

## Article

# Leaching Kinetics of Rare Earth Elements from Fire Clay Seam Coal

Xinbo Yang \* and Rick Q. Honaker

Department of Mining Engineering, University of Kentucky, Lexington, KY 40506, USA; rick.honaker@uky.edu

\* Correspondence: xinbo.yang@uky.edu

Received: 27 April 2020; Accepted: 25 May 2020; Published: 27 May 2020



**Abstract:** Recovery of rare earth elements (REEs) from coal samples collected from the Fire Clay coal seam using diluted mineral acid solutions was investigated. The initial processing step was coal recovery using conventional froth flotation which concentrated the REEs in tailing material resulting in an upgrade to values around 700 ppm on a dry whole mass basis. Leaching experiments were performed on the flotation tailings material using a 1.2 M sulfuric acid solution adjusted to a temperature of 75 °C to study the extractability of REEs from coal material. The effect of particle size, leaching time, leaching temperature, and solid concentration on REE leaching recovery were evaluated. The kinetic data obtained from leaching over a range of temperatures suggested that the leaching process follows the shrinking core model with possibly a mixed control mechanism that may be a result of several heterogeneous materials leaching simultaneously. Leaching recovery increased rapidly at the beginning of the reaction then slowed as the system reached equilibrium. The apparent activation energy determined from test data obtained over a range of temperatures using 1 M sulfuric acid was 36 kJ/mol for the first 20 min of reaction time and 27 kJ/mol for the leaching period between 20 and 120 min. The leaching of light REEs during the initial stage was determined to be driven by a chemical reaction, followed by the formation of a product layer, which required lower activation energy in the later stage of leaching. In regards to the heavy REEs, the major mechanism for leaching is desorption and the product layer formation does not affect the heavy REEs significantly.

**Keywords:** rare earth elements; coal; leaching; kinetics; apparent activation energy

## 1. Introduction

Rare earth elements (REEs) exist in over 200 different mineral types. A portion of the REEs are associated with carbonates and oxides that are easy to extract while others are bonded with silicates and phosphates that are difficult to penetrate [1]. Commercially, REEs are produced from monazite, xenotime, bastnaesite, and clay adsorbed REEs, which is a unique source commonly associated with a commercial production operation in southern China [2,3]. Many studies have focused on developing REE extraction processes from secondary resources including mine waste streams, industrial wastes or byproducts, electronic waste recycling and magnet recycling industries, coal ash, slags and waste water, etc. [3–8]. The limitation of recovering REE from secondary resources is low grade, which limits the effort and cost that can be applied toward the extraction process. However, these resources take advantage of eliminating the mining cost as well as other associated costs such as the chemical cost already expended for treating the waste. Coal-based materials represent a potential secondary source for REEs which may be extracted and concentrated by the use of physical and/or chemical processes [9–11].

Several studies have investigated the REE mode of occurrences and distributions in coals of varying ranks, associated mineral matter, acid mine drainage and sludge, and coal combustion byproducts. Arbuzov et al. (2018) studied peat material collected from western Siberia and concluded that: (1) a

maximum of 25% of the REEs had a mineral association, such as monazite, xenotime, and zircon, etc.; (2) 10%–30% of REEs was in humic substances, and (3) 40%–80% was in a water-soluble form [12]. Studies conducted on the ash product of pre-combustion coal material using a muffle furnace showed that 70% of the light REEs and 50% of the heavy REEs in bituminous coals are predominantly associated with phosphate minerals, and 50%–60% of the REEs in low rank coals are associated with clays [13]. The REEs in low rank coals (i.e., lignite and subbituminous) are primarily associated with the organic matter whereas the association with higher rank coals are with the associated mineral matter including grains of rare earth phosphate minerals that are micro-dispersed within the organic matrix [12,14,15].

The Fire Clay coal seam material appears to be a very suitable source for REEs extraction due to its high concentration of REEs on a dry ash basis as compared to other coal sources. The origin of the REEs in the Fire Clay coal has been associated with volcanic deposition during the coalification period [16]. Mineralogy studies performed on the bituminous coal source using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) detected micro-dispersed rare earth phosphate mineral particles, which are generally difficult to dissolve in strong acid solutions [9]. The finely dispersed inorganic material contained in Fire Clay coal has relatively high concentrations of REEs. Liberation of the rare earth minerals by size reduction provides an opportunity for recovering clean coal from middling streams which is generally discarded or partially blended into coal products to meet contract specifications. This study focused on the leaching characteristics of the REEs associated with various fractions of the Fire Clay coal and associated mineral matter.

## 2. Materials and Method

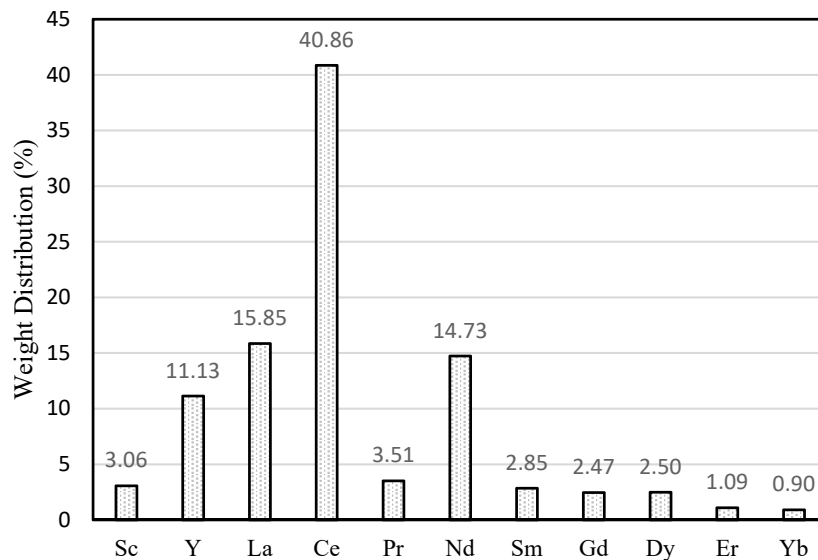
### 2.1. Materials

A representative sample (~200 kg) of a targeted fraction of the Fire Clay seam coal was collected from a coal preparation plant located in eastern Kentucky. The Fire Clay coal source is a high-volatile (30%–40% dry basis), bituminous coal well documented as being enriched with REEs and other critical elements. The sampled process stream was the product of a secondary dense medium vessel, which targeted the recovery of the  $1.4 \times 1.6$  specific gravity (SG) fraction, commonly referred to as middlings, in the  $150 \times 9$  mm particle size fraction of the plant feed.

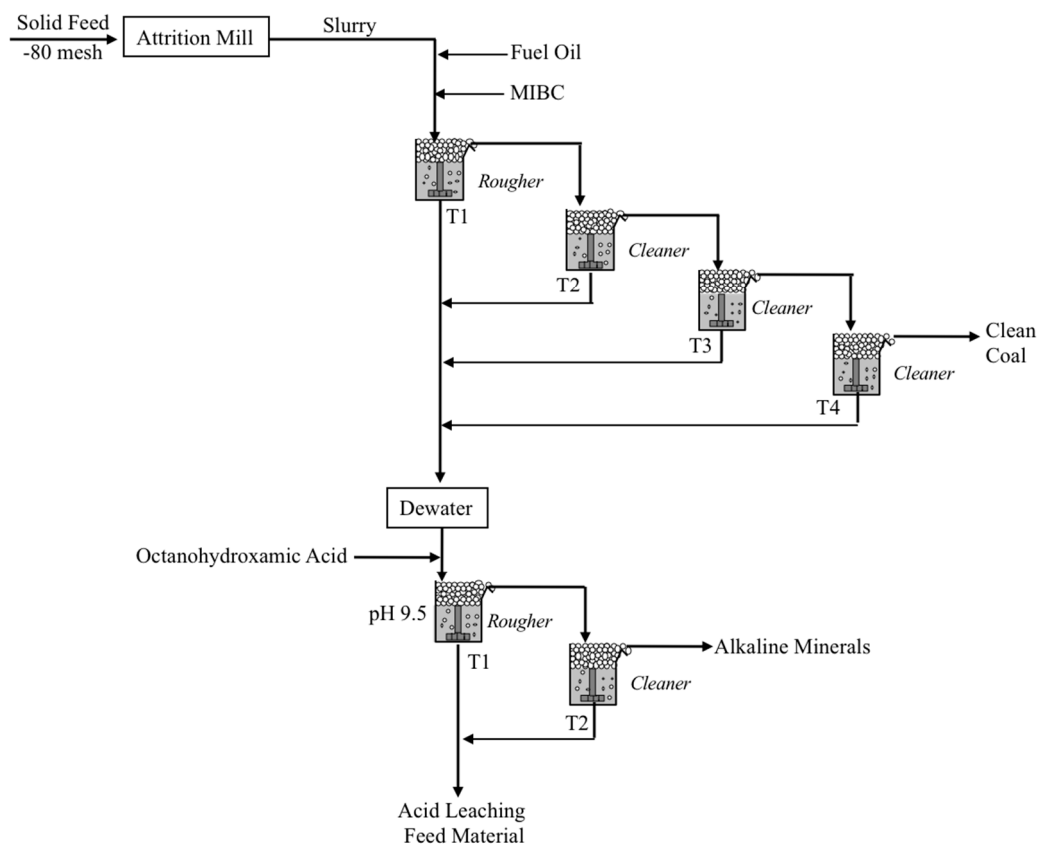
Analysis of a representative sample of the bulk revealed that the middlings material contained 242 ppm REEs on a dry, whole sample basis and 1331 ppm on a dry, ash basis. The ash content of the representative sample was 18.2% on a dry basis. The distribution of the REEs shown in Figure 1 indicates that nearly 24% of the REEs are permanent magnet elements (Nd, Pr, Sm, and Dy) while scandium represents 3.1% of the total, which is valued as a component in high performance aluminum alloy. The high ash-based REE content value provided an indication that the use of grinding to liberate the associated mineral matter could potentially provide a means for significant pre-concentration of the REEs prior to the leaching process while producing a marketable clean coal product.

