

Task Specific Ionic Liquids for the Recovery of Rare Earth Element Europium from Coal Ash

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Abstract

To meet the anticipated global transition to cleaner energy alternatives, the demand for critical metals must be met in all economies. Among the European Union designated critical metals, Rare Earth Elements (REEs) are the ones the supply of which has a current global over-dominance. Notably, Europium (Eu), a REE with a unique electronic structure that renders it critical for the manufacture of high precision luminescent and magnetic equipment has a current limited supply that needs to be addressed. To achieve this objective, its production from sources other than conventional geological deposits must be considered, and the potential for production using coal ash deposits from coal fired power plants deposit is the focus of the present review. Therefore, we have reviewed extensive literature to show the enormous potential of Task Specific Ionic Liquids (TSILs) for the recovery of Europium from coal ash deposits. Accordingly, we have shown that given the versatility in the design and manufacture of TSILs, the potential for the diversification of Europium supply from coal ash to mitigate over-monopoly in the supply chain is attractive and must be explored.

Keywords: rare-earth-elements, europium, ionic liquids, hydrometallurgy, leaching; scanning electron-microscopy

1 Introduction

The outstanding features of the Industrial Revolution were technological, socioeconomic, and cultural, the technological changes involving the use of basic materials, notably iron, steel, and new energy resources. Considering the latter, the use of fossil fuels, notably coal and petroleum in substantial amounts was essential, to meet critical societal goals regarding economic development. The implication was that at the dawn of the Industrial Revolution, the need to exploit available cheaper energy resources in the form of fossil fuels was high on the economic agenda. Consequently, excessive combustion of coal and petroleum derived fuels led to a dramatic increase in the concentration of atmospheric carbon dioxide from 280 ppm in 1860 to 419 ppm in 2023 (Lindsey, 2024).

Broadly speaking, climatic change is the direct result of the exchanges of energy, momentum, and chemicals among the atmosphere, the oceans, and land surfaces, where oceanic and atmospheric circulation, turbulent mixing processes, photochemical effects, and radiative transfer play vital roles (Keeling, 1997). Consequently, sophisticated climate models with evolving complexities, which calculate the interactions among the above listed elements have been used to predict climate change for the past decades (Hausfather, 2017; NASA, 2024). The outcome of such predictive models indicates the urgent need to reduce the concentration of atmospheric carbon dioxide, given its strong absorption in the infrared band of the electromagnetic spectrum (Modest, 2013), which accounts for climate warming. Thus, the absorption of infrared radiation and emission of thermal radiation is a consequence of coupled vibrational and rotational energy transition, where polyatomic molecules, such as carbon dioxide and water vapor undergo such transitions, while the amounts of oxygen gas and nitrogen gas are transparent to infrared radiation as a consequence of their symmetric molecular nature and the absence of permanent dipole moment (Wei, et al., 2018).

Considering the anticipated global environmental catastrophe related to anthropogenic greenhouse gas induced climate warming, a vigorous transition to renewable energy alternatives has been proposed by the United Nations Climate Action Group (UN, 2024; IREA, 2023; UN, 2022). To achieve the objective, emphasis on efficient energy systems is required, which highlights the roles of critical raw materials in the design of modern energy infrastructures (GTK, 2024), with Rare Earth Elements (REEs) being essential for such energy systems as wind turbines, fuel cells, rechargeable batteries, and electric vehicles[USGS]. Moreover, considering the recent discovery of the emerging role of fluorescence technology (Wu, et al., 2023; Hijaz et al, 2021; Prabakaran & Pillay, 2020; Diamandis et al., 1989) in medical diagnosis, Europium (Eu), a REE has been listed as critical. In this regard, Europium (Eu), which is a REE with low toxicity and good biocompatibility, has promising applications in biomedicine. Wu et al. (2023), have reviewed the osteogenic, angiogenic,

neurotogenic, antibacterial, and anti-tumor properties of Eu-containing biomaterials, which has led the way for their biomedical applications.

Currently, there is a global monopoly in the supply of REEs for technological products, where China accounts for 70% of global production and nearly 90% of processing of global output, as well as 90% of rare earth element permanent magnet production (Milewski, 2024). Such a monopoly calls for diversification of the global supply chain and the only way to achieve the objective is to consider viable sources of REEs other than their conventional geological resources, and this is where waste valorization becomes worthy of exploitation (Balaram, 2019; Jaireth et al., 2014).

The geological occurrence of REEs in coal deposits is well known in the geological literature (Seredin, 1996; Coe, et al., 2024), with a global mean concentration of 68 ppm (Ketris & Yudovich, 2009). Moreover, recent studies suggest that coal products contain sub-economic REE concentrations, which may be recovered and upgraded (Seredin et al., 2013). When coal is burnt in thermal power plants, the drastic reduction in volume of the feedstock results in a substantial increase in the concentration of REEs (Seredin et al., 2013) to 404 ppm.

In the chemical industry, the uses of ionic liquids as catalysts (Sheldon, 2001), and reaction media (Banerjee & Subhash, 2005), as stabilization and refolding additives and solvents for proteins (Fujita, 2019), in gas separation systems (Rashid, 2021), purifying cellulose from major waste streams using ionic liquids and deep eutectic solvents (Babara et al., 2023), recycling in biomass processing (Rieland & Love, 2020) and in other industrial processes is well documented due to their environmentally friendly nature (Zhang, et al., 2023; Jhanji, 2024). In this regard, Task-specific ionic liquids (TSILs), is the terminology used to designate functionalized ionic liquids (ILs) which are designed and synthesized with specific goals in mind (Neto et al., 2019). The synthesis is achieved, using the expected combination of IL properties together with a specific property of the selected functionalization. Therefore, the synthesis procedure provides the possibility for countless tailor-made desired ILs.

In 2023, roughly 36% of global electricity came from coal-fired power stations in the first three quarters in the United States (Maguire, 2023). Consequently, considering the current review work, the huge deposits of coal ash in thermal power stations associated with coal combustion and the huge potential for the use of ILs provide the opportunity for the recovery of REEs from coal ash deposits. Accordingly, and considering the role of Eu as a critical REE for electronics and biomedical engineering, we reviewed extensively the role of TSILs in the recovery of this critical metal. The review work is organized as follows:

First, we review the geochemistry and technological relevance of REEs. Next, we review the occurrence of REEs in ores and in coal ash. This is followed by a review of the hydrometallurgical processes involved in the leaching of metals from conventional ores REEs and show how this applies to REEs leaching from coal ash. We then present Europium, its technological uses and sources in coal ash. The generalized concept of TSIL was then presented and its application to Europium extraction was next reviewed. The last part of the review task was accordingly devoted to summary and conclusion.

2. REEs, their Geochemistry and Technological Relevance

Based on the International Union of Pure and Applied Chemistry (Dambus et al., 2005), rare earth comprises 15 lanthanides series (atomic number 57 of lanthanum to 71 of lutetium), including scandium (Sc, atomic number 21) and yttrium (Y, atomic number 21). Generally, the similarity in valence electron of the outermost shell justifies the similarities of the physicochemical properties among the 17 REEs. Considering the differences in electronic structures relating to the number of electrons associated with the 4f orbitals, REEs demonstrate diverse properties of hi-technological relevance (Lian et al., 2013; Cheisson & Schelter, 2019). In this regard, REEs are known to have strong magneto-crystalline anisotropy, which makes them vital components for magnetic instruments. Orbital changes have been known to alter the coupling between ions and their surroundings. Therefore, orbital excitations are critical to our understanding and control of ionic interactions, but control of their 4f magnetic moments and anisotropy has been a major drawback in ultrafast spin physics. However, with the advent of time-resolved X-ray absorption and resonant inelastic scattering, the use of Terbium (Tm) demonstrates that out of ground 4f-electrons excitations multiplet occur after optical pumping. The excitation is driven by inelastic 5d-4f-electron scattering, which has the potential to alter the 4f-orbital state magneto-crystalline anisotropy with important technological implications (Nele-Thielemann-Kühn-et-al., 2024). For instance, a recent study suggests that laser pulses can change the magnetic properties of REE materials through influencing their 4f electrons, which has been experimentally demonstrated, using terbium at major X-Ray facilities. The discovery has the potential to be applied to faster and more data storage solutions, according to the Helmholtz Center for Materials and Energy (HZB, 2024).

