2018

Experimental Study of the Static and Dynamic Extraction of Rare Earth Elements from Coal Using HNO3 and TBP-HNO3 Complex in Supercritical CO2

He Yun
Lehigh University

Recommended Citation

Yun, He, "Experimental Study of the Static and Dynamic Extraction of Rare Earth Elements from Coal Using HNO3 and TBP-HNO3 Complex in Supercritical CO2" (2018). *Theses and Dissertations*. 2994.
https://preserve.lehigh.edu/etd/2994

Experimental Study of the Static and Dynamic Extraction of Rare Earth Elements from Coal Using HNO_3 and TBP-HNO_3 Complex in Supercritical CO_2

by

He Yun

A Thesis
Presented to the Graduate and Research Committee
of Lehigh University
in Candidacy for the Degree of
Master of Science

in
Mechanical Engineering

Lehigh University
(January 2018)

This thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science.

Date

Dr. Arindam Banerjee, Thesis Advisor

Dr. Gary Harlow, Chairperson of Department

ACKNOWLEDGMENTS

I would like to express my greatest appreciation to my thesis advisors, Dr. Arindam Banerjee, Dr. Carlos Romero and Dr. Jonas Baltrusaitis. They have given me a lot of valuable guidance and comments during my academic and research work. Moreover, I would like to thank Mr. Zheng Yao for his suggestions and help during my research projects. Additionally, I would like to thank Mr. Al Kaziunas and all the other staff at Applied Separations, Inc., for teaching me how to use the supercritical separation system and for the warm reception and supporting during every visit.

I am also appreciative of my family for always believing in and encouraging me to pursue my academic dream. Additionally, I would like to thank all the colleagues at Energy Research Center for all the good experience of teamwork. Lastly, special thanks to Dr. Carlos Romero again for his precious time during my stay at the Center.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Solvent extraction was studied for the recovery of Rare Earth Elements (REEs) from refuse coal under static and dynamic conditions. Static extraction was performed using nitric acid (HNO_3) digestion at elevated temperatures, up to 90°C. Dynamic extraction was performed in a flow apparatus using HNO_3 and a complex prepared from TBP and concentrated HNO_3 (TBP-HNO_3 complex) in Supercritical Carbon Dioxide (SC-CO_2) under high pressures, up to 3,000 psig. The reported recovery efficiency for three targeted REEs from refuse coal, Ce, La and Nd was less than 30% under static conditions and less than 5% under dynamic conditions, despite the fact that these three elements exist in the highest concentrations of all of the REEs in the coal samples. However, a hydrometallurgy method for REEs recovery from coal was investigated, providing the opportunity to understand and identify modifications required by the approach to improve REE recovery efficiency. Additionally, the use of SC-CO_2 as a polarity matching stream for REE carry and subsequent reduction, was identified as an important step in a dynamic REE extraction process, which would require process optimization. For static extraction of Ce, La and Nd from refuse coal with heated HNO_3 and TBP-HNO_3 complex digestion, a temperature and time of 90°C and 4 hours were identified from these static experiments, which improve the extraction efficiency of Ce and La with TBP-HNO_3 complex reaching 18.84% and 26.32%, respectively, while with HNO_3, extraction efficiency of 11.90 % and 6.26% were achieved, respectively. Nd was insensitive to this extraction method. For dynamic extraction, with a SC-CO_2 flow rate of 2.5 L/min, pressure and extraction time play an important role in using TBP-HNO_3 complex to extract REE from refuse coal.

CHAPTER1: INTRODUCTION

Rare earth elements (REEs) or rare earth metals, as defined by the International Union of Pure and Applied Chemistry (IUPAC), are elements that belong to a set of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides, as well as scandium and yttrium [1]. Scandium and yttrium are considered REEs since they occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. REEs are cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), Ianthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), promethium (Pm), samarium (Sm), Scandium (Sc), terbium (Tb), thulium (Tm), ytterbium (Yb) and yttrium (Y).

Because of its wide range of uses, REEs are particularly important. REEs are used in many industries, including metallurgy, petrochemical, glass ceramics, and in fluorescent and electronic materials. For example, in the metallurgy industry, REEs and their alloys play an important part in steel-making deoxidation and desulfurization. They can reduce the content of oxygen and sulfur in steel to fewer than 0.001%, change the shape of inclusions and fine granulation, and help improve the processability, strength, toughness, and the corrosion and oxidation resistance of steel. REEs and their alloys are also used for manufacturing of nodular cast iron, high-strength gray iron and vermicular cast iron, helping change the form of graphite in the cast iron, and improve the casting processes and mechanical properties of alloy steel. In addition, a small quantity of rare earth elements added in the smelting of bronze and brass can improve the elongation, heat resistance, conductivity and strength of the alloy. In the glass industry, REE polishing powder also play an important role. For example, CeO_2 is used for increasing glass clarity, Pr_6O_{11} and Nd_2O_3 are used for glass coloring, and La_2O_3, Nd_2O_3 and CeO_2 are used to make special glass. In the ceramics industry, REEs can also be used to make ceramic glazes and refractory materials. For instance, single high-purity rare earth oxides, such as Y_2O_3, Eu_2O_3, Gd_2O_3, La_2O_3, and Tb_4O_7 are used to synthesize various phosphors, such as color TV red phosphor, projection TV white phosphor, ultra-short afterglow phosphor.

REEs are very important to modern life. Pure REEs are used in fluorescent lamps, X-ray screens and light conversion materials. Rare earth metal oxides, like high purity Y_2O_3, Nd_2O_3, Ho_2O_3, Gd_2O_3 are used to make metal halogen lamps. Flint is made of mixed cerium-based rare earth metals. The high-pressure mercury lamps used for lighting on the road is a bright light emitted from europium-doped yttrium vanadate or dysprosium-doped yttrium vanadate phosphor coated on the lamp housing. The lights used for cinema projection are the arc generated by energizing carbon rods doped with rare earth fluoride. Small, portable, neodymium-iron-boron permanent magnets housed in portable stereo headphones are the main source of music. A camera lens that can take a sharp image is made of lanthanum glass. Batteries used in mobile phones are made of lanthanum nickel alloys. The ternary catalyst unit used to purify the exhaust gas emitted by vehicles also contains REEs. In view of this, REEs facilitate people's lives and play an indispensable role in today's world.

A survey of REEs reserves worldwide provided by the US Geological Survey in 2016 [2], shown in Figure 1, indicates that China's REE proven reserves ranks number one in the world, accounting for about 37% of the world's total reserves of 120,000 metric tons. Brazil accounts for about 18.3% as second. India holds about 6,900 metric tons of REEs reserves, third in the world with 0.06%. Australia and United States respectively account for about 0.03% and 0.01% of the world's total REEs reserves, respectively.

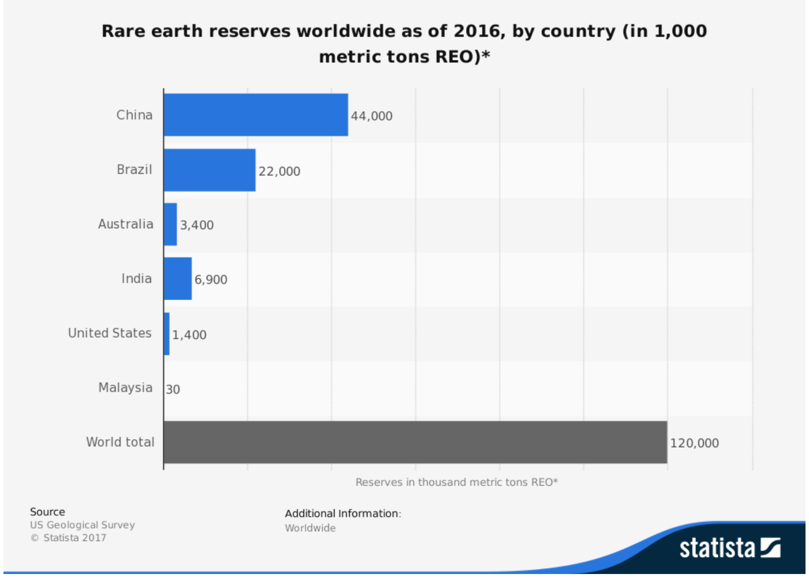


Fig. 1. REEs Worldwide Reserves as of 2016, by Country (in 1,000 metric tons)

It is also worth mentioning that China has the largest scale of REE production in the world [3]. From the survey of distribution of rare earth production worldwide, provided by the US Geological Survey in 2016, China's REE production accounts for 83.33% as number one in world production, almost eight times that of Australia, the second largest producer (see Figure 2).

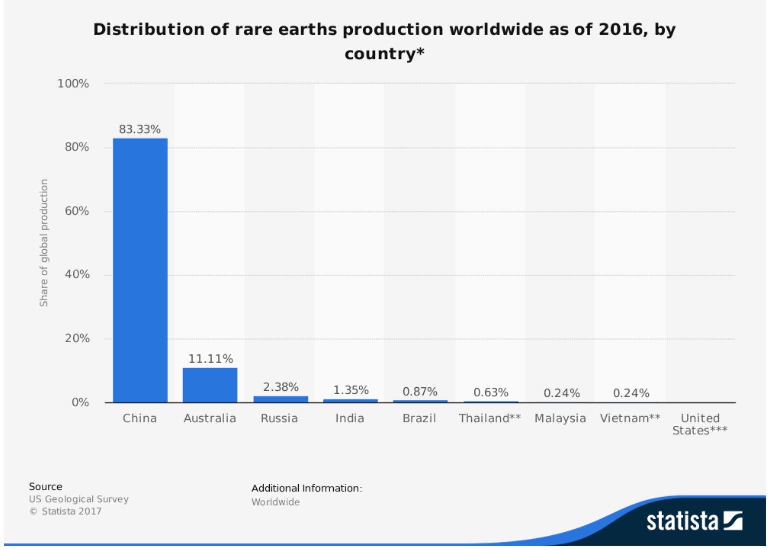


Fig. 2. Worldwide Distribution of REEs Production as of 2016, by Country

Several countries, including the US, the European Union, Japan and South Korea import large quantities of REEs from China, making China a decisive player in setting up REEs undermarked pricing. Since 2009, China began enforcing tighter environmental standards to rare earth producers, while at the same time, requiring them to meet the needs of the domestic market before exporting REEs [4]. This combined situation of new environmental restriction on REEs conventional mining in China and the high demand of REEs in the world, makes REEs extraction an issue of national security for the US.

REEs have become one of the most important strategic resources to the world's largest economies. According to the American Chemistry Council, worldwide demand for REEs would grow more than 5% through 2020, annually [5]. With this significant growth in global REEs demand, cost and availability, countries around the world are increasingly concerned about economically viable rare earth substitutes, as well as new REE extraction methods. One non-traditional source of REEs that has started to receive a good deal of attention is recovery of rare earth from coal and coal bearing resources. Combined with chondrites and shales, many coals worldwide are slightly enriched in heavy rare earth elements (HREE) relative to light rare earth elements (LREE).

In August 2017, the U.S. Department of Energy (DOE) selected four projects to move on to a second phase of research in their efforts to advance recovery of REEs from coal and coal by-products, with an overall research investment of $17.4 million. These projects aim at developing and testing REE recovery concept designed under a prior Phase 1 funding opportunity announcement through the DOE's office of Fossil Energy (FE) [6].

The DOE's REEs from coal and coal by-products program [6] consists of five core technology areas, which are: Resource Sampling and Characterization, Separation Technology

Development, REEs Sensor Development, Process & Systems Modeling, as well as Techno-Economic Analysis. Among them, separation technology development is the most important area since the U.S.'s vast coal resources contain quantities of REEs that offer the potential to reduce the national dependence on other countries for these critical materials and offer new business opportunities to mining and other industries in regions where coal plays an important economic role [7]. It is expected that the development of the novel competitive extraction technologies of REEs from US coals will secure and maintain the national economic growth and security.