The  $150 \times 9$  mm middling bulk sample was crushed using a laboratory jaw crusher and subsequently ground in a hammer mill to achieve a top particle size of 1 mm. The bulk sample was split into multiple representative samples by riffing the hammer mill product. For each test, a representative sample was pulverized to a top size of 80 mesh (177  $\mu$ m) in a smaller hammer mill and then ground in an attrition mill at a pre-selected rotation speed and retention time to achieve the desired particle size reduction. The solids concentration used in the attrition mill was 40 g/L. The ground material was treated in an 8-L Denver conventional flotation system to recover clean coal material using diesel fuel No. 2 as the collector and 4-methyl-2-pentanol as the frother. The chemical concentrations varied from test-to-test based on the feed particle size distribution. As shown in Figure 2, a rougher stage of treatment was followed by three cleaner stages to ensure maximum recovery of the liberated mineral matter and to achieve an ultraclean coal product. The tailings material collected from the coal recovery process was further treated by a second flotation step using octanohydroxamic acid ( $C_8H_{17}NO_2$ ) at a dosage of 1.5 kg/t and a pH value of 9.5 to remove acid consuming materials (e.g., calcite) [17]. No additional

frother was used in the mineral flotation stage due to the frothing property of octanohydroxamic acid. A rougher-cleaner treatment process was used for the alkali mineral rejection to maximize recovery of non-flatable material to the tailings stream. The final tailings material was the material used as feed for the leaching studies.



**Figure 1.** Rare earth element distribution in the nominal  $1.4 \times 1.6$  Specific Gravity (SG) middling fraction of Fire Clay coal as collected from a secondary dense medium vessel product stream.



**Figure 2.** Sample preparation of the Fire Clay middlings for the leaching studies.

## 2.2. Methodology

Leaching experiments were conducted in a triple neck round bottom flask with the middle neck connected to a total reflux condenser, which ensured that a constant volume was maintained. The reactor was placed in a water bath where the solution was heated using an immersion heater and a precise temperature control system to maintain the temperature throughout the duration of the test. Agitation was provided using a magnetic stir at a speed that could be varied up to around 1200 rpm. The leaching experiments were conducted using deionized water and trace metal grade acid (purity > 99.99%).

The investigation involved the evaluation of the following parameters on leaching recovery and kinetics: i) lixiviant type (i.e.,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$ ), ii) acid concentration (i.e., 0.1M, 0.5M, 1M, and 2M etc.), iii) solid-to-liquid ratio (i.e.,  $S/L = 1/100, 1/50, 1/10, 1/5$ , etc.), and iv) solution temperature (i.e., 25 °C, 40 °C, 50 °C, 60 °C, and 75 °C). To assess leaching kinetics, samples were collected at time intervals established from the initial start of the test, i.e., 1 min, 3 min, 5 min, 10 min, 20 min, 30 min, 60 min, 90 min, and 120 min. Micro-filter (0.45  $\mu\text{m}$ ) plunger syringes were used to separate the leachate from the solids to immediately stop the solid–liquid reaction. The final solid residue was filtered and washed with deionized water.

The REE contents in addition to other elements of interest in the leachate and solid residue samples were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The results were used to calculate elemental and overall recovery of the REEs. Solid loss, REE content in the leach solid residue and leachate solution are presented in the supplementary materials (Table S1) that is accessible online. Leach recovery represents the amount of material in the test feed source that was solubilized into solution during the leaching process, which was quantified using the following expression:

$$\text{Leach recovery (\%)} = \frac{c_L * V_L}{c_L * V_L + c_{SR} * m_{SR}} \times 100\% \quad (1)$$

in which  $c_L$  is the elemental concentration in the leachate solution ( $\mu\text{g/mL}$ );  $V_L$  the volume of the analyzed leachate solution (mL);  $c_{SR}$  the elemental concentration in solid residue ( $\mu\text{g/g}$ ); and  $m_{SR}$  the weight of solid residue (g).

## 2.3. Analytical Methods

REE content was determined by digestion and analysis of the resultant solution in an ICP-OES. The solid sample preparation procedure followed the ASTM D6357 method for ashing and digestion of coal and refuse samples with modifications made to the digestion to allow for use of a digestion block apparatus. The ICP-OES unit was calibrated using a standard solution identified as VHGM-SM68 multi standard, which contained 48 elements. The REE recovery of these check standards was maintained at  $\pm 10\%$  relative standard deviation (RSD). A duplicate sample was chosen at random and run through the entire process to verify repeatability at the frequency of not less than one every 40 samples. A certified coal ash sample (1633b) was utilized to ensure the digestion procedure and as a reference standard for peak selection. Three standard sample were repeated with each batch of digestion and the standard deviations for the rare earth elements are: <2% for Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Th, Y, and Yb; <5% for Sm and Tm; <15% for Tb.

X-ray diffraction (XRD) analyses were conducted on feed samples using an Advance D8 instrument produced by the Bruker Company. The scanning was performed from  $10^\circ$  to  $70^\circ$  with a stepwise increase of  $0.02^\circ$  and a scanning speed of  $0.5^\circ/\text{min}$ . The XRD spectra were analyzed to estimate concentrations of major mineral components using the EVA software developed by the same company.

### 3. Results and Discussions

#### 3.1. Particle Size Effect

A reduction in particle size may provide two significant benefits, i.e., (1) liberation of the clay particles and other mineral matter which exposes more surface area and exchangeable REEs for lixiviants to interact and extract the RE ions and/or (2) liberation of nano-sized RE minerals and RE oxides that may be dissolved in acid solutions. Acid leaching on finer size material can also provide faster kinetic rates and higher efficiency for REE extraction. On the negative side, by reducing the particle size to a micron level, the newly generated surface area is increased exponentially which escalates the consumption of hydrogen ions by dissolving more contaminate metal ions. As such, selectivity may be reduced, thereby elevating the cost of leaching and downstream concentration processes. Additional issues are the higher cost of energy for grinding and difficulties associated with thickening and dewatering ultrafine solid residuals.

To assess the effect of particle size on leaching performance, representative samples of the Fire Clay middlings material were ground for different lengths of time before the de-carbonization step to generate samples having a range of 80% passing sizes (P80). Acid leaching tests were conducted using 1.2 mol/L sulfuric acid solution with a solid concentration of 10 g/L at 75 °C. The REE recovery was quantified using test data generated after leaching for five hours and Equation (1).

The results shown in Table 1 indicated that reducing the particle size liberated mineral matter containing higher concentrations of REE. For example, by reducing the particle size to a P80 size of 150 µm (80 mesh top size) in the feed, the flotation tailings material contained 444 ppm of total REEs with a P80 size of 32 µm. The REE concentration of 444 ppm reflects the content of the coarser mineral matter dispersed in the middling particles. By grinding for greater lengths of time resulting in more applied energy, the P80 size was reduced to sub-micron level and the tailing material generated by flotation nearly doubled to 719 ppm of total REEs. This finding indicates that the finest mineral matter dispersed within the Fire Clay coal has the highest concentration of REEs. A previous study found that REEs in the Fire Clay coal were strongly associated with micro-dispersed kaolinite which may be liberated and released through size reduction [9].

