Version of Record: https://www.sciencedirect.com/science/article/pii/S0304386X19307388
Manuscript_f550ba1a92b0013c5324338ca9463f3e

Separation of Thorium, Uranium, and Rare Earths from A Strip Solution Generated from Coarse Coal Refuse

Deniz Talan[1], Qingqing Huang[1*]

[1] Department of Mining Engineering, West Virginia University, 365 Mineral Resources Building, 1374 Evansdale Drive, Morgantown, WV

*Corresponding Author: qingqing.huang@mail.wvu.edu

Abstract

This study systematically evaluated the separation performance of thorium, uranium, and rare earths when coal and coal byproduct were utilized as a non-traditional feedstock for rare earth production. A synthetic solution was prepared following the elemental composition of a strip solution generated from coarse coal refuse and used throughout the study. Various separation techniques including selective precipitation, solvent extraction, and a modified experimental protocol incorporating the two were applied to extract rare earths while minimizing the non-selective recovery of thorium and uranium into the product stream. Test results indicate that selective precipitation was effective for the removal of thorium at a pH value approaching 5 while solvent extraction preferentially removed uranium from rare earths. Therefore, a modified experimental protocol consisting of both selective precipitation and solvent extraction was subsequently developed and implemented. The findings following the modified experimental protocol indicate that extractant concentration, solvent extraction feed pH, and organic to aqueous (O/A) ratio all played a significant role in the removal of uranium. Among all the tests conducted, the best separation performance was achieved using a one-stage precipitation at a pH value of 4.8, 50 v% TBP, solvent extraction feed pH of 3.5, and an O/A ratio of 3, which corresponded to an overall rare earth, thorium, and uranium recovery of 79.6%, 0%, and 3.1%, respectively.

Keywords: Rare earth elements, thorium, uranium, coal, selective precipitation, solvent extraction, separation

1. INTRODUCTION

Rare earth elements (REEs) play an essential role in both national defense and high-tech manufacturing markets such as the industries of permanent magnets, catalysts, lamp phosphors, rechargeable batteries and missiles (Binnemans et al., 2013; Rim et al., 2013; Jha et al., 2016; Van Gosen et al., 2017; Wang et al., 2017; Zhou et al., 2018). The United States (U.S.) has been heavily reliant on foreign countries for the supplies of REEs. The volatility of this supply chain can fatally threaten the U.S. high-tech industries and its national security. The tight export quota favored by the world's leading rare earth producer, China, has led countries and researchers to seek alternative resources for rare earths (Paulick and Machacek, 2017). Recent research efforts have suggested that coal and coal by-products can be a potential feedstock for REEs as opposed to traditional rare earth-bearing minerals such as monazite, xenotime, and bastnaesite (Seredin, 1996; McLellan et al., 2014; Hower et al., 2016; Zhang and Honaker, 2018; Huang et al., 2018; Honaker et al., 2016; Das et al., 2018). The characterization studies of rare earth minerals/elements conducted in various geological locations have been investigated and compiled (Seredin and Dai et al., 2012; Lin et al., 2017; Hu et al., 2006; Karayigit et al., 2000; Zhang et al., 2015; Huang et al., 2019). As a result, it is estimated that the average REE abundance of the world coal is approximately 69 mg/kg on a whole sample basis (Ketris and Yudovich, 2009), which may warrant the economic extraction of REEs from coal and coal byproducts given its vast quantity. While extensive efforts have been focusing on the technical feasibility and economic viability of the REE extraction process, it is equally crucial to ensure that the process is environmentally benign due to the nature of occurrence of REEs (Al-Areqi et al., 2014; Valkov et al., 2014; Zhang et al., 2016, Wang, et al., 2017).

Rare earth-bearing minerals have been known to be associated with naturally occurring radioactive materials (NORM) such as thorium (Th) and uranium (U). The two elements are frequently seen in rare earth deposits due to lattice substitution. In some cases, uranium is also formed by epigenetic infiltration during the lignite-subbituminous stage of coalification (Ault et al., 2015; Zhu et al., 2015; Van Gosen et al., 2017; Qin et al., 2018). Therefore, radioactivity is a typical characteristic of rare earths' mineralization. Three traditional rare earth minerals, namely bastnaesite, monazite, and xenotime, are known to contain a significant amount of radioactive materials with a thorium and uranium dioxide concentration up to 20 wt% and 16 wt%, respectively (Lapidus and Doyle, 2015; Zhu et al., 2015; Van Gosen et al., 2017; Wang et al., 2017). Due to the same reason, monazite has not been produced from heavy-mineral sands industry in Australia since 1990 (Haque et al., 2014; Van Gosen et al., 2017). Bayan Obo, the world's largest rare earth deposit, processes thorium-containing monazite and bastnaesite. Approximately 96% to 98% of the thorium is rejected to the solid waste, which needs to be properly handled in compliance with strict environmental regulations (Ault et al., 2015). Mountain Pass, which owns the only rare earth mining and processing facility in the U.S., treats an ore that contains 0.02 wt% thorium and 7.6 wt% REEs. It indicates that around 2.6 kg of thorium is generated for every ton of rare earths produced that hinders the revival of the U.S. rare earth production (Ault et al., 2015). It was further stated in a study performed by Rim et al. (2013) that refining a ton of rare earths produces approximately 1.4 tons of radioactive wastes.

Therefore, a grave concern is arising that needs to be carefully addressed from the standpoint of environmental control (Haque et al., 2014; Ault et al., 2015).

Coal and coal byproducts, as a non-traditional source for rare earths, are also naturally associated with radioactive materials (Papastefanou, 2007; Department of Energy, 2017; Lange et al., 2017; Dai and Finkelman, 2018). According to a characterization study conducted by USGS with approximately 2,000 U.S. coal samples, the concentration of thorium and uranium has been found to mostly vary between 1 to 4 mg/kg with the highest content value of 20 mg/kg being reported in some cases (United States Geological Survey, 1997). Even though the original concentration of thorium and uranium in coal and coal byproducts is not high compared to that of traditional rare earth minerals, they can be substantially enriched along with the processing stages. Therefore, there exists an urgent need to address the environmental issues associated with the extraction of REEs from coal and coal byproducts. This is especially critical when the primary focus of the ongoing research efforts is on the technical and economic evaluation of the process.

To date, the literature studies predominantly focus on the removal of radioactive materials from traditional rare earth-bearing minerals (Jun et al., 1998; Li et al., 2004; Rabie et al., 2007; Amaral and Morais, 2010; Banda et al., 2012; Zhang et al., 2012; Anufrieva et al., 2014; Panda et al., 2014; Batchu et al., 2015; Borai et al., 2016; Dittrich et al., 2016; Alemrajabi et al., 2017; Kuang et al., 2017). According to a review study performed by Zhu et al. (2015), the removal of uranium and thorium from rare earths is typically achieved via solvent extraction or precipitation. In comparison to solvent extraction, precipitation takes advantage of different precipitation pH of thorium, uranium, and rare earths to achieve the separation. Selective precipitation is a cost-effective and simple operation (Vijayalakshmi et al., 2001; Silva et al., 2018; Zhou et al., 2018). As for solvent extraction, a number of studies have been conducted to investigate the impact of different extractant types, diluents, and operating conditions on the removal of thorium and uranium from traditional rare earth-bearing minerals (Amaral and Morais, 2010; Nasab, 2014; Samsonov et al., 2015; Lu et al., 2016). Various types of extractants including acidic/neutral organophosphorus extractants, amide, amine, and carboxylic extractants have been proved to be effective for the separation of radioactive elements while present with rare earths (Gupta et al., 2002; Belova et al., 2015; Zhu et al., 2015; Zhang et al., 2016, Giri and Nath, 2016). However, most of these extractants are also effective for the recovery of rare earths. Therefore, the challenges lie in how to achieve the desired selectivity and separation efficiency by implementing a specially designed experimental scheme. Besides, the studies pertaining to the separation of hazardous elements and rare earths from coal and coal byproducts are limited, and no insightful information in this regard has been provided to date (Rim et al., 2013; Van Gosen et al., 2017).

To evaluate the separation performance of thorium and uranium from rare earths while using coal and coal byproducts as a feedstock, experimental testing was performed in detail in this study. A synthetic solution was prepared following the elemental composition of a strip solution that was produced from a pilot-scale rare earth plant. Two separation techniques, namely selective precipitation and solvent extraction, were initially applied to explore the potential of selectively removing thorium and uranium from rare earths. A modified experimental procedure consisting of both precipitation and solvent extraction was subsequently developed based on the preliminary studies. Tri-butyl phosphate (TBP) was selected for the solvent extraction study due to its capability to selectively extract thorium and uranium under controlled operating conditions (Habashi, 1997; Zhang et al., 2016). Besides, the effect of different operating parameters including solution pH, extractant concentration and organic to aqueous (O/A) ratio on the recovery of the two hazardous elements (i.e., Th and U) were systematically assessed. X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) analyses were performed as well to facilitate the understanding of the precipitation behavior of different elements. Finally, the response surface methodology and statistical analysis were carried out to develop a statistically significant model that can be utilized to optimize the overall separation performance.

2. EXPERIMENTAL

2.1. Samples and Materials

The feedstock solution used throughout the study was synthetically prepared in accordance with the elemental composition of a strip solution (i.e., REEs, Th, U, and major metals). This strip solution was produced from a pilot-scale rare earth production plant, which used coarse coal refuse as the feedstock. The refuse was collected from a middling stream of an operating coal preparation plant in Southern West Virginia. Preliminary characterization data indicate that the solid sample contained approximately 169 mg/kg of REEs, on a dry whole sample basis, with an ash content of 24.7%. Upon being delivered to the REE production plant, the refuse sample was subjected to hydrochloric acid leaching at a temperature of 75 ˚C, followed by solvent extract and striping. Di-(2-ethylhexyl) phosphoric acid (DEHPA) and 6 M hydrochloric acid was used as the extractant and strippant, respectively. The resultant strip solution was used as the feedstock for the present study, for which a synthetic solution was prepared accordingly.

Standard inductively coupled plasma (ICP) solutions of REEs, Th, and U with a concentration of 1000 mg/L were purchased from Ricca Chemical. Major metal chlorides with a grade greater than 99% were procured from Alfa Aesar. Synthetic feedstock solutions were prepared using both standard ICP solutions and pure chloride minerals. A 6 M hydrochloric acid solution was used as the medium to achieve a starting pH of less than zero. Chemical reagents used for pH adjustment (i.e., sodium hydroxide, potassium hydroxide, and ammonium hydroxide) and TBP with analar grades were purchased from Merck and Sigma Aldrich, respectively. Deionized (DI) water was used throughout the study. The elemental composition of the synthetic feedstock solution is given in Table 1. As seen, the concentration of total REEs in the solution was approximately 37 mg/L, while the concentration of Th and U were 0.50 and 0.86 mg/L, separately. The content of major metals (i.e., Al, Ca, Fe, K, and Mg) was around 74 mg/L, which was noticeably higher than the concentrations of REEs, Th, and U.

Table 1. Elemental composition of synthetic feedstock solution.

Element	Sc	Y	La	Ce	Pr	Nd	Sm	Eu
Concentration (mg/L)	0.00	3.09	1.91	14.47	1.90	9.03	2.67	0.47

Element	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Concentration (mg/L)	2.01	0.10	0.82	0.09	0.33	0.00	0.14	0.01
Element	Th	U	Al	Ca	Fe	K	Mg	
Concentration (mg/L)	0.50	0.86	1.99	55.20	12.85	0.82	2.86	

2.2. Selective Precipitation

Selective precipitation tests were first conducted to selectively precipitate out thorium, uranium, and REEs according to their distinctive precipitation behaviors at different pH values. A 200-ml feedstock solution was prepared and used for the experimental testing. Three commonly used neutralizing reagents, sodium hydroxide (NaOH), potassium hydroxide (KOH), and ammonium hydroxide (NH_3/H_2O) were chosen to adjust the solution pH. These three reagents were also selected to see whether the reagent type had an impact on the precipitation behaviors of different elements. The pH value was elevated gradually by adding each 2 M alkaline solution in a step-wise manner followed by three-min conditioning. When significant precipitation was visually observed, the test was paused. The solution was subjected to settling for a sufficient amount of time until the pH was stable, and the precipitation was fully accomplished. Then the solution was filtered using filter papers with a pore size of 0.45 µm. Afterward, precipitated solids were dried and weighed. A detailed flowsheet governing selective precipitation tests is shown in Figure 1. Representative samples taken from the filtrate and solid sample generated from each stage were subjected to Th, REEs, and major metal analyses using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and U analysis using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS).

