

# Recovery of Rare Earth Elements by Supercritical CO<sub>2</sub>: A Mini Review

Chau Chun Beh, Jordan Evans, Jacques Eksteen

Curtin University, Western Australia School of Mines: Minerals, Energy and Chemical Engineering

**ABSTRACT:** Rare earth elements (REEs) are essential in renewable energy and defence sectors, particularly for the manufacture of high-strength magnets using praseodymium, neodymium, dysprosium, and terbium. Conventional extraction methods of REEs exhibit limitations such as using large amounts of acids and organics that are harmful to the environment and health, and high post-processing costs to subsequently remove the harmful solvents. Supercritical carbon dioxide (scCO<sub>2</sub>) extraction is a potential green alternative to conventional extraction techniques. The study will review and discuss the effects on the extraction efficiency of REEs by varying the scCO<sub>2</sub> operating conditions including pressure, temperature, the addition of chelating agents, and the pre-treatment of the samples.

## INTRODUCTION

Rare earth elements (REEs) are a group of 15 lanthanides, scandium, and yttrium. Rare earth elements are often characterised into sub-groups of light REEs and heavy REEs. REEs are not rare, but abundant on the Earth's crust. However, the supply of REE is vulnerable due to the difficulty of extraction and reliance on sources in China.

Rare earth elements have useful applications such as the growing renewable energy field, and the defence field (Dushyantha, Batapola et al. 2020). One of the major fields that they are being used in is the magnet industry, with the elements Praseodymium (Pr), Neodymium (Nd) and Dysprosium (Dy) being used for the construction of Nd<sub>2</sub>Fe<sub>14</sub>B permanent magnets, which are used in wind turbines, electric motors and computers, as well as larger fields such as the automotive, appliance, automation and medical fields (Brown, Ma et al. 2002, Dushyantha, Batapola et al. 2020). They are also used for a variety of applications such as nickel-metal hydride batteries, glass additives,

lamp phosphors, lasers, alloys and radiation shielding (Dushyantha, Batapola et al. 2020).

The lack of efficient and environmentally friendly extraction and processing techniques is one of the major risks to REE supply. There is a significant push for sustainable technologies that are environmentally friendly to extract REEs. Current REEs recovery techniques are either pyrometallurgy or hydrometallurgy. Pyrometallurgical extraction has high energy requirements while conventional hydrometallurgy typically involves large amounts of acids and organic solvents, which generate hazardous residues and require post-processing purification steps.

The hydrometallurgical recovery processes have a significant environmental impact, as they involve toxic chemicals, leading to pollution of the environment. Providing a green alternative scCO<sub>2</sub> extraction technology helps to address the environmental challenges for REE processing, which inherently helps to reduce the overall environmental footprint. The aim of the current study is to provide a mini review on the use of scCO<sub>2</sub> to recover REEs. Various

experimental parameters will be compared and discussed in the later sections.

## CONVENTIONAL RECOVERY METHODS OF REES

The extraction of REEs from both primary and secondary resources has been studied extensively due to the growing necessity for the resources. Traditional extraction methods for REEs from ores such as monazite and bastnaesite are well-established, and have been in use for many years (Gupta and Krishnamurthy 2005). Originally, the refining methods were predicated on the leaching of components with high-strength mineral acids, namely sulfuric acid, nitric acid, or hydrochloric acid (HCl). The current methods used for extraction vary with ore type. For instance, there are two major extraction methods for bastnaesite ((La,Y) (CO<sub>3</sub>)F). One was developed by Molycorp for their Mountain Pass mine which utilised HCl to extract REEs as chlorides and then extract fluorides by converting them to hydroxides using sodium hydroxide, from which they are leached to chlorides (Gupta and Krishnamurthy 2005, De Lima 2015). The second industrial method is sulfuric acid roasting, which is when bastnaesite concentrate is heated at high temperatures in 98% sulfuric acid (Gupta and Krishnamurthy 2005). However, this process poses serious environmental and health concerns, as the process releases hydrogen fluoride gas.

The extraction measures of monazite have additional concerns due to the presence of radioactive minerals such as uranium and thorium, with thorium content being present between 4 and 12% (De Lima 2015). One of the main leaching technologies currently used is the alkaline method. The REEs are present as refractory phosphates, and they are digested in a hot sodium hydroxide solution at 140°C (Gupta and Krishnamurthy 2005, Kuzmin, Pashkov et al. 2012). The residue is then washed with hot water and leached with a mineral acid of choice. This process results in extraction rates of up to 98%, with even low-grade monazite ore, but it also results in the extraction of thorium, which leads to safety concerns during the separation process, in which thorium accumulation can be dangerous (Kuzmin, Pashkov et al. 2012, De Lima 2015). A few bioprocessing technologies have also been researched (Corbett 2017, Corbett, Eksteen et al. 2017, Corbett, Eksteen et al. 2018, Fathollahzadeh 2018, Fathollahzadeh 2018, Fathollahzadeh, Eksteen et al. 2019, Fathollahzadeh, Khaleque et al. 2019, Van Alin, Corbett et al. 2023, Van Alin, Corbett et al. 2023), which utilise phosphate solubilising microorganisms to leach REEs from their phosphate minerals. However, leach rates are low, and nutrients

and energy sources have to be provided contrary to sulfide mineral-solubilising bacteria, where the chemical energy is provided by the bio-oxidation of the minerals themselves.

Traditional solvent extraction methods use large quantities of acids and organics, a primary environmental concern as they produce toxic waste. Increasing environmental awareness has caused significant increases in legal requirements regarding the disposal of conventional liquid solvents that are considered hazardous, inherently driving the increase in the cost of using these types of solvents for extraction (Wai, Gopalan et al. 2003).

The negative implications of traditional commercial REE extraction methods have led to an increasing focus on alternative technologies that enable similar or higher efficiencies using greener methods. Supercritical fluid extraction is a green alternative extraction technique that has reflected promising results.

## SUPERCRITICAL FLUID EXTRACTION

Supercritical fluid extraction (SFE) is an emerging green technology that has been studied extensively for selective metal extraction, particularly metal chelates. Industrial-scale SFE has been conducted for organics extraction since the 1930s–1940s (Fox, Ball et al. 2004). Supercritical fluid is used to replace conventional solvents, where its supercritical state enables it to have enhanced solvating capabilities. To achieve the supercritical state, the fluid is heated and compressed above its critical temperature and pressure, allowing the supercritical fluid to attain characteristics of both liquids and gases at these conditions in a dynamic equilibrium. The conditions used in SFE to extract REEs from their feed sources depend on various factors such as the type of chelating agents, operating temperature, pressure, and flow rate (Yao, Farac et al. 2018). Supercritical fluid utilises gas-like diffusivity, liquid-like mass transfer and the effective solvating capability to be a more efficient solvent over traditional organic solvents as well as enable the transfer of solutes from porous solids. Supercritical fluid technology underpins the pathway to clean energy. For extraction of REEs by SFE, the quantities of solvent used in conventional processes are reduced significantly, hence, reducing hazardous material utility costs while improving poor environmental practices presently used (Wai, Gopalan et al. 2003).

