used to investigate the possibility for the separation of Ce and Y [47].

2.4. Extraction of cerium from citrate solution

The recovery of cerium(IV) from a solution containing citric acid utilizing D2EHPA in kerosene at pH = 4 was investigated. The species composition extracted was identified to be $[Ce(H_2Cit)_2 \cdot 2A(HA)]$ (where HA denotes D2EHPA). The extraction performance of Ce(IV) and Y(III) was reported to boost by rising the amount of D2EHPA and declining by increasing the citric acid concentration at pH = 4. The recovery of Ce(IV) and Y(III) ions is exothermic with positive entropy. In terms of the conditional extraction constant, separation viability demonstrated that the Ce(IV) and Y(III) boosts by increasing the amount of citric acid while rising the amount of extractant had no impact on the factor of separation and was found to be 12.9 for $\beta_{Y/Ce}$ [48].

2.5. Extraction of cerium from thiocynate solution

The recovery of cerium(III) from thiocyanate medium using two neutral organophosphorus extractants, namely, TBP and TOPO in kerosene or benzene. The recovered constituents were recognized to be Ce(NCS)3·4TBP(org); identical results were reported using TOPO. The method was developed for the spectrophotometric determination of Ce. The IR results indicate that the cerium ion connected with the phosphoryl O atom of the extractants and with the N atom of the thiocyanate [49].

2.6. Future perspectives and conclusions

This study provides a comprehensive view of cerium production from different acidic media with acidic and solvating organophosphorus extractants. Factors that influence the separation process were properly explored, including RE recovery thermodynamics, kinetics, and process mechanisms were discussed briefly. To develop a new extraction approach that is comparable to the existing extraction methods. By comparison with the experimental findings, this complexing recovery process could be proven as an efficient method for isolation of REEs.

- Sulfuric acid is the first choice for the leaching of REEs ores using solvent extraction technique has been extensively reported.
- Cyanex 923 was efficiently used for the solvent extraction of Ce(IV) and fluoride from sulfate medium while Ce(III) shows a little affinity towards Cyanex 923 and can efficiently separate Ce from the latter is almost not extracted.

- The synergistic mixture of Cyanex 923 and D2EHPA enhances the extraction of REEs than the individual extractant.
- RE's recovery by organophosphorus extractants boosts with the rising atomic numbers while also for the amine extractants declines with the rising atomic numbers.
- Aminophosphonate extractants play a crucial key in the extraction of Ce. In this respect, both DEHAPO and DEHAPP extract Ce(IV) more efficiently than some extractors such as P507, Cyanex 923, Cyanex 925, DEHEHP, and Cextrant 230.
- DEHAMP shows high extraction towards Ce(IV) and can be extracted from Th(IV) compared with the less steric than Cextrant 230.
- The recovery of cerium from the medium containing nitrate was also briefly investigated. Acidic organophosphorus extractors such as PC 88A, Cyanex 272, D2EHPA, and P204 were utilized for the recovery of Ce from relatively low HNO_3 amount and were utilized for the extraction of Ce from industrial wastes such as phosphogypsum, red mud, spent FCC catalysts, and NiMH batteries.
- The complex approach to extraction could be regarded as an efficient plan for separating REEs.
- At an industrial scale, separating the actinides from the lanthanides remains a strong technical challenge and requires more investigations.
- Improve the recovery behavior of IL-based extraction approaches for the recovery and isolation of REEs in RE hydrometallurgy is still need more work.

Acknowledgments

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