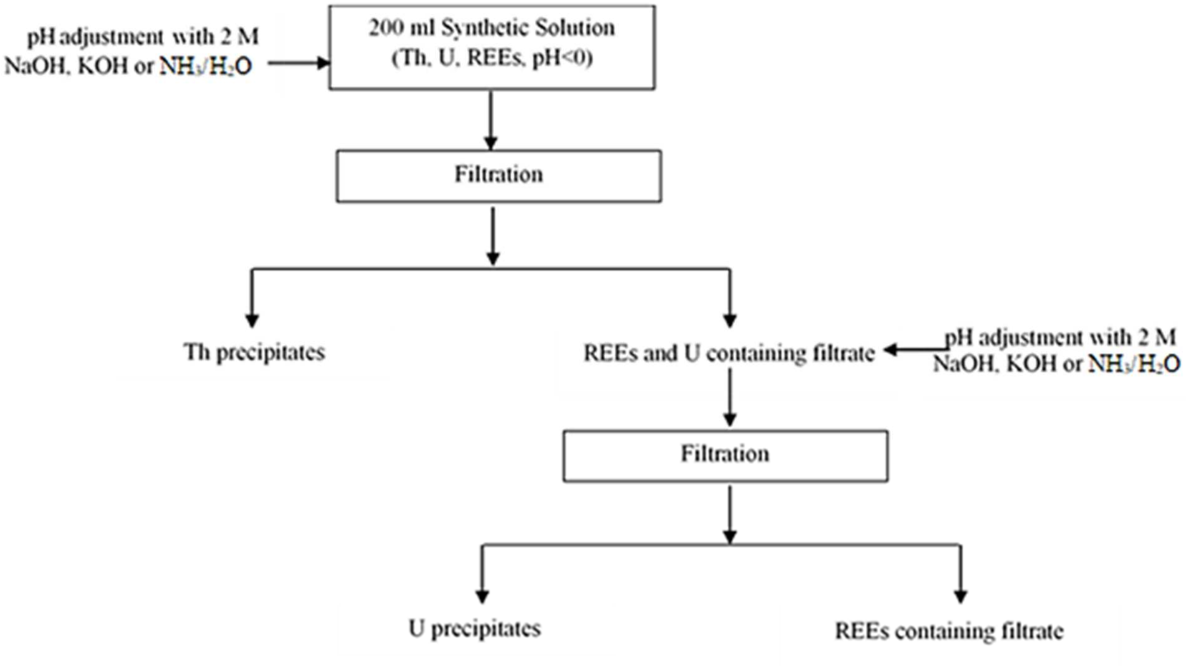


Figure 1. Experimental flowsheet followed during selective precipitation tests.

2.3. Solvent Extraction

In addition to selective precipitation, two sets of solvent extraction tests were also designed and performed to further explore the potential of separating thorium and uranium from rare earths. The corresponding flowsheet with detailed operating procedures is given in Figure 2. As seen, the solvent extraction test consisted of two parts with the first and second part targeting uranium and thorium removal, separately. Tri-butyl phosphate dispersed in a kerosene solution was used as the organic extractant. Kerosene was chosen as the diluent to enhance the extraction capability of TBP and reduce the emulsification of the extractant (Anitha et al., 2014). The scrubbing stage was performed to remove any impurities that may report to the organic phase during uranium extraction. Deionized water was used for the thorium stripping. The retention time was kept at 20 mins throughout the test. Both sets of the solvent extraction tests were conducted under the same conditions except the number of stages applied to extraction, scrubbing, and stripping. For the first set of tests, each unit process (i.e., extraction, scrubbing, stripping) was conducted as a single stage while two stages were carried out for each of the aforementioned processes during the second set of tests. Test results obtained were used to compare the separation efficiencies resulting from various stages of extraction, scrubbing, and stripping.

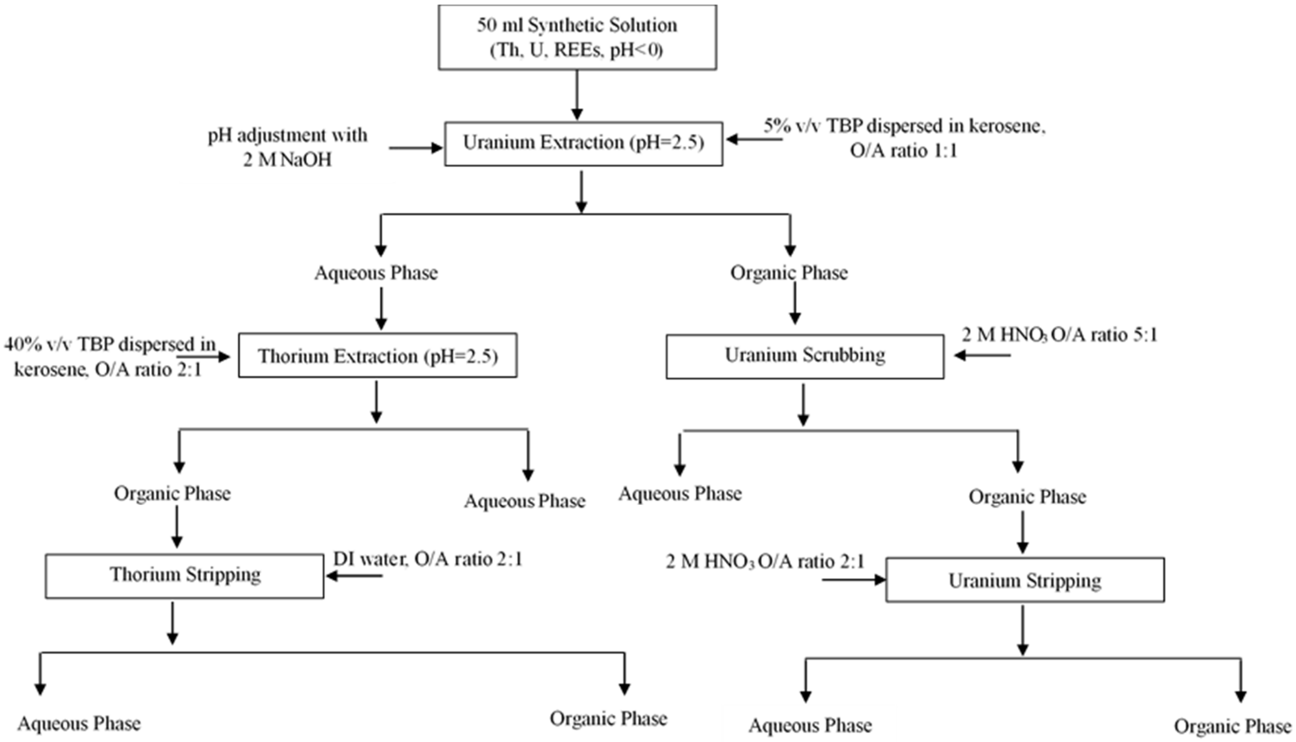


Figure 2. Experimental flowsheet followed during solvent extraction tests.

2.4. Modified Experimental Protocol

Based on the preliminary results obtained from the tests mentioned above, a modified experimental protocol was developed, as shown in Figure 3. The new experimental flowsheet consisted of one-stage selective precipitation followed by two-stage solvent extraction that aimed to achieve enhanced separation of thorium, uranium and REEs. Both selective precipitation and solvent extraction tests were conducted at room temperature (approximately 25°C), and DI water was used throughout the study. A 2 M sodium hydroxide solution was used to gradually increase the pH to a value of around 4.8, under which solid precipitation was first observed. The tests were designed in a manner that precipitation aimed to selectively precipitate out thorium, while the remaining filtrate loaded with uranium and REEs was used as the feedstock for subsequent solvent extraction.

Each solvent extraction test was performed with a 100-ml filtrate obtained from prior selective precipitation. Extraction and stripping were both carried out in two stages. At the end of each solvent extraction test, both REE-enriched (aqueous phase 2 in Figure 3) and uranium-enriched (aqueous phases 3 & 4 in Figure 3) streams were produced. Representative aqueous samples were taken from each step for REE, thorium, and uranium analysis using both ICP-MS and ICP-OES. Various operating parameters were studied during the solvent extraction stage, with details being discussed in the following experimental design section.

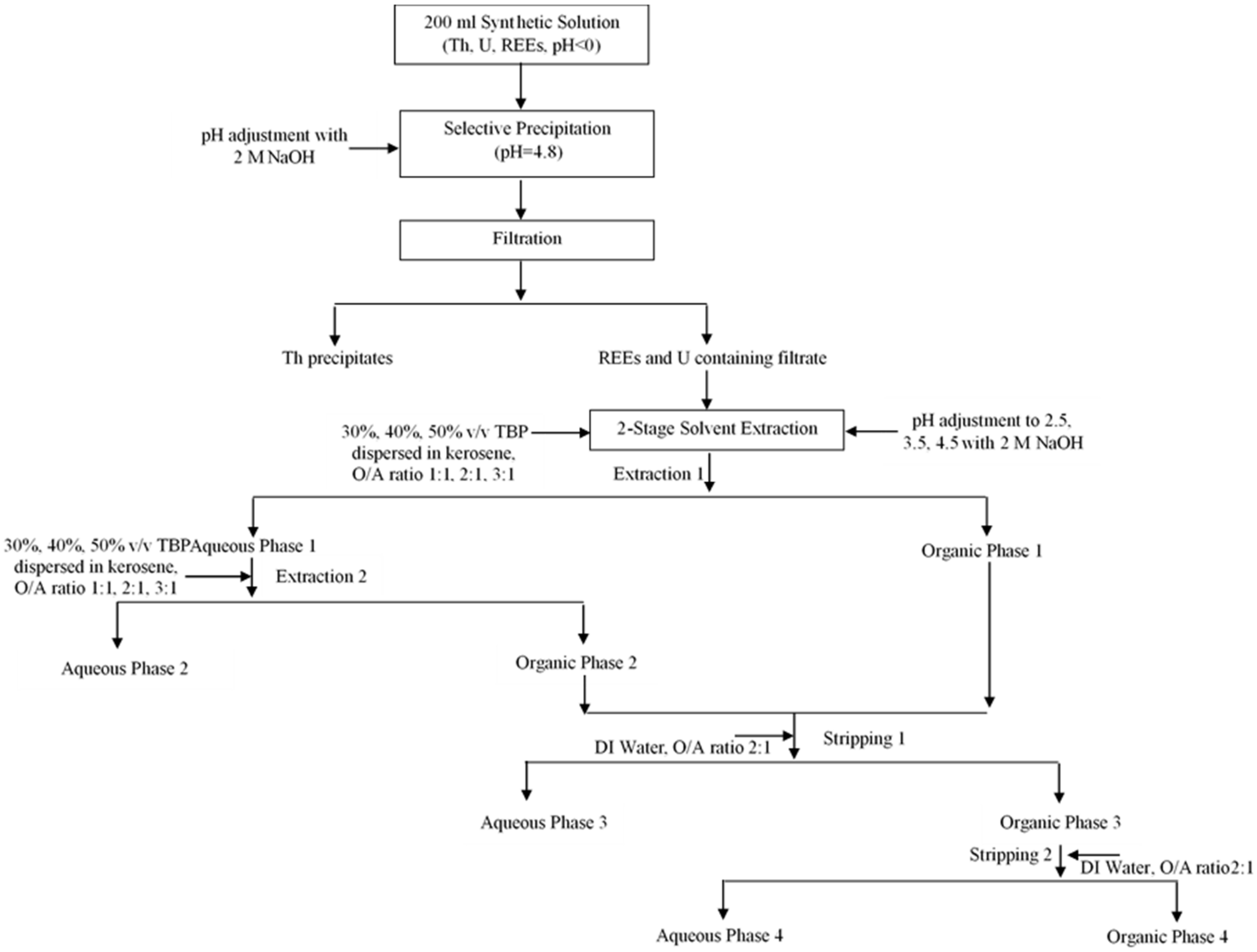


Figure 3. A modified experimental protocol developed for an enhanced separation of Th, U, and REEs.