In this present study, static/dynamic extraction of three rare earth elements was targeted (Ce, La, Nd). Refuse coal was used in the study, with nitric acid (HNO_3) and organophosphorus-HNO_3 complex together in supercritical CO_2 (SC-CO_2). The complexes were prepared by vigorously mixing Tri-n-butyl phosphate (TBP) with concentrated HNO_3 (15.5 mol/L) for 30 minutes in a conical flask and then centrifuged for another 30 minutes. Under static extraction conditions, the total efficiency of those three REEs using HNO_3 and TBP-HNO_3 complex reached 8.34% and 17.33%, respectively. The extraction efficiency of Ce using HNO_3 and TBP-HNO_3 complex reached 11.90% and 18.84%, respectively. Recovery efficiency of La was achieved 6.26% and 26.32%, when using HNO_3 and TBP-HNO_3 complex, respectively; while the extraction efficiency of Nd from coal with both HNO_3 and TBP-HNO_3 complex was less than 1%. Under dynamic extraction, the total extraction efficiency of the three targeted REEs using HNO_3 in SC-CO_2, reached only 4.0%. The reported recovery efficiency for the three targeted REEs in refuse coal, Ce, La and Nd was not significant, despite these three elements exist in the highest concentrations of all of the REEs in the samples. However, two objectives were achieved from this study. A hydrometallurgy method for REE extraction from coal was investigated, offering the opportunity to understand and identify modifications required by the method to improve REE recovery efficiency. It is apparent that ligands would be required to supplement or eliminate acid reagents for REE extraction. There is a long list of chelates, such as humid and nitric acid which have been suggested as good ligands for REE binding and are environmentally benign. Additionally, the use of SC-CO_2 as a polarity-matching reagent for REE carrying and subsequent reduction, was identified as an important step in a dynamic REE extraction process, which would require process optimization. The rest of this thesis reports the experimental methods used in the investigation, describe the analytical results in more detail, and provide conclusions and recommendations for future studies.

CHAPTER 2: LITERATURE REVIEW

To determine the economic feasibility of recovering REEs from domestic coal and coal byproducts, researchers have been introducing novel separation and recovery concepts. In 2016, a team of Penn State University and DOE researchers reported a cost-effective and environmentally friendly method to extract REEs from coal and coal byproducts, using ion exchange [8]. The method also involves extracting coal byproducts with a solvent that releases the REEs bound to it. The new extraction technique combines pressure filtration, using external forces to separate solids from fluids, with an environmentally friendly ion-exchange/ion-chromatography process. In this process, the REE-enriched liquid can be processed to recover the elements while recycling the liquid for reuse in the system.

The National Energy Technology Laboratory (NETL) is working on a research to investigate, characterize, and extract REEs from coal, including coal ash. In this research, a method was investigated that uses 2M hydrochloric acid (HCI) and sodium hydroxide (NaOH) in a hydrothermal pretreatment step to extract the REEs from coal ash [9]. The results report an increased extraction of REE of nearly 90% for coal ash when using the acid digestion, followed by the sodium hydroxide solution pretreatment, instead of limited extraction of REEs using only HCl. Additionally, the same group performed experiments on the sorption of several light and heavy REEs (La, Ce, Sm, Eu, Gd, Ho, Er, Lu) on xylain and humic acids. The results shows that the sorption on xylain was found to be pH and time dependent [9], with a maximal adsorption capacity in the pH range from 3 to 5. Reference 10 reports laboratory-scale dissolution experiments which were conducted to determine REE contents in coal fly ash particles and investigated their dissolution behavior in H_2SO_4 solvents. The results indicate that the dissolution rates of REEs increase with the temperature of the H_2SO_4 solvent in the dissolution tests and that the REE content in coal fly ash specimens completely conformed to the OddoHarkins Rule [10], West Virginia University reports a study on recovery of REEs from coal mine drainage [11]. In this study, these researchers preliminary indicate that Acid Mine Drainage (AMD) sludge could be an important feedstock for REE. To verify their estimates, they sampled two AMD sludges, one from a Kittanning surface mine and another from a Freeport/Kittanning refuse facility. The results shows the summation of aqueous, major ion concentrations accounted for about 30% of the actual sludge solid mass, while accounting for hydroxides in the metal precipitates more than doubled the estimated sludge mass [12].

Solvent extraction has been selected by some researchers to extract REEs from coal and coal by-products due to its efficiency potential, large-scale and continuity of extraction. However, the choice of extraction agent and solvent are critical. In recent years, Supercritical Fluid Extraction (SCFE) has become an increasingly popular method of metal extraction as a useful alternative to conventional solvent extraction methods. The advantage of this option over conventional solvent extraction methods include minimization of liquid waste generation, solute separation and rapid reaction rates. Supercritical fluids (SCFs) can penetrate and transport solutes from different matrices due to its high diffusivity, low viscosity, and liquid-like solvating capability [13-17]. CO_2 provides a good option as an efficient solvent since it has the benefit of easy-to-obtain a medium critical constants ($Tc = 31.1℃$ and $Pc = 7.38$ MPa), as compared to other solvents. Additionally, CO_2 is inert and stable (chemically and radiochemically), inexpensive, easy to supply at high purity, and it is environmentally friendly and widely used [18]. Figure 3 shows the phase diagram of CO_2 [18]. The diagram shows the different phase regions of this medium. The supercritical region, at temperatures greater than 300 K and pressures greater than 100 bar would be the target conditions for the use of SC-CO_2 for REE separation.

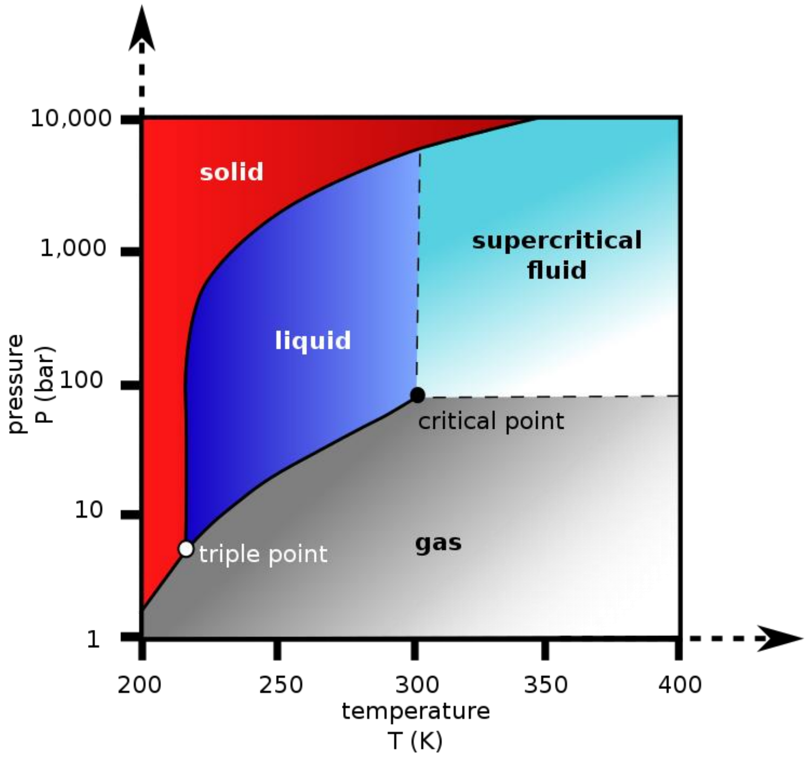


Fig. 3. Carbon Dioxide Pressure-Temperature Phase Diagram

As an effective and reliable solvent, SC-CO_2 has been used for extraction processes in different industries. For example, in the food industry, E. Sabio and M. Lozano [19] performed a method to extract lycopene and β-carotene from tomato processing waste using SC-CO_2. In this study, recovery of lycopene β-carotene was achieved at levels as high as 88% from tomato skins, at 300 bar and 80℃.

However, SC-CO_2 is not always used alone as a solvent. Researchers have reported that it is highly inefficient to direct extract metal ions by SC-CO_2 because of the charge neutralization requirement and the weak solute-solvent interactions. Solution of these metal ions would greatly increase if the metal ions are bound to organic ligands. For example, TBP has shown to play an important role in extraction of metal ions [20]. In this study, the extraction of lanthanide ions from acidic solution (6 M HNO_3-3 M $LiNO_3$) using 30% TBP modified CO_2 yielded extraction efficiencies greater than 85% for Sm^{+3}, Eu^{+3}, Gd^{+3} and Dy^{+3} [20]. Reference 21 studied the density, viscosity and surface tension of the TBP-HNO_3 complex. In reported experiments, the results showed when the concentration of HNO_3 in TBP-HNO_3 complex increases from 1.95 to 5.89 mol/L, the density and the surface tension of the TBP-HNO_3 complex increase from 1.02 to 1.10 g/cm^3 and from 27.5×10^{-3} to 30.0×10^{-3} N/m^3, respectively, while, the viscosity of the TBP-HNO_3 complex decreases from 4.57×10^{-3} to 2.73×10^{-3} $\mathrm{Pa \cdot s}$ (see Figures 4 – 6).

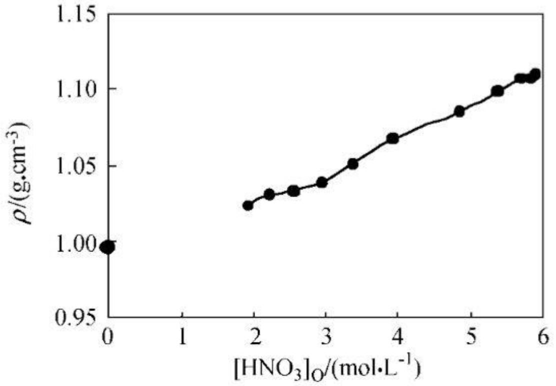


Fig. 4. Density of the TBP-HNO_3 Complex at 15℃ in Reference 21

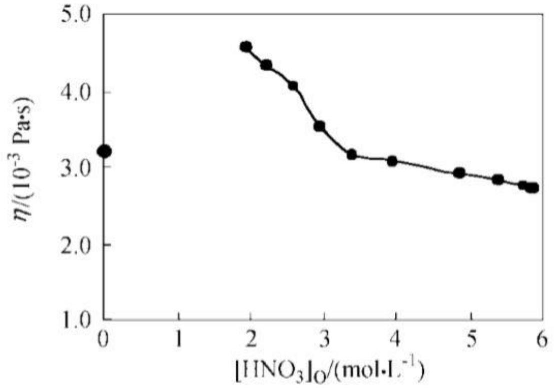


Fig. 5. Viscosity of the TBP-HNO_3 Complex at 15°C in Reference 21

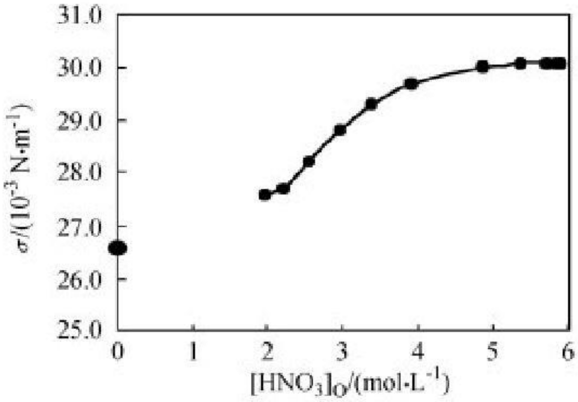


Fig. 6. Surface tension of the TBP-HNO_3 Complex at 15°C in Reference 21

Reference 22 also reported the feasibility of using SC-CO_2 as a substitute extraction solvent in nuclear reprocessing, tested in the extraction of lanthanide ions from an acidic solution. In these experiments, by using tributyl phosphate (TBP) modified CO_2, lanthanides were extracted from 6 M HNO_3-3 M $LiNO_3$ solutions. By using a combination of thenoyltrifluoroacetone (TTA) and TBP-modified CO_2 as the extractant, other separation synergistic effects were also investigated. When TBP-modified CO_2 was used as the extractant, light lanthanides ($Ln(NO_3)_3$•TBP) and heavy lanthanides ($Ln(NO_3)_3$•2TBP) were readily extracted. While when TTA was added to TBP-Modified CO_2, $Ln(TTA)_3$•3TBP and $Ln(TTA)_3$•2TBP adducts were extracted. In Reference 23, the authors report experiments where an adduct was prepared by combining TBP and fuming HNO_3 (90%), and characterized the phase-equilibrium behavior in SC-CO_2. By using the adduct in SC-CO_2, the extraction efficiency of selected rare earth oxides at 338 K and 34.5 MPa were compared with those obtained using another adduct made by concentrated HNO_3 (70%) and TBP. The results showed that all rare earth oxides tested with both adduct species could be extracted with the exception of cerium oxide. It was indicated that water and acid concentrations in the different adducts played an important role in rare earth oxide extraction efficiency.