Coal has provided a sustainable and yet a cheaper source of energy for technological growth since the industrial revolution (SME, 2024). To relate REEs to coal studies, a classification scheme has been developed that divides REEs into Light REEs (LREEs) comprising La-Sm and Heavy REEs (HREEs) comprising Eu-Lu. Moreover, a three-fold classification

scheme has been proposed that divides (Rare Earth Yttrium (REY)) into La-Sm, middle comprising Eu through Dy plus Y, and heavy REEs comprising Ho through Lu (Seredin et al., 2012). Also, a classification permits relating the ratio of LREEs to HREEs to determine the distribution of REEs in both coal and coal derived ash products (Seredin, 1996). Generally, the motivation behind exploiting coal as a viable source of REEs stems from their concentration in coal derived ash following the combustion of coal feedstocks with variable geochemistry and feed conditions under variable operational conditions (Breeze, 2015).

3. The Role of REEs in Energy Transition

3.1 Wind Turbine

Considering their renewability and environmentally friendly nature, the global share of Wind Turbines in the renewable is increasing steadily (Maguire, 2024). In this regard, permanent magnets make possible small, light, space-saving designs for the gearboxes of wind turbines, while enhancing low-voltage ride-through capability, which improves a turbine's capacity to remain connected to the grid. The implication is that the global expansion of wind power raises the prospects of growing imbalances in supply and demand for some REEs, where neodymium, praseodymium and dysprosium are the major concern (Gielen & Lyons, 2022). Moreover, it will not be possible to meet the substantial increase in demand driven by the 2050 global wind power targets unless REEs production rises 11 to 26 times over present levels (Li, et al., 2020). Also, in China, with the greatest supply, Ren, et al. (2021) foresee the demand for REEs increasing 18 times over 2020 levels by 2050 when annual demand for neodymium may equal 1.6-3.3% of the country's reserves and recycled metals will play a growing role in supplying Chinese wind farms.

The share of permanent magnet drives has been growing steadily worldwide, with permanent magnet turbines driving three-quarters of the world's offshore installations in 2018, while gearbox induction generator turbines dominated the onshore market with a 52% share. The dynamics highlights the role of neodymium, praseodymium and dysprosium in the energy transition, rendering them critical REEs in the energy industry.

3.2 Electric Motors

While Rare earth magnets are essential in various automobile components (Fears, 2021), electric motors account for the bulk of their use, where one in four permanent magnets produced worldwide in 2020 was used in transport, mostly for electric motors, but also for micromotors, sensors and speakers (Roskill, 2021; Kane, 2020), with the share expected to grow as the use of electric vehicles (EVs) expands. Moreover, EVs alone are expected to account for around 25% of Neodymium magnets (NdFeB) consumption in 2030 (Adamas-Intelligence, 2021). In this regard, Traction motors for vehicles (including electric bikes, scooters and motorcycles) will consume 23% of the market, while the average hybrid or EV uses between 2 kg and 5 kg of permanent magnets, depending on its design (Onstad, 2021). Considering EVs sales projections together with predictions about the continued use of permanent magnets results in a forecast of up to 225 kt in possible demand for NdFeB magnets in 2030 (Ma & Henderson, 2021).

3.3 Technical Constraints

Based on the current and future trends in the demand for permanent magnets, the most significant bottleneck to meeting higher demand for generators and traction motors using permanent magnets is likely to be upper-limit temperature performance, availability of dysprosium and associated costs, which affect the demand for dysprosium. Therefore, technological breakthroughs will be most keenly felt (Onstad, 2021). Product innovation, for example, can affect REE demand in other ways as well, where the use of reluctance motors already allows low-cost ferrite-based magnets (Huang et al., 2024) to be substituted for the rare earth variety. Such innovations hold the potential to be adapted for use in higher-performance traction motors. Also, improvements in energy density (kilowatts per kg) could lower motors' REE requirement. For example, BMW's i3 EV motor achieves 2.5 kilowatt/kg, substantially higher than the 1-1.5 kilowatt/kg density in a typical hybrid (Onstad, 2021). Currently, NdFeB magnets are essential for optimizing the power-to-weight ratio in motors and generators, but automobile manufacturers are seeking ways to reduce their dependency on them.

4. Occurrence of REEs in Coal Ash

To achieve the principal objective of our review work, the following sections will be devoted to the geochemistry of REEs in coal ash.

4.1 The Chemistry of Coal Derived Ash

Coal ash consists essentially of bottom ash (BA) and fly ash (FA). Bottom ash and boiler slag are composed principally of silica, alumina, and iron, with smaller percentages of calcium, magnesium, sulfates, and other compounds, this composition being controlled by the source of the coal rather than the furnace type (FHART, 2016). Moreover, using X-Ray Fluorescence, the oxide composition has been identified as calcium oxide, silica, alumina, iron oxide and iron with small amounts of calcium, magnesium, sulphate (Ramzi, et al., 2016). From mineralogical and petrological viewpoints,

the latter consists of crystalline minerals, unburnt carbon and non-crystalline aluminosilicate glass (Hower, et al., 2017), where quantitative X-Ray Diffraction (ASTM, 2015) and petrographic examination (Hower, 2012; Hower, et al., 2017) demonstrate the predominant nature of Si-Al glass. Based on inorganic compositions, a classification scheme focusses on inorganic phases as amorphous glass, mullite, crystalline silicates, spinel, lime, sulfates and oxidized minerals (Hower, et al., 2005). Coal fly ash is generally categorized into three phases as glass, mullite-quartzite, and magnetic spinel (Gollakota, et al, 2019; Dai, et al., 2010) being primarily an amorphous material, containing 24.3% crystalline quartz phase, while bottom ash contains 31.1% crystalline quartz, based on X-ray Diffraction (XRD) data (Rahim, et al., 2023). For the mullite phase ($3\text{AlO}_3 \cdot 2\text{SiO}_2$), fly and bottom ash show results of 24.9% and 14.5%, respectively.

4.2 REEs in Coal Ash

While coal combustion generates substantial tonnages of coal ash annually, Fly Ash (FA) is a potential source of REEs (Choudhary, et al., 2024). The mean global concentration of REEs in coal ash is reported as 403.5 mg/kg, although a total REEs concentration of 8000 mg/kg has been reported (Seredin and Dai, 2012). High concentrations of Rare Earth Yttrium (REY) in coal ash ranging from 0.2% to 0.3% were reported in Russian coal, prompting possible recovery (Seredin, 1991). Generally, REEs occurrence is classified as amorphous glassy particles with REE minerals or compounds encapsulated inside (Kolker, et al., 2017; Liu, et al., 2019) amorphous glassy particles with REEs distributed throughout; and discrete REE minerals or compounds. For instance, using SEM, identification of REEs carriers and REEs mineral phases have been achieved, where an irregularly elongated-shaped amorphous carrier and an irregularly shaped REEs bastnasite were observed (Wu, et al., 2022). See Figure 1.

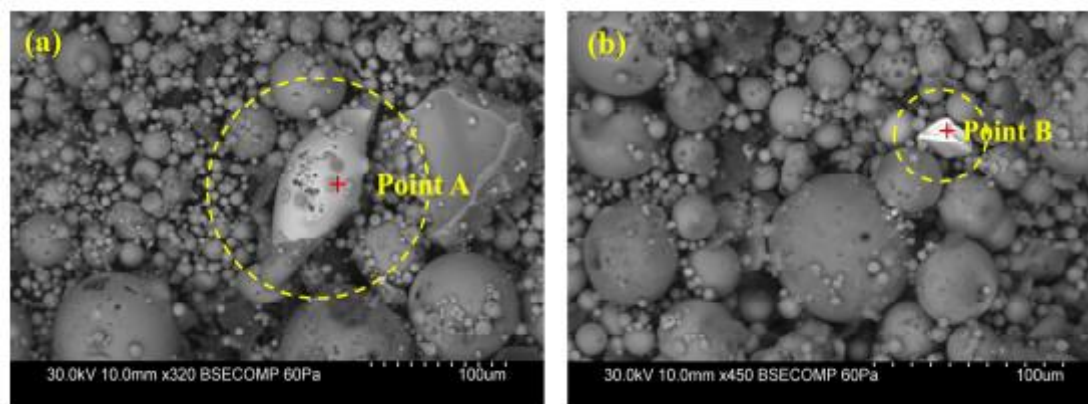


Figure 1. BSE image with element spectra of (a) an irregularly elongated-shaped amorphous carrier and (b) an irregularly shaped REE mineral bastnasite (Wu, et al., 2022)

Figure 2 shows a detailed view of the graphitic carbon at the scale of 10-nm including few-nano-size Ce and Fe particles from a C-rich concentrate using the product of froth flotation of FA where the locations of the Ce $L\beta$ peaks are close to that of the La, Pr, Sm, and Gd peaks (Hower and Groppo, 2021), while Figure 3 shows back scattered electron microscopy

images: A. Thorium bearing monazite, B. allunite supergroup, C,E. authigenic rhabdophane, F. authigenic bastnaesite (Seredin & Dai, 2012).