**Table 1.** Liberation of REEs from the de-carbonized Fire Clay middlings material.

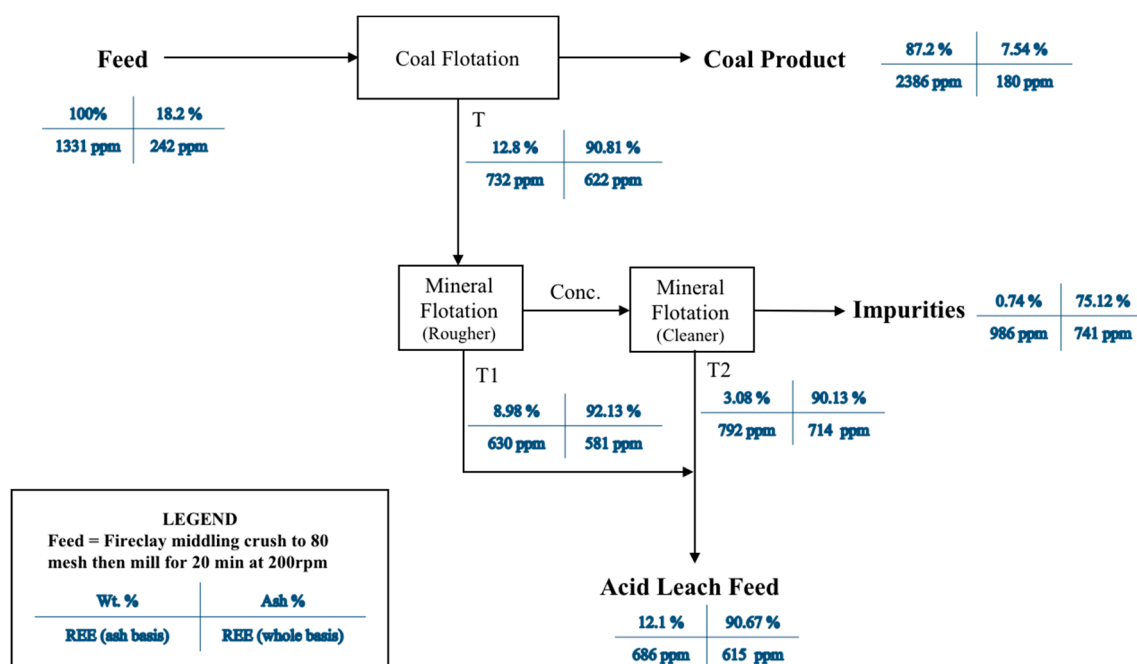
Attrition Mill		P80		Flotation		TREE Concentration		Acid Leaching	
Grinding Time (min)	Rotor Speed (rpm)	Flotation Feed (micron)	Flotation Tailing (micron)	Tailing Yield (%)	Ash Content (%)	Ash Basis (ppm)	Whole Mass Basis (ppm)	Solid Loss (%)	TREE Recovery (%)
Feed					18.2	1331	242		
0	0	150	32.0	3.7	89.1	499	444	11.9	71.2
2.5	150	45	14.5	7.4	85.9	581	499	9.9	74.8
5	200	37	10.2	9.5	87.1	609	531	9.2	79.0
20	200	13	8.7	12.8	90.8	685	622	16.2	83.7
40	200	11	7.3	14.2	91.0	768	699	17.2	84.3
60	200	10	6.5	13.9	91.4	771	705	20.4	83.6
90	200	9	5.0	13.6	90.9	788	716	24.2	82.3
120	200	8	0.9	15.4	91.0	791	719	27.9	82.0

TREE: total rare earth elements.

Reducing particle size resulted in a significant increase in leach recovery from 71.2% to 84.3% over the range of P80 sizes. As such, the size reduction increased the amount of REEs reporting in the leach feed and increased the percentage of the REEs being recovered through leaching. These two positive outcomes suggest that the REEs associated with micro-dispersed mineral matter in the Fire Clay middlings are more concentrated and more easily extractable by leaching relative to the coarser grain fractions. In addition, the finer mineral matter is, in general, more soluble as indicated by an increase in the amount of solid loss during the leaching process. As much as 20% of the solids in the

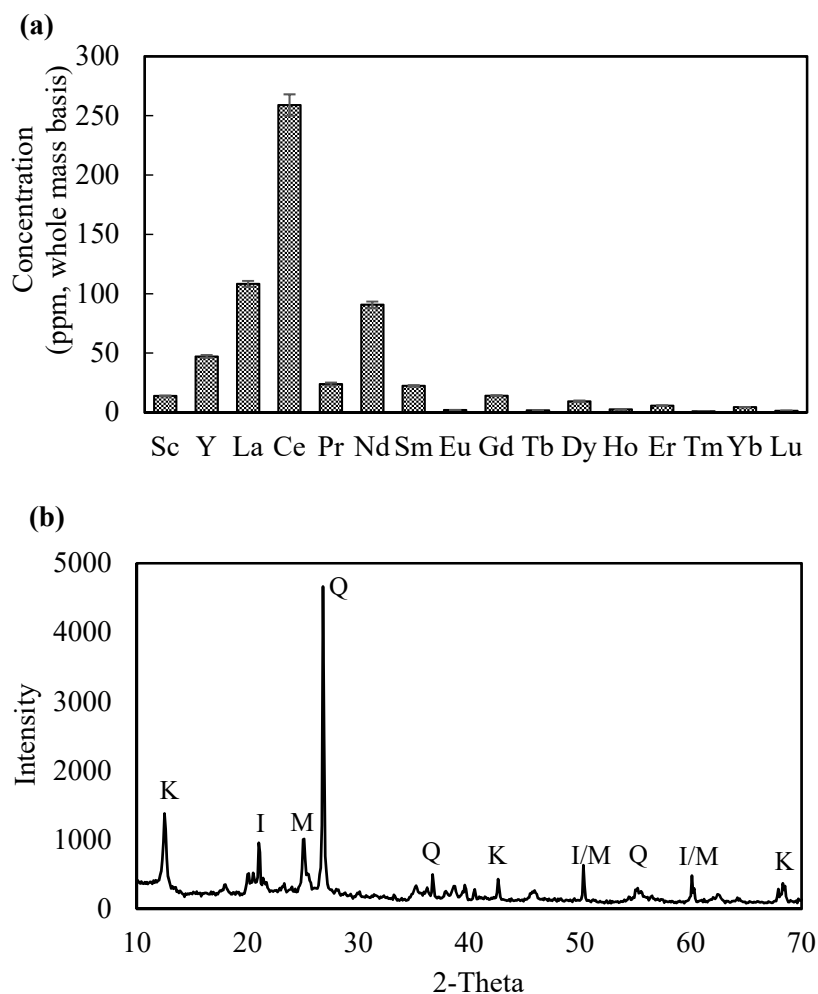
finest sample tested was dissolved under the standard leaching conditions, which may reflect both the solubility of the mineral matter and surface area exposure. A negative impact is an increase in the amount of contaminants in the leachate due to the elevated level of dissolved solids.

Based on the liberation test results, 20 min of grinding time was selected to generate the acid leach feed material used in this study. A flow sheet of the sample preparation process is shown in Figure 3 along with weight yield and content data for each feed and product stream. The decarbonization step resulted in a high-quality clean coal product containing around 7% ash-forming material while the reject material was nearly pure mineral matter as indicated by an ash content of 90.81%. The mineral flotation rougher-cleaner treatment resulted in 0.74% of the total feed reporting to the concentrate having an ash content of 75.12%. The lower ash content in the flotation concentration was an indicator of calcite flotation ( $\text{CaCO}_3$ ). The float product also contained 741 ppm of TREEs, which may be due to RE mineral flotation resulting from the use of octanohydroxamic acid. The flotation tailing material produced from the two stages of flotation represented 12.1% of the feed and contained 615 ppm of TREEs and 90.67% ash-forming material. The REE upgrade is 2.54:1 starting from a feed content of 242 ppm. This material was used as the acid leach feed in the subsequent leaching studies presented in this paper.



**Figure 3.** Schematic of sample preparation for the acid leach feed material using coal and mineral flotation.

Five representative samples of the acid leach feed were analyzed to assess the repeatability of the ICP-OES. The average TREE value was  $607 \pm 18$  ppm (2.97% variation) with thorium content of  $41 \pm 0.6$  ppm (1.46% variation). The Ce content accounted for 42% of the total REEs as shown in Figure 4a. The Fire Clay material was rich in light REEs (i.e., Ce, La, Pr, Nd, Sm, Eu, Gd, Sc) as indicated by a content of 534 ppm or 88.0% of the total. Yttrium was the most abundant heavy REE (i.e., Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu) with a concentration of 47 ppm. The major minerals present in the sample were quartz, kaolinite, illite, and muscovite as shown in the XRD plot in Figure 4b.