2.5. Experimental Design

Tri-butyl phosphate and deionized water were used as the extractant and strippant, respectively, throughout the solvent extraction stage of the modified experimental flowsheet (Figure 3). Various operating parameters, including the extractant concentration, feedstock pH, and O/A ratio during the extraction, were investigated to optimize the overall separation performance, as shown in Figure 4. Three levels of each of the three parameters were studied following the experimental protocol. The levels of each parameter were determined based on prior studies conducted in a similar field (Menzies and Rigby, 1961; Nasab et al., 2011; Biswas et al., 2013; Xie et al., 2014; Jha et al., 2016). A Box-Behnken experimental design technique based on the response surface methodology was used to determine the number of tests that needed to be conducted to evaluate the significance of every input parameter. The retention time was fixed at 20 mins, and kerosene was used as the diluent for the extractant. A volume ratio of O/A=2:1 was maintained for the stripping stage. As a result, a total of 15 tests were conducted according to the following equation:

$$N = 2k(k-1) + C_0 \tag{1}$$

where N is the number of tests required for the experimental design, k the number of variables to be studied (k=3), C_0 the number of center points (C_0=3). The test order and conditions of the 15 tests were determined using the Box-Behnken experimental design and shown in Table 2.

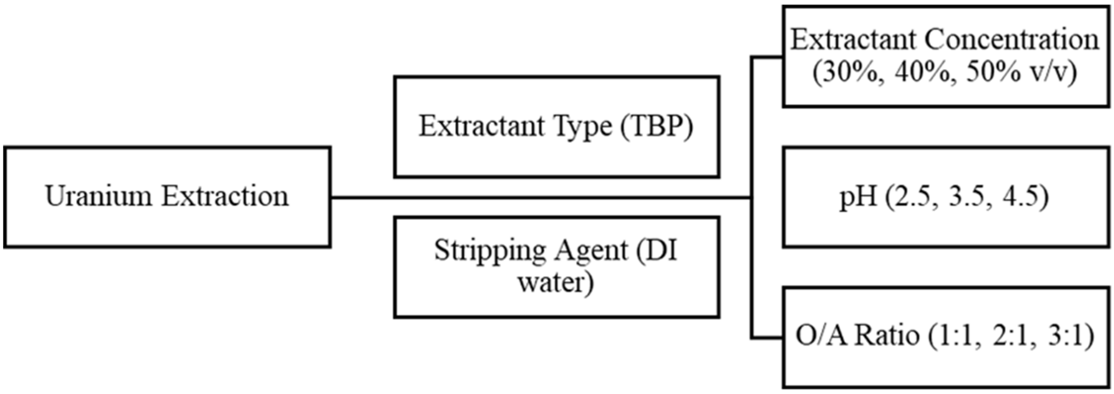


Figure 4. Experimental design for the two-stage solvent extraction targeting uranium separation.

Table 2. Test order and conditions of the solvent extraction stage following the modified experimental protocol

Test No.	**Extractant Concentration (%TBP, by volume)**	**Initial pH**	**O/A Ratio**
1	40	2.5	1
2		4.5	1
3		3.5	2
4		3.5	2
5		3.5	2
6		2.5	3
7		4.5	3
8	50	3.5	3
9		3.5	1
10		4.5	2
11		2.5	2
12	30	2.5	2
13		4.5	2

14		3.5	1
15		3.5	3

2.6. Solids Characterization

The dry solids produced from selective precipitation tests were subjected to X-ray Diffraction (XRD) and Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX) analyses. These analytical techniques were applied to detect the mineralogy, morphology, and elemental compositions of the solid samples. A PANalytical X'Pert Pro X-ray Diffractometer and a Hitachi S4700 Scanning Electron Microscope were used for the characterization studies. For the XRD analysis, the system was set to a continuous scanning mode, and 10°-85° was chosen as the 2-theta angle range. The evaluation and refinement of the diffraction patterns were carried out using the HighScore software. Prior to SEM-EDX analysis, the sample was subjected to sputtering using both Denton Desk V Sputter and Carbon Coater to prevent charging and improve the quality of the image. Accelerating voltage and working distance were kept at 5 kV and 12 mm, respectively, during the analysis.

3. RESULTS AND DISCUSSION

3.1. Selective Precipitation

Selective precipitation test results indicate that there was no significant difference observed between various alkaline solutions with respect to the process separation efficiency. Therefore, the precipitation data obtained from all three pH adjustment reagents were grouped together and shown in Figure 5.

It can be seen from Figure 5 that the first precipitation was observed in a pH range of 4 to 5. Under this condition, over 90% of thorium precipitated out while a small portion of uranium (i.e., 28.7%) and REEs (i.e., 16.3%) co-precipitated with thorium. As indicated in the study of Zhu et al. (2015), the precipitation pH range of thorium is 2.5-5.5, which is consistent with the findings presented in this work. Thorium initially existed in the solution as Th^{4+} followed by being converted to thorium hydroxide with an increase in the solution pH. However, thorium hydroxide is unstable by nature and eventually transforms into thorium dioxide (Brookins 1988). A further increase in the pH to a value of 6.2 resulted in higher thorium and uranium precipitation but also a significant amount of REEs' co-precipitation, which accounted for approximately 34% of initial concentration. The observed phenomena can be attributed to the fact that the precipitation pH range of uranium (i.e., 5.5-7) and rare earths (i.e., 6.8-8) overlaps to some degree, which leads to the co-precipitation of the two (Zhu et al., 2015). It is known that most REEs and U existed in the synthetic solution as $REEs^{3+}$ and U^{6+} along with Th^{4+} since standard ICP solutions had been used for the feedstock preparation. Chemical reactions governing the precipitation behavior of $REEs^{3+}$, Th^{4+}, and U^{6+} are given below (Silva et al., 2018). As such, rare earth hydroxide, thorium oxide, and uranyl hydroxide are formed at their respective precipitation pH regions.

$$REEs^{3+}_{(aq)} + 3OH^{-}_{(aq)} = REEs(OH)_3 \qquad (2)$$

$$Th^{4+}_{(aq)} + 4OH^{-}_{(aq)} = ThO_2 + 2H_2O \qquad (3)$$

$$UO^{2+}_{2(aq)} + 2OH^{-}_{(aq)} = UO_2(OH)_2 \qquad (4)$$

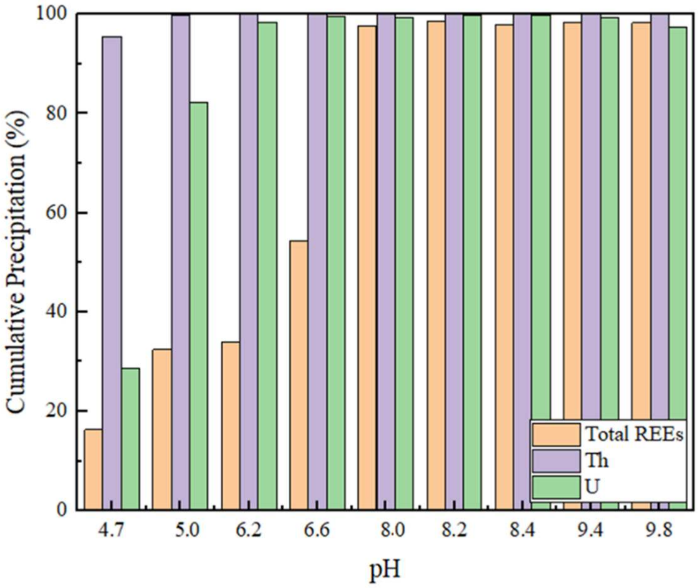


Figure 5. Cumulative precipitation of total rare earths, thorium, and uranium at various pH values using three alkaline solutions (i.e., NaOH, KOH, and NH_3/H_2O).

The precipitation behavior of total, heavy, light, critical, and uncritical REEs are further examined and presented in Figure 6. As seen, the precipitation of heavy/light and critical/uncritical REEs was minimal at a pH value of 4.6. It also suggests that the precipitation of heavy REEs was relatively more significant in a pH range of 5 to 8 compared to light, critical, and uncritical REEs in the same pH region. Approximately 100% of rare earth precipitation was achieved when the pH was above 8. The same trend and findings were observed in the studies carried out by Ponou et al. (2016) and Honaker et al. (2018). Their studies indicate that rare earths precipitation becomes significant when the pH value is beyond 5, and nearly 90% of rare earths precipitation occurs in a pH range of 5 to 10 (Ponou et al., 2016; Honaker et al., 2018). Therefore, it can be concluded that selective precipitation is effective in the removal of thorium from rare earths and uranium at a pH value of less than 5. However, the fact that a further increase in the solution pH led to the co-precipitation of uranium and rare earths indicates an alternative technique ought to be evaluated to fully separate uranium from rare earths.

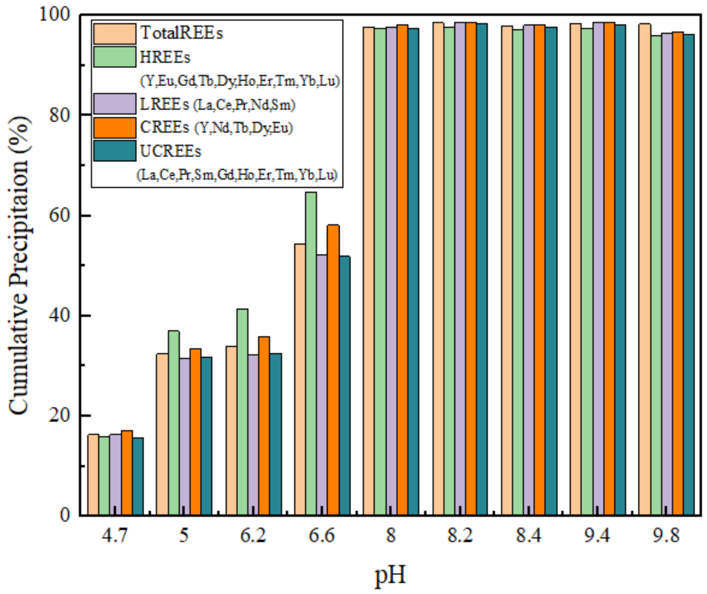


Figure 6. Cumulative precipitation of total, heavy, light, critical, and uncritical rare earths at various pH values using three alkaline solutions (i.e., NaOH, KOH, and NH_3/H_2O).

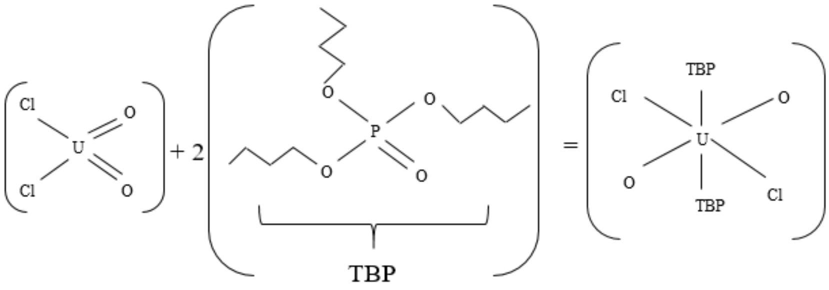
3.2. Solvent Extraction

Rare earth-enriched product, organic, and effluent streams were produced at the end of each set of solvent extraction tests following the experimental flowsheet provided in Figure 2. The results shown in Figure 7 indicate that approximately 97% of REEs and 94% of thorium were recovered into the circuit product stream of the two-stage process. Under the same operational conditions, 43% of uranium was recovered into the circuit product stream. For the one-stage process, the recovery of REEs, thorium, and uranium into the product stream was 90%, 93%, and 51% separately. The recovery data based on the two sets of solvent extraction tests are summarized in Table 3. Regardless of the number of stages conducted for the solvent extraction process (one stage vs. two stages), the recovery of thorium did not fluctuate much; however, a noticeable difference was observed for the recovery of REEs and uranium. When the number of operating stages for extraction, scrubbing, and stripping was increased from one to two, the recovery of uranium was reduced from an initial value of 51% to 43%, while the REE recovery was increased from around 90% to 97%. Therefore, the efficiency of the multi-stage solvent extraction process was indicated as opposed to the single-stage process. However, no significant separation of thorium was observed compared to uranium, which may be explained by their distinct extraction behaviors in hydrochloric acid. It was stated in Nasab's study (2014) that the extraction of uranium is more feasible compared to thorium in a chloride medium. It is because the species formed between uranium and hydrochloride are readily extracted by TBP through forming organic soluble complexes. On the other hand, nitrate is a preferred medium for enhanced extraction of thorium due to an increase in the hydration energy of the anions (Nasab, 2014; Lu et al., 2016).

