Jurnal Sains Nuklear Malaysia, 2026, 38(Special Issue): 37 – 42
ISSN: 2232-0946

ENHANCED CERIUM RECOVERY FROM ACIDIC CHLORIDE VIA SYNERGISTIC EXTRACTION

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ABSTRACT

The increasing demand for light rare earth elements (LREEs), particularly cerium (Ce), has intensified the need for efficient and environmentally sustainable extraction methods. Conventional solvent extraction systems using single extractants often suffer from limited efficiency and raise environmental concerns due to the use of volatile organic compounds (VOCs). Therefore, improving extraction performance while minimizing environmental impact remains a significant challenge. This study aims to evaluate the effectiveness of synergistic extractant systems in enhancing the extraction efficiency of cerium from an acidic chloride medium. The extraction of Ce from an acidic chloride solution was carried out using binary combinations of trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL), di-(2-ethylhexyl) phosphoric acid (D2EHPA), tributyl phosphate (TBP), and trioctylmethylammonium chloride (Aliquat 336), all dissolved in kerosene. Equal volumes of the organic and aqueous phases were mixed at room temperature to assess Ce extraction efficiency. Results showed that all synergistic systems substantially improved Ce extraction over single extractants. The D2EHPA/Cyphos IL system exhibited the highest enhancement in extraction efficiency, achieving a 94.1% improvement, followed by TBP/D2EHPA (70.7%), TBP/Cyphos IL (66.2%), D2EHPA/Aliquat 336 (51.6%), Aliquat 336/Cyphos IL (51.2%), and TBP/Aliquat 336 (42.0%). The superior performance of the D2EHPA/Cyphos IL system can be attributed to strong synergistic interactions between the ionic liquid and acidic extractant, which enhance metal complexation and transfer into the organic phase. In conclusion, synergistic extractant mixtures provide a highly effective and potentially greener approach for cerium recovery under ambient conditions, offering improved efficiency over conventional single-extractant systems while addressing environmental concerns associated with VOC emissions.

Keywords: Rare earth elements, cerium, synergistic, single extractant, efficiency

INTRODUCTION

Rare earth elements (REEs) are critical materials in modern technologies due to their unique magnetic, catalytic, and electronic properties, with demand continuing to rise as a result of their extensive use in a wide range of high-tech applications (Hamzat et al., 2025; Balaram, 2019). Among them, cerium (Ce), a light rare earth element (LREE), is one of the most abundant and widely used, particularly in catalytic converters, glass polishing, and fuel additives. Its high industrial demand, coupled with its relatively large proportion in REE ores such as monazite, makes cerium an important target for recovery and separation processes (Allahkarami & Rezai, 2021). Despite its abundance, the selective recovery of cerium remains challenging due to the similar chemical properties shared among REEs. Efficient separation is especially critical when cerium coexists with other LREEs in mixed mineral sources (Suyanti et al., 2024; Allahkarami & Rezai, 2021). Therefore, developing improved

extraction systems specifically tailored for cerium is necessary to enhance recovery efficiency and meet industrial demand.

In industrial hydrometallurgical processes, acidic chloride media are commonly used for REE leaching due to their high solubility and compatibility with downstream separation techniques. Compared to other media, chloride systems offer advantages such as faster kinetics and easier phase separation (Afonin et al., 2024; Wei et al., 2020). However, extracting cerium from such environments still requires highly efficient and selective extractants.

Solvent extraction is the most widely applied technique for REE separation. Conventional single extractants, however, often suffer from limitations such as low extraction efficiency, poor selectivity, and operational issues including emulsion formation and extractant loss. Although previous studies have explored various extractants, there remains a need for more effective systems that can enhance cerium recovery under practical conditions (Lake et al., 2025; Merroune et al., 2024; Zhang et al., 2022).

To overcome these challenges, synergistic extraction using mixed extractants has emerged as a promising approach. This method enhances extraction efficiency, improves selectivity, and increases the stability of the organic phase, offering a more effective route for high-purity REE separation (Ning et al., 2025; Wei et al., 2020; Ghani et al., 2020) While this method has shown improved performance for general REE separation, its application specifically for cerium recovery in chloride media remains insufficiently explored. In particular, the synergistic interactions between ionic liquids and conventional extractants have not been fully investigated.