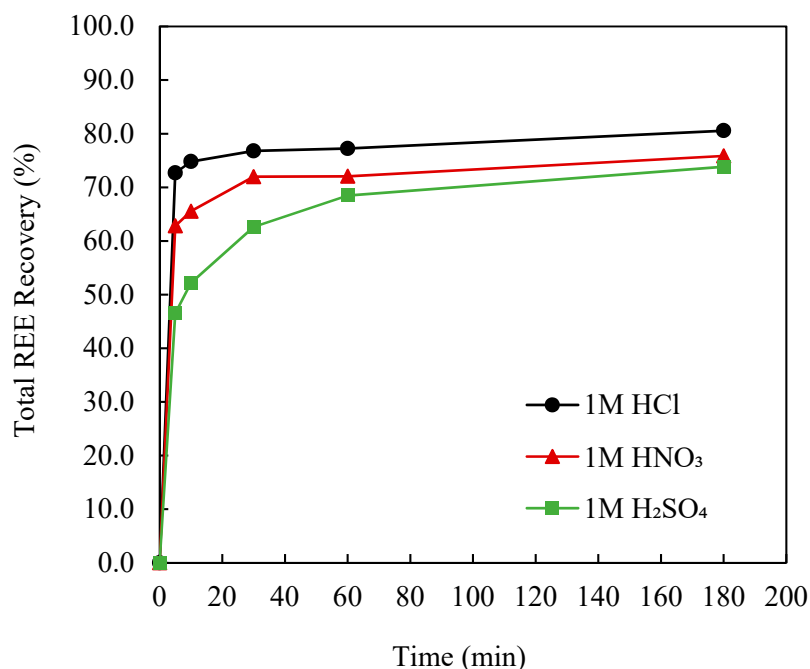


**Figure 4.** The composition of the acid leaching feed material used in this study on the basis of (a) rare earth content and (b) mineralogy as determined by X-ray diffraction analysis (Q—quartz, K—kaolinite, I—illite, M—muscovite).

### 3.2. Effect of Major Variables on REE Leaching

#### 3.2.1. Effect of Acid Type

The lixiviant type affects the REE leaching characteristics by changing the solution speciation stabilities due to the existence of various anions in varying concentrations. Sulfate ions were reported to have a higher coordination ability with rare earths than chloride ions even in high monovalent concentration solutions [18]. Leaching experiments were conducted using different inorganic acids at an acid concentration of 1M, solid/liquid ratio of 10 g/L, and a temperature of 75 °C. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), hydrochloric acid (HCl), and nitric acid ( $\text{HNO}_3$ ) were used to study the effect on REE leaching recovery and reaction rate as shown in Figure 5. Total REE (TREEs) recovery values of 80%, 76%, and 74% were achieved after 3 h of leaching using HCl,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  solution, respectively. The pH of the leachate solutions at the end of the tests were 0.105, 0.113, and 0.112, respectively.



**Figure 5.** Effect of acid type on the leaching recovery of total rare earth elements contained in the Fire Clay coal middlings (75 °C, 530 rpm, solid-to-liquid ratio (S/L) = 10 g/L,  $d_{80}$  = 8.7  $\mu$ m).

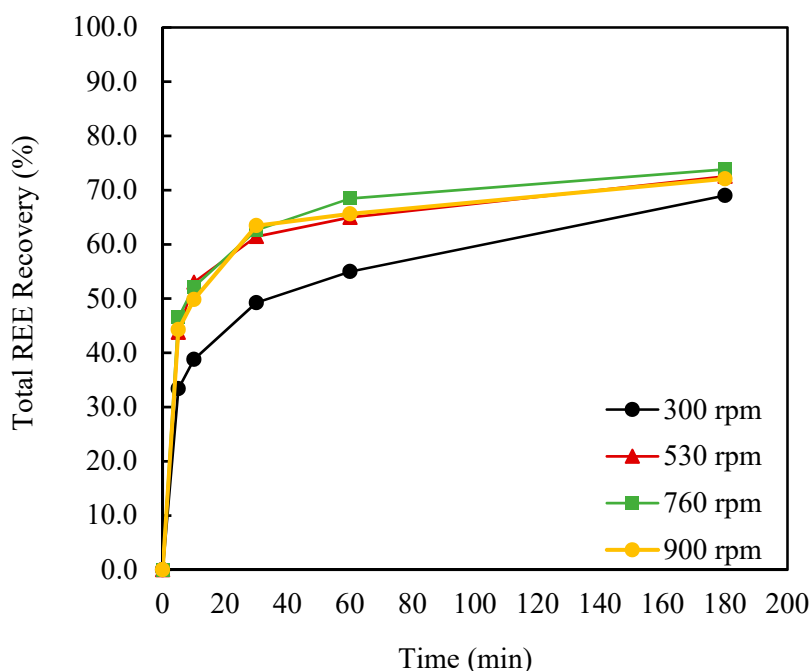
Hydrochloric acid provided the fastest leaching rate, which achieved 73% recovery after the first 5 min of leaching, and slowly reached equilibrium after 3 h. Nitric acid also provided fast leaching rate within the first 30 min. Sulfuric acid was the least effective under the leaching conditions and provided the slowest leaching rate. This finding was likely due to the fact that sulfate ions have a higher coordination ability with rare earths than chloride ions even in high monovalent concentration solutions [19].

The coal-based leachate contained high concentrations of trivalent ions that may coordinate with sulfate ions resulting in depression of the rare earth-sulfate coordination. In addition, sulfuric acid requires two steps of dissociation reaction to release  $H^+$  into solution whereas hydrochloric acid and nitric acid dissociates more rapidly into solution. Viscosity of the sulfuric acid solution is another factor that could have resulted in the slower reaction rate as the wetting rate of the solid particle surfaces is reduced when the solution viscosity is high. Despite the negative aspects of sulfuric acid, the lixiviant is still considered a viable lixiviate due to its relatively low cost and the negative aspects of the other lixiviants including the volatility of hydrochloric acid and the decomposability of nitric acid under 75 °C [20].

### 3.2.2. Stirring Speed Effect

Stirring speed affects the thickness of the film layer surrounding a solid particle suspended in the lixiviate solution. A high stirring speed creates an enhanced shear rate in solution which reduces the film layer thickness thereby increasing the mass transfer rate through the film diffusion layer [21]. The effect of stirring speed was evaluated at 300 rpm, 530 rpm, 760 rpm, and 900 rpm as shown in Figure 6. The leaching condition included 1M  $H_2SO_4$  solution and a solid/liquid ratio of 10 g/L at 75 °C. The test results indicated that a stirring speed of 300 rpm did not provide sufficient agitation due to inadequate suspension of the slurry based on visual observations, while stirring speeds of 530 rpm to 900 rpm provided nearly equal kinetics. The recovery achieved using a 900-rpm stirring speed was slightly lower than that obtained at 760 rpm. A stirring speed of 530 rpm was established as an adequate value for the standard test conditions.





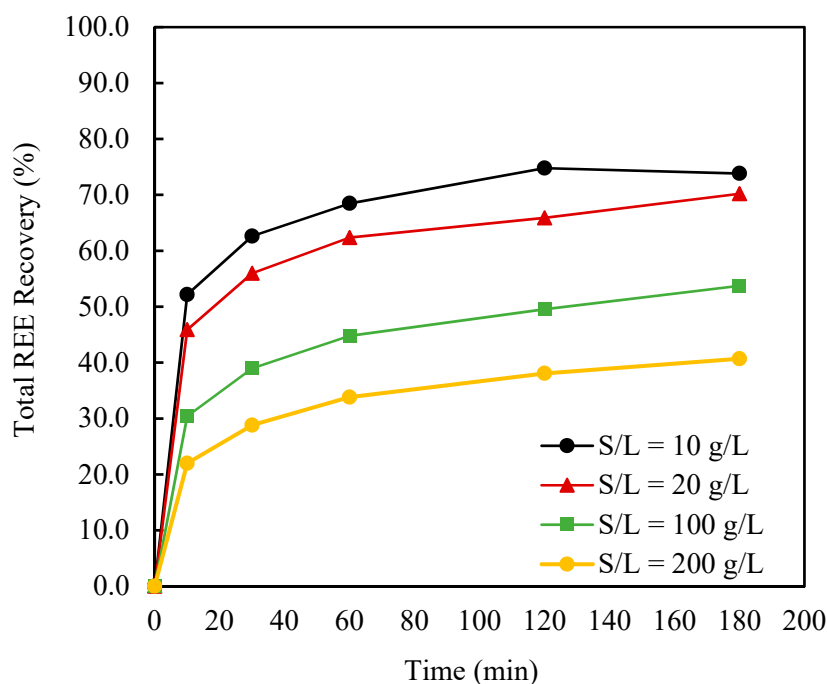
**Figure 6.** Effect of stirring speed on the leaching recovery of total rare earth elements contained in the Fire Clay coal middlings (75 °C, 1 M H<sub>2</sub>SO<sub>4</sub>, S/L = 10g/L, d<sub>80</sub> = 8.7 µm).