Finally, Wuhua and Cao performed experiments on the effect of static and dynamic extraction of Nd [24]. Their results showed acidity of the TBP-HNO_3 complex has a great influence on static extraction efficiency, while temperature and pressure have little effect on the static extraction efficiency. At an optimized volume of TBP-HNO_3 complex of 8 ml per 0.5 g of Nd_2O_3, the extraction efficiency of Nd was 94.69% with the TBP-HNO_3 complex ([H+] = 4.54 mol/L) at 323.15 K and 15 MPa. Samsonov and Trofimov also reported the recovery of REEs (Uranium and Thorium) from monazite concentrate (MC) by SCFE [25]. In the study, quantitative recovery of Th and U was not possible, and there was an indication that the components needed to be more soluble compounds. Microwave (MV) radiation was additionally tried for MC pretreatment by sintering with Na_2CO_3 in the presence of coal. The resulting product consisted of two phases. One of them contains REEs (~50%) that are recyclable with TBP or adducts of HNO_3 with SC-CO_2. The second stage was a solid solution of Ce, and Th and U oxides and the remaining REEs. Using HDEHP under SC-CO_2 allowed the recovery of Th and U from hydrochloric acid solution [25].

CHAPTER 3: EXPERIMENTAL

This chapter describes the experimental setup used for extraction of the REEs from coal under static condition and dynamic conditions. The corresponding experimental procedures are also described in this chapter.

Separation extraction is the premise used in this study for recovery of REEs from coal and coal by-products. Fractional crystallization and fractional precipitation are the basic separation methods of REEs, which have been commonly and widely used in the past; however, these methods have started to be replaced by ion exchange and solvent extraction [26]. In fractional crystallization, a portion of the salt in the solution is precipitated by temperature changes or by evaporation of a saturated solution. Due to the different solubility of the components, the composition of the crystals formed is different when compared to the original solution. The result is a crystalline crop that contains less soluble components and a more soluble component-rich solution. A variety of rare earth salts and soluble salts have been used for separation of isolated crystals [27]. For example, dibasic ammonium nitrate has been used for the removal of lanthanum and the separation of praseodymium and neodymium. In fractional precipitation, by adding a chemical reagent, a part of the REEs is removed from the solution to form a less soluble compound. The remaining REEs in solution are recovered by further precipitation as the same or different compound [27]. Several compounds have been used for fractional precipitation of REEs, with hydroxides and bisulfates being the most widely used [28]. Ion exchange is used to treat low concentrated REEs solutions as well as is used in applications requiring high purity REEs [29]. In ion exchange resins or ion exchangers, negative or positive ions attach to the insoluble organic matrix. In cation exchange resins, ions are positive while the ions are negative in anion exchange resins. When the resin is in contact with the salt solution, the ions in the organic resin can be replaced by the ions in the solution. In general, ions with a lower charge are replaced by the one with a higher charge, and ions with a larger radius displaces the ion with a smaller radius if the ions have the same charge [29]. After the adsorption phase, ions in the solution are loaded into the resin, and ions are desorbed from the resin into solution during the resin elution phase. Ion exchange can be referred to as ion exchange separation if the solution contains several ions that exhibit selectivity during the exchange. The component distribution between two phases has a constant value under equilibrium conditions [29]. Solvent extraction, also called liquid-liquid extraction, is the most common technique used in REEs separation. Acidic, basic, and neutral extractants are the most common industrial extractants, including TBP, 2-ethylhexyl (2-ethylhexyl) phosphonate (EHEHPA), bis (2-ethylhexyl) phosphoric acid (D2EHPA) [28], and Aliquat 336 (see Figure 7 from Reference 28).

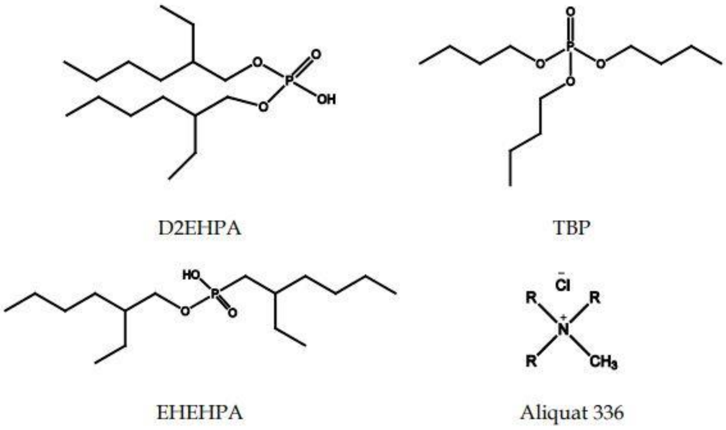


Fig. 7. Structures of D2EHPA, TBP, EHEHPA and Aliquat 336 in Reference 28.

Acidic extractants, include organophosphorus acids, carboxylic acids and naphthenic acids [30]. The hydrogen in the extractant is usually replaced by the extracted metal and then form a neutral organic soluble complex. This process is controlled by pH of the aqueous solution [28]. The cation exchange reaction [31] is:

$$Ln^{3+}\ (aq) + 3HL\ (org) \rightarrow [LnL](org) + 3H^{+}\ (aq)$$

Basic extractants, include long-chain quaternary ammonium salts $R_3CH_3N^+X^-$. R_3 is a C_8-C_{12} group and X is thiocyanate. The degree of extraction and stripping depends on the concentration of the X-ray aqueous phase. There is a different extraction behavior in thiocyanate and nitrate systems. Specifically, in the thiocyanate system, the extraction efficiency increases with an increasing atomic number, while the effect is the opposite in the nitrate system. The corresponding reaction is an anion exchange reaction [29]:

$$Ln^{3+}\ (aq) + 3X^{-}\ (aq) +\ R_3CH_3N^{+}X^{-}\ (org) \rightarrow [LnX_4^{-}R_3CH_3N^{+}](org)$$

Neutral extractants, include phosphate esters, phosphonate esters, phosphine oxides and phosphinate esters. TBP is the most commonly neutral extractant [32, 33]. The solvation reaction is [31]:

$$Ln^{3+}\ (aq) + 3NO_3^{-}\ (aq) + 3TBP\ (org) \rightarrow [Ln(NO_3)_3(TBP)_3](org)$$

TBP works well in nitrate media. In the present work, solvent extraction was considered as the extraction method in experiments run under static extraction and dynamic extraction. Static extraction was performed using nitric acid digestion at elevated temperatures, while, dynamic extraction was performed in a flow apparatus using nitric acid and a complex prepared from nitric acid and Tri-Butyl-Phosphate (TBP) in supercritical carbon dioxide under high pressures, up to 3,000 psig. Corresponding procedures are introduced in this Chapter.

3.1 Reagents

The main reagents used in this study include supercritical carbon dioxide (SC-CO_2), nitric acid (HNO_3) and TBP-HNO_3 complex prepared from TBP and concentrated HNO_3. HNO_3 (15.5 mol/L) was purchased from Right Price Chemicals and Lab Equipment Inc. In order to consider different concentrations of nitric acid on REEs extraction, concentrated HNO_3 (15.5 mol/L) and dilute HNO_3 (3%) in water were investigated in the experiments. TBP (98%) was purchased from Fisher Scientific Inc. TBP was used in combination with HNO3 and it was prepared by vigorously mixing TBP and concentrated HNO_3 (15.5 mol/L) with a volume ratio of 1:1 for 30 minutes in a conical flask and then centrifuged for another 30 minutes. The density of the TBP-HNO_3 complex was calculated by weighing a known sample volume. This data was used in further calculations about in the recovery efficiency of REEs. SC-CO_2 used in the dynamic extraction was original provided by Praxair, Inc..

3.2 Equipment

Two setups were used in these experiments, a setup for static conditions testing and a flow apparatus for dynamic condition experimentation. The main part of the equipment consists of a separation system device and a liquid pump, which were used for the dynamic extractions, and a stirring hotplate and an atomic absorption spectrometer used for the static extractions. For the static conditions testing, the stirring hotplate was used to heat and dissolve mixtures of refuse coal and an extracting solution. The hotplate is Fisher Scientific, Inc., with static conditions indicated in Table 1.

Table 1. Specifications of Thermix® Stirring Hotplate

Surface Area Heating	7.25 * 7.25 in.
Top Plate Material	Ceramic
Hertz	50/60 Hz
Dimensions (L * W * H)	13 * 8.2 * 3.8 in.
Max. Temperature	540℃
Surface Area (Metric) Heating	18.4 * 18.4 cm
Voltage	110-120V
Electrical Requirements	100-120 V 50/60 Hz

An atomic absorption spectrometer (Model: AAnalyst 200) from PerkinElmer, Inc. was used in combination with the hotplate experiment to detect metallic ions (Fe^{3+}, Ca^{2+}, Mg^{2+}). Condition information for the atomic absorption spectrometer are listed in the Table 2. These three metallic ions were targeted as an internal step in assessing the next of recovering element from a coal matrix.

Table 2. PinAAcle Instrument and Analytical Specifications (Model: AAnalyst 200)

Parameter	Cu	Fe	Mg	Zn	Na	Ca
Wavelength (nm)	324.75	248.33	285.21	213.86	589.00	422.67
Slit (nm)	0.7	0.2	0.7	0.7	0.2	0.7
Air Flow (L/min)	2.5	2.5	2.5	2.5	2.5	2.5
Acetylene Flow (L/min)	10	10	10	10	10	10
Acquisition Time (sec)	3	3	3	3	3	3
Replicates	3	3	3	3	3	3
Sample Flow Rate (ml/min)	6	6	6	6	6	6
Intermediate Standard (mg/L)	1	2	1	2	20	20
Auto-Diluted Calibration Standards (mg/L)	[0.05] [0.1] [0.25] [0.5] [1]	[0.1] [0.2] [0.5] [1] [2]	[0.05] [0.1] [0.25] [0.5] [1]	[0.1] [0.2] [0.5] [1] [2]	[0.5] [1.0] [2.0] [5.0]	[1.0] [2.0] [5.0] [10.0]
Calibration Curve Type	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero	Non-Linear Through Zero

The flow separation system device for dynamic operation is mainly composed of a SC-CO_2 storage cylinder, a SC-CO_2 pump, a heating oven, a pressurized vessel (SS 316) and a sealed glass recovery tank. This setup was provided by Applied Separations, Inc.. Detail information of this separation system was shown in Table 3 and Figure 8.