In some applications, SFE has shown to consume less energy and result in higher recovery than other extraction techniques, such as acid leaching, which could lead to high energy costs and environmental impacts (Yao, Farac et al. 2018). Phase separation of the solvent and solute is achieved easily through depressurisation (Wai, Gopalan et

al. 2003). This thus motivated the research into the potential to use scCO<sub>2</sub> as a possible mobilising agent for REEs. As the maturity of the application of scCO<sub>2</sub> in this field is limited, the current review may be valuable as a foundation for continued research.

### **Supercritical Carbon Dioxide Extraction for the Recovery of REEs**

Carbon dioxide is commonly used in SFE due to its wide availability, inexpensive, non-toxic, non-flammable, inert, and ease of recyclability (Beh, Mammucari et al. 2017, Beh, Wong et al. 2019). Supercritical CO<sub>2</sub> has a moderate critical temperature of 31.1 °C and critical pressure of 7.37 MPa, implying that it is easy to obtain supercritical conditions for this fluid. Supercritical CO<sub>2</sub> is used in various applications including the pharmaceutical, food, and agriculture industries for extracting organics such as organic solvents from pharmaceutical products as well as essential oils from herbs and flowers such as rosemary, turmeric and chamomile (Das, Gaustad et al. 2018). Supercritical CO<sub>2</sub> extraction is also useful in the energy industry for the direct liquefaction of coal (Zhang, Anawati et al. 2022). In addition, scCO<sub>2</sub> has been applied as a solvent for extracting inorganics, including REEs, under various experimental conditions (Das, Gaustad et al. 2018). The high solvation strength of scCO<sub>2</sub> on REEs has been demonstrated with recovery efficiencies as high as 99% from the literature. Supercritical CO<sub>2</sub> extraction requires minimal reagent input, especially compared to conventional extraction.

The use of scCO<sub>2</sub> as a solvent for inorganic material has been developed as a selective extraction method due to its tuneable properties by varying the density of scCO<sub>2</sub>. Generally, scCO<sub>2</sub> is a poor solvent for polar or ionic compounds due to CO<sub>2</sub> being a linear molecule with no dipole moment. Therefore, chelating agents are required to dissolve the REEs as CO<sub>2</sub>-soluble metal chelates in scCO<sub>2</sub>. Subsequently, the metal-chelates in scCO<sub>2</sub> can be chemically reduced to the elemental state for metal deposition in the fluid phase (Wai, Gopalan et al. 2003). Lastly, REEs can be recovered upon depressurisation of the scCO<sub>2</sub> extraction system.

Laintz and co-authors reported the first use of a chelating method to extract transition metals with scCO<sub>2</sub> in 1992. The study investigated the impact of introducing fluorinated dithiocarbamate chelating agent into scCO<sub>2</sub> extraction system to extract metal Cu<sup>2+</sup> ions from both an aqueous solution and solid surface. The study found that the absence of the chelating agent led to no metal ion extraction (Laintz, Wai et al. 1992). In addition, other chelating agents such as β-diketones, organophosphorus

reagents, and macrocyclic ligands were also studied for the extraction of metal species using scCO<sub>2</sub> extraction (Wai 2002, Vincent, Mukhopadhyay et al. 2009). In the recent decade a novel chelating agent tributyl phosphate-nitric adduct (TBP-HNO<sub>3</sub>), has been investigated for the extraction of REEs from their oxide form using scCO<sub>2</sub>. Table 1 summarises the recent literature recovering REEs by scCO<sub>2</sub> extraction under various operating conditions.

### **PARAMETERS AFFECTING RECOVERY OF REES BY SUPERCRITICAL CO<sub>2</sub> EXTRACTION**

Supercritical fluid extraction has been shown to have a high potential as an effective and environmentally friendly technique for extracting REEs from multiple sources. The extraction process is influenced by various parameters such as temperature, pressure, REE sources, chelating agents, mechanical activation, impurities, water content, pH, residence time, agitation, presence of solvent modifier and flow rate of solvent. The major parameters are described in the sections below.

#### **REE Sources**

Sources of REEs are found all over the world, with the largest reserves located in China. Other significant sources of REEs include Australia, United States, Brazil, India, and Malaysia. These elements can be found in primary sources such as minerals and clays within the earth's crust. Secondary sources such as the recycling of electronic products is also becoming an important source of REEs. As the demand for REEs continues to grow, it is important to diversify the sources of these crucial minerals to prevent over-reliance on any one country, region, or source (Gupta and Krishnamurthy 2005).

#### **Primary Sources**

Mineralised ore bodies are considered the primary sources of REEs as well as in phosphates and ion adsorption clays deposits. These top three sources with high rare earth oxide (REO) contents are bastnaesite [(Ce, La,Y)CO<sub>3</sub>(OH,F)], monazite [(REEs,Th)PO<sub>4</sub>], and xenotime [Y(PO<sub>4</sub>)] (Gupta and Krishnamurthy 2005).

Bastnaesite deposits are fluocarbonates with approximately 70% REO by weight in the mineralisation, with mostly lighter element and lower or no thorium concentrations. Monazite deposits contain REEs that are phosphates with the presence of thorium. The presence of significant levels of fluoride and thorium in these ore bodies make them toxic and radioactive, which pose safety challenges for processing. Xenotime deposits exhibit similar properties

Table 1. Summary of recent literature studying the use of scCO<sub>2</sub> extraction for the recovery of REEs