Therefore, this study focuses on evaluating the performance of selected synergistic extractant systems for the extraction of cerium from an acidic chloride solution. By comparing different binary extractant combinations, this work aims to identify an efficient and stable system that enhances cerium recovery and contributes to the development of improved separation technologies.

MATERIALS AND METHODS

Materials

Distilled kerosene and HCl solution (37%) were purchased from R&M Chemical Company. Tributyl phosphate (TBP), Di-(2-ethyl hexyl) phosphoric acid (D2EHPA), Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL), Trioctylmethylammonium chloride (Aliquat 336) were four types of extractants selected for this research. All the other reagents were of analytical grade and used without further purification.

Methods

The rare earth chloride solution was prepared by dissolving an appropriate amount of the corresponding rare earth oxide powder in concentrated hydrochloric acid, followed by dilution with distilled water to the desired concentration. The organic phase was prepared by dissolving a specified amount of extractants in distilled kerosene under continuous stirring to ensure complete homogenization.

Extraction

Solvent extraction experiments were conducted in an acidic chloride medium (0.2 M) at room temperature (298 K) by contacting equal volumes (15 mL each) of the organic and aqueous phases, maintaining an organic-to-aqueous (O/A) phase ratio of 1:1. Synergist extractants between TBP, D2EHPA, Cyphos IL and Aliquat 336 was prepared as shown in Table 1. The mixtures were placed in covered Erlenmeyer flasks and vigorously agitated for 15 minutes using a mechanical shaker equipped with a magnetic stirrer to ensure that equilibrium was achieved. Following agitation, the phases were allowed to separate undisturbed for at least 10 minutes. Extraction experiments were performed in triplicate under identical conditions, and efficiencies are reported as mean ± standard deviation to ensure reproducibility.

Table 1: Synthesis of synergist extractants

Sample ID	Ratio	Extractant 1	Extractant 2
S01	-	TBP	-
S02	-	D2EHPA	-
S03	-	Aliquat 336	-
S04	-	Cyphos IL	-
S05	1:1	TBP	D2EHPA
S06	1:1	TBP	Aliquat 336
S07	1:1	TBP	Cyphos IL
S08	1:1	D2EHPA	Aliquat 336
S09	1:1	D2EHPA	Cyphos IL
S10	1:1	Aliquat 336	Cyphos IL

The concentrations of Ce(IV) in the aqueous phase, were determined using energy-dispersive X-ray fluorescence (ED-XRF). The extraction efficiency of Ce(IV), E was determined using Equation 1.

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_o is the initial concentration of Ce in aqueous phase and C_e is the final concentration of Ce in aqueous phase after extraction.

RESULTS AND DISCUSSION

Extraction of Ce

The effect of varying extractants on cerium (Ce) extraction was investigated. The extraction process involves two immiscible phases: an aqueous phase containing rare earth elements (REEs) in an acidic chloride medium, and an organic phase comprising synergistic extractants. In this study, the organic phase utilized a combination of extractants, including TBP, D2EHPA, Cyphos IL, and Aliquat 336. These extractants were selected based on their known affinities for lanthanides and compatibility with acidic chloride media. The efficiency of Ce extraction between different extractants are shown in Table 2.

Table 2: Extraction efficiency of Ce using TBP, D2EHPA, Cyphos IL, and Aliquat 336

Sample ID	Extraction	Efficiency of Ce extraction
S01	Single	2.44
S02	Single	46.2
S03	Single	39.7
S04	Single	73.2
S05	Synergist	70.7
S06	Synergist	42.0
S07	Synergist	66.2
S08	Synergist	51.6
S09	Synergist	94.1
S10	Synergist	51.2

As shown in Table 2, the individual extractants exhibited moderate extraction efficiencies when employed separately. Among them, D2EHPA (S02) displayed enhanced selectivity toward Ce, relative to TBP (S01) and Aliquat 336 (S03), likely due to its strong cation-exchange properties. Remarkably, the combination of D2EHPA with Cyphos IL (S09) in a synergistic extraction system significantly improved the extraction efficiency, reaching up to 94.1% under ambient conditions, followed by TBP/D2EHPA (S05), TBP/Cyphos IL (S07), D2EHPA/Aliquat 336 (S08), Aliquat 336/Cyphos IL (S10) and TBP/Aliquat 336 (S06) as illustrated in Figure 1.