Table 3. Operating Parameters of Flow Separation System Device

Instruments	Maximum Pressure	Maximum Temperature
SC-CO_2 pump	6,000 psig	120℃
Heating Oven	10,000 psig	240℃
Vessel	10,000 psig	240℃

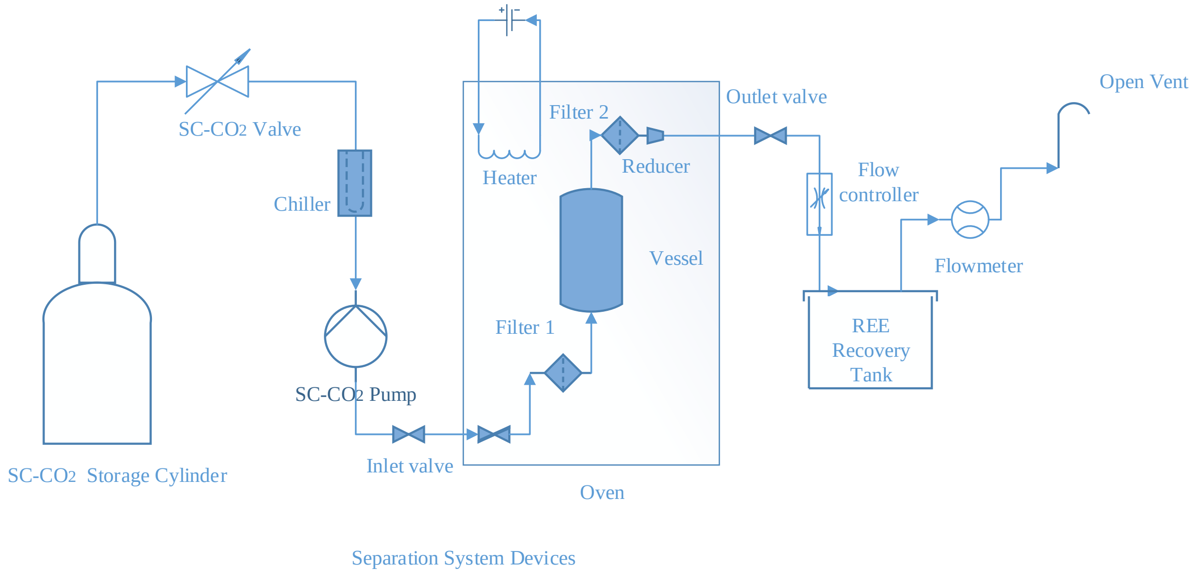


Fig. 8. Diagram of Flow Separation System Devices

A liquid pump (Model: LC-10AT VP) was used to pump the solvent to the separation system device and it was purchased from Shimadzu Corporation, Inc. Table 4 shows the operating parameter.

Table 4. Specifications of Liquid Pump (Model: LC-10AT VP)

Setting Item	Setting Range	Setting Steps	Initial Value	Mode
Flow	0 – 9.999 ml/min	0.001 ml/ min	0 ml/min	Constant flow delivery
Press	1.0 – 40.0 MPa 10 – 400 kgf/cm^2 10 – 400 bar 140 – 5,700 psig	0.1 MPa 1 kgf/cm^2 1 bar 10 psig	1.0 MPa 10 kgf/cm^2 10 bar 140 psig	Constant Pressure Delivery
P-max	2.0 – 40.0 MPa 10 – 440 kgf/cm^2 10 – 430 bar 140 – 6,200 psig	0.1 MPa 1 kgf/cm^2 1 bar 10 psig	10 MPa 100 kgf/cm^2 100 bar 1,400 psig	
P-min	0 – 43.0 MPa 0 – 440 kgf/cm^2 0 – 400 bar 140– 6,200 psig	0.1 MPa 1 kgf/cm^2 1 bar 10 psig	0 MPa 0 kgf/cm^2 0 bar 0 psig	

3.3 Procedures

Experiments using static and dynamic conditions were run sequentially. Initially, static extraction experiments were run to extract metallic elements from refuse coal samples provided by a mine located in West Virginia. Refuse coal is a byproduct of the coal cleaning process used by coal mining companies. On this process, coal extracted from the mine goes through a series of screens, froth flotation, spirals, etc. to obtain coal with a quality specified by coal buyers. The reject or refuse coal is typically landfilled. It is expected that this coal is richer in REE. The analysis of the refuse coal as tested by Geochemical Lab are included in Table 5.

Table 5. Laboratory Results of Refuse Coal provided by Geochemical Testing

Analyses	Result	Low Limit	Units
Silicon Dioxide	60.97	2.00	% Dry
Aluminum Oxide	24.47	0.02	% Dry
Iron Oxide	9.08	0.02	% Dry
Calcium Oxide	1.15	0.02	% Dry
Magnesium Oxide	0.95	0.02	% Dry
Sodium Oxide	0.56	0.04	% Dry
Potassium Oxide	2.39	0.02	% Dry
Sulfur Trioxide	1.00	0.02	% Dry
Manganese Dioxide	0.11	0.02	% Dry
Strontium Oxide	0.07	0.02	% Dry
Barium Oxide	0.13	0.02	% Dry
Cerium	93.3	8.21	mg/Kg-dry
Dysprosium	<8.21	8.21	mg/Kg-dry
Erbium	<8.21	8.21	mg/Kg-dry
Europium	<8.21	8.21	mg/Kg-dry
Gadolinium	6.12	1.64	mg/Kg-dry
Holmium	<8.21	8.21	mg/Kg-dry
Lanthanum	41.3	8.21	mg/Kg-dry
Lutetium	<8.21	8.21	mg/Kg-dry
Neodymium	29.6	8.21	mg/Kg-dry
Scandium	30.5	1.64	mg/Kg-dry
Terbium	<8.21	8.21	mg/Kg-dry
Thulium	<8.21	8.21	mg/Kg-dry
Ytterbium	<8.21	8.21	mg/Kg-dry
Yttrium	17.5	8.21	mg/Kg-dry

Three elements in the refuse coal were targeted to demonstrate the feasibility of acid digestion using heated HNO_3. The three elements are Fe, Ca and Mg. These experiments were also performed to optimize operating conditions of the static setup duration of digestion to extrapolate conditions of temperature and digestion time on the extraction of REE from refuse coal. The results of these experiments assessed the merit of acid digestion on metals inserted in the coal matrix and optimized operating conditions for subsequent experiments with REEs. The static experiments gave place them to a tried on dynamic extraction to explore the effect of solvent strength and the type of solvent on REE recovery from coal.

3.3.1 Static Extraction – Heated Digestion

To investigate extraction of high concentrated metals from refuse coal, under static digestion conditions, fifteen experiments were run over a range of recovery time and operating temperatures. Details of the experimental conditions are shown in Table 6.

Table 6. Operating Conditions for Extraction of Metallic Elements under Static Conditions with HNO_3

Test Number	Refuse Coal	Testing Duration	Testing Temperature	Total Efficiency (%)
1	0.5 gram	2 hours	70°C	46
2			80°C	74
3		3 hours	70°C	77
4			80°C	71
5			90°C	81
6		4 hours	70°C	45
7			80°C	55
8			90°C	93
9		5 hours	70°C	65
10			90°C	71

In these static experiments, the stirring hotplate was preheated to the desired temperatures of 70, 80 or 90℃. For each test, 0.5 gram of refuse coal was weighted and then placed into a glass container labeled in advanced for the corresponding test number. A designed volume of 50 ml of HNO_3 was then added into the glass container. The glass container was sealed and placed on the preheated hotplate and heated for the corresponding time of the experiment. After the end of the each experiment, 15 ml of the upper layer liquid of the solution was extracted and placed into a vial for analysis.

Optimal temperature and duration of digestion was selected based on the total extraction efficiency of Fe, Ca and Mg, using HNO_3 as the digestion media. Additionally, two additional tests were run with TBP added to the solution under static extraction to consider the effect of organic acid ions on the efficiency of REEs extraction. Table 7 indicates the operating conditions for these tests. A similar procedure as the one described before for HNO_3 was followed for the test with the TBP-HNO_3 complex.

Table 7. Operating Conditions for Static Extraction of REEs with HNO_3 and TBP-HNO_3 Complex

Tests Number	Refuse Coal	Range of Testing Duration	Range of Testing Temperature	Solvent	Volume of Solvent
11	1.0 gram	0.5-5 hours	70-90℃	HNO_3 (15mol/L)	100 ml
12				TBP-HNO_3 complex	

3.3.2 Dynamic Extraction – Separation System Devices

The schematic diagram of the dynamic extraction system is shown again in Figure 9, with added details of the components which participate in the experimental procedure to be described next. As mentioned in the previous sections, the main part of this system consists of the separation system devices and a liquid pump. This schematic corresponds to the system from Applied Separation Model Speed SFE 2. Operating conditions for the operation of dynamic extraction experiments are shown in Table 8.

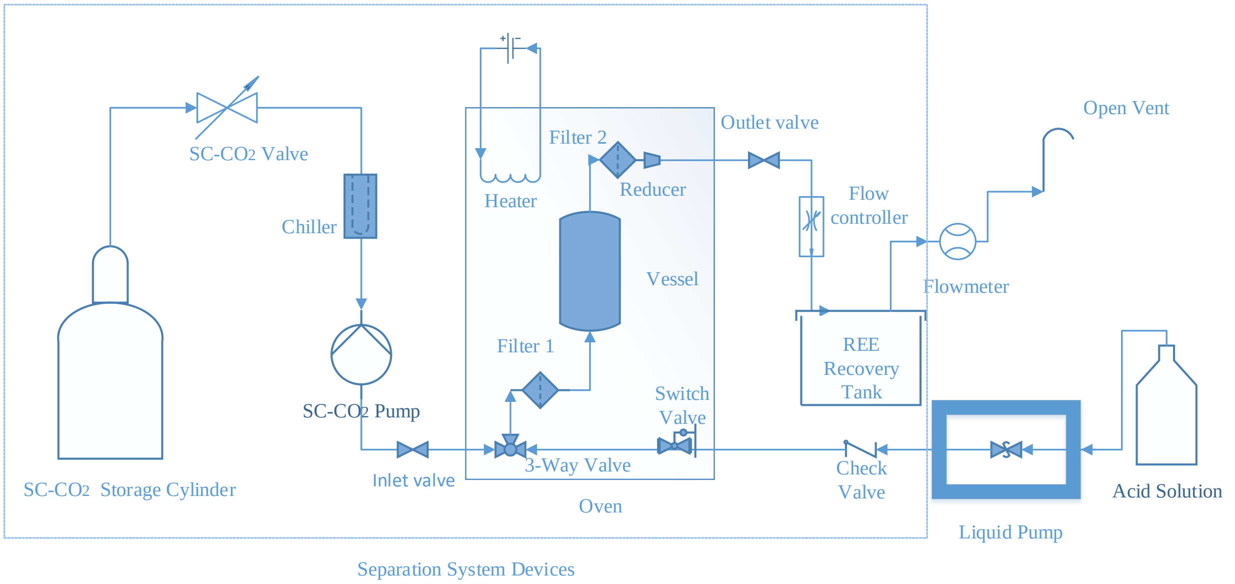


Fig. 9. Schematic Diagram of the Dynamic Extraction

Table 8. Operating Conditions for Dynamic Extraction of REEs

Test number	Refuse Coal	Glass Beads	Solvent	Duration	Liquid Volume	SC-CO$_2$ Flow Rate	SC-CO$_2$ Pressure
13	3 gram	3 gram	HNO$_3$ (0.6 mol/L)	30 min	1 ml/min	2.5 L/min	3,000 psig
14			TBP-HNO$_3$ complex				

Five steps were involved in these tests, that is: sample preparation, setting the liquid pump, check for air tightness, running the system and system cleaning. The specific steps are described below:

(1) Sample Preparation:

1. Make sure the SC-CO_2 valve, the SC-CO_2 pump, the inlet valve, the 3-way valve, the outlet valve, as well as the flow controller and the switch valve are closed.
2. Weight 3 gram of refuse coal and 3 gram of glass beads separately, and then mix them together evenly to make a mixture. Adding glass beads provided a media in the reactor vessel to reduce the possibility of clogging, it also help the solution containing SC-CO_2 and HNO_3 fully contact with the coal inside the reactor vessel inside the oven.
3. Add glass wool at the top and the bottom of the vessel to prevent coal with size less than the filters filled in the vessel entering the outlet pipe.
4. Prior to tightening the vessel and install it, press the package to compact the mixture, in order to allow the SC-CO_2 to contact sufficiently with the coal when the system is running.