### 3.2.3. Solid-to-Liquid Ratio Effect

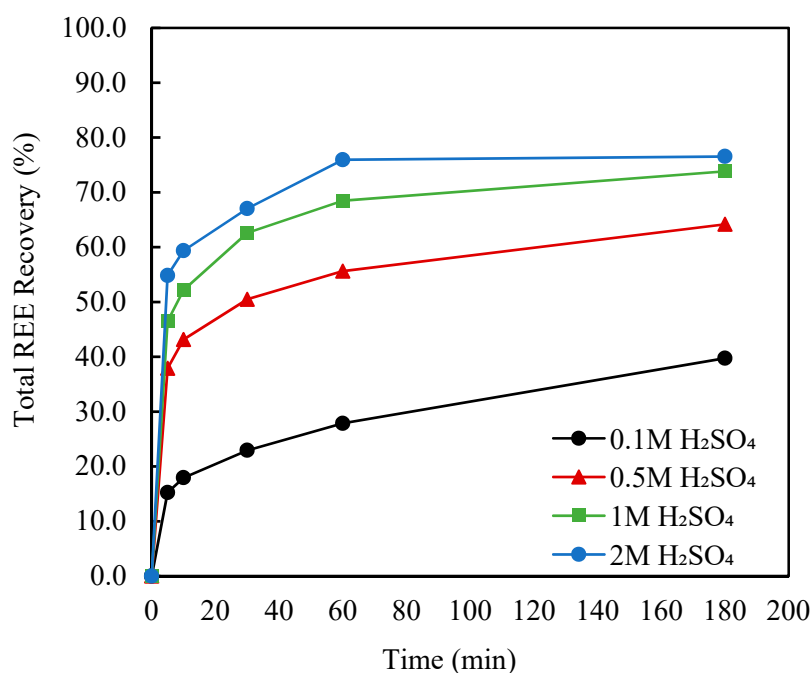
The solid-to-liquid (S/L) ratio establishes to the stoichiometric ratio of reactants, which directly affects the reaction equilibrium. The effect of the S/L ratio on rare earth leaching recovery was investigated in the range of 10 g/L to 200 g/L while maintaining the other parameters constant at 75 °C, 1 M H<sub>2</sub>SO<sub>4</sub>, and 530 rpm. The association between reactants decreased with an increase in the solid/liquid ratio, which resulted in a decrease in the extraction rate as shown in Figure 7. Leach recovery was reduced from 74% to 40% after increasing the S/L ratio from 10 g/L to 200 g/L. The magnitude of the recovery reduction is not commonly observed in other metal leaching operations. In the metallic copper leaching process, the leaching reaction was more effective when the Cu<sup>2+</sup> concentration in solution was higher due to Cu<sup>2+</sup> reacting with metallic Cu to Cu<sup>+</sup> [22]. This type of reaction mechanism does not occur in a REE solution since the REEs exist mostly as a compound. Niobium leaching from titanium oxide residues did not show any effect from the S/L ratio on leaching recovery [21]. However, Li et al. (2013) reported on a rare earth concentrate leaching study that found the S/L ratio to have a negative effect on the leaching of a rare earth concentrate when the ratio was higher than 100 g/L [23]. Therefore, the solid/liquid ratio effect varies from source-to-source in different leaching environments.

### 3.2.4. Effect of Acid Concentration

The effect of sulfuric acid concentration on leaching recovery was studied using 0.1 M, 0.5 M, 1 M, and 2 M acid concentrations using the standard values for temperature, stirring speed, and solid-to-liquid ratio. The initial acid concentrations of 0.1 M, 0.5 M, 1 M, and 2 M resulted in ending pH values of 1.04, 0.38, 0.11, and −0.25, respectively, after 3 h of leaching. As shown in Figure 8, the total REE recovery increased substantially from 40% to 74% by elevating acid concentration from 0.1 to 1 M. However, from 1 M to 2 M, the increase was marginal at around 2.5 absolute percentage points. The optimal acid concentration was selected to be 1 M since higher concentrations of acid did not provide a significant increase in recovery of REEs.

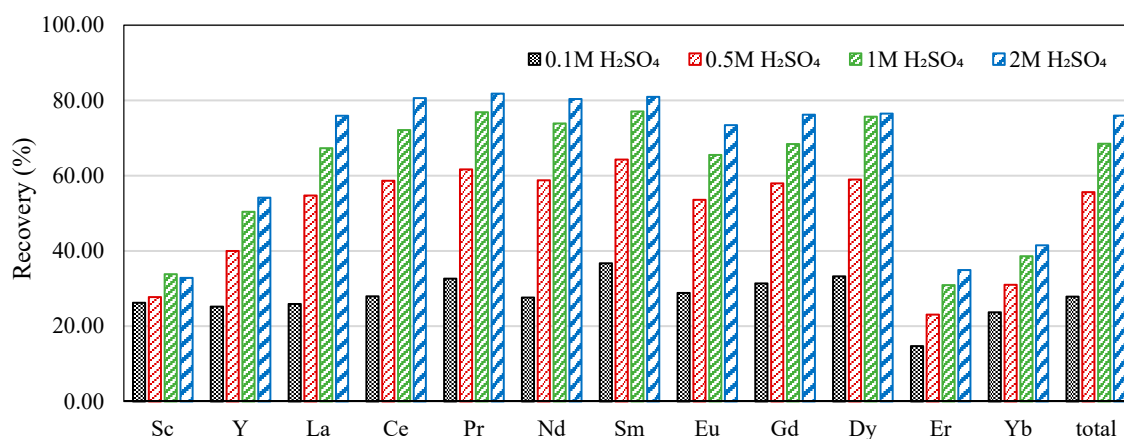


**Figure 7.** Effect of solid-to-liquid ratio on the leaching recovery of total rare earth elements contained in the Fire Clay coal middlings (75 °C, 1 M H<sub>2</sub>SO<sub>4</sub>, 530 rpm, D<sub>80</sub> = 8.7 μm).



**Figure 8.** Effect of sulfuric acid solution concentration on the leaching recovery of total rare earth elements contained in the Fire Clay coal middlings (75 °C, 530 rpm, S/L = 10g/L, D<sub>80</sub> = 8.7 μm).

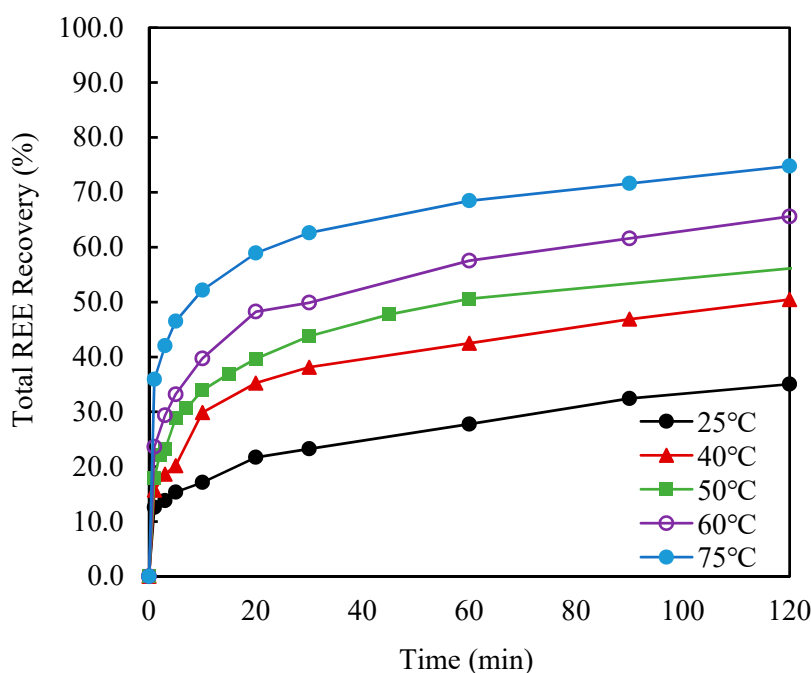
The effect of acid concentration on individual RE leaching recovery is shown in Figure 9. Recovery of the light REEs significantly increased when acid concentration was elevated from 0.1 M to 1 M and very little improvement was realized when using a 2 M acid solution. Scandium was the least sensitive to acid concentration. The remaining un-leached portion of Sc is likely associated with a mineral structure that requires a higher level energy to break down. Yang et al. (2018) improved the scandium leaching recovery from 31% to 74% after treated by roasting with no chemical additives at 750 °C for 2 h from a coal-based material [24].



**Figure 9.** Effect of sulfuric acid solution concentration on individual rare earth element leaching recovery (2 h, 75 °C, 530 rpm, S/L = 10 g/L,  $D_{80}$  = 8.7  $\mu$ m).