REE Source	REEs		Chelating agents	Pressure (MPa)	Temperature (°C)	Residence Time (h)	Efficiency (%)	Pre-treatment/ Other Additions	Reference
	wt%								
Monazite concentrate	La (15.2)		TBP(HNO <sub>3</sub> )	20.27	45	1	La (91.82)	Pre-treatment with Na <sub>2</sub> CO <sub>3</sub>	(Samsonov, Trofimov et al. 2015)
	Ce (30.6)		HDEHP-HNO <sub>3</sub>				Ce (93.53)		
	Pr (3.4)						Pr (94.28)		
	Nd (13.0)						Nd (95.15)		
	Sm (1.4)						Sm (95.74)		
	Eu (0.06)						Eu (96.28)		
	Gd (0.8)						Gd (94.63)		
	Tb (0.09)						Tb (94.47)		
Monazite concentrate	La (16.75)		D2EHPA-HNO <sub>3</sub>	20.27	45		La (72.80)	Pre-treatment with Na <sub>2</sub> CO <sub>3</sub>	(Samsonov, Trofimov et al. 2016)
	Ce (33.72)						Ce (92.30)		
	Pr (3.72)						Pr (92.6)		
	Nd (14.32)						Nd (94.8)		
	Sm (1.58)						Sm (99.39)		
	Eu (0.06)						Eu (99.49)		
	Gd (0.93)						Gd (98.76)		
	Tb (0.10)						Tb (98.88)		
Bastnasite concentrate	La (20.7)		TBP/HNO <sub>3</sub>	34	65	2	La (72)	Roasted at 730 °C for 3 hrs	(Sinclair, Baek et al. 2017)
	Ce (34.1)						Ce (96)		
	Pr (3.0)						Pr (88)		
	Nd (8.0)						Nd (90)		
	Sm (0.6)								
	Eu (>0.2)								
	Gd (0.2)								
	Tb (0.1)								
	Ba (4.3)								
Ca (0.9)									
Sr (4.2)									

Table 1. Summary of recent literature studying the use of scCO<sub>2</sub> extraction for the recovery of REEs (continued)

REE Source	REEs		Chelating agents		Pressure		Temperature (°C)	Residence Time (h)	Efficiency (%)	Pre-treatment/ Other Additions	Reference
	wt%	REEs			(MPa)						
Bastnasite concentrate	La (25.1)	TBP/HNO <sub>3</sub>	34	65	1.5	La (93) Ce (100) Pr (99) Nd (101)	NaOH digest	(Sinclair, Baek et al. 2017)			
	Ce (33.1)										
	Pr (3.0)										
	Nd (7.7)										
	Sm (0.5)										
	Eu (>0.2)										
	Gd (0.2)										
	Tb (0.1)										
Ba (3.6)											
Ca (1.0)											
Sr (>1.7)											
NiMH battery	La (18)	TBP(HNO <sub>3</sub> )x(H <sub>2</sub> O)y	31.0	35.0	2	La (86) Ce (86) Pr (88) Nd (90)	Methanol added	(Yao, Farac et al. 2018)			
	Ce (7.3)										
	Pr (2.4)										
	Nd (2.1)										
Fluoride lamp	Y (41.2)	TBP/HNO <sub>3</sub> and H <sub>2</sub> O	31	40	3	Y (70) Eu (70) La, Ce, Tb (50)		(Zhang, Anawati et al. 2022)			
	Eu (2.7)										
	Ce (8.5)										
	Tb (3.0)										
	La (11.0)										
Fluoride lamp (Y and Eu oxides, La and Ce phosphates, and Tb in unidentified form)	Y (29.6)	TBP/HNO <sub>3</sub> and H <sub>2</sub> O	15	60	2	Y (99.7) Eu (99.8) La, Ce, Tb all <7		(Shimizu, Sawada et al. 2005)			
	Eu (2.3)										
	La (10.6)										
	Ce (5.0)										
Tb (2.6)											
Fluoride lamp	Y (3.27)	TBP/HNO <sub>3</sub>	31	40	3	Ce (56.1) Y (71.2) Tb (51.3) La (55.4)		(Zhang and Azimi 2020)			
	La (0.55)										
	Tb (0.22)										
	Ce (0.43)										
Nd <sub>2</sub> O <sub>3</sub> powder	>99%	TTA-TBP	15	50	2	Nd (67.5)	Methanol added	(Vincent, Mukhopadhyay et al. 2009)			

**Table 1. Summary of recent literature studying the use of scCO<sub>2</sub> extraction for the recovery of REEs (continued)**

REE Source	REEs		Pressure		Residence Time (h)	Efficiency (%)	Pre-treatment/ Other Additions	Reference
	wt%	Chelating agents	(MPa)	Temperature (°C)				
Nd <sub>2</sub> O <sub>3</sub> Ce <sub>2</sub> O <sub>3</sub>		TBP/HNO <sub>3</sub>	21	60	3	Nd (>95) Failed to extract Ce		(Duan, Cao et al. 2010)
Nd <sub>2</sub> O <sub>3</sub>		TBP/HNO <sub>3</sub>	21	60	1	Nd (>96)		(Zhu, Duan et al. 2009)
Lanthanide oxide Nd <sub>2</sub> O <sub>3</sub> Gd <sub>2</sub> O <sub>3</sub>	10–3 mol each	TBP/HNO <sub>3</sub>	12	40		Nd (51) Gd (46)		(Tomioka, Enokida et al. 1998)
Lanthanide oxides (Y <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub> , Eu <sub>2</sub> O <sub>3</sub> , Tb <sub>2</sub> O <sub>3</sub> , Dy <sub>2</sub> O <sub>3</sub> )		TBP/HNO <sub>3</sub>	34.5	65	1.5	Y (>99) Ce (0.12) Eu (>99) Tb (92.1) Dy (98.5)		(Baek, Fox et al. 2016)
NdFeB	Nd (18.5) Pr (3.6) Dy (0.1)	TBP/HNO <sub>3</sub>	20.7	55	1	Nd (94) Pr (91) Dy (98)	Methanol added	(Zhang, Anawati et al. 2018)
NdFeB	Nd (32.36) Nd (32.36)	Malic acid Citric acid	12	90	0.5	Nd (99.4) Nd (50.5)		(Reisdörfer, Berruol et al. 2020)
NdFeB	Nd (25.19) Nd (25.19)	Malic acid Citric acid	10	90	2	Nd (99.5) Nd (30.6)	Roasted at 900 °C for 480 min	

**Acronyms**

NiMH: Nickel-metal hydride battery  
 TBP: Tributyl phosphate  
 TTA: Thenoyl tri fluoroacetone  
 HNO<sub>3</sub>: Nitric acid  
 NdFeB: Neodymium magnet made from alloy of neodymium, iron, and boron  
 NaOH: Sodium hydroxide  
 Na<sub>2</sub>CO<sub>3</sub>: Sodium carbonate



as monazite, but with higher HREE (yttrium) content. The overall REO content of xenotime is approximately 67% (Gupta and Krishnamurthy 2005). However, there is no published literature describing the recovery of REEs from xenotime using  $\text{scCO}_2$  extraction to date.