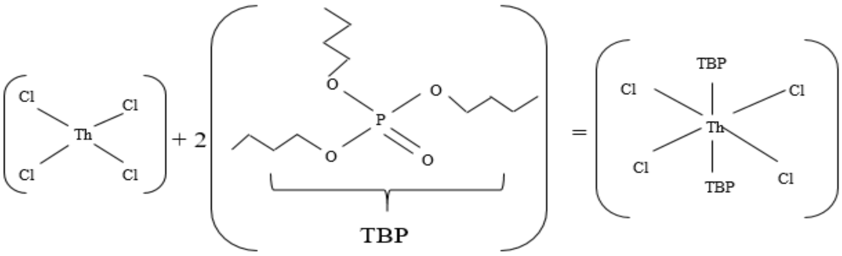
Table 3. Total recovery of rare earths, thorium, and uranium into the product stream based on both the one-stage and two-stage solvent extraction process.

Process	Recovery of REEs (%)	Recovery of Th (%)	Recovery of U (%)
One-Stage	90	93	51
Two-Stage	97	94	43

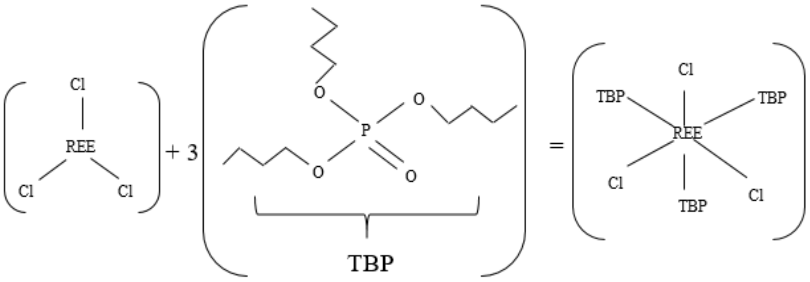
The extraction of REEs, Th, and U in a chloride medium using TBP follows the order of $UO_2^{2+} > Th^{4+} > REE^{3+}$ (Zhang et al., 2016). When present with the three ion groups, TBP forms complexes with the ions in the solution according to their distinctive capabilities to bind with the extractant (Rand et al., 2008). The complexation reactions occurring between TBP and the three ion groups (i.e., U, Th, and REE) are given in Eqs. (5)-(7).



(5)

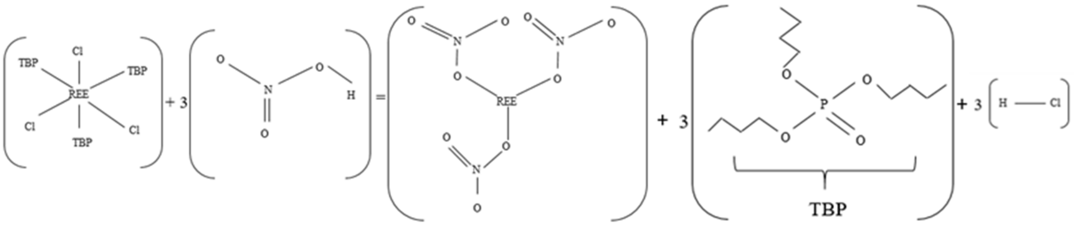


(6)

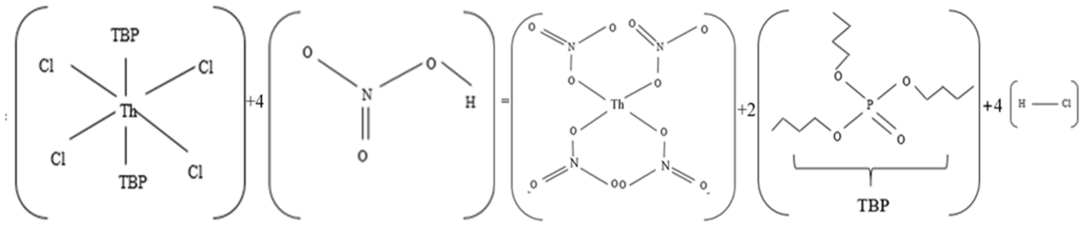


(7)

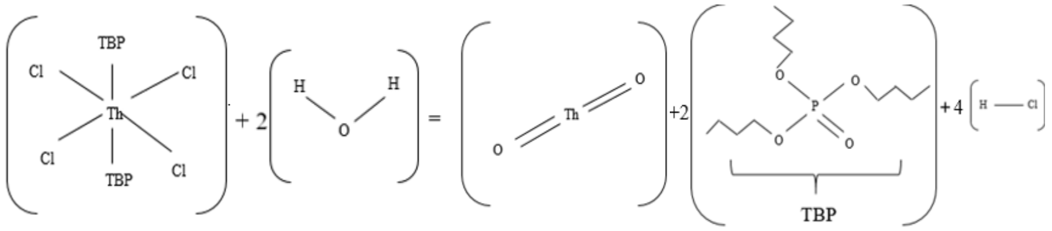
In addition, 2 M HNO_3 was used as the scrubbing reagent to remove entrained REEs and Th from the U-laden organic phase following the reactions given in Eqs. (8)-(9). Afterward, DI water and 2 M HNO_3 was applied as the stripping reagent for Th and U, separately, and the corresponding equations governing the complexation reactions are shown in Eqs. (10)-(11).



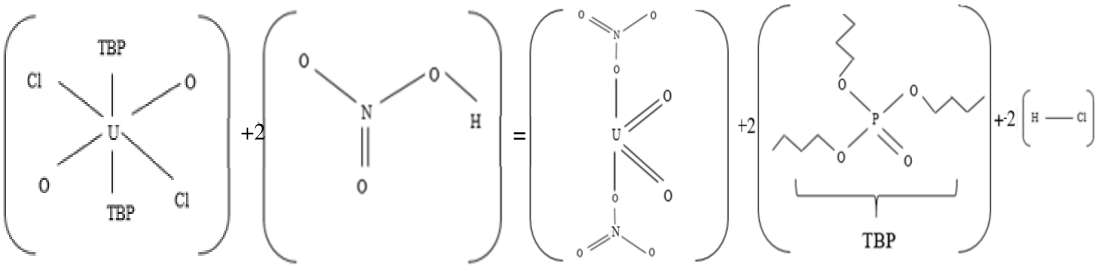
(8)



(9)



(10)



(11)

The recovery of individual rare earth element into the product stream is shown in Figure 8. The dataset indicates that the majority of the elements achieved a recovery above 90% while a relatively lower recovery was noticed for scandium (<90%). Moreover, Figure 9 suggests that no substantial difference was observed for the recovery of HREEs, LREEs, CREEs, and UCREEs between the two sets of solvent extraction tests with an improved recovery being obtained for the two-stage process.

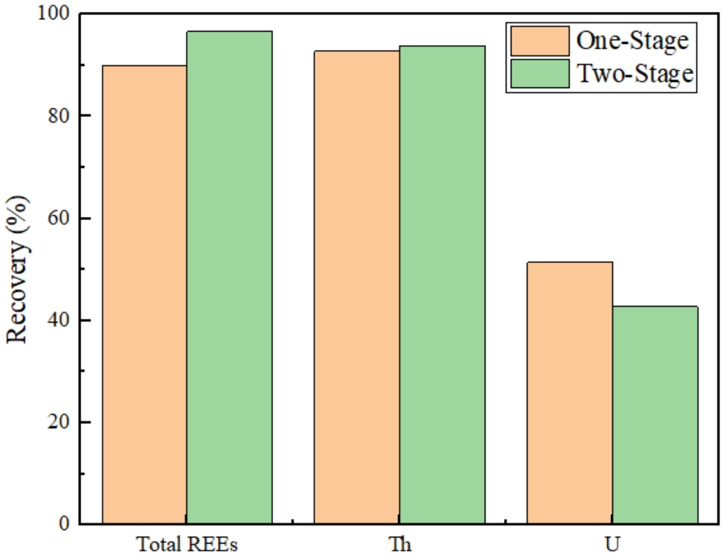


Figure 7. Recovery of total rare earths, thorium, and uranium into the product stream based on the one-stage and two-stage solvent extraction process.

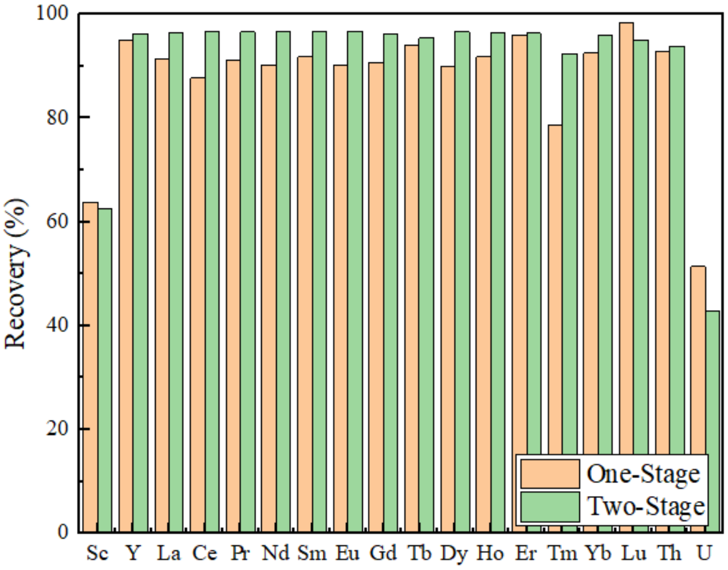


Figure 8. Recovery of individual rare earth, thorium, and uranium into the product stream based on the one-stage and two-stage solvent extraction process.

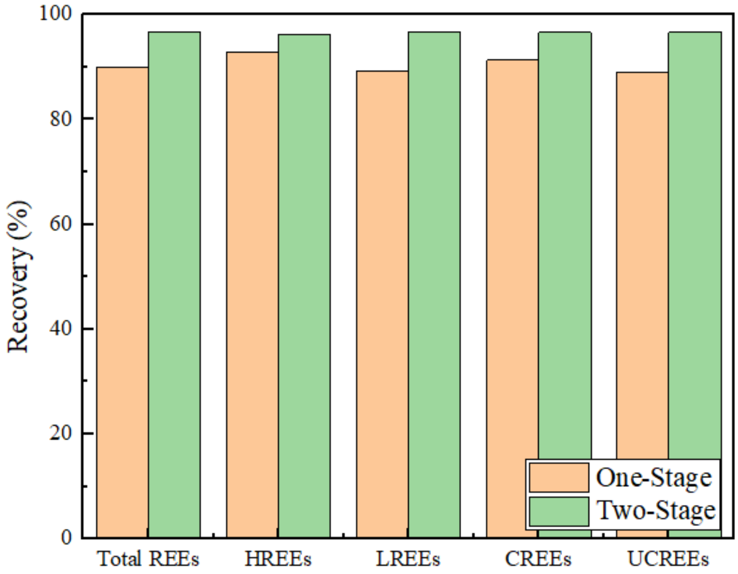


Figure 9. Recovery of total, heavy, light, critical, and uncritical REEs based on the one-stage and two-stage solvent extraction process.

3.3. Modified Experimental Testing

3.3.1. One-stage Precipitation

As seen from the results presented earlier, selective precipitation successfully precipitated out thorium, while solvent extraction was noticeably more effective in removing uranium from rare earths. Therefore, a modified experimental protocol consisting of one-stage precipitation and two-stage solvent extraction was developed, the procedure of which was strictly followed for improved separation of the radioactive elements from rare earths.

Individual REE content, as well as the concentration of thorium and uranium of the filtrate obtained at the precipitation pH of 4.8, are shown in Table 4. All the data reported are the average of three replicate selective precipitation tests. It can be seen from Table 4 that all Th present in the feedstock solution precipitated out as solids, and no content was detected in the remaining solution, which further confirms the findings previously discussed in the stage-wise precipitation. Besides, the amount of REEs, thorium, uranium, and major metals precipitated at a pH of 4.8 is shown in Figure 10. As seen, 100% of thorium precipitated out, while approximately 19.3% of REEs and 47.9% of uranium co-precipitated at the same pH value.