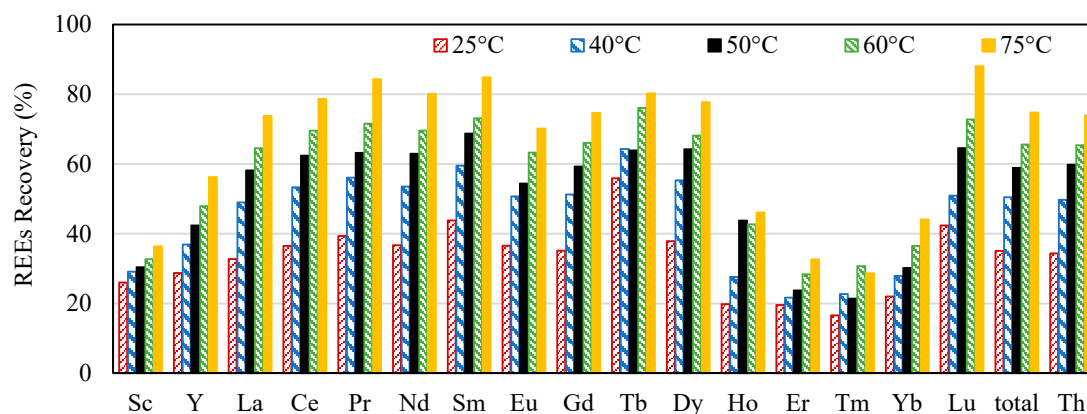
### 3.2.5. Effect of Temperature

A leaching process that is mainly controlled by a diffusion process is more dependent on mixing conditions whereas temperature has a more significant effect on chemical reaction controlled processes [25]. The effect of temperature on REE leaching using 1 M H<sub>2</sub>SO<sub>4</sub> was investigated using a stirring speed of 530 rpm and S/L ratio of 10 g/L for 2 h. Samples were taken over shorter time increments due to the relatively fast kinetics during the first 20–30 min. Figure 10 shows that REE leach recovery increased significantly with an elevation in leaching temperature. When the temperature was increased from 298 K (25 °C) to 348 K (75 °C), leaching recovery increased from 35% to 75% after 2 h of leaching. The data suggests the existence of a relatively fast leaching process during the first 20 min followed by a slow process. As such, two or more reaction mechanisms may be occurring when leaching the coal source.



**Figure 10.** Effect of leaching reaction temperature on the leaching recovery of total rare earth elements contained in the Fire Clay coal middling (1 M H<sub>2</sub>SO<sub>4</sub>, 530 rpm, S/L = 10g/L,  $D_{80}$  = 8.7  $\mu$ m).

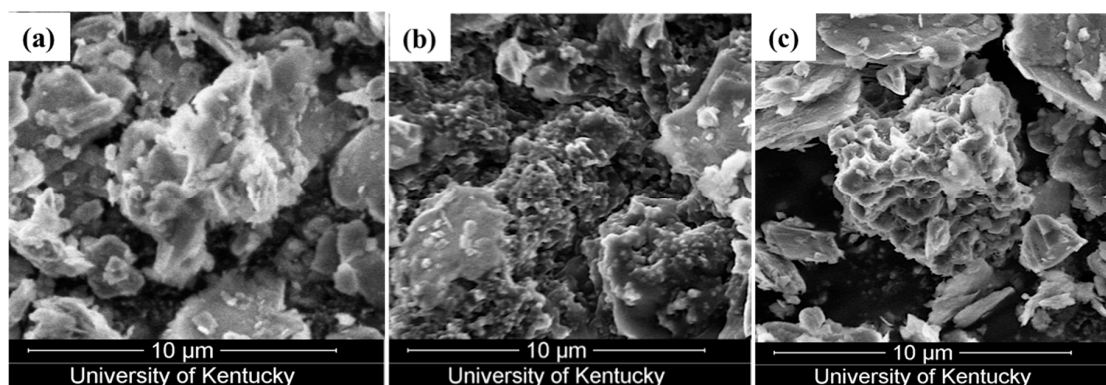
The effect of temperature on individual REEs is shown in Figure 11. Most of the light REEs (i.e., La, Ce, Pr, Nd, Sm) appeared to be very sensitive to temperature, which indicated that the leaching mechanism of light REEs was mostly chemical reaction controlled. The recovery of Ce, Pr, and Nd increased from 36%, 39%, and 36% to 79%, 84%, and 80%, respectively, by increasing the temperature from 25 °C to 75 °C. The heavy REEs and scandium recovery improved with higher temperature, but the increase was not as significant. Scandium recovery rose from 29% to 36%. For the recovery of elements that were relatively insensitive to temperature, the activation energy is generally low and more likely to be a result of a diffusion controlled process [26].



**Figure 11.** Effect of leaching reaction temperature on the leaching recovery of individual rare earth element (1 M H<sub>2</sub>SO<sub>4</sub>, 530 rpm, S/L = 10 g/L, D<sub>80</sub> = 8.7 µm, retention time of 120 min).

### 3.2.6. Morphology

The morphology of the Fire Clay coal middling particles before and after sulfuric acid leaching was studied using SEM. As shown in Figure 12a, the feed material consisted of heterogeneous particles comprised of mostly quartz and clay, which agrees well with the XRD analysis shown in Figure 12b. After 2 h of leaching at 50 °C, the particles were found to have a porous structure on the surface with a micro pore structure as shown in Figure 12b. After 2 h of leaching at 75 °C, the porous structure on some of the particle surfaces appeared larger in size as shown in Figure 12c. The images show no visible layer on the surface instead of porous structure due to dissolution. Therefore, the diffusion process in this reaction may be the results of interfacial transfer of the products and the reagent diffusion through the porous structure of solid particles.



**Figure 12.** SEM images of particles found in (a) leaching feed material; (b) solid residue after 2 h leaching at 50 °C; (c) solid residue after 2 h leaching at 75 °C (1 M H<sub>2</sub>SO<sub>4</sub>, 530 rpm, S/L = 10 g/L, D<sub>80</sub> = 8.7 µm).

The leaching process involved several simultaneous reactions due to the mineral composition and the variety of REE associations. The REEs were found to exist in crystallized structures (mostly silicates and phosphate compounds), which usually require decomposition to be extracted under the current leaching conditions. A small portion of the REEs are present as RE ion substitution form in clays whereas most are associated with soluble RE containing minerals. Based on the results shown in Section 3.2.5, extraction of light REEs in this coal source was more sensitive to temperature thus the light REEs were more likely to be mineral associated, whereas the heavy REEs extraction was more independent to temperature thus more likely to be soluble metal oxides and adsorbed ions onto clay minerals.

### 3.3. Kinetic Analysis

The leaching process is classified as a fluid–particle heterogenous reaction in which a liquid reacts with a solid by contacting and transforms the solid into a product. A solid particle that reacts with a liquid and shrinks in size during the reaction can be described by a shrinking core model. The reaction is a five-step process, i.e., (1) diffusion through the film layer, (2) diffusion through the product layer, (3) chemical reaction on the surface, (4) product diffusion through the product layer and (5) product diffusion through the film layer to the solution. The slowest step is known as the rate determining process. The activation energy of a certain leaching step can be quantified by selecting the most accurate rate equation to represent the reactions [25].

A variety of rate equations have been developed and reported in literature that describe the leaching rate process [25,27,28]. Among the equations, the rate equation (Equation (2)) developed by Crank–Ginstling–Brounshtein, which describes the mass transfer across product layer, fits the experimental data well, i.e.,

$$k_d t = \left[ 1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}} \right] \quad (2)$$

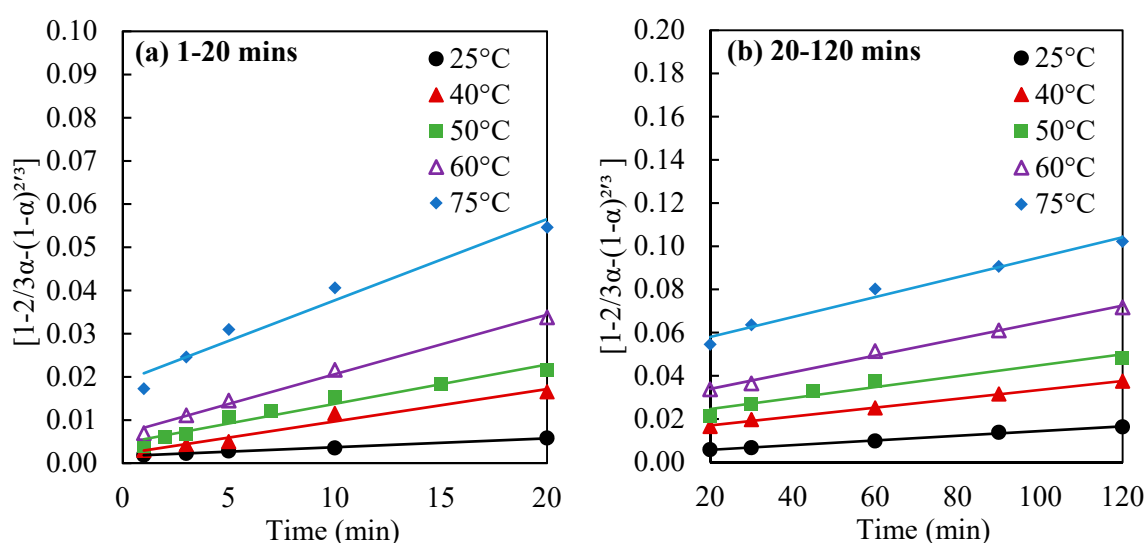
here  $\alpha$  is the fraction that reacted;  $k_d$  is the kinetic constant.