### **Secondary Sources**

Secondary sources refer to recycled or reused materials that contain REEs. These sources can include electronic waste, magnets, batteries, and industrial waste streams and have become increasingly important sources of REEs, particularly due to the limited accessibility and economic viability of primary sources (Binnemans, Jones et al. 2013). Urban mining of end-of-life products is advantageous to an environmentally sustainable approach to sourcing REEs as it reduces the scarcity of REE supply and diminishes the volume of landfill waste. Applying green  $\text{scCO}_2$  extraction technology to the secondary sources mitigates environmental and health concerns regarding using traditional hazardous solvents and producing toxic wastes.

**Fluorescent lamp waste.** The use of fluorescent lighting (FLs) has been dominating the market due to its energy conservation advantage, with a 75% energy consumption reduction compared to incandescent lights. These FLs comparatively also have an increased life expectancy. The increase in usage has resulted in growing waste stockpiles of FLs. Rare earth elements are widely used as functional material within these lamps, and currently, FLs are being investigated as a secondary source of REEs, with up to 28% of the FL phosphors by weight being REEs in a more concentrated abundance than primary ore sources (Zhang, Anawati et al. 2022).

The investigation of FL lamps has previously been not considered practical due to a lack of available processing methods; however, SFE technology has enabled the expansion of extraction capacity for REEs. Experimental studies such as Shimizu et al. and Zhang et al. have demonstrated the use of SFE to achieve selective extraction of yttrium (Y) and europium (Eu) from the FL phosphors containing a mixture of various complex REE-containing compounds, including red phosphors, green phosphors and blue phosphors. The literature also showed that SFE was less selective to extract lanthanum (La), terbium (Tb) and cerium (Ce) (Shimizu, Sawada et al. 2005, Zhang, Anawati et al. 2022).

Shimizu et al. reported that the REE content within the FL was – Y – 29.6%, Eu – 2.3%, La – 10.6%, Ce 5.0%, Tb 2.6% while Zhang et al. also reported similar contents with exception to the larger weight of Y to be 41.2% (Shimizu, Sawada et al. 2005, Zhang, Anawati et al. 2022). From these

studies, it has been identified that this secondary feed is more consistent with its feed of REE ratios; hence this may enable the extraction process conditions to be optimised to suit most FL feed sources to produce reliable extraction efficiency of REEs. This reflects that waste phosphors are a potentially significant secondary feed source with relative certainty of feed material characteristics (Shimizu, Sawada et al. 2005).

**Nickel-metal hydride battery.** Spent nickel metal hydride (NiMH) batteries are the most efficient rechargeable batteries on the market and play a fundamental role in hybrid electric cars. The use of hybrid cars is growing traction due to their environmental advantages, inadvertently driving the production of NiMH batteries. Rare earth elements account for 33% of the weight of these batteries, which is a viable REE source. Currently, Umicore, Japan Metals & Chemicals Co, and Honda Motor Co. Ltd are processing recycled spent NiMH batteries utilising conventional hydrometallurgical methods resulting in alloy products containing base metals and REOs. The amenability of this feed source to SFE has been experimentally explored by Yao and co-authors, who reported recovery efficiencies of La (86%), Ce (86%), Pr (88%), and Nd (90%) at 35 °C and under 31.0 Mpa (Yao, Farac et al. 2018).

**Neodymium-iron-boron magnets.** Neodymium-iron-boron magnets, also known as NdFeB magnets, are the strongest permanent magnets currently available in the market. They are made from a combination of neodymium, iron, and boron, and are often coated in nickel or zinc to prevent corrosion. NdFeB magnets are a crucial component in modern technology with the use having a tie to the increasing global focus on reducing greenhouse gas emissions with their use in wind turbines and electronic cars. Investing in these technologies that provide cleaner energy production and consumption options, evidently increases the use and production of NdFeB magnets.

Pyrometallurgy and hydrometallurgy are traditional methods of recycling the materials in NdFeB magnets, however  $\text{scCO}_2$  extraction has been investigated to recover Nd as an alternative green technique recently. The magnets contain approximately 22–33% by weight REEs which is higher in concentration than primary sources, making them a desirable source of REEs (Zhang, Anawati et al. 2018, Reisdörfer, Bertuol et al. 2020). In addition, NdFeB magnets require pre-treatment to demagnetise, remove external coating and reduce particle size prior to  $\text{scCO}_2$  extraction. The recovery of REEs from NdFeB magnets by  $\text{scCO}_2$  extraction is summarised in Table 1.

## Temperature

Temperature is a critical factor in SFE, as it directly affects the solubility of the REEs, the viscosity and density of the  $\text{scCO}_2$ , and the diffusion rates. In general, high operating temperature results in high extraction efficiency of REEs in SFE. As temperature increases, the solubility of REEs in  $\text{scCO}_2$  increases due to the weakening of intermolecular forces as well as the viscosity and density of the  $\text{scCO}_2$  decrease, leading to better penetration of  $\text{scCO}_2$  and hence, improved extraction efficiency and faster extraction. However, there is an upper limit to temperature as high temperatures can cause thermal degradation of the system (Shimizu, Sawada et al. 2005).

The effect of temperature on the extraction efficiency of REEs was investigated by Zhu et al., where the pressure was fixed at 21 MPa and the temperature varied between 35 and 60 °C for the  $\text{scCO}_2$  extraction of  $\text{Nd}_2\text{O}_3$  with a TBP- $\text{HNO}_3$  adduct (Zhu, Duan et al. 2009). Zhu and co-authors concluded that an increase in temperature leads to greater extraction efficiency, which is consistent with the findings by others (Zhu, Duan et al. 2009, Duan, Cao et al. 2010). This effect on the system may be due to the increased reaction between chelating complex and the metal oxide to form the metal-chelating agent complex (Zhu, Duan et al. 2009). The increase in temperature would lead to a significant increase in operational cost and safety concerns for the system. To optimise the system both operational efficiency and cost efficiencies must be considered for the overall viability of the project.

## Pressure

Pressure is an important parameter as pressure affects the solubility of the REEs in  $\text{scCO}_2$ , which, in turn, impacts extraction efficiencies of REEs. An increase in pressure generally increases the density of  $\text{scCO}_2$ , making it easier to dissolve the REEs. Shimizu and co-authors confirmed that higher pressure levels result in higher extraction efficiencies by comparing the extraction of REEs at atmospheric and critical pressures. It was found that greater extraction efficiency could be achieved with pressures within the supercritical range. The results reflected that Y and Eu extraction efficiencies were 37.4 and 36.8% for atmospheric pressure, respectively, compared to 99.7 and 99.8% for the same feed material under supercritical pressure of 15 MPa (Shimizu, Sawada et al. 2005). These results confirm the theoretical understanding of supercritical fluid behaviour with fluids experiencing enhanced solvating and diffusion capabilities.