Furthermore, nearly 25% of major metals, including aluminum, calcium, iron, and magnesium, were transformed into solid forms under identical conditions. Approximately 65.6% of iron precipitated, followed by around 38.5% of aluminum, 17.1% of calcium, and 14.2% of magnesium. The findings presented here are consistent with prior studies (Xie et al., 2014; Balintova and Petrilakova, 2011). It is known that the precipitation of iron in the presence of oxygen starts at a pH value of 3.5, and $Fe(OH)_3$ is formed as a result of iron oxidization (Seo et al., 2017). In the present study, iron had existed in the solution as ferric iron, which was ready to precipitate with an increase in the pH, as seen in Eq. (12). On the other hand, the precipitation of aluminum typically initiates around a pH value of 5 (Balintova and Petrilakova, 2011), which results in the formation of $Al(OH)_3$ in the presence of OH^- ions following Eq. (13). Therefore, a substantially higher amount of iron precipitated out as opposed to aluminum, which also agrees well with the study carried out by Seo et al., (2017). High $Fe(OH)_3$ precipitation may partially contribute to the co-precipitation of rare earths due to its capability of absorbing particles onto the lattice sites of the iron crystals (Silva et al., 2018).

Table 4. Individual rare earth, thorium, and uranium concentration (mg/L) of the filtrate obtained at the pH value of 4.8.

pH	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
4.8	0.00	0.50	0.33	2.55	0.25	1.49	0.67	0.08	0.29	0.03	0.13	0.02	0.06	0.00	0.02	0.00	0.00	0.13

$$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} = Fe(OH)_3 \tag{12}$$

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} = Al(OH)_3 \tag{13}$$

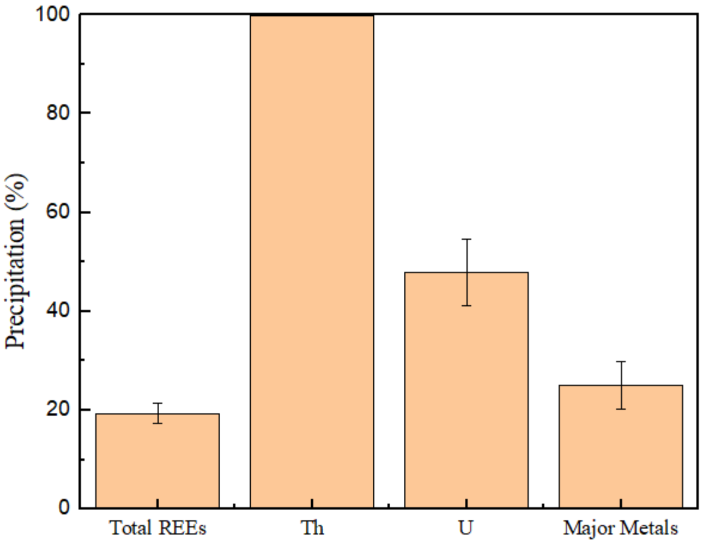


Figure 10. Average precipitation of total REEs, Th, U, and major metals at the pH value of 4.8 using 2 M NaOH. Error bars represent one standard deviation of three replicate tests.

Supplemental information can be obtained by further analyzing the REE precipitation data, as shown in Figure 11. It suggests again that heavy REEs tend to preferentially precipitate out compared to light REEs, which leads to a precipitation difference of approximately 4.5 percent. However, this difference is less than one standard deviation, which may not be statistically significant.

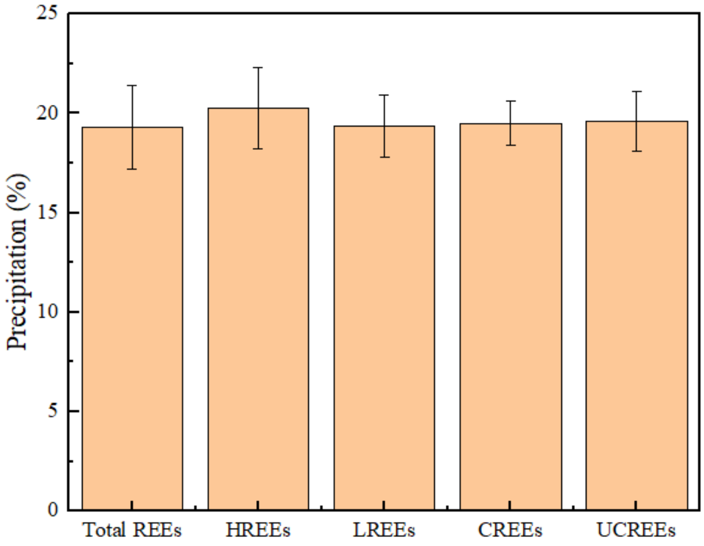


Figure 11. Average precipitation of total, heavy, light, critical, and uncritical rare earths at the pH value of 4.8 using 2 M NaOH. Error bars represent one standard deviation of three replicate tests.

3.3.2. Solids Characterization

The X-ray diffraction pattern of the solid sample obtained from the one-stage precipitation is shown in Figure 12. It can be seen that precipitated solids predominantly consisted of halite, which is attributed to the use of sodium hydroxide and hydrochloric acid for pH adjustment purposes. In addition to halite, a relatively small amount of hematite was also detected. It corroborates the prior finding that approximately 66% of iron precipitated out from the feedstock solution, and was later transformed from the hydroxide complex into hematite following the olation process (Jolivet et al., 2004). Elemental identification of the solid sample was provided by the SEM-EDX analysis as opposed to the qualitative analysis provided by XRD. As seen in Figure 13, the highest intensity peaks were observed for the elements of sodium (Na), oxygen (O), and chloride (Cl), which is consistent with the findings obtained from the XRD analysis. In addition to the three elements, a portion of rare earths and Th were also detected in the EDX spectrum; however, the intensities are considerably low compared to Na, O, and Cl. The identification of rare earths and thorium can be explained by their respective precipitation behavior shown earlier in Figure 10. The carbon peak seen in the EDX spectrum is due to the carbon tape substrate used during sample preparation. Moreover, SEM images presented in Figure 14 show the rough surfaces of the solid particles. The microscopic pictures observed under high magnifications further indicate that tiny nuclei in nanoscale initially precipitated out and deposited on top of the particles. Those nuclei acted like the nucleating agents and led to the subsequent growth of the particles in the form of roughly spherical crystallites.

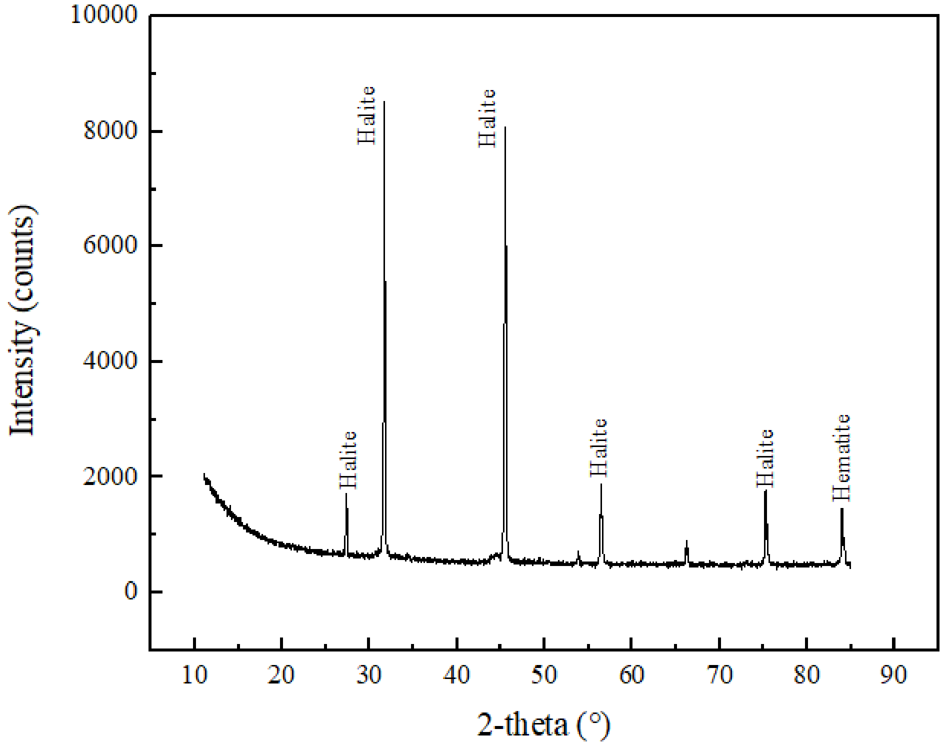


Figure 12. The X-ray diffraction pattern of the solid samples obtained from selective precipitation at a pH value of 4.8.

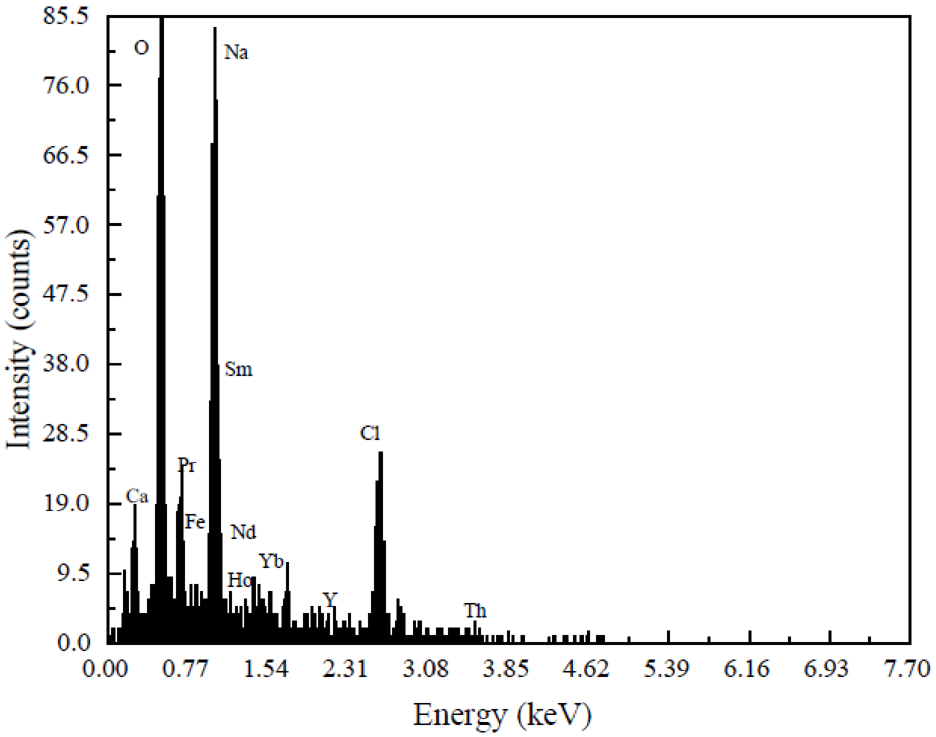


Figure 13. Elemental identification of the solid samples obtained from selective precipitation at a pH of 4.8 using SEM-EDX analysis.

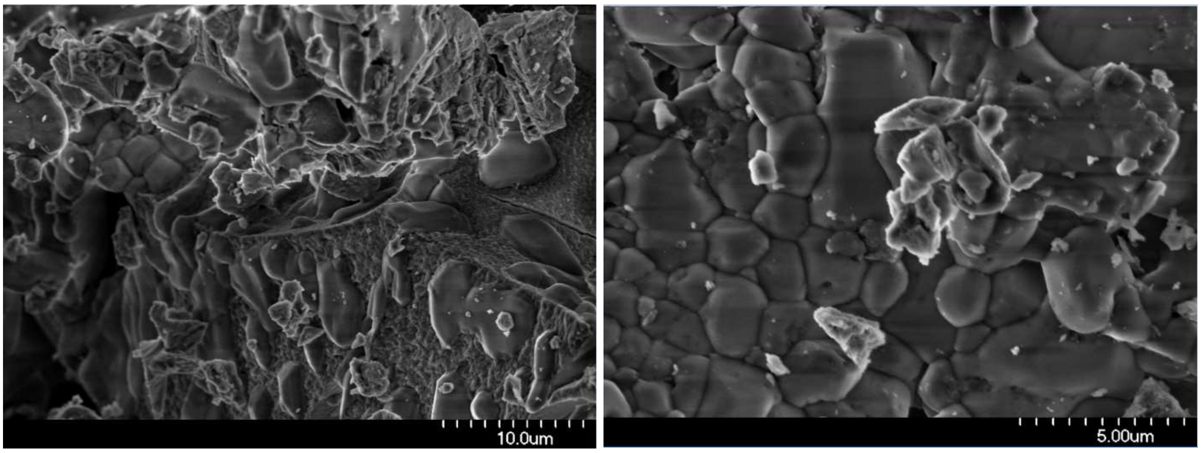


Figure 14. Scanning electron microscopy images of precipitated solids (at a pH of 4.8) observed under various magnifications.