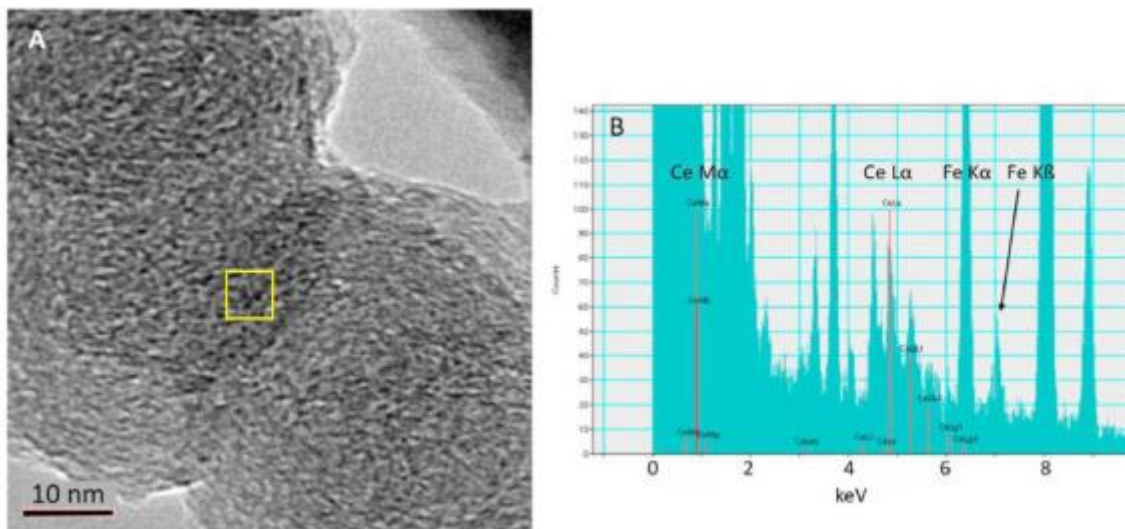


Figure 2. (A) HR-TEM image of a graphitic carbon contains Ce and Fe (yellow box), as indicated by EDS spectra (B). Images from Hower, et al. (2017).

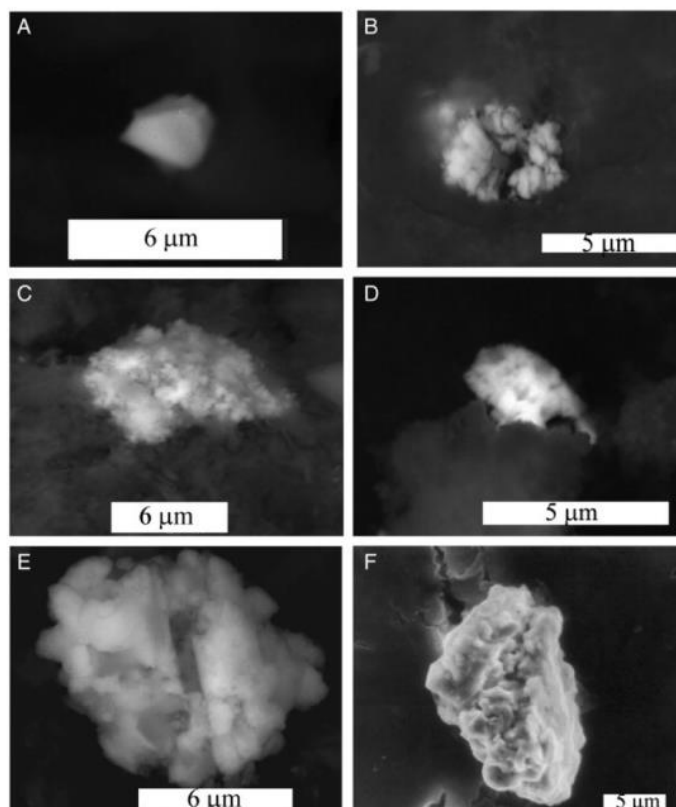


Figure 3. Scanning electron microscopy (in back scattered electron: BSE mode) images of A. Th-bearing monazite, B. allunite supergroup minerals, C-E. authigenic rhabdophanes; F. authigenic bastnaesite. (Seredin & Dai, 2012)

5. Extraction of Metals from Ores: Hydrometallurgical Routes

Hydrometallurgy involves the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials, having lots of advantages of low energy consumption and a simple operational procedure. It involves

four fundamental processes, namely leaching, solution concentration and purification, and metal recovery. In the hydrometallurgical technique for the recovery of metals from waste, the process mainly consists of four steps: involving roasting, leaching, purification, and electrowinning. Generally, hydrometallurgy is the choice for extracting non-ferrous metals, such as zinc, lead, copper and so on. In this regard, alkaline leaching has been used for the recovery of zinc from stainless steel (Lindlom, et al., 2002; Kelebek, et al., 2004), where the most significant zinc recovery rate was 74% following a 4 h leaching with a 6 M NaOH solution (Dutra and Tavares, 2006).

Recently, a novel hydrometallurgical process exploiting mechanical activation and chemical leaching of lead (Pb) from a funnel Cathode Ray Tube (CRT) glass using a strong alkaline solution was proposed (Zhang, et al., 2013), being acknowledged as more effective than mechanical activation followed by leaching. Mechanical activation is a pre-process applied to increase the reactivity of the mineral during state changes in these processes prior to a basic metallurgical process, using grinding mills (Cao, et al., 2020). The most important effect of mechanical activation in mineral preparation processes is the milling of mineral particles, which leads to a change in their physicochemical properties. During the process, the crystal structure of the mineral deteriorates and more reactive species form. Consequently, under extreme conditions, the milled mineral is rendered more active during the metallurgical process to be carried out which enhances the process speed. Therefore, reducing the reaction temperature, increasing the amount of solubility and speed, preparation of water-soluble compounds, simple and cheaper reactor production and shorter reaction time requirements are some of the advantages of mechanical activation in mineral processing. Accordingly, more than 97% of Pb in the CRT funnel glass could be extracted with a stirring ball mill leaching process in a 5 M sodium hydroxide at 70 °C. Recently Yuan, et al. (2012) introduce the hydrothermal sulfidation method to separate lead from scrap cathode ray tube funnel glass following hydrothermal treatment after mechanical activation. In the hydrothermal environment, hydroxyl ions were formed through an ion exchange process between metal ions in mechanically activated funnel glass and water, which accelerated sulfur disproportionation. Accordingly, lead contained in funnel glass was converted to lead sulfide with high efficiency. The following section will be devoted to the chemistry of acid leaching.

5.1 Acid Leaching

Acid leaching is commonly performed by agitating an ore-leach mixture for time frames ranging from 4 to as long as 48 hours at an ambient temperature. Except in special circumstances, sulfuric acid is the lexiviant used (Khalid, et al., 201; Peng, et al., 2018; Trinh, et al., 2020; Lundström, et al., 2024) because of the low cost (Walawalkar, et al., 2016). The simple leaching reaction by sulfuric acid based on a metal sulfide ore can be expressed as follows (Xio, et al., 2020):



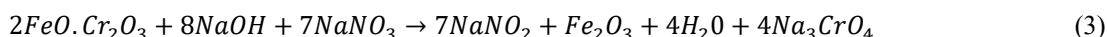
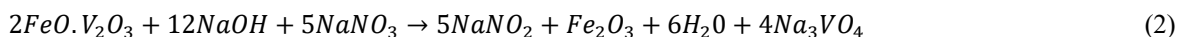
In this equation, MeS is metal sulfide, S is sulfur, Me represents the metal, and H⁺ represents hydrogen ion.