The Crank–Ginstling–Brounshtein equation was used to linearize the extraction fraction ( $\alpha$ ) among all the temperatures using the experimental data for the first 20 min of leaching and the following 20–120 min of the reaction as shown in Figure 13. The correlation coefficient values ( $R^2$ ) and the corresponding slopes ( $k$ ) of the plots are listed in Table 2. Rate constants were calculated and the Arrhenius plots of  $\ln(k)$  versus  $1/K$  are as shown in Figure 14 for the two leaching stages. The activation energy determined for the first 20 min was 36 kJ/mol and 27 kJ/mol for the following 20–120 min of leaching. The activation energy values for both leaching periods were close to the energy barrier that is typically used to identify a diffusion controlled or chemical reaction controlled process, which is around 20 kJ/mol [26].

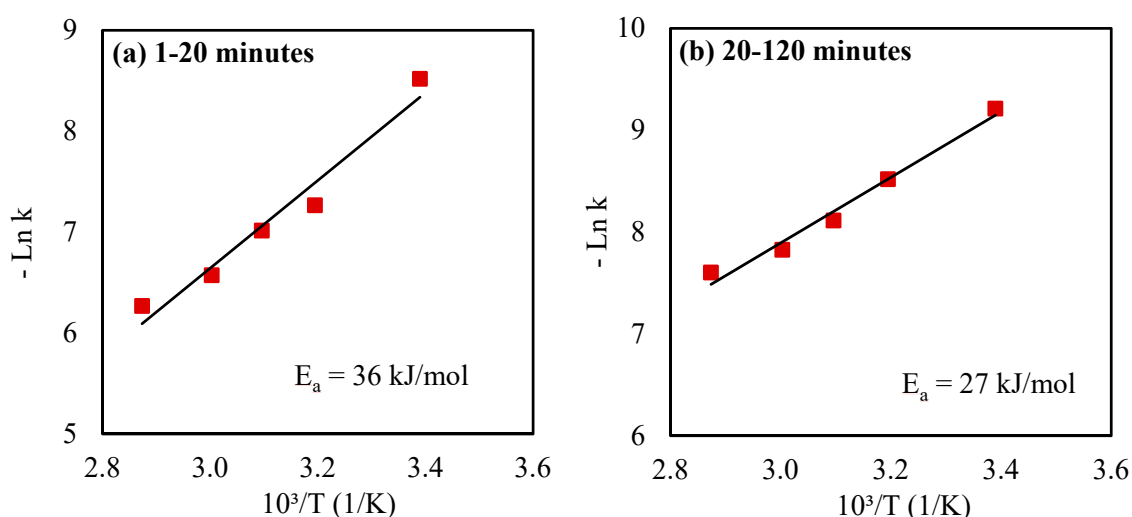
**Table 2.** Correlation coefficients of diffusion-controlled kinetics models at different temperatures for total REEs.

Temperature		Diffusion 1–20 min			Diffusion 20–120 min		
°C	K	k	a	R <sup>2</sup>	k	a	R <sup>2</sup>
25	298	0.0002	0.0017	0.9949	0.0001	0.0036	0.996
40	313	0.0007	0.0022	0.9648	0.0002	0.0129	0.9977
50	323	0.0009	0.0046	0.9616	0.0003	0.0196	0.9402
60	333	0.0014	0.0068	0.9919	0.0004	0.0262	0.9934
75	348	0.0019	0.0189	0.9627	0.0005	0.0487	0.9796

Note: k denotes the slope of the regression line, and a denotes the intercept of the regression line.



**Figure 13.** Kinetic modeling of total REEs recovery during the (a) first 20 min, and (b) 20–120 min of leaching at various temperatures for the Fire Clay middlings (1 M H<sub>2</sub>SO<sub>4</sub>, 530 rpm, S/L = 10 g/L, D<sub>80</sub> = 8.7 μm, retention time of 120 min).



**Figure 14.** Arrhenius plot for the total REEs leached from the Fire Clay coal middlings during the (a) first 20 min, and (b) 20–120 min of leaching (1 M H<sub>2</sub>SO<sub>4</sub>, 530 rpm, S/L = 10 g/L, d<sub>80</sub> = 8.7 micron).

Since the coal tailing material is a heterogeneous material that contains a number of potential modes of occurrence of REEs, the leaching process is not a single reaction. The resulting requirement for activation energy is a combination of the various forms of REEs. In addition, the material contains both calcite and pyrite among other soluble minerals that create a complex solution environment where the localized pH elevation on the solid particle surface could cause a product layer to be formed. The interfacial transfer of product through the porous structure of the solid particles requires high activation energies as reported by Li et al. (2010 and 2013), which can be as high as 40 kJ/mol [23,29].

To support the hypothesis, the activation energies for light and heavy REE groups were calculated using the data provided in Tables 3 and 4, respectively. The activation energy values for leaching the light REEs over the first 20 min and the period between 20 and 120 min were 41.8 kJ/mol and 28.1 kJ/mol, respectively. On the other hand, the activation energy values for the leaching of heavy REEs for the first 20 min and the 20–120 min of reaction were 24.2 kJ/mol and 26.1 kJ/mol, respectively. These values indicate that the leaching of the light REEs during the initial stage is more of a chemical reaction followed by the formation of a product layer and a reduced activation energy. The activation

energy required for leaching the heavy REEs during the initial stage was significantly lower than that of the light REEs. This finding implies that the major rate controlling mechanism for heavy REEs leaching is diffusion.

**Table 3.** Correlation coefficients of diffusion-controlled kinetics models at different temperatures for light REEs.

Temperature		Diffusion 1–20 min			Diffusion 20–120 min		
°C	K	k	a	R <sup>2</sup>	k	a	R <sup>2</sup>
25	298	0.0002	0.0016	0.9975	0.0001	0.0034	0.9971
40	313	0.0005	0.0017	0.9963	0.0002	0.0115	0.9931
50	323	0.001	0.0042	0.9712	0.0003	0.0214	0.9542
60	333	0.0015	0.0068	0.9929	0.0004	0.0278	0.9928
75	348	0.0021	0.0198	0.9648	0.0005	0.0571	0.9888

Note: k denotes the slope of the regression line, and a denotes the intercept of the regression line.

**Table 4.** Correlation coefficients of diffusion-controlled kinetics models at different temperatures for heavy REEs.

Temperature		Diffusion 1–20 min			Diffusion 20–120 min		
°C	K	k	a	R <sup>2</sup>	k	a	R <sup>2</sup>
25	298	0.0002	0.0028	0.9593	0.00005	0.0049	0.9634
40	313	0.0004	0.0032	0.9943	0.00008	0.104	0.98
50	323	0.0005	0.0051	0.939	0.00009	0.0127	0.9704
60	333	0.0007	0.0068	0.9803	0.0002	0.016	0.9972
75	348	0.0008	0.013	0.941	0.0002	0.0251	0.9857

Note: k denotes the slope of the regression line, and a denotes the intercept of the regression line.

It was noted that the reaction kinetics was extremely fast within the first 1 min of the reaction. A possible explanation is that, due to the different modes of occurrence of REEs in coal-based material, the easy-to-leach REEs was instantaneously released at the beginning of the leaching process, and the hard-to-leach fraction controlled the reaction rate. The mode of occurrence of REEs can be categorized into different forms (i.e., ion exchange form, carbonate form, metal oxide form, acid soluble form, and insoluble form) with different levels of activation energy needed for extraction [24]. Zhang and Honaker (2020) studied the REE mode of occurrence in coal using the sequential chemical extraction method and quantified the REEs associated with each mode [30]. The REEs associated with ion exchangeable form and carbonates are likely to be released instantaneously at the beginning of the extraction process under the leaching conditions of the current study.

#### 4. Conclusions

The Fire Clay coal is an excellent source for REE extraction due to its elevated REE contents and high leaching recovery values. Reducing the particle size of the middings material prior to de-carbonization resulted in the liberation of the associated micro-dispersed mineral matter that contained significantly higher concentrations of REEs. Decreasing the P80 particle size from 38  $\mu\text{m}$  to 5  $\mu\text{m}$  nearly doubled the concentration of REEs in the tailings of the flotation steps, which was the material used a feed for the leaching tests. The major minerals present in the sample were quartz, kaolinite, illite, and muscovite. Exponentially increasing the particle surface area through grinding resulted in higher solid dissolution which elevates the consumption of hydrogen ions and the concentration of contaminant metal ions.

The type of inorganic acid does not affect leaching recovery significantly but has an impact on the initial leaching rate. The mixing condition is sufficient at rotational speed values above 500 rpm.



Furthermore, solid concentration and acid concentration have a significant effect on leaching recovery of REEs. Scanning electron microscope (SEM) images showed no visible product layer or coating product on the particle surfaces. Therefore, the diffusion process in this reaction may be contributed by the interfacial transfer of the products and the reagent diffusion through the porous structure of solid particles.