3.3.3. Two-stage Solvent Extraction

The recovery of rare earths and uranium into the final rare earth product stream, based solely on the solvent extraction circuit, are given in Figure 15. Likewise, the overall recovery of rare earths and uranium, taking into account both selective precipitation and solvent extraction, is shown in

Figure 16. All the data shown in Figures 15 &16 are based on the 15 tests generated from the experimental design (Table 2). As shown in Figure 15, the rare earth recovery obtained from the solvent extraction circuit varied from 90% to 98.9%, while the corresponding uranium recovery changed between 5.9% and 89.4%. This noteworthy fluctuation in uranium recovery simply implies that the chosen variables had an impact on the removal of uranium. On the other hand, the rare earth recovery values close to each other suggests that the same variables had less profound or a minimal impact on the recovery of rare earths.

Figure 16 indicates the overall recovery of rare earths and uranium based on the experimental route incorporating selective precipitation. After taking into account the amount of rare earths and uranium that had precipitated out as solid forms, the overall recovery of rare earths and uranium both decreased to a value varying between 72.6%-79.8% and 3.1%-46.5%, respectively. Data from Figures 15 & 16 indicate the best results regarding the recovery of rare earth and uranium were obtained by Test 8 under the following conditions: 50 v% TBP, feed pH value of 3.5, an O/A ratio at 3. An overall rare earth recovery of approximately 79.8% with a corresponding uranium recovery of 3.1% was produced under the same operating conditions. Detailed data of REE and U extraction/stripping during each of the two-stage extraction and stripping processes have also been provided in Table 5 with respect to the test order and conditions contained in Table 2.

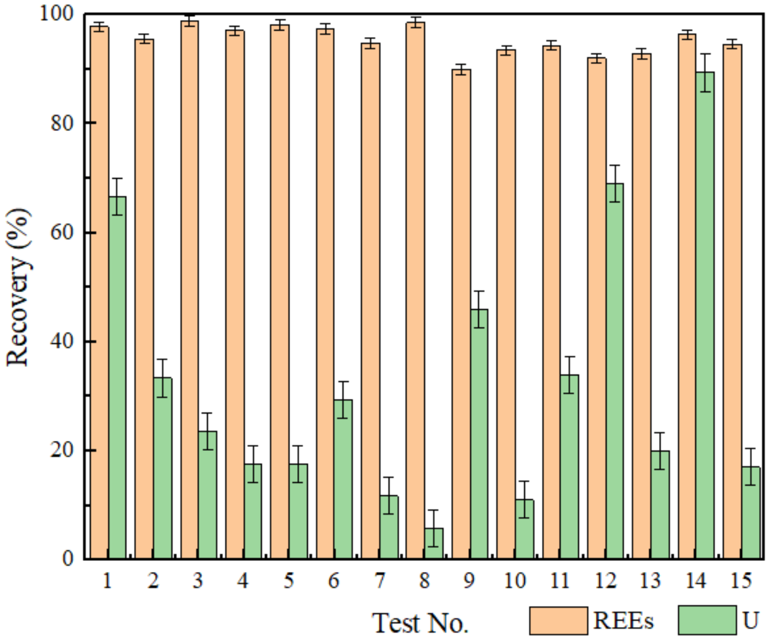


Figure 15. Recovery of total rare earths and uranium into the final product stream based solely on the solvent extraction circuit. Error bars represent one standard deviation of three replicate tests.

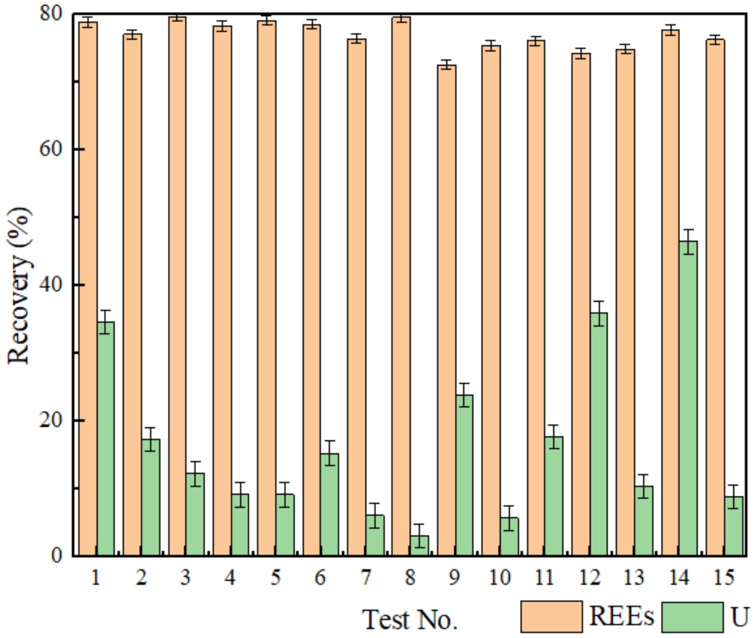


Figure 16. Recovery of total rare earths and uranium with respect to the overall experimental flowsheet. Error bars represent one standard deviation of three replicate tests.

Table 5. Total rare earth and uranium extraction and stripping with respect to test conditions provided in Table 2.

Test No.	First Extraction		Second Extraction		First Stripping		Second Stripping	
	TREEs Extraction to Organic Phase (%)	Uranium Extraction to Organic Phase (%)	TREEs Extraction to Organic Phase (%)	Uranium Extraction to Organic Phase (%)	TREEs Reporting to Aqueous Phase (%)	Uranium Reporting to Aqueous Phase (%)	TREEs Reporting to Aqueous Phase (%)	Uranium Reporting to Aqueous Phase (%)
1	1.98	0.00	100.00	33.33	84.30	100.00	7.90	0.00
2	4.48	33.33	0.00	50.00	60.07	50.00	4.59	0.00
3	0.00	47.06	0.01	55.56	0.00	50.77	0.00	0.00
4	2.26	47.06	0.00	66.67	100.00	42.86	0.00	0.00
5	0.00	52.94	0.00	62.50	0.00	40.39	0.00	0.00
6	0.00	47.50	0.00	44.44	0.00	75.00	0.00	0.00
7	0.00	70.59	5.13	60.00	46.15	20.00	2.66	0.00
8	0.00	71.34	0.00	100.00	0.00	52.79	1.38	5.41
9	8.49	22.00	1.58	41.02	40.50	48.15	12.37	7.14
10	5.54	63.00	0.04	70.27	26.40	35.60	33.24	3.51
11	4.34	33.00	0.03	49.25	45.14	75.76	49.79	12.50
12	7.05	11.00	0.07	22.47	26.32	70.97	26.76	0.00
13	6.17	65.00	0.13	42.86	51.09	20.00	43.54	6.25
14	0.04	0.00	0.03	6.67	100.00	100.00	0.00	0.00
15	2.97	31.71	0.00	75.00	79.73	79.44	85.00	0.00

3.4. Statistical Analysis and Modeling

Following data analysis, the impact of three operating variables (i.e., extractant concentration, feed solution pH, and O/A ratio) on the recovery of rare earth and uranium were analyzed using the Design Expert statistical analysis software. A statistical model was developed to determine the operational sensitivity of the rare earth and uranium recovery with respect to the input parameters based on the two-stage solvent extraction circuit.

The uranium recovery obtained from all the 15 tests were applied to develop the statistical model, which is shown in Eq. (14). It can be seen from the quadratic model that all three variables have a significant impact on the non-selective recovery of uranium into the REE product stream.

$$Uranium\ Recovery = +596.01 - 12.38 * A - 85.85 * B - 110.80 * C + 0.65 * AB + 0.80 * AC + 3.92 * BC + 0.09 * A^2 + 4.81 * B^2 + 10.88 * C^2 \quad (14)$$

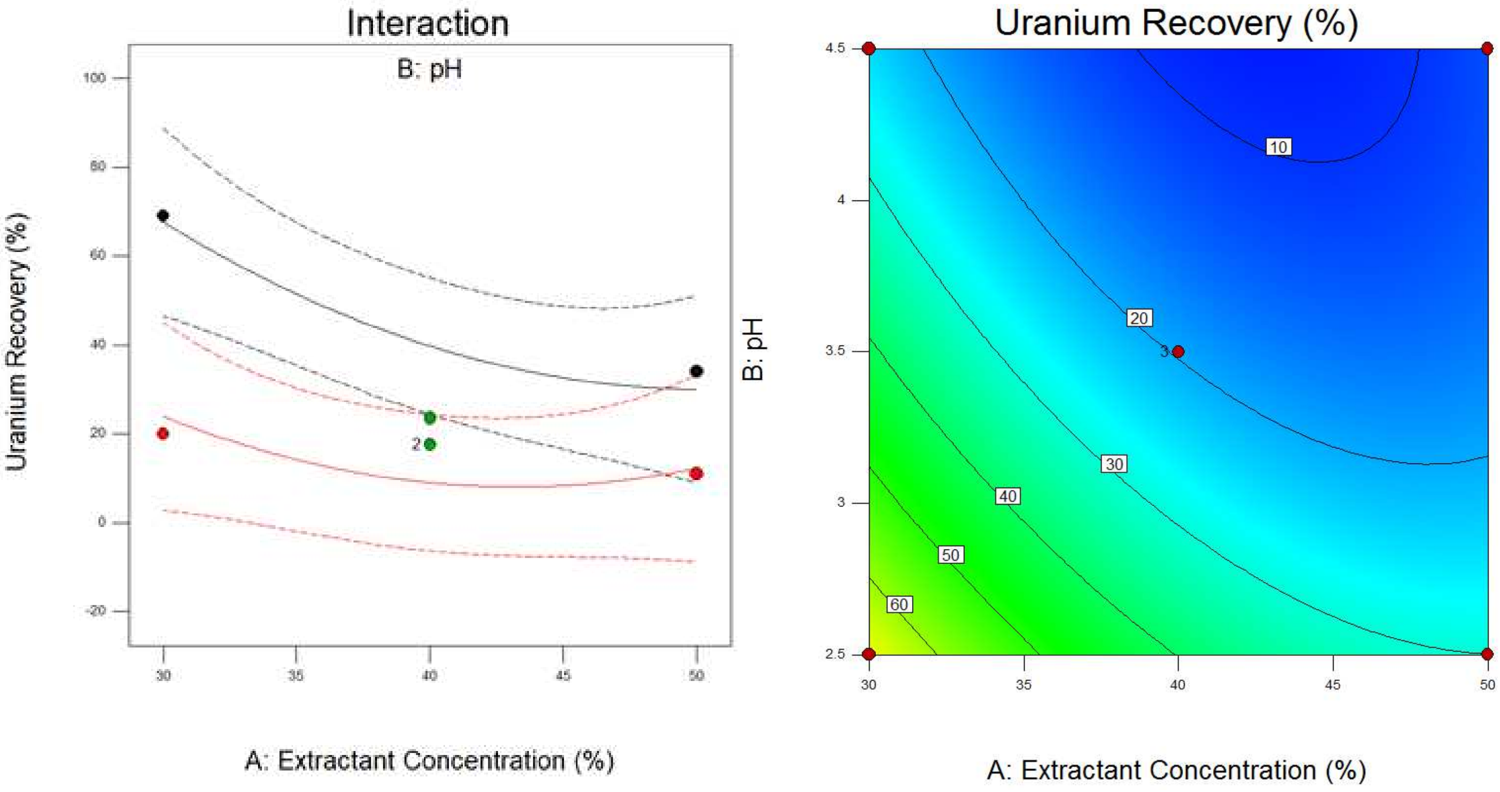
where the uncoded model terms A, B, and C correspond to the extractant concentration, feed solution pH, and O/A ratio, respectively. It should be noted that the extractant concentration in volume percentage and the pH value were used for developing this model. If different forms were used to express the model terms, such as using the concentration of H^+ instead of the pH value, the model and its significance will be impacted.