Thermodynamically, the reaction is feasible at room temperature, and the added advantage is that the toxic hydrogen sulfide released in the leaching process can be converted to elemental sulfur, which has a market value (Nasato, et al., 1994; Sung, et al., 1998).

In the hydrometallurgical process, the above reaction can be used selectively in multiple sulfide ores to dissolve the sulfides of iron, cobalt and nickel from low-nickel materials into a solution, leaving cuprous sulfide and inert noble metals in the residue. The advantage stems from the fact that it circumvents the conventional process of preparing high-nickel matte by conversion, which cannot be achieved without reduced loss of cobalt (Xio, et al., 2020).

5.2 Alkaline Leaching

In addition to the conventional acid leaching process in hydrometallurgy, the alkali route is common. For instance, a novel process for tungsten hydrometallurgy based on direct solvent extraction in alkaline medium has been reported (Zhang, et al., 2016). Wang, et al., (2014) developed an eco-friendly method to process vanadium slag using a combination of sodium hydroxide and sodium nitrate in a binary molten salt medium under significantly lower temperature conditions (200–400°C) compared to traditional sodium salt roasting (850°C). The process provides enhanced extraction rates of up to 95% for V and 90% for Cr while having enormous potential to minimize the discharge of harmful gases and toxic waste. Kim, et al., (2016) observed that under atmospheric conditions, the alkaline leaching of Cr(III) from slug stainless steel oxides is minimal, and to enhance the thermodynamics and kinetics of Cr dissolution, they focused on chromium leaching under oxidative pressurized conditions at elevated temperatures, demonstrating that Cr(III) is not present as Cr₂O₃ but rather in the more complex spinel phases: FeCr₂O₄, MgCr₂O₄ and CaCr₂O₄. In the alkaline leaching process, Liu, et al., (2013), have demonstrated that NaOH and NaNO₃ create an excellent medium for the decomposition of vanadium slag and the extraction of chromium and vanadium. In this process, the inclusion of a strong oxidant accelerates the oxidation of V and Cr spinel FeO·V₂O₃ and FeO·Cr₂O₃, which facilitates the formation of water-soluble compounds - Na₃VO₄ and Na₂CrO₄ (Vincent, 2001; DesMarias & Costa, 2019). The leaching kinetics can be described by the following reactions (Saidi, et al., 2024):

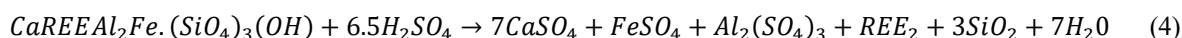


The main rare earth ores are monazite, bastnaesite and xenotime with monazite being the principal sources for light rare earth (La, Ce, Pr, Nd) often associated with mineral sands, which are usually mined primarily for ilmenite, rutile and zircon (Forsyth & Hinton, 2015). Geologically, monazite (LnPO₄) is the most abundantly observed in natural rock (granites, gneisses, and pegmatites) samples (Bohrea, et al., 2017). Considering the similarities in geochemistry regarding REEs ores and those of conventional metal ores, both acid and alkali leaching processes have been applied to hydrometallurgical processes in involving their extraction. In the following sections, we review the hydrometallurgical processes involving REEs acid and alkali leaching.

6. Application to RREs Ores

6.1 Acid Leaching of REEs Ores

Sulfuric acid-based decomposition of rare earth minerals was originally invented as a batch process, (Eyring, 1964), but current industrial operations based on rotary kiln facilitate continuous operation (Lynas-Corporation, 2011). Alanite, also known geologically as orthite is associated with metamorphosed clay rich sediments and felsic igneous rocks, belonging to a sorosilicate group of minerals found in the broader epidote group. It contains a significant amount of REEs. It has the general formula A₂M₃Si₃O₁₂[OH], where the A sites can contain large cations, such as Ca²⁺, Sr²⁺, and REEs, while the M sites admit Al³⁺, Fe³⁺, Mn³⁺, Fe²⁺, or Mg²⁺ among others (Dollase, 1971). The following represents the acid leaching reaction of REEs leaching from alanite (Liu, et al., 2014):



In the acid leaching process, the REEs are converted to sulfates by reaction with concentrated sulfuric acid at elevated temperatures, which are then dissolved during the water leaching step (Demol, et al., 2019). In this process, the REEs sulfate's reaction products are insoluble in concentrated sulfuric acid in the digestion stage.

REEs are also extracted from xenotime either by leaching with sulfuric acid or by alkali leaching, the process being essentially similar to those utilized for the treatment of monazite (Alex, et al., 1998). Alkali pre-treatment effects on acid leaching recovery of rare earth elements from coal waste of the Western Kentucky No. 13 and Fire Clay seams has also been reported (Li, et al., 2022; Gasser, et al., 2022). In this process, the enhancements in the recovery of light REEs (LREEs) are more significant than those of heavy REEs (HREEs). In this regard, after treating 5 M NaOH at 90°C, the recovery of LREEs from the Western Kentucky No. 13 coal waste increased from 26% to 71%, while the recovery of HREEs only increased from 29% to 41%.

6.2 Alkali Leaching of REEs

In this process, sodium hydroxide is used as the lixiviant to digest RE phosphate. The chemical reactions for the alkali decomposition of monazite at elevated temperatures can be represented as follows (Abdel-Rahim, 2002; Habashi, 2013).



In Eq. (5), the alkali dissolved REEs of the ore, which are precipitated in the hydroxide form in accordance with the following equation (Fan, et al., 2022).



Phosphate decomposition by alkaline roasting to concentrate REEs from monazite is another form of the alkali process, where application of the shrinking core model, a mixed control of diffusion through a residual layer and surface chemical reaction (Purwanti, et al., 2020) is valid. In both acid and alkali hydrometallurgical processes, sulfuric acid and alkali corrosions (APIRP-571, 2020; Karlsson, et al., 2012) are imminent problems. Therefore, less corrosive hydrometallurgical process involving less-corrosive acids (Figure 4) and greener chemicals have been proposed, and the following section will be devoted to reviewing the processes involved.

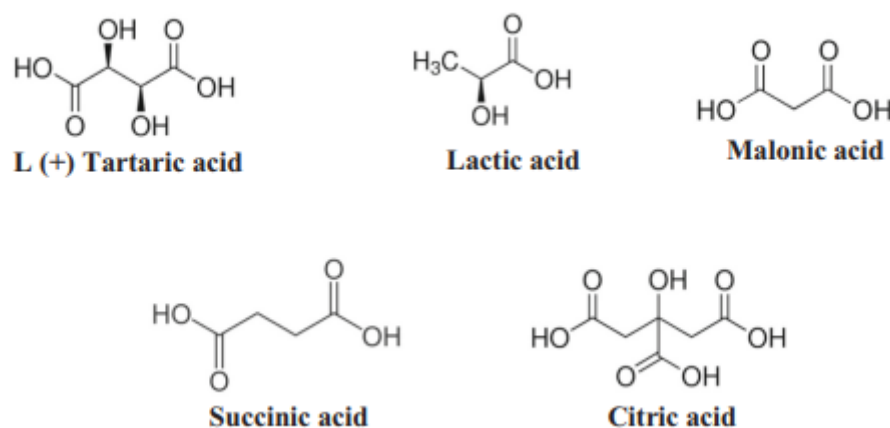


Figure 4. Chemical structure of chosen organic acids (Banerjee et al., 2021)