The varying pressures from 15 to 30 MPa were investigated at a constant temperature of 50 °C by Zhu et al. This report found that the increase in pressure had a

negative impact on extraction efficiency. It was noted that the change in pressure may have impacted the reactivity of the TBP- $\text{HNO}_3$  complex to be reduced (Zhu, Duan et al. 2009). Typically, pressure would have a positive impact on SFE system, however this study reflected that the additional components such as the chelating agent used in the system are important in determining the optimal conditions as they directly impact the extraction efficacy.

Based on the literature in Table 1, the optimal  $\text{scCO}_2$  extraction pressure will be within 15 to 25 MPa to achieve the highest extraction efficiencies of REEs. Higher pressures for this system would also be avoided if lower pressures were as efficient due to the increased operational cost and safety concerns with higher pressures.

## Chelating Agents

The use of chelating agents has been investigated throughout literature for SFE with the chosen optimal agent being highly dependent on the system. The selection is essential for the efficiency and efficacy of the SFE, and extraction would not be possible without these chelating agents, where the  $\text{scCO}_2$  serves as the solvent and diluent for these ligands. The ligands widely explored for use in SFE include dithiocarbonates,  $\beta$ -diketones, organophosphorus agents, and macrocyclic compounds (Burford, Ozel et al. 1999). Organophosphorus agents are the most used chelating agents for both conventional solvent extraction and SFE. Generally, REEs in their oxide form are extracted by  $\text{scCO}_2$  with tributyl phosphate (TBP) as a chelating agent which is classified as an organophosphorus agent (Ding, Liu et al. 2017). The high extraction efficiencies of REEs using chelating agents are evident in Table 1.

Baek et al. investigated TBP and nitric acid (TBP- $\text{HNO}_3$ ) as chelating agents, modifying it to create a new adduct TBP- $[(\text{HNO}_3)1.7(\text{H}_2\text{O})0.6]$ , which was prepared by using fuming (90%)  $\text{HNO}_3$  and TBP. The extraction occurred at 65.85 °C under 34.5 MPa. Baek et al. reported under these conditions collectively one of the most optimal recovery efficiencies seen within the literature for light REE extraction. The efficiencies were Y (>99%), Ce (0.12%), Eu (>99%), Tb (92.1%) and Dy (98.5%) (Baek, Fox et al. 2016).

The efficiencies achieved through  $\text{scCO}_2$  extraction are highly dependent on the choice of agent as the solubility of agent in  $\text{scCO}_2$ . The greater the solubility of the agent in  $\text{scCO}_2$  the higher efficiencies that can be achieved (Zhu, Duan et al. 2009). This explains the optimal recoveries achieved by Baek et al. as TBP and  $\text{HNO}_3$  have high solubility in  $\text{scCO}_2$  and notably, according to Wai, Gopalan



and Jacobs, at conditions of 14 MPa and 50 °C, the complex is entirely miscible (Wai, Gopalan et al. 2003).

Equations 1 and 2 reflect TBP and HNO<sub>3</sub> acting as chelating agents by interacting with the trivalent lanthanides to produce a CO<sub>2</sub>-soluble complex. The nitrate anions act to form a nitrate salt with the trivalent lanthanide, and then with polar phosphate group on the TBP molecules substituting for coordinated water around the metal cation, the complex then becomes soluble (Sinclair, Baek et al. 2017). The change in solubility of the metal cation is due to the shielding mechanism provided by the non-polar butyl groups, allowing charge neutralization of the ion to become soluble in scCO<sub>2</sub> (Burford, Ozel et al. 1999, Sinclair, Baek et al. 2017). This shielding mechanism is essential for the extraction as it makes the solubilisation of the metal cation into scCO<sub>2</sub>. This solubility is highly influenced by the extraction conditions, however, due to metal organophosphate complexes involving ion-pair extraction, it is challenging to obtain solubility data (Smart, Carleson et al. 1997).



There are two mechanisms for deploying chelating agents in SFE, these are in-situ or on-line. In-situ is where scCO<sub>2</sub> is introduced and interacts with the chelating agent first, or where the chelating agent interacts with the metal prior to the introduction of scCO<sub>2</sub> as a batch process. The on-line method feeds the extraction system with scCO<sub>2</sub> and

metal complexes at specified flow rates through a mixing joint, Sawada et al. utilised this method when conducting an Nd extraction with SFE (Sawada, Hirabayashi et al. 2008, Ding, Liu et al. 2017). The main distinction between the techniques is the different mixing and dissolution processes, however it has been noted within literature that both methods have led to efficient extraction.

A chelating agent is a type of chemical compound such as Di-(2ethylhexyl)phosphoric acid (D2EHPA) and TBP which are explored for REE extraction. These compounds have the ability to bond with metal ions by forming multiple bonds between the agent and the metal. This bond involves coordination between the metal ion and the donor atoms in the chelating agent, forming a stable complex. This complex enables the metal to become soluble in scCO<sub>2</sub>. Figure 1 compares the recovery of REEs using two organophosphate chelating agents, D2EHPA and TBP.

It is evident that TBP has resulted in higher extraction efficiencies for the lighter REEs, which gradually decrease for the heavier REEs. Overall, D2EHPA reflects the higher extraction efficiencies, especially for the heavier REEs. This may be due to D2EHPA creating a more stable and soluble REE complex to be extracted. The use of chelating agent will depend on which REE extraction is most desired as different chelating agents will have greater selectivity and interaction with some REE over others.

### Pre-Treatment

Pre-treatment is required for REEs because these elements occur together in minerals and or secondary sources and

