

Article



# Recovery of Rare Earth Elements from Coal Fly Ash with Betainium Bis(trifluoromethylsulfonyl)imide: Different Ash Types and Broad Elemental Survey

Ting Liu<sup>1</sup>, James C. Hower<sup>2,3</sup> and Ching-Hua Huang<sup>1,\*</sup>

- <sup>1</sup> School of Civil and Environmental Engineering, Georgia Institute of Technology, 200 Bobby Dodd Way, Atlanta, GA 30332, USA; tliu335@gatech.edu
- <sup>2</sup> Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA; james.hower@uky.edu
- <sup>3</sup> Department of Earth & Environmental Sciences, University of Kentucky, Lexington, KY 40506, USA
- \* Correspondence: ching-hua.huang@ce.gatech.edu; Tel.: +1-404-894-7694

Abstract: Previously, proof-of-concept studies have demonstrated that rare-earth elements (REEs) can be preferentially extracted from coal fly ash (CFA) solids using a recyclable ionic liquid (IL), betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf<sub>2</sub>N]). When the suspension of aqueous solution—IL-CFA—is heated above 65  $^{\circ}$ C, the majority of REEs will separate from the bulk elements in the solids and partition to the IL phase. Acid stripping of the IL removes REEs and regenerates the IL for reuse in additional extraction cycles. The objective of this study is to showcase the applicability and effectiveness of the optimized method to recover REEs from various CFAs. Six CFA samples with different characteristics (feed coal basins, coal beds, and ash collecting points) and classifications (Class C and Class F) were examined. The process performance was evaluated for a broad range of elements (33 total), including 15 REEs, two actinides, six bulk elements, and 10 trace metals. Results confirmed good recovery of total REEs (ranging from 44% to 66% among the CFA samples) and the recovery process' high selectivity of REEs over other bulk and trace elements. Sc, Y, Nd, Sm, Gd, Dy, and Yb consistently showed high leaching and partitioning into the IL phase, with an average recovery efficiency ranging from 53.8% to 66.2%, while the other REEs showed greater variability among the different CFA samples. Some amounts of Al and Th were co-extracted into the IL phase, while Fe co-extraction was successfully limited by chloride complexation and ascorbic acid reduction. These results indicated that the IL-based REE-CFA recovery method can maintain a high REE recovery efficiency across various types of CFA, therefore providing a promising sustainable REE recovery strategy for various coal ash wastes.

Keywords: rare-earth elements; ionic liquids; coal combustion residuals; resource recovery; sustainability

# 1. Introduction

The rare-earth elements (REEs) are a group of 17 elements, including 15 lanthanides, yttrium, and scandium [1–7]. Due to their nature of electronic configuration and a typically stable +3 oxidation state, REEs have valuable properties that are crucial to a wide range of modern technologies in the fields of catalysts, magnets, batteries, metallurgy and alloys, polishing, ceramics and glass, medical applications, and military defense [2–10]. With emerging clean energy technologies, the global market for REEs will continue to expand in the coming decades. By far, few artificial alternatives to REEs have been found, and substitutes compromise efficiency or product quality [2,4]. Therefore, a steady supply is essential to support the growing demand in the long term. The majority of the current world's REE production comes from mining, such as the Bayan Obo deposit in Inner Mongolia, Mount Weld in Australia, and Mountain Pass in the U.S. [3–5,8,10–12]. REEs have an average concentration of 150 to 220 ppm in the earth's crust, where the concentrations of the widely



Citation: Liu, T.; Hower, J.C.; Huang, C.-H. Recovery of Rare Earth Elements from Coal Fly Ash with Betainium Bis(trifluoromethylsulfonyl)imide: Different Ash Types and Broad Elemental Survey. *Minerals* **2023**, *13*, 952. https://doi.org/10.3390/ min13070952

Academic Editors: Jan Zawala and Sudip Maity

Received: 15 May 2023 Revised: 10 July 2023 Accepted: 14 July 2023 Published: 17 July 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). used copper and zinc are 55 ppm and 70 ppm, respectively [4,8]. However, REEs often occur with other elements in the ore deposits, and the economically extractable concentrations of REEs stated by the U.S. Department of Energy's (DOE) National Energy Technology Laboratory are 300 ppm [3–5]. As a result, REE mining requires complex procedures, generates considerable waste, including radioactive thorium and uranium contaminants, and may have a negative impact on the environment and human health [3,4,10,13,14]. To ensure more sustainable REE availability, the European Commission categorized REEs as critical materials in 2010. In the same year, the U.S. DOE also emphasized the importance of recycling REEs from REE-rich wastes [2,5,6].

Coal fly ash (CFA), a fine powder waste from coal combustion, has recently been considered a potential source for REE recovery. In 2021, the U.S. generated approximately 28 Mt of CFA, of which about 67% were reused and the rest were stored in landfills or impoundments [15]. Compared to rare earth mines, most CFAs have higher total REE contents and a full range of REEs. Seredin et al. [16] indicated that the average REE contents for the world CFA were 483 ppm. The REE contents of CFA are highly determined by the characteristics of the feed coal. U.S. coal mainly comes from three basins: the Appalachian basin (App), the Illinois basin (IL), and the Powder River basin (PRB). Taggart et al. [17] studied 35 CFA samples burning feed coals from those basins and found that CFA from the App basin had the highest total REE contents (591 ppm) compared to CFA from IL basin (403 ppm) and PRB (337 ppm) basins. Specifically, CFA from burning eastern Kentucky's Fire Clay coal was found to have high REE concentrations ranging from 1200 to 1670 ppm [17–19]. Another factor affecting REE contents is the ash collection location in the utility [18,20]. The CFA in the flue gases from the boiler is usually captured at electrostatic precipitator (ESP) hoppers. Studies showed that the REE contents of collected CFA slightly decreased as the temperature dropped from the first through the following rows of ESP [18,20]. Besides high REE contents, CFA contains significant amounts of toxic heavy metals, such as As, Cr, and Pb, that can be leached together with REEs [21–25]. Most current REE-CFA recovery methods use strong acids, such as concentrated HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> solutions, to treat CFA solids or generate CFA leachate [17,26–28]. Direct acid extraction on solids resulted in low REE recovery and, therefore, was combined with alkaline roasting or hydrothermal pretreatment to improve recovery efficiency [26,29]. Such methods have low selectivity between REEs and bulk elements and require high chemical consumption and intense operational conditions, including high temperature, high pressure, and highly corrosive solutions. A sustainable recovery method should effectively extract and separate REEs from the bulk material with minimal chemical and energy costs, reduced waste generation, and simplified downstream processing.