6.3 Acid and Alkali Leaching of REEs in Coal Ash

Considering the occurrence of REEs in coal ash (See Section 3), their acid and alkali leaching is hydrometallurgically feasible, using conventional mineral acids (Peiravi, et al., 2017) and less corrosive organic acids (Banerjee, et al., 2021). Thus, Equation (1) through (6) are theoretically applicable. Consequently, Schwartz, et al., (2018) have ranked coal ash materials for their potential to leach arsenic and selenium and the relative importance of ash chemistry and site biogeochemistry using four different leaching tests, namely the toxicity characteristic of the leaching protocol, natural pH, aerobic sediment microcosms, and anaerobic sediment microcosms on 10 different coal ash materials. The research demonstrated the potential of categorizing high and low-leaching potential ash materials, which can impact extraction economics. Shoppert, et al (2023) have also researched the potential for REEs extraction from low alkali desiccated coal fly ash using a combination of ammonium salt and sulfuric acid, demonstrating that total dissolution of the amorphous aluminosilicate phases from the surface of mullite leading to the formation of low alkali mullite concentrate prior to sulfuric acid dissolution in the presence of ammonium sulfate has the potential to accelerate REEs extraction. Considering the potential for REEs extraction from the globally abundant coal ash deposits, Thomas, et al., (2024) have reviewed the fundamental understanding and the ongoing advancements. In this regard, the cited literature focuses on the characterization of coal ash using techniques such as SEM-EDX, XRD, synchrotron-based μ -XRF and μ -XANES which advance our understanding of the occurrence of REEs with various mineral in coal ash, which can impact hydrometallurgical processes of REEs recovery. In addition, the review work of the cited literature focused on such hydrometallurgical processes as direct acid leaching, solvo-metallurgical pathways based on deep eutectic solvents and ionic liquids, including the subsequent metal recovery processes using solvent separation process, electrochemical separation, and membrane separation technique. The goal of REEs leaching whether from conventional ores or from coal ash is to hydrometallurgically recover REEs from aqueous phase of the liquor, and the fundamental approach is that involving liquid-liquid solvent extraction (Belfqueh, et al., 2024; Yuksekdog et al, 2022; Gergori,c et al., 2017). In solvent extraction, water is one of the phases and the other is an organic liquid phase. Generally, immiscibility of solvents (polar and low polarity solvents), good solubility of the target compounds, poor solubility of impurities, volatility of the extracting solvent, and toxicity and safety properties of the extracting solvent are the key governing factors in the design of liquid-liquid extraction (Alberta-University, 2025). Consequently, in recent times, the use of ionic liquids (ILs) in hydrometallurgy has received global attention, given their globally proven environmental safety (Park, et al., 2014; Binnemans & Jones, 2023; Wellens, et al., 2012).

ILs are generally, highly viscous fluids, with viscosities being several orders of magnitude higher than those of water and widely utilized organic solvents and this undesirable property poses one of the major obstacles to successful applications of these novel solvents (Paduszyński & Domańska, 2014). Consequently, research has focused on the development of new low-viscous ILs critical for future industrial applications (Barthen et al.,2015; Zhao, et al., 2022; MacFarlane et al.,2001). For instance, Zhao, et al (Zhao, et al., 2022) synthesized a low viscosity IL ($[N_{8881}][NIA]$). Also, the tricyanomethanide anion has been known to favor low viscosity of the pure ionic liquid and its aqueous mixtures (Chabana, 2015). Tan et al (2012) have reviewed the physicochemical properties of the host of library of ether- and alcohol-functionalized ILs, highlighting the role of ionic structure on features such as viscosity, phase behavior/transitions, density, thermostability, electrochemical properties, and polarity (e.g., hydrophilicity and hydrogen bonding capability). In the following section, we focus on the review of the fundamental chemical properties of ILs involving the potential to tailor their chemical properties, which has facilitated the development of Task Specific Ionic Liquids (TSILs) of hydrometallurgical importance (Visser, et al., 2001; Sowińska et al., 2006; Llaver, et al., 2022).

6.4 Chemical Reduction Process

Trivalent europium can be reduced to divalent europium by zinc and remain stable in aqueous solution for a period (Li et al., 2025). Therefore, in the metallurgical process, Europium can also be easily separated from other lanthanides by reducing it to divalent form. The remaining dissolved lanthanides are then separated using solvent extraction. Other bastnasite ores are treated in a similar manner, but the exact reagents and processes used vary depending on the constituents found in the various ore bodies.

In the lanthanothermic process (Tanaka et al., 2020), oxides of the rare earths being extracted (samarium, europium, thulium, and ytterbium) are mixed with fine chips of lanthanum metal. They are then heated to 1,400 – 1,600 °C, depending on the desired metal. The lanthanum metal reacts with oxide to form lanthanum oxide, and the desired metal evaporates and collects on a condenser. The metals can be further purified by resubliming.

6.5 Calciothermic Process

In the Calciothermic process (Huang, et al., 2023), a rare earth oxide is converted to the fluoride by heating it with anhydrous hydrogen fluoride, where the fluoride powder is mixed with calcium metal, placed in a tantalum crucible, and heated to 1,450 °C or higher, depending upon its melting point. The process causes calcium to react with the rare earth trifluoride to form calcium fluoride and the rare earth metal which are immiscible, allowing for the separation of the metal, which is then heated in a high vacuum to above its melting point to evaporate the excess calcium. The metal is then further purified by sublimation or distillation. This procedure is used to prepare all the rare earths except samarium, europium, thulium, and ytterbium. The fluoride can also be made by dissolving the oxide in aqueous hydrochloric acid and then adding aqueous hydrofluoric acid to precipitate the rare earth trifluorides from the solution. The Calciothermic process provides the best metallurgical route for the recovery of pure REEs from their ores

6.6 A Protein-Based Process for Recovery and Separation of Rare Earth Elements

Recovering REEs from abundant waste products, such as coal fly ash and red mud, provides a potential means to diversify the REEs supply chain while avoiding pollution associated with conventional mining. However, the leachate solutions generated from such low-grade REE-bearing wastes contain high levels of metal ion impurities, such as Al^{3+} , Ca^{2+} , and Fe^{3+} , rendering it problematic for conventional liquid–liquid extraction approaches (Runqian-Zhang, 2023; Pramanik, et al., 2024). A common example is where Al^{3+} is commonly coextracted with REEs in liquid–liquid extraction, resulting in low REE purity and the formation of emulsions or a third phase via gelatinous hydroxides (Zhang & Azimi, 2023). Other impurities, such as Ca^{2+} , have also been known to cause fouling in liquid–liquid extraction processes through gypsum formation (Peng, et al., 2024). Therefore, leachate solutions are commonly subjected to a pretreatment precipitation step to remove impurities before feeding into a liquid–liquid extraction unit. However, while selective precipitation is effective for removing certain impurities, such as Fe^{3+} , the complete removal of Al^{3+} presents a major challenge as REE hydroxides coprecipitate with aluminum hydroxide (Gao, et al., 2024). Consequently, a REE extraction method with high REE selectivity over non-REE impurities, particularly Al^{3+} and Ca^{2+} , is highly desirable.

The implication of the above problem is that the extraction and subsequent separation of individual rare earth elements (REEs) from their feedstocks represent a challenging yet essential task for the growth and sustainability of renewable energy technologies. To overcome the technical and environmental limitations of current REE processing methods, (Dong, et al., 2021) have demonstrated a biobased, all-aqueous REE extraction and separation scheme using the REE-selective lanmodulin protein. In this process, Lanmodulin was conjugated onto porous support materials using thiol-maleimide chemistry to enable tandem REE purification and separation based on flow-through conditions. Immobilized lanmodulin maintains the attractive properties of the soluble protein, including remarkable REE selectivity, the ability to bind REEs at low pH, and high stability over numerous low-pH adsorption/desorption cycles. Accordingly, Dong, et al., 2021 have demonstrated lanmodulin (LanM) column-based REE extraction and separation concepts using an exceptionally low-grade leachate (0.043 mol % REE, excluding monovalent ions) prepared from Powder River Basin (PRB), USA, fly ash. To assess the REE purity of the adsorbed metal content, the metal ion composition was determined following nonselective desorption using a pH 1.5 solution enabling over 96.5% of the REEs to be desorbed within the most concentrated fractions. Figure 5 shows the process flow diagram while Figures. 6, A to C. show the molecular chemistry of the protein-based approach.