(2) Setting the Liquid Pump:

Before setting the liquid pump, purging is required in case any bubbles in the system, resulting in blockage of the system.

1. Take 100 ml of the same solvent that is going to be used for the following test and added it into a beaker.
2. Make sure the switch valve is off to keep the HNO_3 from entering the vessel before the liquid pump is going to be switched on.
3. Select purging model until there is no more bubbles in the tubes.
4. Re-take 100 ml of solvent and get ready to run the test.

(3) Check-up for Air Tightness:

1. Turn the heater on to heat the oven and the flow controller until reading temperatures of 90 and 60℃, respectively, so that CO_2 could be kept above its critical temperature in the vessel and the SC-CO_2 could be also converted to gaseous CO_2 in the outlet pipe.
2. Turn the chiller on and set the temperature as -5℃.
3. Open the 3-way valve before closing the door of the oven.
4. Then open the SC-CO_2 valve, the inlet valve and the outlet valve.
5. Turn on the SC-CO_2 pump and set it to a designed value of 3,000 psig.
6. Adjust the flow rate of SC-CO_2 to 2.5 L/min by rotating the flow controller and listen carefully to see if there is any leak inside the oven. If so, sequentially turn of the SC-CO_2 valve and regulate the SC-CO_2 pump to a minimum, and adjust the flow controller until the float inside the flowmeter reach the zero graduation line and the pressure shown on the SC-CO_2 pump returns to its original value around of 780 psig. Then unload the vessel to check for possible reasons of the leaking. Any potential factors regarding leaking will be covered in the following section.
7. Repeat the above steps until no leaks are achieved. If no more leaks, then move to the next step of running system.

(4) Running the System:

1. Make sure the temperature of the heater, the flow controller and the chiller have already reached 90, 60 and -5℃ respectively.
2. Open the SC-CO_2 valve, SC-CO_2 pump, inlet valve, as well as the 3-way valve and outlet valve.

3. Check if the pressure of the SC-CO_2 shown on the SC-CO_2 pump reaches the value of 3,000 psig.
4. Check if the flow rate of SC-CO_2 reaches 2.5 L/min.
5. Turn on the switch valve.
6. Turn on the liquid pump and select the model as running, and run for 30 minutes.
7. After 30 minutes, replace the REEs recovery tank with a waste liquid tank.
8. Turn off the liquid pump and SC-CO_2 valve sequentially.
9. Keep the inlet valve and outlet valve on.
10. Slowly regulate the knob of the SC-CO_2 pump and the flow controller, until the pressure drops to the initial value of 780 psig and the float inside the flowmeter reach to the zero graduation line.
11. Close the inlet valve and the outlet valve.
12. Open the door of the oven and carefully remove the vessel.
13. Take away the solid part inside the vessel and measure 5 ml of the upper liquid in the REEs recovery tank for further laboratory analysis.

During the period of system running, carefully observe and record the level changes of the solvent in the beaker. It is also necessary to keep an eye on the REEs recovery tank to see if there is liquid outflow, if not, it means that there is clogging inside the vessel. The corresponding solution of this issue will be described in the next section.

(5) System Cleaning:

1. Install a jumper in the oven just like installing the vessel.
2. Close the inlet valve.
3. Keep the switch valve, the 3-way valve, as well as the outlet valve on.

4. Turn the liquid pump on with a maximum flow rate of 9.999 ml/min to clean the system including the tubing, valves, as well as the filters and the flow controller for 5 minutes, using distilled water.
5. Stop the liquid pump and close the switch valve and the 3-way valve and outlet valve.
6. Remove the jumper.
7. Duly handle the liquid in the waste liquid tank.

3.4 Experimental Potential Risk and Protective Measures

This experimental study involves corrosive acid and high-pressure gas, it is very necessary and critically important to be aware of any potential risk and take protective measures. In the static extraction experiment, in order to prevent inhalation of acid vapors, all the acid manipulation should be run under averted hood and all the experimenters should performed with gloves and face masks covering the eyes, because the concentrated HNO_3 vaporizes on heating.

Compared with the static extraction experiments, the dynamic extraction experiments are more dangerous. Leaks, blockages and decompression are the major issues in these latter experiments. Leakage is likely to occur during the inspection of the air tightness prior to run the system. This may be caused by failed O-rings and seals inside the vessel. Before tightening the vessel, a set of O-rings and backup rings should be installed at the top and bottom of the vessel. Both of these O-rings and backup rings are made of acid-resistant material. If the two sets of rings are not placed correctly, this will result in being unable to be fully tightened of the vessel. Air tightness check-up can timely find this problem. By contrast, clogging is more likely to occur during system operation. To solve this problem, two persons are needed to observe at the experiment at the same time, one person should observe whether there is a change in the liquid level in the beaker containing solvent and the other person should focus on whether the liquid is collected in the REEs recovery tank. As time goes on, if the liquid level in the beaker remains the same, or no liquid flows out from the outlet pipe, this means that there is a blockage inside the vessel. There are two possible causes of this. The first one is due to the fact there may be some bubbles in the tubing or even in the liquid pump, which could be easily observed. In this case, stop the liquid pump and select the purge model until there is no more bubbles. However, the operator should need to re-add the solvent to the initial value after purging. The second reason for the blockage may be that the coal and glass beads were not mixed evenly in the step of sample preparation. Based on practical experience, an efficient solution is to rapidly increase the flow rate of the liquid pump and decrease it to the initial value. For example, increase the flow rate from 1 ml/min to 5 ml/min for 5 seconds and quickly decrease it to 1 ml/min again. The last potential risk is in the setup decompression. When the experiment is over, it should be avoided to remove the vessel immediately because there may still be same amount of SC-CO_2 with a high pressure of 3,000 psig inside. The correct step is to firstly close the SC-CO_2 valve so that new SC-CO_2 will not enter the vessel. At the same time, shut down the liquid pump and close the switch valve so that no more solvent will be injected into the vessel. The next step should be turning the knob of the SC-CO_2 pump to its minimum level. However, the actual pressure shown on the display of the SC-CO_2 pump will not immediately reach the lowest value of 780 psig due to the small size of the tubing connected to the filter. Thus, turn the outlet valve to increase the flow rate slowly while paying attention to the float within the flowmeter in case of rushing it to its maximum value resulting in a broken flowmeter. Once the float drops down to the zero graduation line, it means that the SC-CO_2 inside the vessel has been drained completely. It is then safe to unload the vessel at this time.

CHAPTER 4: RESULTS AND DISCOSSION

This chapter discusses results of the testing performed in this study, as well as, it reports the recovery efficiency of selected REEs targeted in the study. The amount of REEs recovered was determined by the analytical laboratory at the Center for Applied Energy Research at the University of Kentucky. Extraction efficiency (E) was defined as follows:

$$E = \frac{M_{collected}}{M_0} \times 100\% \tag{3}$$

Where M_0 and $M_{collected}$are the quantity of REE in the material sample loaded into the reaction vessel and in the collection vessel, respectively. The units of M_0 and $M_{collected}$ are gr and they are defined as follows:

$$M_0 = M_{test,dry} \cdot W_{total\ content\ in\ sample} \cdot 10^{-6} \tag{4}$$

$$M_{collected} = \left(M_{test,dry} + M_{solvent}\right) \cdot W_{total\ content\ in\ test} \cdot 10^{-6} \tag{5}$$

$$M_{test,dry} = M_{test} \cdot (1 - H) \tag{6}$$

Where $M_{test,dry}$ is the dry quantity of refuse coal in a particular test. $W_{total\ content}$ and $W_{total\ content\ in\ test}$ are the total content of REEs in the original refuse coal and in the test with in sample units of ppm, respectively. $M_{solvent}$ is the quantity of solvent used in a test in gr. H is the moisture level of the refuse coal.

Additionally, metals in the coal ash were targeted in a first round of testing to assess the next of acid extraction. These elements, Fe, Ca and Mg were selected due to it large concentration in coal. The extraction efficiency ($E^{'}$) of metallic elements were defined as follows:

$$E^{'} = \frac{M_{collected}^{'}}{M_0^{'}} \times 100\% \tag{7}$$

Where $M_0^{'}$ and $M_{collected}^{'}$ are the quantity of the three targeted metallic elements from refuse coal loaded under static extraction conditions, and the material collected in the collection vessel, respectively. The units of $M_0^{'}$ and $M_{collected}^{'}$ are gr and they are defined as follows:

$$M_0^{'} = \frac{A_r \cdot M_{oxide}}{A_{r,oxide}} \tag{8}$$

$$M_{oxide} = M_{test,dry}^{'} \cdot W_{oxide}^{'} \tag{9}$$

$$M_{test,dry}^{'} = M_{test}^{'} \cdot (1 - H) \tag{10}$$

$$M_{collected}^{'} = V_{solvent}^{'} \cdot W_{b,test}^{'} \tag{11}$$

$$W_{b,test}^{'} = W_{a,test}^{'} \cdot R \tag{12}$$

Where M_{oxide} is the quantity of oxide of the elements since the targeted metallic element concentrations reported in the refuse coal in the form of their oxides, such as ferric oxide (Fe_2O_3), calcium oxide (CaO) and magnesium oxide (MgO). Equation (8) was used to estimate in the content of the elements. A_r is the relative atomic number of the element, and $A_{r,oxide}$ is the relative atomic number of the oxide of the element. $M_{test,dry}^{'}$ is the quantity of dry coal used in each test, m, and $W_{oxide}^{'}$ is the mass fraction of oxide in refuse coal (see Table 9). $M_{test}^{'}$ is the quantity of refuse coal used per run in gr. $V_{solvent}^{'}$ is the volume of solution in a particular test, which is 50 ml per run for the static extraction test. R is the dilution ratio since the solution need to be diluted to be subsequently analyzed by atomic absorption spectroscopy. Different elements had different dilution ratio (see Table 10). $W_{b,test}^{'}$ and $W_{a,test}^{'}$ are the content of each element before and after solution was diluted, with an unit of mg/L. The data in Table 9 and Table 10 were provided by Geochemical Lab, Inc..

Table 9. Mass Fraction of Oxide in Refuse Coal

Oxide in Refuse Coal	Mass Fraction in Refuse Coal ($W_{oxide}^{'}$)
Fe_2O_3	9.08%
CaO	1.15%
MgO	0.95%

Table 10. Dilution Ratio of Different Metallic Elements for Analysis Using Atomic Absorption Spectrometer

Metallic Elements	Dilution Ratio (R)
Fe	100
Ca	1
Mg	50

4.1 Results of Static Extraction of Metallic Elements from Refuse Coal.

As mentioned in Chapter 3, before running tests to recover REEs under static conditions, testing was performed to explore appropriate digestion temperature and with HNO_3 timing to be applied in experiments on recovery of REEs. The procedure used in these experiments was described in Chapter 3. After filtering and diluting the recovered test samples, the contents of the three elements, Fe, Ca and Mg analyses are shown in Tables 11 and 12, for pre-dilution and post-dilution.