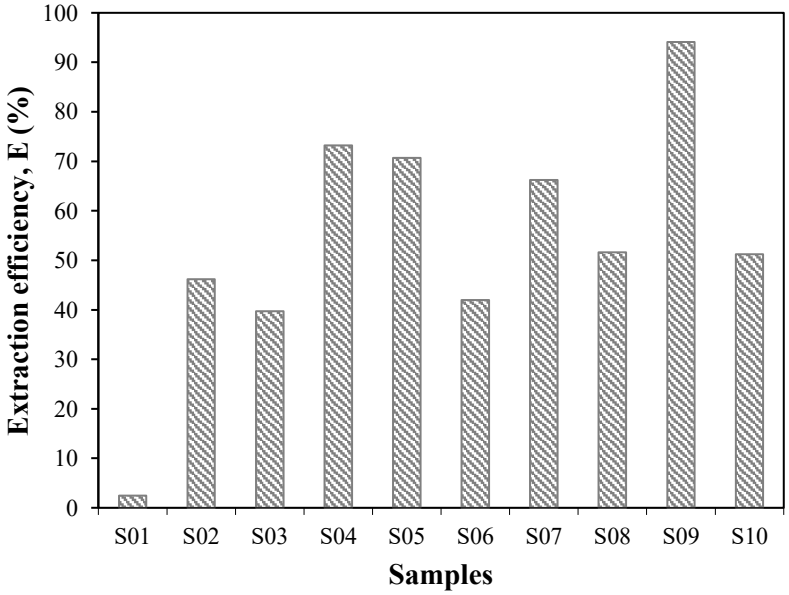

Figure 1: Extraction efficiency of Ce using TBP, D2EHPA, Cyphos IL, and Aliquat 336 [Fixed conditions: T= room temperature; O/A ratio = 1/1]

The improved extraction efficiency of the D2EHPA/Cyphos IL (S09) system is attributed to a synergistic interaction between the acidic organophosphorus extractant and the ionic liquid. D2EHPA facilitates the extraction of Ce^{3+} via a proton exchange mechanism, while Cyphos IL enhances the solvation and stabilization of the extracted metal complex, thereby promoting favorable phase transfer kinetics and increasing the metal-loading capacity. The combined action of both components reduces interfacial tension, leading to more efficient partitioning of Ce^{3+} into the organic phase.

No significant third-phase formation was observed, as confirmed by visual inspection of the phases, indicating good phase compatibility and stability of the extractant system under the tested conditions. Furthermore, the D2EHPA/Cyphos IL (S09) system demonstrated selective extraction of Ce over other lanthanides present in the leachate, such as La and Nd, under the same experimental conditions. This selectivity is advantageous for downstream separation and purification processes.

CONCLUSION

Rare earth chlorides were successfully extracted from monazite mineral via solvent extraction. Laboratory-scale studies demonstrated that Ce could be efficiently recovered from an acidic chloride medium using synergistic extractant systems. Among the extractants evaluated, the combination of D2EHPA and Cyphos IL exhibited the highest extraction efficiency for cerium, achieving 94.1%. The synergistic system outperformed individual extractants under ambient conditions, indicating a significant enhancement in extraction performance through synergism.

ACKNOWLEDGEMENTS

This research was supported by the Ministry of Science, Technology and Innovation (MOSTI) of Malaysia through DSTIN Thorium Flagship Fund - Development of Innovative Nuclear Reactor Technology (with the Spin-Off) Based on Thorium (2015 - 2019). This research paper also was a part of the PQRD project (NM-R&D-21-77) entitled “Synergistic Solvent Extraction of Cerium from Monazite Mineral”.

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