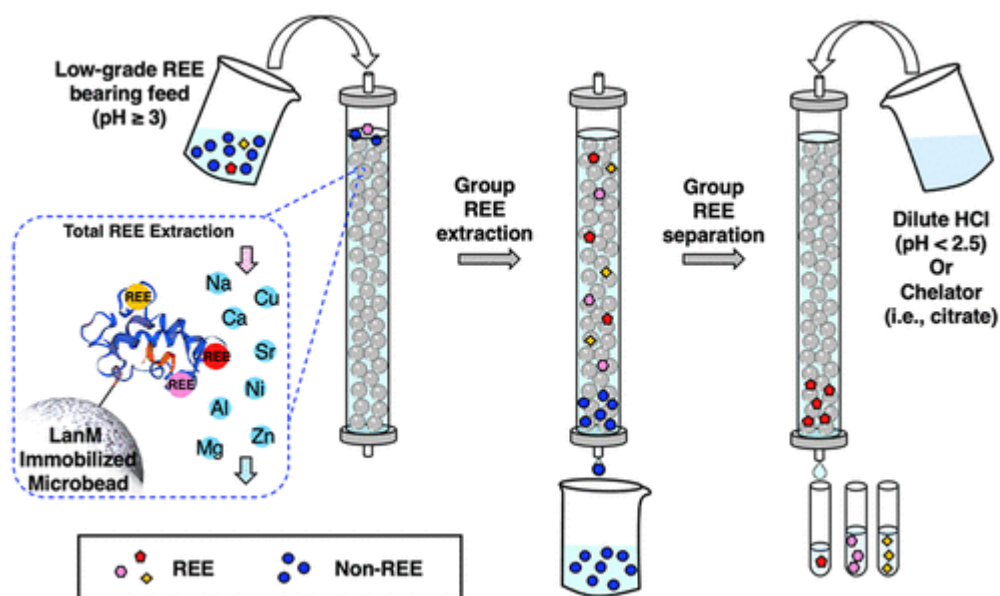
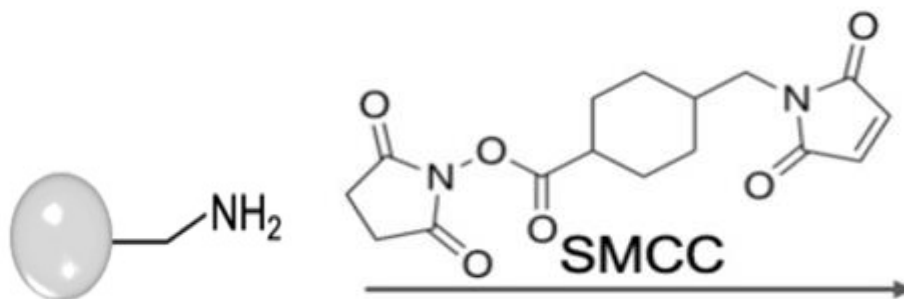


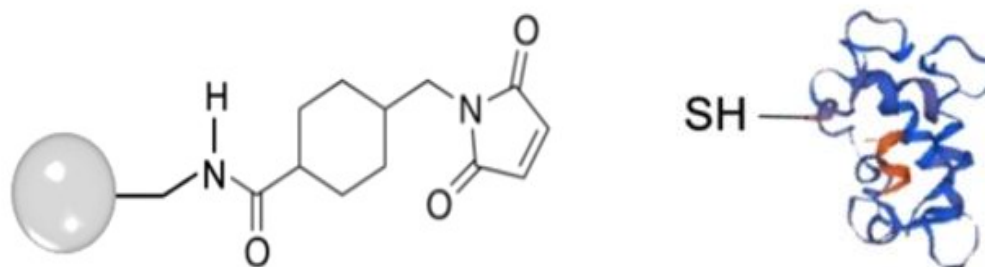
Figure 5. Process flow diagram for the protein-based extraction

A



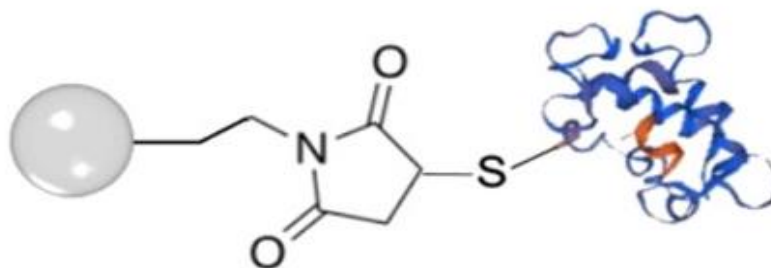
Amine functionalized agrose

B



Cysteine LanM

C



LanM-agrose

Figure 6. Chemistry of the protein-based approach (Dong, et al., 2021)

The authors further demonstrated the ability of immobilized lanmodulin to achieve high-purity separation of the clean-energy-critical REE pair Nd/Dy and to transform a low-grade leachate (0.043 mol % REEs) into separate heavy and light REE fractions (88 mol % purity of total REEs) in a single column run based on ~90% of the column capacity. The bio-based approach has demonstrated for the first time the ability to achieve tandem extraction and grouped separation of REEs from very complex aqueous feedstock solutions without requiring organic solvents, establishing this lanmodulin-based approach as an important advance for sustainable hydrometallurgy.

7. Europium

7.1 Uses of Europium in Biotechnology

Europium compounds belong to those formed by Europium. It generally exhibits the three oxidation states, such as EuCl_3 , $\text{Eu}(\text{NO}_3)_3$ and $\text{Eu}(\text{CH}_3\text{COO})_3$, though compounds in the most stable oxidation state of 2 in aqueous media exist. Many europium compounds fluoresce under ultraviolet light due to the excitation of electrons to higher energy levels, which has applications in magnetic imaging. Consequently, europium-based nanoparticles have been found to be better candidates for immunoassay and imaging compared to quantum dots due to their stable luminescence, long fluorescence lifetime, sharp emission peaks with band width, lack of blinking, and biocompatibility (Syamchand & Sony, 2015). In view of its paramagnetic nature, Europium possesses an outstanding luminescent property, which render their complexes formed by the second oxidation state ideal for fluorescence imaging (FI) agents. In this regard, +2 Europium complexes possess satisfactory relaxivity and optical properties, having the potential to realize magnetic resonance (MRI)-FI dual imaging applications when used with appropriate cryptands that can boost its oxidative stability. Moreover, based on the chemical exchange saturation transfer mechanism, the +3 oxidation state form complexes that can enhance magnetic resonance imaging when used with optimal cryptands (Syamchand & Sony, 2015). The osteogenic, angiogenic, neurotogenic, antibacterial, and anti-tumor properties of Eu-containing biomaterials and the potential biomedical applications has been demonstrated as has the application of fluorinated Eu^{+2} and Eu^{3+} containing probes for hypoxia quantification (Subasinghe, et al., 2023) and luminescence-guided surgery and 1 photon post-surgical luminescence microscopy of solid tumors (Boros, et al., 2023)

Several of the lanthanide elements, including Europium possess larger and excellent capture cross sections for thermal neutrons in nuclear reactors, allowing them to absorb more neutrons per unit area. For instance, data for cross section regarding samarium, europium, gadolinium, and dysprosium are 5600, 4300, 49000, and 1100 respectively (Pecharsky & Gschneidner Jr., 2024). Consequently, Europium is incorporated into control rods use to regulate nuclear reactors. In this regard, naturally, Europium absorbs 4.0 neutrons per atom, dysprosium 2.4, samarium 0.4, and gadolinium 0.3 respectively, before being incapacitated as neutron absorbers, making Europium an attractive neutron absorber.