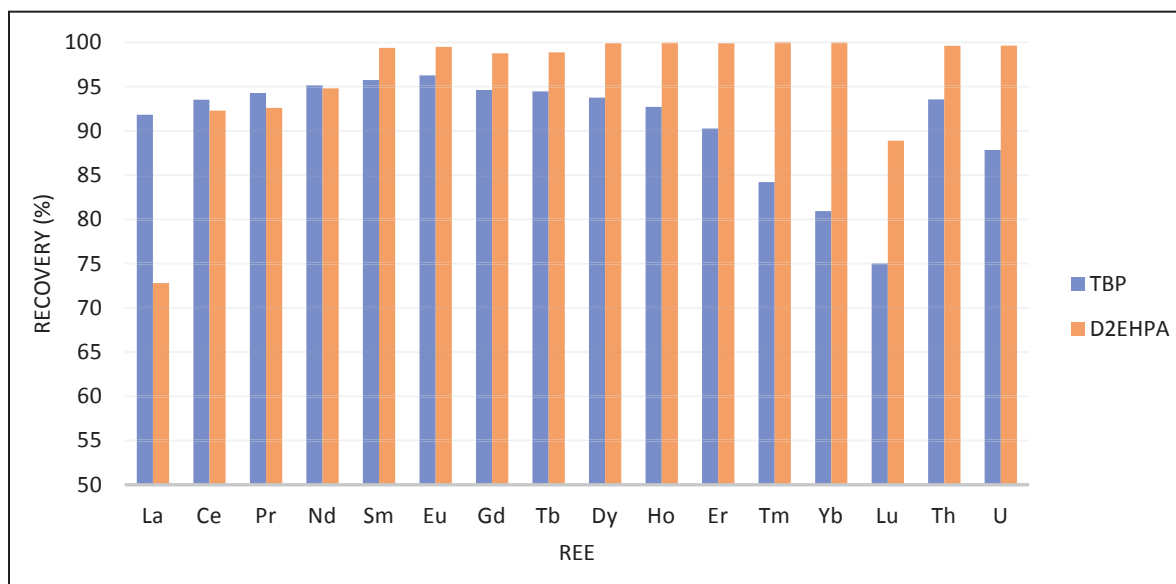


Figure 1. Effect of chelating agents on the recovery of REEs by scCO<sub>2</sub> extraction (Chart plotted using data from (Samsonov, Trofimov et al. 2015, Samsonov, Trofimov et al. 2016)

are often difficult to separate. The pre-treatment process involves separating the REEs from other elements and impurities so that they can be extracted and purified more efficiently. For instance, roasting step is required to break down the fluorocarbonate structure. Roasting temperature varies with the ore type. Bastnaesite is generally oxidised to form oxyfluorides while CO<sub>2</sub> gas is released after roasting at 400–500 °C. Subsequently, oxyfluorides are turned into acid-soluble oxides and insoluble trifluorides while releasing HF gas at temperature of 500–700 °C. After that, Ce is oxidised to produce insoluble cerianite at 700–1000 °C, which can be separated from other REEs in the subsequent leaching process (Sinclair, Baek et al. 2017). Figure 2 represents a comparison of two types of pre-treatments on the same ore source for scCO<sub>2</sub> extraction of REEs. Cerium is unique amongst the REEs due to its potential to be oxidised to the 4+ oxidation state, thereby simplifying some separations.

Roasting and NaOH digest were the commonly used industrial pre-treatment procedures. Sinclair et al. applied a roasting pre-treatment of bastnaesite concentrate at 730 °C for 3 hours to break down the fluorocarbonate structure to enable contraction and increase solubility of REEs (Sinclair, Baek et al. 2017). Similarly, the NaOH digest also breaks down the structure to enable contraction and increase solubility of REEs however it produces an acid-soluble rare earth hydroxide. The NaOH digest was able to achieve a greater extraction efficiency for all REEs. This may be due to the faster reaction rate of NaOH digested material. However, it is important to determine overall performance of both pre-treatment options, including environmental impact, infrastructure and operational cost.

## Water and pH

For samples where the REO is contained within a solid, water molecules in the system can act as modifiers to accelerate desorption of metal chelates from a solid sample. This process improves the extraction efficiency through increasing the dissolved metal chelate complexes. However, excess water has been noted to decrease extraction efficiency as water molecules will form stable adducts with metal chelates, making them less amendable to extraction (Ding, Liu et al. 2017).

Excess water was found from the reaction of the complex and metal oxides during the scCO<sub>2</sub> extraction process conducted by Shimizu et al. Evidently, water saturation comes from preparing the chelating complex as shown in Equation 1 with HNO<sub>3</sub> containing a mixture of HNO<sub>3</sub> and H<sub>2</sub>O. When extraction occurs, the water separates and forms small water droplets in the scCO<sub>2</sub> extraction system. The metal ions become trapped in these droplets, reducing extraction efficiency (Shimizu, Sawada et al. 2005). Shimizu et al. investigated a technique to prevent these droplets from forming, and this involved the control of the molecular ratio of TBP:HNO<sub>3</sub>:H<sub>2</sub>O within the complex by using anhydrous TBP to prevent water precipitation. The study compared the extraction efficiencies of REEs using hydrated and anhydrous TBP, which found that the anhydrous TBP achieved slightly higher efficiencies with a more significant impact on the Ce and La (Shimizu, Sawada et al. 2005).

Rare earth element extraction benefits from higher acid content within the system as it promotes the formation of rare earth nitrate complexes which positively impacts extraction efficiency (Yao, Farac et al. 2018). Furthermore,

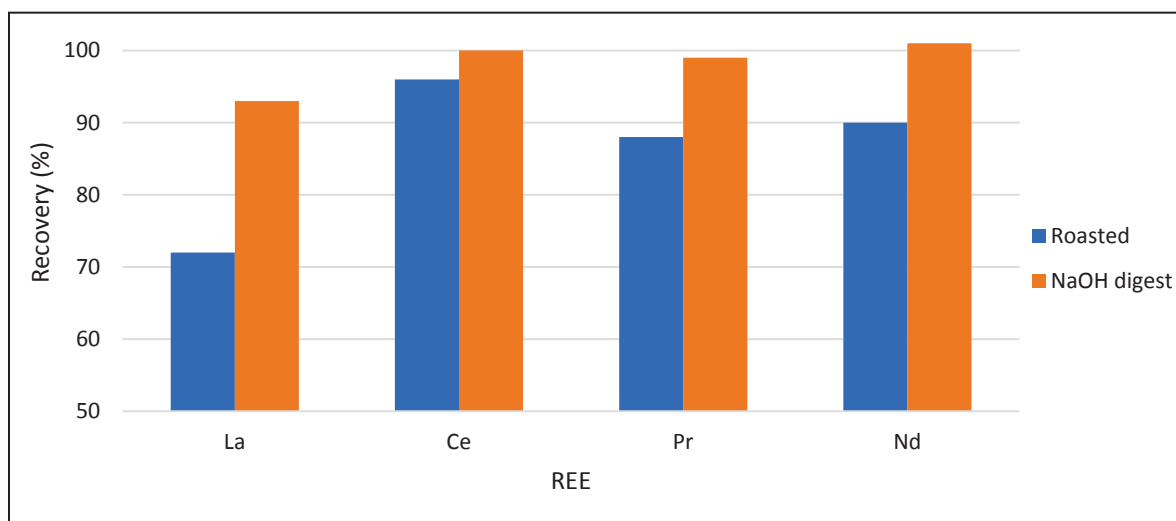


Figure 2. Effect of pre-treatment techniques on the extraction efficiencies of REEs by scCO<sub>2</sub> extraction (Chart plotted using data from (Sinclair, Baek et al. 2017))

an experimental study undertaken by Zhang, Anawati and Azimi confirmed the importance of an acidic system as it found that REE extraction systems are notably sensitive to increases in pH. An increase in pH caused the REE-phosphates to precipitate, resulting in high calcium extraction and a significant reduction in REE extraction efficiency (Zhang, Anawati et al. 2022).