The Analysis of Variance (ANOVA) table provided detailed information on the significance of the model, as shown in Table 6. The model F-value of 9.84 implies the model is significant, and the probability of an F-value to become this large is 1.07% (<5%, which is the critical P-value used to determine the significance). Model terms are considered as significant within a 95% confidence level, or in other words, values of "prob>F" less than 0.05 indicate that terms are significant. Terms A (extractant concentration), B (pH), and C (O/A ratio) are all significant model terms according to the data obtained from ANOVA, and they all have a profound impact on uranium recovery. The "lack-of-fit" model is insignificant based on a p-value greater than 5%, which further supports the statistical significance of the model. An R-squared value of 0.9466 and an adjusted R-squared value of 0.8503 again validate the model.

Even though the coefficients associated with high-order terms are not high compared to that of the first-order terms, they are still needed to justify the significance of the model. Changing from the quadratic model to the linear model will drastically reduce the statistical significance of the model. The quadratic model also gives a low standard deviation and pure-error sum of squares compared to the linear model. The necessity of high-order terms is also suggested in the two plots provided in Figure 17. Both the interaction plot and the elliptical 2D contour plot support and indicate a strong interaction between the variables, namely the extractant concentration and feed solution pH.

Table 6. ANOVA analysis of the quadratic model for the prediction of uranium recovery.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	7992.72	9	888.08	9.84	0.0107	Significant
Lack of Fit	428.26	3	142.75	12.39	0.0756	Not significant
A-Extractant Concentration	1214.51	1	1214.51	13.46	0.0145	
B-pH	1890.82	1	1890.82	20.95	0.0060	
C-O/A Ratio	3666.25	1	3666.25	40.62	0.0014	
AB	169	1	169	1.87	0.2295	
AC	258.41	1	258.41	2.86	0.1514	
BC	61.54	1	61.54	0.68	0.4466	
A^2	304.75	1	304.75	3.38	0.1256	
B^2	85.25	1	85.25	0.94	0.3758	
C^2	436.87	1	436.87	4.84	0.0791	
R-Squared	0.9466					
Adj R-Squared	0.8503					
Pred R-Squared	0.1824					
Adeq Precision	10.172					



A

B

Figure 17. Interaction plot (A) and 2D contour plot (B) suggesting a strong interaction between the extractant concentration and feed solution pH.

3D response surface plots shown in Figure 18 indicate the impact of two input variables on uranium recovery while the level of the third variable was fixed at the middle-range value. Figure 18 (A) shows the effect of extractant concentration and feed solution pH on uranium recovery while the O/A ratio was maintained as a constant value of 2. As seen, a high pH value and high extractant concentration tend to generate enhanced separation results. This is corroborated by the experimental results that the lowest recovery of uranium into the rare earth product stream (i.e., 5.9%) was obtained with 50% TBP by volume. For the tests conducted with low TBP concentrations and low pH values, the amount of uranium reporting to the final product stream increased substantially. Similarly, the effect of extractant concentration and O/A ratio on uranium recovery was indicated in Figure 18 (B) with a constant feed solution pH value of 3.5. The uranium recovery decreases with an elevation in both extractant concentration and O/A ratio. It is also supported by experimental results obtained from Test 8 (i.e., 50 v% TBP, O/A of 3) and Test 14 (i.e., 30 v% TBP, O/A of 1) where the lowest and highest uranium recovery were achieved, respectively. As the O/A ratio and pH increase, the recovery of uranium into the final product stream decreases, as reflected by Figure 18 (C).

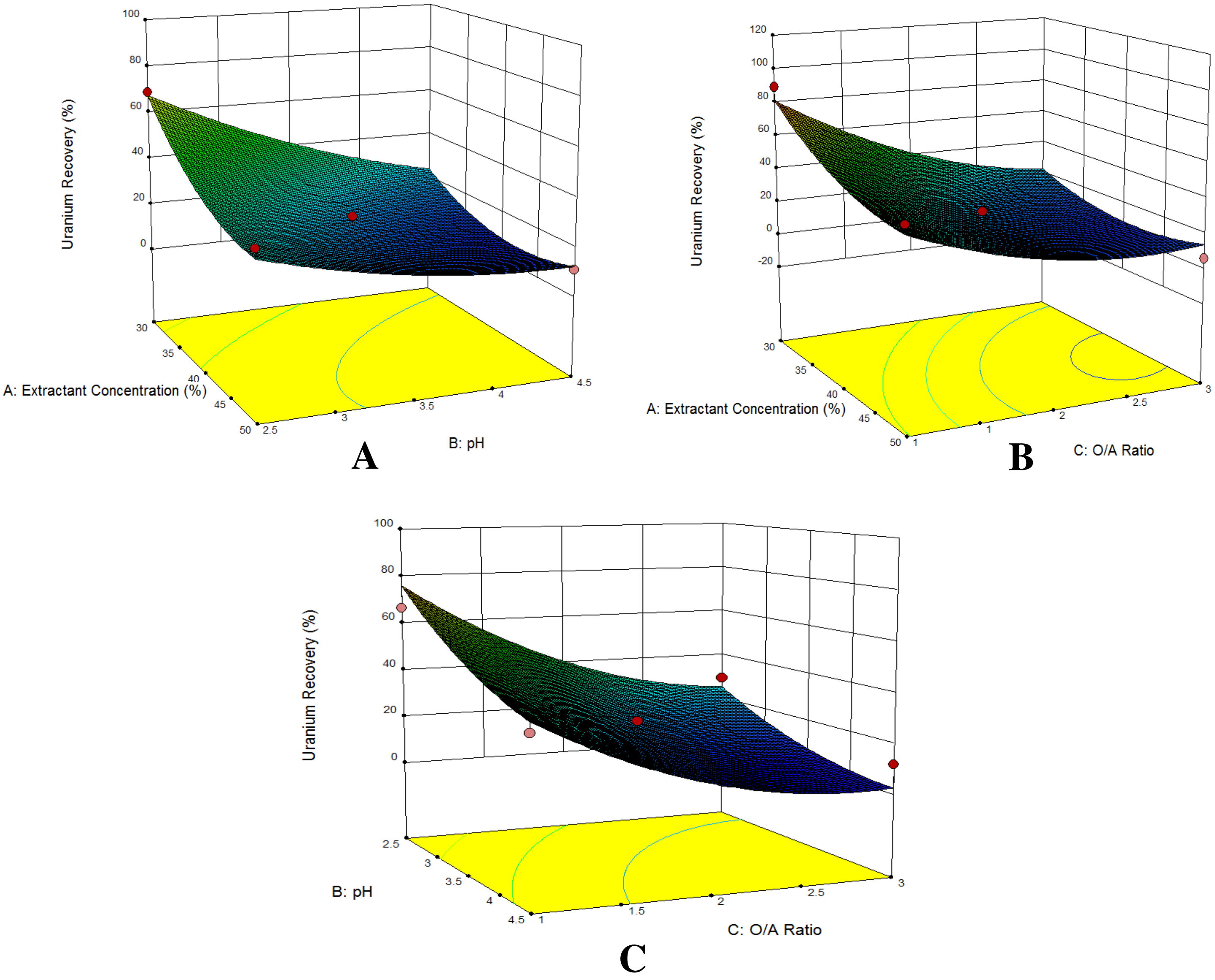


Figure 18. 3D surface response graphs obtained from the statistical analysis using Design-Expert.

4. CONCLUSIONS

Experimental studies were performed on a synthetic solution, which emulated a strip solution generated from coarse coal refuse and aimed to separate radioactive elements (i.e., Th and U) from rare earths. Selective precipitation and solvent extraction were initially applied to assess the separation potential, based on the findings of which a modified experimental protocol incorporating both separation methods were developed and strictly followed. A Box-Behnken design technique on the basis of response surface methodology was utilized for the experimental design and statistical analysis, which later shed light on the process operating parameters that had a profound impact on the removal of radioactive elements from rare earths. Specific findings from the study include:

1. Selective precipitation was an effective technique for the removal of thorium. Nearly 100% of thorium precipitated out at a solution pH value of 4.8, while 19.3% of rare earths and 47.9% of uranium co-precipitated at the same pH. A further increase in the solution pH led to the co-precipitation of rare earths and uranium due to their overlapping precipitation pH regions.
2. At the same pH value of 4.8, approximately 65.6% of iron precipitated out, followed by around 38.5% of aluminum, 17.1% of calcium, and 14.2% of magnesium precipitation.
3. Solvent extraction preferentially extracted uranium compared to thorium from the REE-containing solution. A two-stage solvent extraction process proved to be more efficient than the single-stage process, during the former process of which approximately 97%, 94%, and 43% of REEs, thorium, and uranium were recovered into the circuit product stream, respectively.
4. A modified experimental protocol incorporating both one-stage selective precipitation and two-stage solvent extraction was developed for enhanced removal of thorium and uranium. The impact of various operating parameters was systematically investigated using a Box-Behnken experiment design.
5. Test results following the modified experimental protocol indicate that extractant concentration, solvent extraction feed pH, and O/A ratio during extraction, all played a significant role in the removal of uranium from rare earths, which were further corroborated by the statistical model developed using Box-Behnken.
6. The optimum separation performance was identified throughout the study, which corresponded to an overall rare earth, thorium, and uranium recovery of 79.6%, 0%, and 3.1%, separately. The optimum separation was obtained under the following operating condition: one-stage precipitation at a pH value of 4.8, solvent extraction feed pH of 3.5, 50 v% TBP, O/A ratio at 3:1.
7. A detailed assessment of the process's economic viability is beyond the scope of the present study; however, it will be performed in the future to indicate the economic benefits that can be potentially gained from the optimized separation process.

ACKNOWLEDGEMENT

The findings presented in this manuscript were based on a study that was supported by the Department of Energy under Award Number DE-FE0027035. Disclaimer: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The view and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The authors would like to express their gratitude towards the Department of Mining Engineering at the University of Kentucky and National Research Center for Coal and Energy (NRCCE) at West Virginia University for the elemental analysis reported in this study.

REFERENCES

Al-Areqi, W., Majid, A., & Sarmani, S. (2014). Thorium, Uranium and Rare Earth Elements Content in Lanthanide Concentrate (LC) and Water Leach Purification (WLP) Residue of Lynas Advanced Materials Plant (LAMP). *American Institute of Physics Conference Proceedings*, (pp. 93-96).

Alemrajabi, M., Rasmuson, A., Korkmaz, K., & Forsberg, K. (2017). Recovery of Rare Earth Elements from Nitrophosphoric Acid Solutions. *Hydrometallurgy*, 253-262.

Amaral, J., & Morais, C. (2010). Thorium and Uranium Extraction from Rare Earth Elements in Monazite Sulfuric Acid Liquor Through Solvent Extraction. *Minerals Engineering*, 498-503.

Anitha, M., Kotekar, M., Singh, D., Vijayalakshmi, R., & Singh, H. (2014). Solvent Extraction Studies on Rare Earths from Chloride Medium with Organophosphorous Extractant Dinonyl Phenyl Phosphoric Acid. *Hydrometallurgy*, 128-132.

Anufrieva, A., Buinovskii, A., Guluyta, M., Molokov, P., Ageeva, L., & Verkhoturova, V. (2014). Processing of REE-containing Ores and Concentrates. *Procedia Chemistry*, 119-125.

Ault, T., Krahn, S., & Croff, A. (2015). Radiological Impacts and Regulations of Rare Earth Elements in Non-Nuclear Energy Production. *Energies*, 2066-2081.

Balintova, M., & Petrilakova, A. (2011). Study of pH Influence on Selective Precipitation of Heavy Metals from Acid Mine Drainage. *Chemical Engineering Transactions* , 345-350.

Banda, R., Jeon, H., & Lee, M. (2012). Solvent Extraction Separation of Pr and Nd from Chloride Solution Containing La using Cyanex 272 and Its Mixture with Other Extractants. *Separation and Purification Technology*, 481-487.

Batchu, N., Jeon, H., & Lee, M. (2015). Solvent Extraction of Praseodymium (III) from Chloride Solutions by A Mixture of Cyanex 301 and LIX 63. *Journal of Industrial and Engineering Chemistry*, 286-290.

Belova, V., Egorova, N., Voshkin, A., & Khol'kin, A. (2015). Extraction of Rare Earth Metals, Uranium and Thorium from Nitrate Solutions by Binary Extractants. *Theoretical Foundations of Chemical Engineering*, 545-549.

Binnemans, K., Jones, P., Blanpain, B., Gerven, T., Yang, Y., Walton, A., & Buchert, M. (2013). Recycling of Rare Earths: A Critical Review . *Journal of Cleaner Production* , 1-22.