7.2 Sources of Europium

Geologically, Europium is genetically related to bastnasite, a carbonate fluoride mineral found in association with some iron ores (magnetite, hematite, goethite, and limonite), where the concentration of the mineral is 4-17%. Bastnasite contains about 0.1–0.5% of europium (Worrell & Reuter, 2014). Monazite is a common mineral in magmatic, metamorphic, and ore-forming environments (Stein, 2014), that also contains Europium concentrations. Apart from these two sources of monazite and bastnasite, coal deposits have been reported to be enriched in REEs worldwide. For instance, coal samples from the East Kootenay coalfields in British Columbia, Canada were examined for the presence of REEs in

run-of-mine coal samples and flotation products, the result of the examination revealing the concentration of REEs ranging from 174-1038 mg/kg (Kuppusamy & Holuszko, 2019). The identification of REEs in Kentucky deposits has also been confirmed (KGS, 2023). Bituminous coal has also been reported to host rare earth minerals (Birk & White, 1991). Therefore, apart from the conventional geological sources of rare earth minerals associated with iron ore rocks, coal deposits are potential sources of high concentrations of rare earth minerals when burnt in thermal power plants. Thus, in coal and in some sedimentary rocks, REEs are concentrated in minerals, such as monazite ($(Ce,La,Nd,Th)PO_4$), allanite ($(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$), zircon ($ZrSiO_4$), and xenotime (YPO_4), all of which occur in trace amounts (USGS, 2019). The implication is that acid or alkaline leaching of REEs from coal ash provides a proven hydrometallurgical opportunity for their extraction using solvent extraction where the role of TSILs can be exploited. Accordingly, Table 1 shows the concentration of total and critical REEs (yttrium (Y), neodymium (Nd), europium (Eu), terbium (Tb), dysprosium (Dy), and erbium (Er)) (Seredin & Dai, 2012).

Table 1. Concentration of total and critical RREs in coal ash from different coal sources (Seredin and Dai, 2012)

Sample	Coal Basin	Total REEs-ppm	Critical REEs-%
A	Jungar, Inna Mongolia, China	192.1	28.8
B	Jungar, Inna Mongolia, China	229.7	28.7
C	Jungar, Inna Mongolia, China	313.8	39.2
D	Powder River Bssin+ Appalchian Basin mixed	365.8	37.3
E	Powder River Basin+ Appalachian Basin mixed	523.6	39.7
F	Unspecified mixed	523.6	39.7
G	Unspecified mixed	635.2	44.5
H	Central Appalachian Basin	524.5	39.5
I	Eastern Interior (Illinois Basin)	366.5	39.4
J	Powder River Basin	345.2	34.5
K	Central Appalachian, Fire clay coal	1534.3	34.7
L	Central Appalachian, Fire clay coal	1667.6	36.5
M	Central Appalachian Basin	401.5	38.6

8. Task Specific Ionic Liquids (TSILs)

TSILs, also known as functionalized ILs, can be broadly defined as any salt that has the typical properties of an IL in which a functional group with a target application is covalently bonded to the cation and/or anion (Singh & Savoy, 2020) to achieve desired performance properties. Therefore, TSILs represent a sub-family of ionic liquids characterized by their high specificity towards a target analyte or group of analytes. Figure 7 shows a base IL 1-alkyl-3-methylimidazolium with a host of ions that can be used for the synthesis of TSILs. Broadly speaking, 1-Alkyl-3-methylimidazolium-based ILs are polar in nature, being miscible in polar solvents like methylene chloride (dichloromethane, chloroform) and immiscible in hexane, water. Therefore, to reduce their polarity for use in industrial processes where a level of miscibility with nonpolar solvents is desired, they must be specifically functionalized.

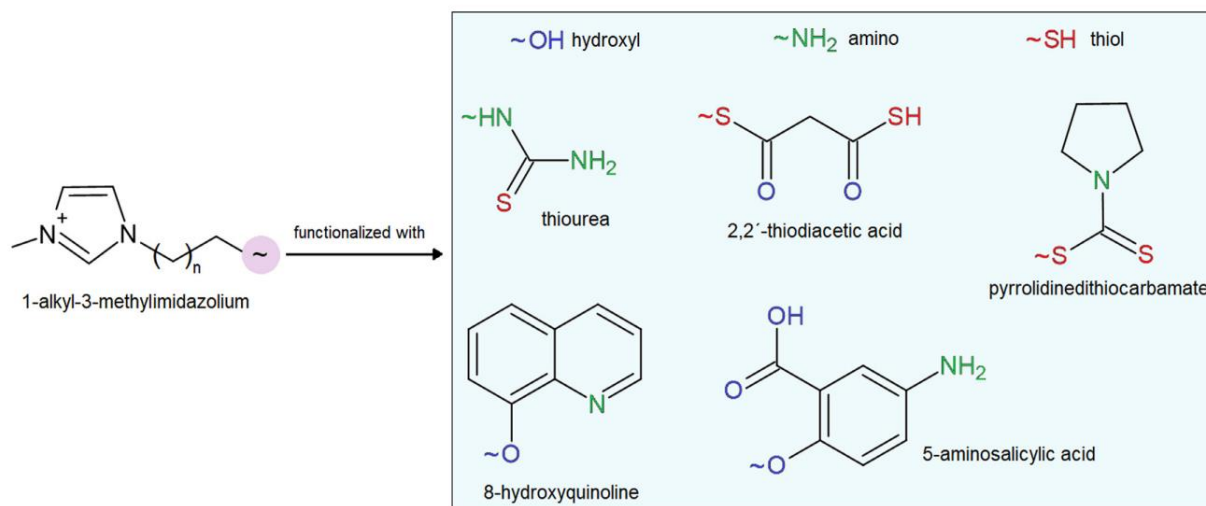


Figure 7. Functionalization of 1-Alkyl-3-methylimidazolium-based ILs with different ions (Llaver, et al., 2022)

For instance, analysis shows that polycrystalline copper is a hydrophobic metal. Therefore, extraction of copper requires a hydrophobic extractant (Valette, 1982; Sang, et al., 2015). To achieve the objective, thiourea has been used to functionalize 1-Alkyl-3-methylimidazolium-based ILs. For instance, two thiourea based hydrophobic ILs were screened and synthesized, which were used as efficient extractants to extract Cu^{2+} by introducing ethyl and carboxyl groups as functional groups (Zhang, et al., 2023). Also, 2,2'-thiodiacetic acid can be used to functionalize the base IL for the synthesis of an IL with a Lewis acid catalyst property (Estager et al., 2010). Research findings, suggest that to eliminate undesirable effects of the scale layer, natural wool needs to be surface-modified before further application in textile engineering to enhance shrink-resistance, washing/felting and dyeing. Traditional methods involve the use of absorbable organic halogens with disadvantages. In this regard, thiol-based ionic liquids have proven to be the best for surface modification (Jiang, et al., 2021). Therefore, functionalization of the base IL (1-Alkyl-3-methylimidazolium) will lead to a TSIL for industrial processes involving textile engineering in hydrophobic media. In the following sections, we review the application of TSILs to the extraction of Eu from aqueous media resulting from the leaching of REEs.

9. TSILs for Eu Extraction

Chloride occurring in aqueous media are ubiquitous as aliquots in hydrometallurgical leaching of ores using acids. The extraction of Eu^{3+} from chloride medium using bifunctional ionic liquid extractants (Bif-ILEs), tri-n-octylmethyl ammonium bis(2-ethyl hexyl) phosphate ([A336][D2EHP]), and trihexyltetradecyl phosphonium bis(2-ethylhexyl) phosphate ([P₆₆₆₁₄][D2EHP]) using kerosene as a diluent to exploit green chemistry approach has been reported (Mishra & Devi, 2022). The study demonstrated that ammonium-based ionic liquid [A336][D2EHP] shows better extraction efficiency for Eu^{3+} than that of phosphonium-based ionic liquid [P₆₆₆₁₄][D2EHP]. Quantitative extraction of Eu^{3+} was achieved with 0.05 mol/L [A336][D2EHP], compared to 0.1 mol/L of [P₆₆₆₁₄][D2EHP] for achieving the same extraction rate.

ILs such as, methyltrioctylammonium chloride (Aliquat 336), methyltrioctylammonium nitrate, and trihexyl (tetradecyl)phosphonium chloride (Cyphos IL 101) are commercially available and substantially hydrophobic in nature. In this regard, the highly hydrophobic cation restricts any loss of ionic liquid cation in the extraction process (Rout, et al., 2013; Regadío, et al., 2018), rendering them suitable ionic cationic source for the design of a wide range of ionic liquids for solvent extraction by combining them with suitable anions. Consequently, ILs derived from methyltrioctylammonium cation have been used as suitable diluents in solvent extraction (Rout, et al., 2013), where the cations of Aliquat 336 or Cyphos IL 101 ionic liquid has been successfully combined with other complex anions for designing strongly organophilic ionic liquids. Such ionic liquids have the potential to resist cation as well as anion exchange.