The kinetic data obtained from leaching over a range of temperatures suggested that the leaching process follows the diffusion control shrinking core model. The activation energy determined from test data obtained over a range of temperatures using 1 M sulfuric acid was 36 kJ/mol for the first 20 min of reaction time and 27 kJ/mol for the leaching period between 20 and 120 min. The leaching of light REEs during the initial stage is much greater than the typical energy barrier of 20 kJ/mol, which indicates that a mixed control mechanism may occur as a result of several heterogeneous materials leaching simultaneously. The energy required for later stage of leaching reduced significantly. The activation energy required for leaching the heavy REEs during the initial stage was significantly lower than that of the light REEs, which implies that the major rate controlling mechanism for heavy REE leaching is the diffusion.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2075-163X/10/6/491/s1>, Table S1: Solid loss and REs content in leaching solid residue and leachate solution.

**Author Contributions:** Conceptualization, X.Y. and R.Q.H.; methodology, X.Y. and R.Q.H.; software, X.Y.; validation, X.Y.; formal analysis, X.X.; investigation, X.Y. and R.Q.H.; resources, R.Q.H.; data curation, X.Y.; writing—original draft preparation, X.Y.; writing—review and editing, R.Q.H.; visualization, X.Y.; supervision, R.Q.H.; project administration, R.Q.H.; funding acquisition, R.Q.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the U.S. Department of Energy, Grant Number DE-FE0029900.

**Acknowledgments:** This material is based upon work supported by the Department of Energy under Award Number DE-FE0029900. 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 views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Kumari, A.; Panda, R.; Jha, M.K.; Lee, J.Y.; Kumar, J.R.; Kumar, V. Thermal treatment for the separation of phosphate and recovery of rare earth metals (REMs) from Korean monazite. *J. Ind. Eng. Chem.* **2015**, *21*, 696–703. [\[CrossRef\]](#)
2. Chi, R.; Zhang, X.; Zhu, G.; Zhou, Z.A.; Wu, Y.; Wang, C.; Yu, F. Recovery of rare earth from bastnasite by ammonium chloride roasting with fluorine deactivation. *Miner. Eng.* **2004**, *17*, 1037–1043. [\[CrossRef\]](#)
3. Jha, M.K.; Kumari, A.; Panda, R.; Rajesh Kumar, J.; Yoo, K.; Lee, J.Y. Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* **2016**, *165*, 2–26. [\[CrossRef\]](#)
4. Binnemans, K.; Jones, P.T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M. Recycling of rare earths: A critical review. *J. Clean. Prod.* **2013**, *51*, 1–22. [\[CrossRef\]](#)
5. Wu, G.; Li, J.; Xu, Z. Triboelectrostatic separation for granular plastic waste recycling: A review. *Waste Manag.* **2013**, *33*, 585–597. [\[CrossRef\]](#)
6. Peelman, S.; Sun, Z.H.I.; Sietsma, J.; Yang, Y. Chapter 21—Leaching of Rare Earth Elements: Review of Past and Present Technologies; Rare Earths Industry, Elsevier Inc.: Delft, The Netherlands, 2016; ISBN 9780128023280. [\[CrossRef\]](#)
7. Lin, R.; Bank, T.L.; Roth, E.A.; Granite, E.J.; Soong, Y. International Journal of Coal Geology Organic and inorganic associations of rare earth elements in central Appalachian coal. *Int. J. Coal Geol.* **2017**, *179*, 295–301. [\[CrossRef\]](#)



8. Lin, R.; Howard, B.H.; Roth, E.A.; Bank, T.L.; Granite, E.J.; Soong, Y. Enrichment of rare earth elements from coal and coal by-products by physical separations. *Fuel* **2017**, *200*, 506–520. [\[CrossRef\]](#)
9. Zhang, W.; Yang, X.; Honaker, R.Q. Association characteristic study and preliminary recovery investigation of rare earth elements from Fire Clay seam coal middlings. *Fuel* **2018**, *215*, 551–560. [\[CrossRef\]](#)
10. Honaker, R.Q.; Zhang, W.; Yang, X.; Rezaee, M. Conception of an integrated flowsheet for rare earth elements recovery from coal coarse refuse. *Miner. Eng.* **2018**, *122*, 233–240. [\[CrossRef\]](#)
11. Honaker, R.; Groppo, J.; Bhagavatula, A.; Rezaee, M.; Zhang, W. *Recovery of Rare Earth Minerals and Elements from Coal and Coal Byproducts*; International Coal Preparation Conference: Louisville, KY, USA, 2016.
12. Arbuzov, S.I.; Maslov, S.G.; Finkelman, R.B.; Mezhibor, A.M.; Ilenok, S.S.; Blokhin, M.G.; Peregudina, E.V. Modes of occurrence of rare earth elements in peat from Western Siberia. *J. Geochem. Explor.* **2018**, *184*, 40–48. [\[CrossRef\]](#)
13. Finkelman, R.B.; Palmer, C.A.; Wang, P. Quantification of the modes of occurrence of 42 elements in coal. *Int. J. Coal Geol.* **2018**, *185*, 138–160. [\[CrossRef\]](#)
14. Dai, S.; Graham, I.T.; Ward, C.R. A review of anomalous rare earth elements and yttrium in coal. *Int. J. Coal Geol.* **2016**, *159*, 82–95. [\[CrossRef\]](#)
15. Riley, K.W.; French, D.H.; Farrell, O.P.; Wood, R.A.; Huggins, F.E. Modes of occurrence of trace and minor elements in some Australian coals. *Int. J. Coal Geol.* **2012**, *94*, 214–224. [\[CrossRef\]](#)
16. Hower, J.C.; Ruppert, L.F.; Eble, C.F. Lanthanide, yttrium, and zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky. *Int. J. Coal Geol.* **1999**, *39*, 141–153. [\[CrossRef\]](#)
17. Zhang, W.; Honaker, R.; Groppo, J. *Fundamental Study of the Monazite Calcite Flotation Separation*; Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, QC, Canada, 2016.
18. Xiao, Y.F.; Chen, Y.Y.; Feng, Z.Y.; Huang, X.W.; Huang, L.; Long, Z.Q.; Cui, D.L. Leaching characteristics of ion-adsorption type rare earths ore with magnesium sulfate. *Trans. Nonferrous Met. Soc. China Engl. Ed.* **2015**, *25*, 3784–3790. [\[CrossRef\]](#)
19. Xiao, Y.; Feng, Z.; Huang, X.; Huang, L.; Chen, Y.; Liu, X.; Wang, L.; Zhiqi, L. Recovery of rare earth from the ion-adsorption type rare earths ore: II. Compound leaching. *Hydrometallurgy* **2016**, *163*, 83–90. [\[CrossRef\]](#)
20. Yu, J.; Guo, Z.; Tang, H. Dephosphorization Treatment of High Phosphorus Oolitic Iron Ore by Hydrometallurgical Process and Leaching Kinetics. *ISIJ Int.* **2013**, *53*, 2056–2064. [\[CrossRef\]](#)
21. Makanyire, T.; Jha, A.; Sutcliffe, S. Kinetics of hydrochloric acid leaching of niobium from TiO<sub>2</sub> residues. *Int. J. Miner. Process.* **2016**, *157*, 1–6. [\[CrossRef\]](#)
22. Wang, Z.; Guo, S.; Ye, C. Leaching of copper from metal powders mechanically separated from waste printed circuit boards in chloride media using hydrogen peroxide as oxidant. *Procedia Environ. Sci.* **2016**, *31*, 917–924. [\[CrossRef\]](#)
23. Li, M.; Zhang, X.; Liu, Z.; Hu, Y.; Wang, M.; Liu, J.; Yang, J. Kinetics of leaching fluoride from mixed rare earth concentrate with hydrochloric acid and aluminum chloride. *Hydrometallurgy* **2013**, *140*, 71–76. [\[CrossRef\]](#)
24. Yang, X.; Werner, J.; Honaker, R.Q. Leaching of rare Earth elements from an Illinois basin coal source. *J. Rare Earths* **2019**, *37*, 312–321. [\[CrossRef\]](#)
25. Levenspiel, O. *Chemical Reaction Engineering-3rd edition*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1999; Volume 38, ISBN 9780471530169.
26. Free, M.L. *Hydrometallurgy: Fundamentals and Applications*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013; ISBN 978-1-118-23077-0.
27. Salmi, T.; Grenman, H.; Warna, J.; Murzin, D.Y. New modelling approach to liquid-solid reaction kinetics: From ideal particles to real particles. *Chem. Eng. Res. Des.* **2013**, *91*, 1876–1889. [\[CrossRef\]](#)
28. Dickinson, C.F.; Heal, G.R. Solid-liquid diffusion controlled rate equations. *Thermochim. Acta* **1999**, *340–341*, 89–103. [\[CrossRef\]](#)
29. Li, M.; Wei, C.; Qiu, S.; Zhou, X.; Li, C.; Deng, Z. Kinetics of vanadium dissolution from black shale in pressure acid leaching. *Hydrometallurgy* **2010**, *104*, 193–200. [\[CrossRef\]](#)
30. Zhang, W.; Honaker, R. Characterization and recovery of rare earth elements and other critical metals (Co, Cr, Li, Mn, Sr, and V) from the calcination products of a coal refuse sample. *Fuel* **2020**, *267*, 117236. [\[CrossRef\]](#)