Biswas, S., Pathak, P., Singh, D., & Roy, S. (2013). Comparative Evaluation of Tri-n-butyl Phosphate (TBP) and Tris(2-ehylhexyl) Phosphate (TEHP) for the Recovery of Uranium from Monazite Leach Solution. *Separation Science and Technology*, 2013-2019.

Borai, E., El-Ghany, M., Ahmed, I., Hamed, M., El-Din, A., & Aly, H. (2016). Modified Acidic Leachinh for Selective Separation of Thorium, Phosphate, and Rare Earth Concentrates from Egyptian Crude Monazite. *International Journal of Mineral Processing*, 34-41.

Brookins, D. (1988). *Eh-pH Diagrams for Geochemistry.* Albuquerque: Springer-Verlag.

Dai, S., & Finkelman, R. (2018). Coal As A Promising Source of Critical Elements: Progress and Future Prospects. *International Journal of Coal Geology*, 155-164.

Das, S., Gaustad, G., Sekar, A., & Williams, E. (2018). Techno-Economic Analysis of Supercritical Extraction of Rare Earth Elements from Coal Ash. *Journal of Cleaner Production*.

Department of Energy . (2017). *Report on Rare Earth Elements from Coal and Coal Byproducts.* Washington DC.

Dittrich, C., Kaya, S., Diekmann, F., & Yagmurlu, B. (2016). Recovery of Rare Earth Elements and Scandium from European Deposits by Solvent Extraction. *ALTA Uranium-REE Proceedings*, (pp. 123-135).

Giri, R., & Nath, G. (2016). Physicochemical Study of Extractants for Extraction of Rare Earth Element . *Journal of Analytical Science and Technology* .

Gupta, B., Malik, P., & Deep, A. (2002). Extraction of Uranium, Thorium and Lanthanides using Cyanex 923: Their Separations and Recovery from Monazite. *Journal of Radioanalytical and Nuclear Chemistry*, 451-456.

Habashi, F. (1997). *Handbook of Extractive Metallurgy.* Germany: Wiley-VCH.

Haque, N., Hughes, A., Lim, S., & Vernon, C. (2014). Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact. *Resources*, 614-635.

Honaker, R., Groppo, J., Bhagavatula, A., Razaee, M., & Zhang, W. (2016). Recovery of Rare Earth Minerals and Elements from Coal and Coal Byproducts. Louisville, KY.

Honaker, R., Zhang, W., Yang, X., & Razaee, M. (2018). Conception of An Integrated Flowsheet for Rare Earth Elements Recovery from Coal Coarse Refuse. *Minerals Engineering*, 233-240.

Hower, J., Granite, E., Mayfield, D., Lewis, A., & Finkelman, R. (2016). Notes on Contributions to the Science of Rare Earth Element Enrichment in Coal and Coal Combustion Byproducts. *Minerals*, 1-9.

Hu, J., Zheng, B., Finkelman, R., Wang, B., Wang, M., Li, S., & Wu, D. (2006). Concentration and Distribution of Sixty-One Elements in Coals from DPR Korea . *Fuel*, 679-688.

Huang, Q., Noble, A., Herbst, J., & Honaker, R. (2018). Liberation and Release of Rare Earth Minerals from Middle Kitanning, Fire Clay, and West Kentucky No. 13 Coal Sources. *Powder Technology*, 242-252.

Huang, Q., Talan, D., Restrepo, J., Baena, O., Kecojevic, V., & Noble, A. (2019). Characterization Study of Rare Earths, Yttrium and Scandium from Various Colombian Coal Samples and Non-Coal Lithologies. *International Journal of Coal Geology*, 14-26.

Jha, M., Kumari, A., Panda, R., Kumar, J., Yoo, K., & Lee, J. (2016). Review on Hydrometallurgical Recovery of Rare Earth Metals. *Hydrometallurgy*, 2-26.

Jolivet, J., Chaneac, C., & Tronc, E. (2004). Iron Oxide Chemistry. From Molecular Clusters to Extended Solid Networks. *The Royal Society of Chemistry*, 481-487.

Jun, L., Zhenggui, W., Deqian, L., Gengxiang, M., & Zucheng, J. (1998). Recovery of Ce (IV) and Th (IV) from Rare Earths (III) with Cyanex 923. *Hydrometallurgy*, 77-87.

Karayigit, A., Gayer, R., Querol, X., & Onacak, T. (2000). Contents of Major and Trace Elements in Feed Coals from Turkish Coal-Fired Power Plants. *International Journal of Coal Geology*, 169-184.

Ketris, M., & Yudovich, Y. (2009). Estimations of Clarkes for Carbonaceous Biolithes: World Averages for Trace Element Contents in Black Shales and Coals. *International Journal of Coal Geology*, 135-148.

Kuang, S., Zhang, Z., Li, Y., Wei, H., & Liao, W. (2017). Synergistic Extraction and Separation of Rare Earths from Chloride Medium by the Mixture of HEHAPP and D2EHPA. *Hydrometallurgy*, 78-83.

Lange, C., Camargo, I., Figueiredo, A., Castro, L., Vasconcellos, M., & Ticianelli, R. (2017). A Brazilian Coal Fly Ash As A Potential Source for Rare Earth Elements. *Journal of Radioanal Nucl. Chem.*, 1235-1241.

Lapidus, G., & Doyle, F. (2015). Selective Thorium and Uranium Extraction from Monazite: I. Single-Stage Oxalate Leaching. *Hydrometallurgy*, 102-110.

Li, D., Zuo, Y., & Meng, S. (2004). Separation of Thorium (IV) and Extracting Rare Earths from Sulfuric and Phosphoric Acid Solutions by solvent Extraction Method . *Journal of Alloys and Compounds*, 431-433.

Lin, R., Bank, T., Roth, E., Granite, E., & Soong, Y. (2017). Organic and Inorganic Associations of Rare Earth Elements in Central Appalachian Coal. *International Journal of Coal Geology*, 295-301.

Lu, Y., Wei, H., Zhang, Z., Li, Y., Wu, G., & Liao, W. (2016). Selective Extraction and Separation of Thorium from Rare Earths by a Phosphorodiamidate Extractant. *Hydrometallurgy*, 192-197.

McLellan, B., Corder, G., Golev, A., & Ali, S. (2014). Sustainability of the Rare Earths Industry. *Procedia Environmental Sciences*, 280-287.

Menzies, I., & Rigby, F. (1961). Separation of Thorium from Uranium and Rare Earth Elements by Solvent Extraction with Tri-n-Butyl Phosphate-Xylene. *J. Appl. Chem.*, 104-113.

Nasab, M. (2014). Solvent Extraction Separation of Uranium (VI) and Thorium (IV) with Neutral Organophosphorus and Amine Ligands. *Fuel*, 595-600.

Nasab, M., Sam, A., & Milani, S. (2011). Determination of Optimum Process Conditions for the Separation of Thorium and Rare Earth Elements by Solvent Extraction. *Hydrometallurgy*, 141-147.

Panda, R., Kumari, A., Jha, M., Hait, J., Kumar, V., Kumar, J., & Lee, J. (2014). Leaching of Rare Earth Metals (REMs) from Korean Monazite Concentrate. *Journal of Industrial and Engineering Chemistry*, 2035-2042.

Papastefanou, C. (2007). Radioactivity of Coals and Fly Ashes. *Journal of Radioanalytical and Nuclear Chemistry*, 29-35.

Paulick, H., & Machacek, E. (2017). The Global Rare Earth Element Exploration Boom: An Analysis of Resources Outside of China and Discussion of Development Perspectives. *Resources Policy*, 134-153.

Ponou, J., Dodbiba, G., Anh, J., & Fujita, T. (2016). Selective Recovery of Rare Earth Elements from Aqueous Solution Obtained from Coal Power Plant Ash. *Journal of Environmental Chemical Engineering*, 3761-3766.

Qin, S., Lu, Q., Li, Y., Wang, J., Zhao, Q., & Gao, K. (2018). Relationships Between Trace Elements and Organic Matter in Coal. *Journal of Geochemical Exploration*, 101-110.

Rabie, K., Sayed, S., Lasheen, T., & Salama, I. (2007). Europium Separation from A Middle Rare Earths Concentrate Derived from Egyptian Black Sand Monazite. *Hydrometallurgy*, 121-130.

Rand, M., Fuger, J., Grenthe, I., Neck, V., & Rai, D. (2008). *Chemical Thermodynamics of Thorium.* Oxford.

Rim, K., Koo, K., & Park, J. (2013). Toxicological Evaluations of Rare Earths and Their Health Impacts to Workers: A Literature Review. *Safety and Health at Work*, 12-26.

Samsonov, M., Trofimov, T., Kulyako, Y., Vinokurov, S., Malikov, D., Batorshin, G., & Myasoedov, B. (2015). Recovery of Rare Earth Elements, Uranium and Thorium from Monazite Concentrate by Supercritical Fluid Extraction. *Radiochemistry*, 343-347.

Seo, E., Cheong, Y., Yim, G., Min, K., & Geroni, J. (2017). Recovery of Fe, Al and Mn in Acid Coal Mine Drainage by Sequential Selective Precipitation with Control of pH. *Catena*, 11-16.

Seredin, V. (1996). Rare Earth Element-Bearing Coals from the Russian Far East Deposit. *International Journal of Coal Geology*, 101-129.

Seredin, V., & Dai, S. (2012). Coal Deposits as Potential Alternative Sources for Lanthanides and Yttrium. *International Journal of Coal Geology*, 67-93.

Silva, R. G., De Morais, C. A., & Teixeria, L. V. (2018). Selective Removal of Impurities from Rare Earth Sulphuric Liquor Using Different Reagents. *Minerals Engineering*, 238-246.

United States Geological Survey. (1997). Retrieved from Radioactive Elements in Coal and Fly Ash: Abundance, Forms, and Environmental Significance: https://pubs.usgs.gov/fs/1997/fs163-97/FS-163-97.html

Valkov, A., Sergievskiy, V., Sofronov, V., Kalaev, M., & Ermakova, Y. (2014). Studies in the Field of Rare Earth Elements. *Procedia Chemistry*, 171-175.

Van Gosen, B., Verplanck, P., Seal, R. I., Long, K., & Gambogi, J. (2017). *Rare-Earth Elements, Chap.O ofSchulz, K.J, DeYoung, J.H. Jr, Seal, R.R., II, and Bradley, D.C.,eds. Critical Mineral Resources of United States-Economic and Environmental Geology and Prospects for Future Supply: U.S. Geological Survey Professional Paper.*

Vijayalakshmi, R., Mishra, S., Singh, H., & Gupta, C. (2001). Processing of Xenotime Concentrate by Sulphuric Acid Digestion and Selective Thorium Precipitation for Separation of Rare Earths. *Hydrometallurgy*, 75-80.

Wang, L., Huang, X., Yu, Y., Zhao, L., Wang, C., Feng, Z., . . . Long, Z. (2017). Towards Cleaner Production of Rare Earth Elements from Bastnaesite in China. *Journal of Cleaner Production*, 231-242.

Xie, F., Zhang, T., Dreisinger, D., & Doyle , F. (2014). A Critical Review on Solvent Extraction of Rare Earths from Aqueous Solutions. *Minerals Engineering*, 10-28.

Zhang, J., Zhao, B., & Schreiner, B. (2016). *Separation Hydrometallurgy of Rare Earth Elements.* Saskatoon: Springer.

Zhang, W., & Honaker, R. (2018). Rare Earth Elements Recovery Using Stages Precipitation from A Leachate Generated from Coarse Coa Refuse. *International Journal of Coal Geology*, 189-199.

Zhang, W., Rezaee, M., Bhagavatula, A., Li, Y., Groppo, J., & Honaker, R. (2015). A Review of the Occurance and Promising Recovery Methods of Rare Earth Elements from Coal and Coal By-Products. *International Journal of Coal Preparation and Utilization* , 295-330.

Zhang, Y., Xu, Y., Huang, X., Long, Z., Cui, D., & Hu, F. (2012). Study on the Thorium Recovery from Bastnaesite Treatment Process. *Journal of Rare Earths*, 374-377.

Zhou, H., Wang, Y., Guo, X., Dong, Y., Su, X., & Sun, X. (2018). The Recovery of Rare Earth by A Novel Extraction and Precipitation Strategy using Functional Ionic Liquids. *Journal of Molecular Liquids*, 414-420.

Zhu, Z., Pranolo, Y., & Cheng, C. (2015). Separation of Uranium and Thorium from Rare Earths for Rare Earth Production - A Review. *Minerals Engineering*, 185-196.