Table 11. Analyzed Results of Static Extraction of Targeted Metallic Elements After Dilution

Test Number	Refuse Coal	Testing Duration	Testing Temperature	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)
1	0.5 gram	2 hours	70°C	2.323	27.924	0.178
2			80°C	3.782	43.968	0.303
3		3 hours	70°C	4.110	27.330	0.372
4			80°C	3.659	25.583	0.530
5			90°C	4.155	43.981	0.630
6		4 hours	70°C	2.277	23.139	0.323
7			80°C	2.867	26.058	0.233
8			90°C	4.982	34.259	0.277
9		5 hours	70°C	3.115	53.570	0.328
10			90°C	3.579	50.017	0.262

Table 12. Analyzed Results of Static Extraction of Targeted Metallic Elements Before Dilution

Test Number	Refuse Coal	Testing Duration	Testing Temperature	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)
1	0.5 gram	2 hours	70°C	232.3	27.9	8.9
2			80°C	378.2	44.0	15.2
3		3 hours	70°C	411.0	27.3	18.6
4			80°C	365.9	25.6	26.5
5			90°C	415.5	44.0	31.5
6		4 hours	70°C	227.7	23.1	16.2
7			80°C	286.7	26.1	11.7
8			90°C	498.2	34.2	13.9
9		5 hours	70°C	311.5	53.6	16.4
10			90°C	357.9	50.0	13.1

Efficiency result, calculated by Equations (8) – (12), are included in Table 13.

Table 13. Efficiency of Each Targeted Metallic Elements (E')

Test Number	Refuse Coal	Testing Duration	Testing Temperature	Fe (%)	Ca (%)	Mg (%)
1	0.5 gram	2 hours	70℃	48	45	20
2			80℃	78	70	35
3		3 hours	70℃	85	44	43
4			80℃	76	41	61
5			90℃	86	70	73
6		4 hours	70℃	47	37	37
7			80℃	59	42	27
8			90℃	100	55	32
9		5 hours	70℃	64	86	38
10			90℃	74	80	30

Figures 10 – 12 report recovery efficiency of Fe, Ca and Mg under static digestion conditions with HNO_3. It can be described from the figures and the data in Tables 11 and 12 that higher digestion temperatures promote extraction of the metals into solution. The extraction efficiency of the three different outline elements is not comparable for all of them, with Fe being easier to be recovered. This may be due to the form and components associated with each of the elements in the coal matrix. For example, Fe is known to be mainly bound with sulfur in the form of pyrite (FeS_2). Iron sulfide is easy to separate from coal by gravity and other physical-chemical process. In regard to impact of process. The time in the recovery process under static conditions, it seems that 4 hours was a reasonable time to use in the subsequent experiments with REE. Thus, a temperature of 90℃ and a digestion time of 4 hours were used in the digestion experiments for REE extraction。 Table 13 summarize the extraction experiment in terms of total efficiency of recovery for the sum of the three targeted metals, Fe, Ca and Mg.

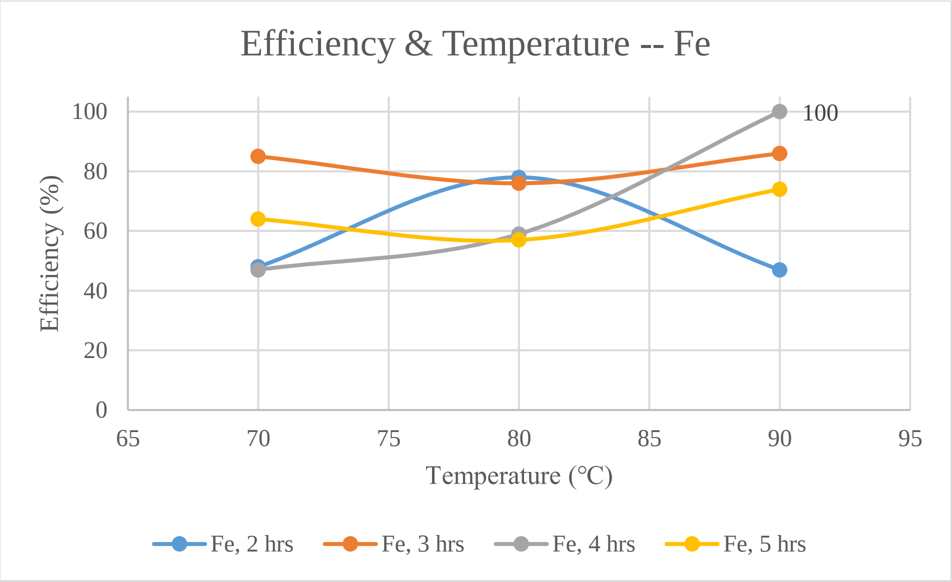


Fig. 10. Efficiency VS. Temperature of Fe Using Heated HNO_3 Digestion

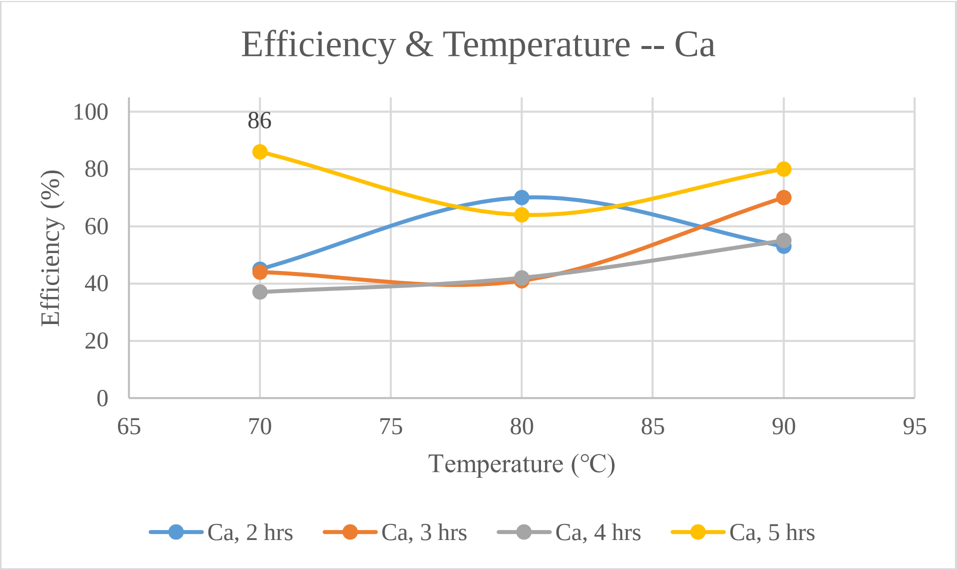


Fig. 11. Efficiency VS. Temperature of Ca Using Heated HNO_3 Digestion

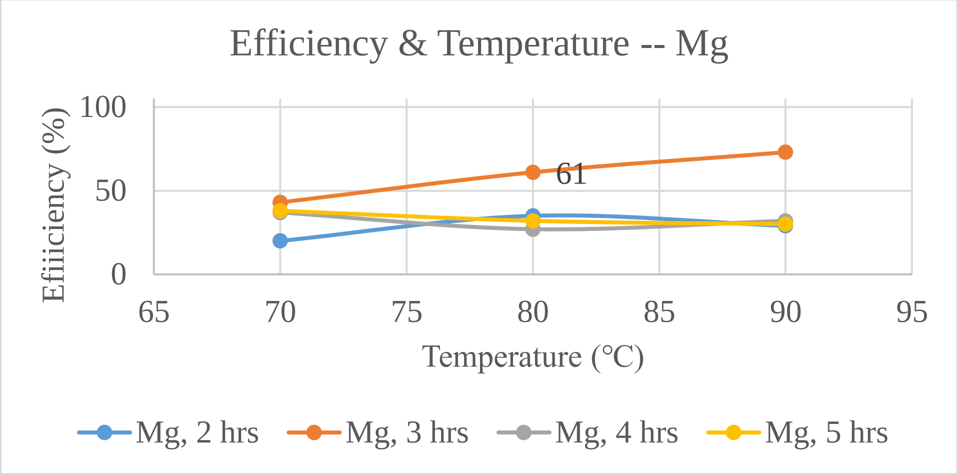


Fig. 12. Efficiency VS. Temperature of Mg Using Heated HNO_3 Digestion

Table 14. Efficiency of Static Extractions for These Three Targeted Metallic Elements

Test Number	Refuse Coal	Testing Duration	Testing Temperature	Total Efficiency (%)
1	0.5 gram	2 hours	70°C	46
2			80°C	74
3		3 hours	70°C	77
4			80°C	71
5			90°C	81
6		4 hours	70°C	45
7			80°C	55
8			90°C	93
9		5 hours	70°C	65
10			90°C	71

4.2 Static Extraction of REEs from Refuse Coal

Based on the results of the extraction experiment with metallic elements, REEs extraction experiments with refuse coal, using heated HNO_3 digestion and heated TBP-HNO_3 complex digestion, were performed at experimental conditions of 90°C and 4 hours. Three REEs were targeted, Ce, La, Nd. Individual and total extraction results and efficiency of these three REEs are shown in Table 15. The extraction efficiency of Ce, La, Nd, as well as the total REE result based on those three elements, using heated TBP-HNO_3 complex digestion, are reported in Table 16. 1 gr of refuse coal and a volume of solvent of 100 ml were used in those experiments.

Table 15. Results of Static Extraction for REEs using Heated HNO_3 Digestion

Test Number	REEs	Original Value in Refuse Coal (ppm)	Test Value in HNO_3 Solution (ppm)	Test Weight of Refuse Coal(gram)	Volume of HNO_3 (ml)	Efficiency (%)
11	Ce	93.3	0.06	1	100	11.90
	La	41.3	0.04			6.26
	Nd	29.6	<0.001			0
	Total	164.2	0.1			8.34

Table 16. Results of Static Extraction for REEs using Heated TBP-HNO_3 Complex Digestion

Test Number	REEs	Original Value in Refuse Coal (ppm)	Test Value in HNO_3 Solution (ppm)	Test Weight of Refuse Coal(gram)	Volume of TBP-HNO_3 Complex (ml)	Efficiency (%)
12	Ce	93.3	0.13	1	100	18.84
	La	41.3	0.03			26.32
	Nd	29.6	<0.001			0
	Total	164.2	0.16			17.33

Efficiency values were calculated using Equation (3) - (6). Tables 17 – 22 include details of the results obtained with REEs on Test 11 and 12.