The influence of pH on the formation of REE cation was investigated by Vincent et al. A lower pH has been demonstrated to promote higher ionisation which enabled a higher conversion of REE cations to form complexes that could be extracted by scCO<sub>2</sub> (Vincent, Mukhopadhyay et al. 2009).

### Solvent Modifier

The use of solvent modifiers in extracting REEs by SFE has been found to significantly enhance the efficiency and selectivity of the process. Most commonly, methanol, ethanol, acetone, and various surfactants are used as solvent modifiers. Solvent modifiers change polarity of supercritical fluid and react with metal complexes (Ding, Liu et al. 2017). Solvent modifiers have been demonstrated to greatly enhance extraction efficiency, as evidenced by Yao and co-authors. Specifically, the addition of methanol increased extraction efficiency by 20% (Yao, Farac et al. 2018). The positive impact was also noted in a study extracting Hg<sup>2+</sup> where 5% methanol addition improved the SFE, however, addition of too much may have a negative impact (Ding, Liu et al. 2017).

### CONCLUSION

Supercritical CO<sub>2</sub> extraction has been demonstrated to recover REEs with relatively high extraction efficiency from various primary and secondary resources. Supercritical CO<sub>2</sub> is a more environmentally and economically sustainable alternative to traditional solvents. The extraction efficiency of REEs using scCO<sub>2</sub> extraction is highly dependent on experimental conditions and the feed sources of REEs. The literature review has highlighted the many influencing factors that require optimisation to achieve the high extraction efficiencies of REEs using scCO<sub>2</sub> extraction. This work has provided valuable insights for future work into the extraction of REEs and aided in understanding the impact extent of these influencing factors on REEs extraction by scCO<sub>2</sub> technique. This mini review reflected that the choice of chelating agent is the most highly influential parameter on the system and that most studies have been conducted using TBP as the chosen chelating agent due to its high solubility in scCO<sub>2</sub>. Furthermore, temperature and pressure of the solvent system play the next most

critical roles in determining the extraction efficiency as they maintain the system within a supercritical state. The other parameters less significantly aid in achieving an optimally efficient system and are highly influenced by the type of feed source.

### REFERENCES

- Baek, D. L., R. V. Fox, M. E. Case, L. K. Sinclair, A. B. Schmidt, P. R. McIlwain, B. J. Mincher and C. M. Wai (2016). "Extraction of Rare Earth Oxides Using Supercritical Carbon Dioxide Modified with Tri-Butyl Phosphate-Nitric Acid Adducts." *Industrial & Engineering Chemistry Research* **55**(26): 7154–7163.
- Beh, C. C., R. Mammucari and N. R. Foster (2017). "Neoteric Media as Tools for Process Intensification." *29th Symposium of Malaysian Chemical Engineers (Somche) 2016* **206**.
- Beh, C. C., M. G. Wong, V. Olet and N. Foster (2019). "Development of a novel continuous dense gas process for the production of residual solvent-free self-assembled nano-carriers." *Chemical Engineering and Processing-Process Intensification* **143**.
- Binnemans, K., P. T. Jones, B. Blanpain, T. Van Gerven, Y. X. Yang, A. Walton and M. Buchert (2013). "Recycling of rare earths: a critical review." *Journal of Cleaner Production* **51**: 1–22.
- Brown, D., B. M. Ma and Z. M. Chen (2002). "Developments in the processing and properties of NdFeb-type permanent magnets." *Journal of Magnetism and Magnetic Materials* **248**(3): 432–440.
- Burford, M. D., M. Z. Ozel, A. A. Clifford, K. D. Bartle, Y. H. Lin, C. M. Wai and N. G. Smart (1999). "Extraction and recovery of metals using a supercritical fluid with chelating agents." *Analyst* **124**(4): 609–614.
- Corbett, M. K., J. J. Eksteen, X. Z. Niu, J. P. Croue and E. L. J. Watkin (2017). "Interactions of phosphate solubilising microorganisms with natural rare-earth phosphate minerals: a study utilizing Western Australian monazite." *Bioprocess and Biosystems Engineering* **40**(6): 929–942.
- Corbett, M. K., J. J. Eksteen, X. Z. Niu and E. L. J. Watkin (2018). "Syntrophic effect of indigenous and inoculated microorganisms in the leaching of rare earth elements from Western Australian monazite." *Research in Microbiology* **169**(10): 558–568.
- Corbett, M. K., Eksteen, J.J., Niu, X.Z., Watkin, E.L.J. (2017). "Incorporation of indigenous microorganisms increases leaching rates of rare earth elements from Western Australian monazite." *Solid State Phenomena* **262**: 294–298.