Rout and Ramanathan (2020) used methyltrioctylammonium bis (trifluoromethanesulfonyl) imide as a diluent for extraction of Europium using bis (2-ethylhexyl) diglycolamic acid as the extractant, improving the distribution ratios compared with the use of organic diluent. Moreover, the 1-octyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide was reported as the best diluent with the potential to achieve a distribution-ratio over 400 in the extraction of Eu. Hidayah and Abidin (2019) used conventional extractants bis (2-ethylhexyl) phosphoric acid and 2-thenoyltrifluoroacetone (HTTA), both cation exchange extractants and Aliquat 336 (A336) which is a quaternary ammonium salt diluted in imidazolium-based ILs to extract a wide range of REEs demonstrating that oxygen-containing

extractants in ILs achieved a complete extraction of praseodymium. Considering that Eu and Pr are among the critical REEs, this extraction approach could be applied to Eu extraction.

A new non-fluorinated malonamide-based TSIL extractant was synthesized and evaluated for the extraction behavior of europium (III) from nitric acid medium (Rout & Binneman, 2014). The extractant was the functionalized ionic liquid trihexyl (tetradecyl)phosphonium N,N,N',N'-tetra(2-ethylhexyl) malonate, [P66614][MA], in combination with the non-fluorinated ionic liquid trihexyl (tetradecyl)phosphonium nitrate, [P66614][NO₃], as diluents. Figure 8 shows the molecular structure of the functionalized IL. The TSIL is easily recyclable compared to other fluorinated functionalized ionic liquids. With a concentration of 0.5 M, 100% Eu can be recovered albeit the relatively high viscosity of the IL diluent A [P₆₆₆₁₄][NO₃], the formation of a 1 : 3 (or possibly 1 : 4) complex between [P₆₆₆₁₄][MA] and europium (III). The extraction system also demonstrates favorable thermodynamics with negative values of free energy and enthalpy changes with positive entropy change with the potential to regenerate TSIL.

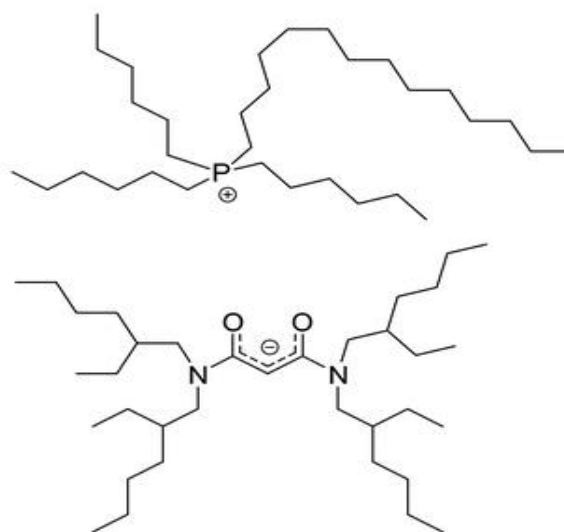


Figure 8. functionalized ionic liquid (Rout & Binneman, 2014)

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Chloride occurring aqueous media are ubiquitous as aliquots in hydrometallurgical leaching of ores using acids. The extraction of Eu³⁺ from chloride medium using bifunctional ionic liquid extractants (Bif-ILEs), tri-*n*-octylmethyl ammonium bis(2-ethyl hexyl), phosphate ([A336][D2EHP]) and trihexyltetradecyl phosphonium bis(2-ethylhexyl), phosphate ([P₆₆₆₁₄][D2EHP]) using kerosene as a diluent to exploit green chemistry approach has been reported (Mishra & Devi, 2022). The study demonstrated that ammonium-based ionic liquid [A336][D2EHP] shows better extraction efficiency for Eu³⁺ than phosphonium-based ionic liquid [P₆₆₆₁₄][D2EHP]. Quantitative extraction of Eu³⁺ was achieved with 0.05 mol/L [A336][D2EHP], compared to 0.1 mol/L of [P₆₆₆₁₄][D2EHP] for achieving the same extraction rate.

10. Current Limitations and Future Trends in Task Specific Ionic Liquids

Metal salts are intermediate products in hydrometallurgical process related to metal recoveries (Ma, et al., 2020). Generally, for electrochemical and solvent extraction technologies, ionic liquids should have high solubility powers for metal salts, including metal oxides (Nockemann, et al., 2006). Good solubility is encountered where aluminum chloride based ILs, such as mixtures of 1-ethyl-3-methylimidazolium chloride and aluminum chloride ([C₂mim]Cl–AlCl₃) Wilkes, et al., (1982), and mixtures of 1-butylpyridinium chloride and aluminum chloride (BPC–AlCl₃) (Gale, et al., 1978) are encountered. Unfortunately, these systems suffer from extreme water sensitivity because in the presence of water, there is evolution of corrosive hydrogen chloride gas from the ionic liquid. On the other hand, compounds, such as the 1-alkyl-3-methylimidazolium hexafluorophosphates, [C_{*n*}mim][PF₆], are room-temperature ionic liquids demonstrating much lower sensitivity toward aqueous phases (Wilkes & Zaworotko, 1992). However, these ionic liquids and related ones, such as the 1-alkyl-3-methylimidazolium tetrafluoroborates (Holbrey & Seddon, 1999) or the 1-alkyl-3-

methylimidazolium bis(trifluoromethylsulfonyl)imides (Bonhote, et al., 1996) have low solubility for metal salts due to the weakly coordinating properties of the constituting anions and cations. Therefore, the solvation energy is not high enough to break the binding interactions between the ions or molecules of the metal-containing compounds in the solid state. To overcome the solubility problems, researchers are developing the so-called (TSILs), having functional group covalently tethered to the cationic or anionic part (Davis, 2004). The goal is to allow functional groups to coordinate to the metal ion, preferably as a bidentate or a polydentate ligand, to facilitate the dissolution of metal oxides or metal salts into the ionic liquid. Consequently, such TSILs are not used as single-component ionic liquids, but as mixtures with more conventional ionic liquids. The motivation to use mixtures rather than pure TSILs is that they often have a higher melting point and a higher viscosity than conventional ionic liquids (Nockemann, et al., 2006). In addition, the conventional ionic liquids are in general much cheaper than the TSILs. However, the major drawback of these TSILs is that they are often only accessible after a multistep synthetic procedure. Moreover, their preparations are time-consuming, which

restricts their use in large-scale industrial applications. Therefore, the development of TSILs that can readily be prepared from cheap raw materials is an important principal research focus, and TSILs that can be prepared using renewable natural resources could be the major targets.

11. Summary and Conclusion

REEs are not only essential for the anticipated energy transition, but also for biomedical applications involving the manufacture of improved method of fluorescence imaging based on Targeted Molecular Eu^(III) Probes (Lengacher, et al., 2023). The principal source of Eu is monazite and bastnaesite, which are obtained from rocks and coal deposits. However, while igneous and metamorphic rocks contain known commercial deposits of these minerals, they occur as minor substances in coal deposits, and the combustion of coal results in their concentration in coal ash, from which Eu can be extracted. In this review, we have shown how TSILs can be used to enhance Eu extraction from leachates containing Eu. In conclusion:

1. The statistics of coal ash deposits show significant percentage of critical REEs including Europium,
2. Advances in the design and synthesis of TSILs provide the opportunity and versatility for the extraction of Europium from leachates containing Europium,
3. All TSILs for the recovery of Europium from leachates can be regenerated, and
4. Based on the experimental results of reviewed TSILs for Europium extraction, opportunity exists for their commercialization.

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Authors contributions

Professor. Adango Miadonye and Dr. Mumuni Amadu were responsible for study design and conception of the manuscript. Both drafted the manuscript while Prof. Adango Miadonye edited the manuscript. Dr Mumuni Amadu wrote the introductory section of the manuscript while Professor Adango Miadonye was responsible for reading through and making recommendations. Both authors jointly carried out data analysis and review. Each author read and approved of the final manuscript. Both authors contributed meaningfully and equally.

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Informed consent

Obtained.

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The Publication Ethics Committee of the Canadian Center of Science and Education.

The journal's policies adhere to the Core Practices established by the Committee on Publication Ethics (COPE).

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The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Data sharing statement

No additional data is available.

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