Table 17. Process of Efficiency of Ce in Test 11

Process	Results	Units
Ce from Refuse Coal ($W_{total\ content}$)	93.3	ppm
Refuse Coal used in Test 11 (M_{test})	1.0	gram
Moisture (H)	5.11	%
Dry Coal used in Test 11 ($M_{test,dry}$)	0.95 (use Equation 6)	gram
Ce loaded in Reaction Vessel (M_0)	7.11×10^{-5} (use Equation 4)	gram
Ce from Test 11	0.06	ppm
Volume of Solvent (HNO_3)	100	Ml
Density of Solvent (HNO_3)	1.4	g/ml
Mass of Solvent ($M_{solvent}$)	140	gram
Ce collected in Test 11 ($M_{collected}$)	8.46×10^{-6} (use Equation 5)	gram
Efficiency of Ce in Test 11	11.90	%

Table 18. Process of Efficiency of La in Test 11

Process	Results	Units
La from Refuse Coal ($W_{total\ content}$)	41.3	ppm
Refuse Coal used in Test 11 (M_{test})	1.0	gram
Moisture (H)	5.11	%
Dry Coal used in Test 11 ($M_{test,dry}$)	0.95 (use Equation 6)	gram
La loaded in Reaction Vessel (M_0)	3.15×10^{-5} (use Equation 4)	gram
La from Test 11	0.02	ppm
Volume of Solvent (HNO_3)	100	Ml
Density of Solvent (HNO_3)	1.4	g/ml
Mass of Solvent ($M_{solvent}$)	140	gram
La collected in Test 11 ($M_{collected}$)	1.97×10^{-6} (use Equation 5)	gram
Efficiency of La in Test 11	6.26	%

Table 19. Process of Efficiency of Total Three Targeted REEs in Test 11

Process	Results	Units
Total REEs from Refuse Coal ($W_{total\ content}$)	164.2	ppm
Refuse Coal used in Test 11 (M_{test})	1.0	gram
Moisture (H)	5.11	%
Dry Coal used in Test 11 ($M_{test,dry}$)	0.95 (use Equation 6)	gram
Total REEs loaded in Reaction Vessel (M_0)	1.25×10^{-4} (use Equation 4)	gram
Total REEs from Test 11	0.1	ppm
Volume of Solvent (HNO_3)	100	Ml
Density of Solvent (HNO_3)	1.4	g/ml
Mass of Solvent ($M_{solvent}$)	140	gram
Total REEs collected in Test 11 ($M_{collected}$)	1.04×10^{-5} (use Equation 5)	gram
Efficiency of total REEs in Test 11	8.34	%

Table 20. Process of Efficiency of Ce in Test 12

Process	Results	Units
Ce from Refuse Coal ($W_{total\ content}$)	93.3	ppm
Refuse Coal used in Test 12 (M_{test})	1.0	gram
Moisture (H)	5.11	%
Dry Coal used in Test 12 ($M_{test,dry}$)	0.95 (use Equation 6)	gram
Ce loaded in Reaction Vessel (M_0)	7.11×10^{-5} (use Equation 4)	gram
Ce from Test 12	0.13	ppm
Volume of Solvent (TBP-HNO_3)	100	ml
Density of Solvent (TBP-HNO_3)	1.025	g/ml
Mass of Solvent ($M_{solvent}$)	102.5	gram
Ce collected in Test 12 ($M_{collected}$)	1.34×10^{-5} (use Equation 5)	gram
Efficiency of Ce in Test 12	18.84	%

Table 21. Process of Efficiency of La in Test 12

Process	Results	Units
La from Refuse Coal ($W_{total\ content}$)	93.3	ppm
Refuse Coal used in Test 12 (M_{test})	1.0	gram
Moisture (H)	5.11	%
Dry Coal used in Test 12 ($M_{test,dry}$)	0.95 (use Equation 6)	gram
La loaded in Reaction Vessel (M_0)	3.15×10^{-5} (use Equation 4)	gram
La from Test 12	0.01	ppm
Volume of Solvent (TBP-HNO_3)	100	ml
Density of Solvent (TBP-HNO_3)	1.025	g/ml
Mass of Solvent ($M_{solvent}$)	102.5	gram
La collected in Test 12 ($M_{collected}$)	8.28×10^{-6} (use Equation 5)	gram
Efficiency of La in Test 12	26.32	%

Table 22. Process of Efficiency of Total Three Targeted REEs in Test 12

Process	Results	Units
Total REEs from Refuse Coal ($W_{total\ content}$)	93.3	ppm
Refuse Coal used in Test 12 (M_{test})	1.0	gram
Moisture (H)	5.11	%
Dry Coal used in Test 12 ($M_{test,dry}$)	0.95 (use Equation 6)	gram
Total REEs loaded in Reaction Vessel (M_0)	1.25×10^{-4} (use Equation 4)	gram
Total REEs from Test 12	0.16	ppm
Volume of Solvent (TBP-HNO_3)	100	ml
Density of Solvent (TBP-HNO_3)	1.025	g/ml
Mass of Solvent ($M_{solvent}$)	102.5	gram
Total REEs collected in Test 12 ($M_{collected}$)	2.17×10^{-5} (use Equation 5)	gram
Efficiency of total REEs in Test 12	17.33	%

From the above two groups of experimental results, run at 90°C for 4 hours, using HNO_3 or the TBP-HNO_3 complex, it was apparent that REEs is hardly to extract using acid digestion. Ce and La exhibited about 8.34% extraction efficiency, while Nd was hardly shown in the remaining solvent. Specifically, when the volume ratio of TBP/HNO_3 was 1:1, the extraction efficiency of Ce using the TBP-HNO_3 complex was 18.84%, which was improved from extraction efficiency result obtained with HNO_3 solvent, which was 11.90% for Ce. Extraction of La with the TBP-HNO_3 complex reached extraction efficiencies of 26.32% and 6.26% with HNO_3, respectively. When the total REE result are compiled, it was found that the TBP-HNO_3 complex results in a recovery efficiency of those three REEs of 17.33%, compared to 8.34% with HNO_3 only.

4.3 Dynamic Extraction of REEs from Refuse Coal

A second set of experiment was performed for REE extraction from refuse coal using a flow setup. This setup would provide dynamic extraction conditions using the TBP-HNO_3 complex in SC-CO_2. It was rationalized the supercritical fluid phase would help to promote extraction of REE from the coal matrix. Procedures were followed as described in Chapter 3. TBP-HNO_3 complex and 3% dilute HNO_3 were the two solvents, considered for extraction. Use of 3% diluted nitric acid was expected to promote concentration of H^+ on the extraction. The effect of the TBP/HNO_3 volume ratio on extraction of REE from refuse coal under static conditions seems worthy to further discuss. The result achieved with Ce and La showed that higher level of TBP/HNO_3 volume ratio improve the recovery efficiency of REE. This indicates that TBP help promoting Ce- and La-TBP complex in solution. It was expected that HNO_3 would be help dissolving REEs, due to the acidity of it and the effect of dissolving the REEs, but it was not the case. However, acid such as HNO_3, which are insolvable in CO_2 would become solvable by the complexation with a base such as TBP and help promote REE extraction under dynamic conditions.

Results of experiments using 3% dilute HNO_3 and a TBP-HNO_3 complex (with TBP/HNO_3 volume ratio of 1:1) under dynamic extraction conditions with SC-CO_2 are reported Table 23 and Table 24, respectively. The SC-CO_2 and solvent flow rate used in these experiments was 2.5 L/min and 1.0 ml/L, respectively. The pressure of SC-CO_2 was set at 3,000 psig. A total of 3 gr of refuse coal were used in the test. Test duration was 30 minutes.

Table 23. Results of REEs Recovery using 3% Dilute HNO_3 in SC-CO_2

Test Number	REEs	Original Value in Refuse Coal (ppm)	Test Value in HNO_3 Solution (ppm)	Test Weight of Refuse Coal (gram)	Volume of 3% Dilute HNO_3 (ml)	Efficiency (%)
13	Ce	93.3	0.24	3	30	2.56
	La	41.3	0.22			5.41
	Nd	29.6	0.20			6.72
	Total	164.2	0.66			4.03

Table 24. Results of REEs Recovery using TBP-HNO_3 Complex in SC-CO_2

Test Number	REEs	Original Value in Refuse Coal (ppm)	Test Value in HNO_3 Solution (ppm)	Test Weight of Refuse Coal (gram)	Volume of TBP-HNO_3 (ml)	Efficiency (%)
14	Ce	93.3	0.095	3	30	1.15
	La	41.3	<0.001			0
	Nd	29.6	0.087			3.31
	Total	164.2	0.182			1.25

A comparison of Tables 23 and 24, it shows that the extraction efficiency of Ce, La and Nd, from refuse coal using 3% dilute HNO_3 and TBP-HNO_3 is negligible. The results are discouraging. This may be caused by the concentration of HNO_3 in TBP-HNO_3 complex or testing duration. Wuhua and Zhu reported a study on the impact of TBP-HNO_3 complex used for direct dissolution of lanthanide and actinide oxides in SC-CO_2 [21] (see Figure 13). In figure 13 from Reference 21, it is shown that as the concentration of HNO_3 in the TBP-HNO_3 complex is increased from 2 to 6 mol/L and the acidity of the equilibrated aqueous phase is increased from 3 to about 15 mol/L, the high acid content of the TBP-HNO_3 is important in dissolving REEs. In the experiments reported in Reference 21, high recovery of REE are achieved in excess of 60%. The volume ratio of HNO_3/TBP used in this study was of the ratio of 1:1.

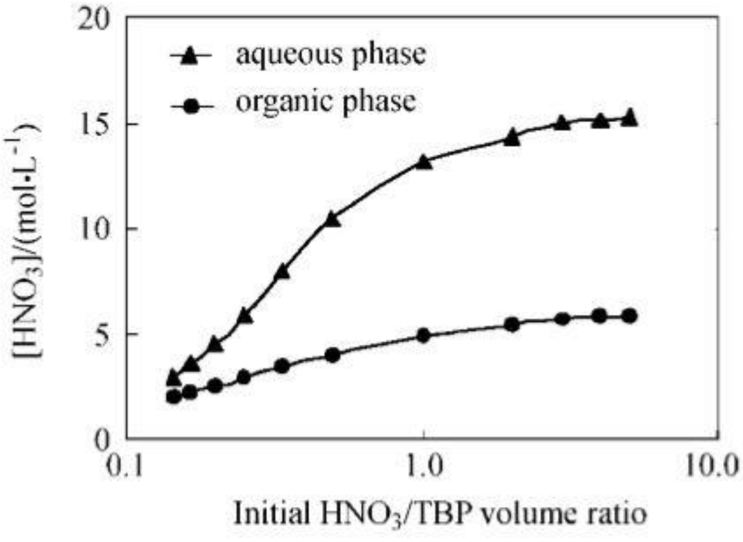


Fig. 13. Concentration of HNO_3 in the Organic and Aqueous Phases from Reference 21

Other results by Reference 24, using Nd_2O_3 and TBP-HNO_3 complex at 30℃, show that the highest extraction efficiency occurred at a concentration of HNO_3 of 2.01 mol/L (the concentration of HNO_3 used in this study was 4.70 mol/L). Recovery efficiencies as high as 90+% were achieved for Nd_2O_3, but at contact time greater than one hour. Figure 14 shows that the relationship between extraction efficiency and time is very strong. In the four curves shown in Figure 14, from 0 to 60 minutes, the extraction efficiency increases rapidly, contact time is important, mass transfer is also important in the flow setup. In Figure 14, the efficiency corresponding to the curve of concentration of H^+ with 4.54 mol/L was still increasing slowly after 60 minutes and eventually reached saturation until 180 minutes. This may point to one of the reaons of why the REE extraction efficiency in this study was so small.

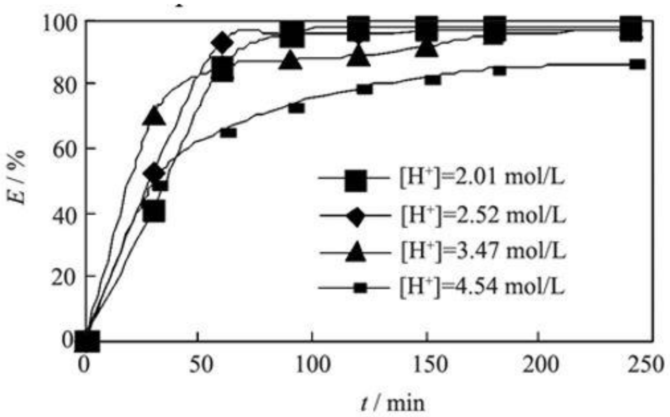
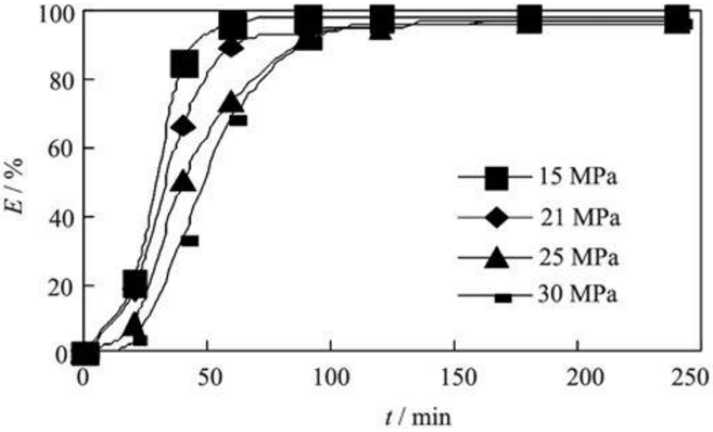


Fig. 14. Effect of Different H^+ in the TBP-HNO_3 Complex on Extraction Efficiency of REEs from Reference 24

Additionally, comparing Table 16 and Table 24, the effect of SC-CO_2 on the extraction of Ce, La and Nd from refuse coal using TBP-HNO_3 complex can be discussed. The results show that the dissolution and extraction of Ce and La from refuse coal using TBP-HNO_3 complex in SC-CO_2 may be impacted by the high-pressure of SC-CO_2 and the limited test duration. Wuhua and Cao reported in a study the effect of pressure of SC-CO_2 on the Nd extraction efficiency from Nd_2O_3, using TBP-HNO_3 in SC-CO_2 [24]. From the Figure 15, it can be seen that the extraction efficiency of Nd is inversely proportional to SC-CO_2 pressure, in the range from 15 to 30 MPa (2,176 to 4,351 psig). The CO_2 pressure used in this study was around 21 MPa (3,045 psig). The data in Figure 20 shows that an increase in SC-CO_2 pressure from 15 to 30 MPa would increase REE recovery at 30 minutes from 25 to 85%.