- Das, S., G. Gaustad, A. Sekar and E. Williams (2018). "Techno-economic analysis of supercritical extraction of rare earth elements from coal ash." *Journal of Cleaner Production* **189**: 539–551.
- De Lima, I. B., and Walter Leal Filho (2015). *Rare earths industry: Technological, economic, and environmental implications*, Elsevier.
- Ding, X., Q. L. Liu, X. P. Hou and T. Fang (2017). "Supercritical Fluid Extraction of Metal Chelate: A Review." *Critical Reviews in Analytical Chemistry* **47**(2): 99–118.
- Duan, W. H., P. J. Cao and Y. J. Zhu (2010). "Extraction of rare earth elements from their oxides using organophosphorus reagent complexes with HNO<sub>3</sub> and H<sub>2</sub>O in supercritical CO<sub>2</sub>." *Journal of Rare Earths* **28**(2): 221–226.
- Dushyantha, N., N. Batapola, I. M. S. K. Ilankoon, S. Rohitha, R. Premasiri, B. Abeysinghe, N. Ratnayake and K. Dissanayake (2020). "The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production." *Ore Geology Reviews* **122**.
- Fathollahzadeh, H., Becker, T., Eksteen, J.J., Kaksonen, A.K. and Watkin, E.L.J. (2018). "Microbial contact enhances bioleaching of rare earth elements." *Bioresource Technology Reports* **3**: 102–108.
- Fathollahzadeh, H., J. J. Eksteen, A. H. Kaksonen and E. L. J. Watkin (2019). "Role of microorganisms in bioleaching of rare earth elements from primary and secondary resources." *Applied Microbiology and Biotechnology* **103**(3): 1043–1057.
- Fathollahzadeh, H., Hackett, M.J., Khaleque, H.N., Eksteen, J.J., Kaksonen, A.H. and Watkin, E.L.J. (2018). "Better together: Potential of co-culture microorganisms to enhance bioleaching of rare earth elements from monazite." *Bioresource Technology Reports* **3**: 109–118.
- Fathollahzadeh, H., H. N. Khaleque, J. Eksteen, A. H. Kaksonen and E. L. J. Watkin (2019). "Effect of glycine on bioleaching of rare earth elements from Western Australian monazite by heterotrophic and autotrophic microorganisms." *Hydrometallurgy* **189**.
- Fox, R. V., R. D. Ball, P. D. Harrington, H. W. Rollins, J. J. Jolley and C. A. Wai (2004). "Praseodymium nitrate and neodymium nitrate complexation with organophosphorus reagents in supercritical carbon dioxide solvent." *Journal of Supercritical Fluids* **31**(3): 273–286.
- Gupta, C. K. and N. Krishnamurthy (2005). *Extractive Metallurgy of Rare-Earths*, CRC Press.
- Kuzmin, V. I., G. L. Pashkov, V. G. Lomaev, E. N. Voskresenskaya and V. N. Kuzmina (2012). "Combined approaches for comprehensive processing of rare earth metal ores." *Hydrometallurgy* **129**: 1–6.
- Laintz, K. E., C. M. Wai, C. R. Yonker and R. D. Smith (1992). "Extraction of Metal-Ions from Liquid and Solid Materials by Supercritical Carbon-Dioxide." *Analytical Chemistry* **64**(22): 2875–2878.
- Reisdörfer, G., D. A. Bertuol and E. H. Tanabe (2020). "Extraction of neodymium from hard disk drives using supercritical CO<sub>2</sub> with organic acids solutions acting as cosolvents." *Journal of Co<sub>2</sub> Utilization* **35**: 277–287.
- Samsonov, M. D., T. I. Trofimov, Y. M. Kulyako, D. A. Malikov and B. F. Myasoedov (2016). "Supercritical fluid extraction of rare earth elements, thorium and uranium from monazite concentrate and phosphogypsum using carbon dioxide containing tributyl phosphate and di-(2-ethylhexyl)phosphoric acid." *Russian Journal of Physical Chemistry B* **10**(7): 1078–1084.
- Samsonov, M. D., T. I. Trofimov, Y. M. Kulyako, S. E. Vinokurov, D. A. Malikov, G. S. Batorshin and B. F. Myasoedov (2015). "Recovery of Rare Earth Elements, Uranium, and Thorium from Monazite Concentrate by Supercritical Fluid Extraction." *Radiochemistry* **57**(4): 343–347.
- Sawada, K., D. Hirabayashi and Y. Enokida (2008). "Fundamental studies on extraction of actinides from spent fuels using liquefied gases -: Conversion of copper into nitrate with NO<sub>2</sub> and extraction of Nd(III) nitrate by CO<sub>2</sub> with TBP." *Progress in Nuclear Energy* **50**(2–6): 483–486.
- Shimizu, R., K. Sawada, Y. Enokida and I. Yamamoto (2005). "Supercritical fluid extraction of rare earth elements from luminescent material in waste fluorescent lamps." *Journal of Supercritical Fluids* **33**(3): 235–241.
- Sinclair, L. K., D. L. Baek, J. Thompson, J. W. Tester and R. V. Fox (2017). "Rare earth element extraction from pretreated bastnasite in supercritical carbon dioxide." *Journal of Supercritical Fluids* **124**: 20–29.
- Smart, N. G., T. Carleson, T. Kast, A. A. Clifford, M. D. Burford and C. M. Wai (1997). "Solubility of chelating agents and metal-containing compounds in supercritical fluid carbon dioxide." *Talanta* **44**(2): 137–150.
- Tomioka, O., Y. Enokida and I. Yamamoto (1998). "Solvent extraction of lanthanides from their oxides with TBP in supercritical carbon dioxide." *Journal of Nuclear Science and Technology* **35**(7): 515–516.

- Van Alin, A., M. K. Corbett, H. Fathollahzadeh, M. C. Tjiam, A. Putnis, J. Eksteen, A. H. Kaksonen and E. Watkin (2023). "Adhesion Behaviour during Biofilm Formation on Monazite." *Microorganisms* **11**(5).
- Van Alin, A., M. K. Corbett, H. Fathollahzadeh, M. C. Tjiam, W. D. A. Rickard, X. Sun, A. Putnis, J. Eksteen, A. H. Kaksonen and E. Watkin (2023). "Biofilm formation on the surface of monazite and xenotime during bioleaching." *Microbial Biotechnology* **16**(9): 1790–1802.
- Vincent, T., M. Mukhopadhyay and P. K. Wattal (2009). "Direct in situ supercritical fluid extraction of neodymium ion from its oxide using thenoyl tri fluoro acetone-tri butyl phosphate-methanol in carbon dioxide." *Journal of Supercritical Fluids* **48**(3): 230–237.
- Wai, C. M. (2002). Metal Processing in Supercritical Carbon Dioxide. *Supercritical Fluid Technology in Materials Science and Engineering*. Y.-P. Sun, Marcel Dekker: New York: 351–386.
- Wai, C. M., A. S. Gopalan and H. K. Jacobs (2003). "An introduction to separations and processes using supercritical carbon dioxide." *Supercritical Carbon Dioxide: Separations and Processes* **860**: 2–8.
- Yao, Y. X., N. Farac and G. Azimi (2018). "Recycling of Rare Earth Element from Nickel Metal Hydride Battery Utilizing Supercritical Fluid Extraction." *Selected Proceedings from the 233rd Ecs Meeting* **85**(13): 405–415.
- Zhang, J. K., J. Anawati and G. Azimi (2022). "Urban mining of terbium, europium, and yttrium from real fluorescent lamp waste using supercritical fluid extraction: Process development and mechanistic investigation." *Waste Management* **139**: 168–178.
- Zhang, J. K., J. Anawati, Y. X. Yao and G. Azimi (2018). "Aerionmetallurgical Extraction of Rare Earth Elements from a NdFeB Magnet Utilizing Supercritical Fluids." *Acs Sustainable Chemistry & Engineering* **6**(12): 16713–16725.
- Zhang, J. K. and G. Azimi (2020). "Supercritical Fluid Extraction of Rare Earth Elements from Waste Fluorescent Lamp." *Rare Metal Technology 2020*: 93–105.
- Zhu, L. Y., W. H. Duan, J. M. Xu and Y. J. Zhu (2009). "Kinetics of Reactive Extraction of Nd from Nd<sub>2</sub>O<sub>3</sub> with TBP-HNO<sub>3</sub> Complex in Supercritical Carbon Dioxide." *Chinese Journal of Chemical Engineering* **17**(2): 214–218.