The flow rate of CO_2/(ml/min): ■ 2.51±0.28; ♦ 2.56±0.23;
▲ 2.61± 0.20; –■– 2.58±0.28

Fig. 15. Effect of Pressure on the Extraction Efficiency from Reference 24

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

A study was conducted to explore recovering of REEs from coal. Two set of experiments were performed under static and dynamic conditions using HNO_3, a TBP-HNO_3 complex and adding SC-CO_2 to help the REE extraction under flow conditions.

The reported recovery efficiency for three targeted REEs from refuse coal, Ce, La and Nd was not significant, less than 30%, despite the fact that these three elements exist in the highest concentrations of all of the REEs in the samples. However, the outline of this study can be portrayed as: a hydrometallurgy method for REE extraction from coal was investigated, providing the opportunity to understand and identify modifications required by the approach to improve REE recovery efficiency. Additionally, the use of SC-CO_2 as a polarity matching stream for REE carry and subsequent reduction, was identified as an important step in a dynamic REE extraction process, which would require process optimization. Specifically, several conclusions can be made:

1. For static extraction of Ce, La and Nd from refuse coal with heated HNO_3 and TBP-HNO_3 complex digestion, higher process temperatures and recovery time help recovery of REE. A temperature and time of 90°C and 4 hours were identified from these static experiments.
2. For static extraction, the recovery efficiency of Ce and La from refuse coal using heated TBP-HNO_3 complex digestion is more efficient than using heated plain nitric acid. Nd was insensitive to this extraction method.
3. For dynamic extraction, with a SC-CO_2 flow rate of 2.5 L/min, the pressure of SC-CO_2 plays an important role in using TBP-HNO_3 complex to extract REE from refuse coal. Extraction efficiencies achieved were less than 5% for Ce, La and Nd.

However, there are still some points that need further investigations. Future directions in REEs extraction from coal and fly ash should focus in two directions:

1. Utilizing ligands alternative and more benign than TBP, such as biomass derived carboxylic acids. Some of the acids proposed are derived from natural sources and some from glycerol partial oxidation thus enabling very important routes for utilization of other energy industry, such as biomass into biodiesel, byproducts. While HNO_3 based extraction is intuitive and well defined, presence of organic ligands to facilitate the extraction is not yet well explored.
2. Concentration of REEs from the diluted acidic aqueous streams is of critical importance due to the high water heat capacity and the energy needed to evaporate it. As a research direction SC-CO_2 is promising but its various aspects related to the novel REE-organic carboxylic acid molecular complex formation need to be explored. Those include measuring partition coefficients of REE organic ligand complexes in SC-CO_2. Said technology, however, will utilize numerous advantages over the existing processes. First, it will utilize environmentally benign and recyclable CO_2 in its supercritical state for the extraction. It will operate in the continuous manner and will allow instantaneous extract fractionation by changing its solubility in SC-CO_2 by adjusting the pressure of the system. It will also depart from typically utilized harsh extraction conditions, such as concentrated (6M) HNO_3, as well as the need to utilize hazardous ligands, such as TBP. Finally, instrumental design of extractors to accommodate mass transfer between two different complex phases (water and SC-CO_2) needs to perfected.

REFERENCES

[1] Henderson,P. ed, 2013. “Rare earth element geochemistry (Vol.2)”. Elsevier.

[2] US Geological Survey, 2016. “Rare earth reserves worldwide as of 2016 by country”. Statistic.

[3] US Geological Survey, 2016. “Distribution of rare earths production worldwide as of 2016 by country”. Statistic.

[4] Zhanheng, C.H.E.N., 2011. “Global rare earth resources and scenarios of future rare earth industry.” *Journal of rare earths*, 29(1), pp. 1-6

[5] ASM International, 2016. “Rare earths extracted from coal byproducts”.

[6] ENERGY NEWS, 2017. “DOE invests $17.4 Million in projects to advance recovery of rare earth elements from coal and coal byproducts”.

[7] The National Academics of Science Engineering Medicine, 2007. “Research and development to support national energy policy”.

[8] Penn State University News, 2016. “Extracting rare earth elements from coal could soon be economical in U.S.”

[9] US DEPARTMENT OF ENERGY, 2016. “Recovery of rare earth elements (REEs) from coal ash with a closed loop leaching process”. Battelle Memorial Institute, Columbus, Ohio

[10] Kashiwakura S, Kumagai Y, Kubo H, and Wagatsuma, K., 2013. “Dissolution of rare earth elements from coal fly ash particles in a dilute H_2SO_4 solvent”. *Open Journal of Physical Chemistry*, 3(02), p.69.

[11] West Vigrgina Acid Mine Dranage Task Force Symposium, 2016. “Recovery of rare earth elements (REEs) from coal mine drainage”.

[12] Merten, D. and Bechul, G., 2004. “Determination of rare earth elements in acid mine drainage by inductively coupled plasma mass spectrometry”. Microchim. Acta 148, pp. 163-170.

[13] Noyori, R., 1999. “Supercritical fluids: introduction”

[14] Eckert, C.A., 1996. “Supercritical fluids as solvents for chemical and materials processing”. *Nature*, 383, pp. 313-318.

[15] Kamat, S., Barrera,J., Beckman, J. and Russell, A.J., 1992. “Biocatalytic synthesis of acrylates in organic solvents and supercritical fluids: I. Optimization of enzyme environment”. *Biotechnology and bioengineering*, 40(1), pp. 158-166.

[16] Subramaniam, B. and McHugh, M.A., 1986. “Reactions in supercritical fluids-a review”. *Industrial & Engineering Chemistry Process Design and Development*, 25(1), pp. 1-12.

[17] DeSimone, J.M., Guan, Z. and Elsbernd, C.S., 1992. “Synthesis of fluoropolymers in supercritical carbon dioxide”. *Science*, 257(5072), pp. 945-947.

[18] Brunner, G., 2013. “Gas extraction: an introduction to fundamentals of supercritical fluids and the application to separation processes (Vol.4)”. Springer Science & Business Media.

[19] Sabio, E., Lozano, M., Montero de Espinosa, V., Mendes, R.L., Pereira, A.P., Palavra, A.F. and Coelho, J.A., 2003. “Lycopene and β-carotene extraction from tomato processing waste using supercritical CO_2”. *Industrial & Engineering Chemistry Research*, 42(25), pp. 6641-6646.

[20] Page, S.H., Sumpter, S.R., Goates, S.R., Lee, M.L., Dixon, D.J. and Johnston, K.P., 1993. “Tri-n-butylphosphate/CO_2 and acetone/CO_2 phase behaviors and utilities in capillary supercritical-fluid chromatography”. *The Journal of Supercritical Fluids*, 6(2), pp. 95-101.

[21] Duan, W.H., Zhu, L.Y., Jing, S., Zhu, Y.J. and Chen, J., 2007. “Study on properties of TBP-HNO_3 complex used for direct dissolution of lanthanide and actinide oxides in supercritical fluid CO_2”. *Chinese Journal of Chemistry*, 25(3), pp. 319-322.

[22] Joung, S.N., Yoon, S.J., Kim, S.Y. and Yoo, K.P., 2000. “Extraction of lanthanide ions from aqueous solution by modified supercritical CO_2: tri-n-butylphosphate + CO_2 and bis-2-ethylhexyl phosphoric acid + CO_2”. *The Journal of Supercritical Fluids*, 18(2), pp. 157-166.

[23] Baek, D.L., Fox, R.V., Case, M.E., Sinclair, L.K., Schmidt, A.B., Mcllwain, P.R., Mincher, B.J. and Wai, C.M., 2016. “Extraction of rare earth oxides using supercritical carbon dioxide modified with Tri-n-butyl phosphate – nitric acid adducts”. *Industrial & Engineering Chemistry Research*, 55(26), pp. 7154-7163.

[24] Wuhua, D.U.A.N., Pijia, C.A.O, and Yongjun, Z.H.U., 2010. “Extraction of rare earth elements from their oxides using organophosphorus reagent complexes with HNO_3 an H_2O in supercritical CO_2”. *Journal of Rare Earths*, 28(2), pp. 221-226.

[25] Samsonov, M.D., Trofimov, T.I., Kulyako, Y.M., Vinokurov, S.E., Malikov, D.A., Batorshin, G.S. and Myasoedov, B.F., 2015. “Recovery of rare earth elements, uranium, and thorium from monazite concentrate by supercritical fluid extraction”. *Radiochemistry*, 57(4), pp. 343-347.

[26] Sato, T., 1989. “Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds”. *Hydrometallurgy*, 22(1-2), pp. 121-140.

[27] Royen, H. and Fortkamp, U., 2016. “Rare earth elements – purification”, *Separation and Recycling*.

[28] Gupta, C.K. and Krishnamurthy, N., 2004, “Extractive metallurgy of rare earths”. CRC Press, Boca Raton, Florida, 1-504.

[29] Izatt, S.R., McKenzie, J.S., Izatt, N.E., Bruuening, R.L., Krakowiak, K.E. and lzatt, R.M., 2016. “Molecular recognition technology: A green chemistry process for separation of individual rare earth metals”. *White Paper on Separation of Rare Earth Elements.*

[30] Kao, H.C., Yen, P.S. and Juang, R.S., 2006. "Solvent extraction of La (III) and Nd (III) from nitrate solutions with 2-ethylhexylphosphonic acid mono – ethylhexylester". *Chem. Eng. J. (Amsterdram, Neth.),* 119(2-3), pp. 167-174.

[31] SIIRI PERAMAKI, 2014. "Method development for determination and recovery of rare earth elements from industrial fly ash". Academic Dissertation for the Degree of Doctor of Philosophy. University of University of Jyväskylä

[32] Kraikaew, J., Srinuttrakul, W. and Chayavadhanakur, C., 2005. "Solvent extraction study of rare earths from nitrate medium by the mixtures of TBP and D2EHPA in kerosene". *J. Met., Mater. Miner*. 15(2), pp 89-95.

[33] Preston, J.S., Cole, P.M., Craig, W.M. and Feather, A.M., 1996. "The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: Leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction". *Hydrometallurg*y, 41(1), pp. 1-19.

VITA

He Yun (Andy) was born on November 10, 1992 in Lanzhou, China, son of Jinchun He and Hua Yun. He earned his Bachelor of Science degree in Process Equipment and Control Engineering from University of Shanghai for Science and Technology in Shanghai, China in 2015 after finishing high school in Beijing, China. He entered Lehigh University in Spring 2016 as a masters student in Mechanical Engineering department and joined in Energy Research Center as a graduate research assistant at Lehigh University since November 2016.