In previous publications, we developed a novel recovery method by using a recyclable ionic liquid (IL), betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf<sub>2</sub>N], Figure 1), to preferentially extract REEs from CFA [30]. ILs are molten salts that have become promising extraction solvents in the past decades due to favorable properties, for example, high tuneability, low melting points (below 100 °C), negligible vapor pressure, low flammability, and high thermal stability [31,32]. Nockemann et al. [32] demonstrated that [Hbet][Tf<sub>2</sub>N] exhibited a thermomorphic behavior with water, that is, a 50 wt% [Hbet][Tf<sub>2</sub>N] mixture with water formed a homogeneous phase when heated above 55 °C, and the mixture returned to two phases after cooling to ambient temperature. When [Hbet][Tf<sub>2</sub>N] is miscible with water, the mixture has a lower viscosity, thereby accelerating the mass transfer of REEs from CFA solids to the solution. The leaching mechanism relies on exchanging three protons on the carboxylic group of the IL cations with each REE ion (Equation (1)):

$$\operatorname{REE}^{3+} + 3[\operatorname{Hbet}][\operatorname{Tf}_2 N] \to [\operatorname{REE}(\operatorname{bet})_3][(\operatorname{Tf}_2 N)_3] + 3\mathrm{H}^+ \tag{1}$$



Figure 1. Molecular structure of [Hbet][Tf<sub>2</sub>N].

The extracted REEs were removed from the IL phase as dissolved salts through a mild acid stripping process, and the regenerated [Hbet][Tf<sub>2</sub>N] was reused for more extraction processes [32–34].

Our previous study applied [Hbet][Tf<sub>2</sub>N] to three representative types of CFA and achieved high REE leaching efficiencies (approaching 100%). The recalcitrant Class F ashes were pretreated with an alkaline solution to promote extraction and separation behavior, and no significant loss of REEs was found during the pretreatment. Adding excess betaine to the aqueous phase further shifted the distribution of REEs toward the IL phase [30]. Optimizations of iron removal were developed by chloride complexation and ascorbic acid reduction. The combination of alkaline pretreatment, additional betaine, chloride complexation, and ascorbic acid reduction generated a mildly acidic REE-rich solution with limited iron coextraction (approximately 68.6 wt% REEs recovered and approximately 2.7 wt% Fe coextracted from CFA) [35]). The recyclable IL was successfully applied for multiple cycles without a significant decrease in leaching efficiency or partitioning [30]. Our most recent study expanded the elemental survey from seven REEs and four bulk elements (11 total) to eleven REEs, two actinides, six bulk elements, and ten trace elements (29 total) and confirmed the preference of [Hbet][Tf<sub>2</sub>N] for REEs over other elements. Optimizations of operational conditions found that a pH range of 2–7 had no impact on the extraction behaviors of elements studied, and the optimal leaching temperature and duration were 75-85 °C and 3 h of the studied 45-85 °C and 0.5-12 h range, respectively [36].

In this study, we investigated four additional REEs (Pr, Gd, Ho, and Er) and applied the optimized IL-based recovery method to six types of CFA. The study objectives were to first determine the leaching and partitioning behaviors of all elements in CFAs and, second, explore the impact of different CFA properties on process efficiency.

# 2. Materials and Methods

#### 2.1. Chemicals, Materials, and Characterization

All chemicals used are described in Supporting Information Text S1. [Hbet][Tf<sub>2</sub>N] was synthesized following the steps from previous work (Text S2) [30,32]. Six CFAs were examined (Table 1): four fly ashes derived from Appalachian coals, one from the Illinois basin, and one from the Powder River basin. Fly ash 93927 was derived from a power plant burning Class C PRB coals [17,37]. Fly ash sample 92801 was collected from a 220-MW power plant utility that exclusively burned single-seam Dean (a correlative of the Fire Clay) coal from a mine in Knox County, eastern Kentucky [20]. Fly ash 93932 was sampled from a 633-MW boiler burning Fire Clay-dominated coal from southern Leslie County, eastern Kentucky [38,39]. Fly ash 93951 was collected from a fly ash storage silo at a 130-MW boiler [40]. The unit burned Fire Clay coal from eastern Kentucky, but to the north-northwest of the coal source of sample 93932 [38]. Fly ash 93964 was collected from a Kentucky power plant burning Illinois basin coals [41,42]. Sample 94012 was from the same utility as fly ash 93951, but was derived from a mix of Central Appalachian coals [41,42].

Sample ID	Power Plant ID (Location)	ССР Туре	Feed Coal Basin (Coal Bed)	Reference
93927	Plant LA (Missouri)	Fly ash	PRB	[17,37]
92801	Plant I, unit 2 (Kentucky)	ESP fly ash	App (Fire Clay coal)	[20]
93932	Plant W (South Carolina)	ESP fly ash	App (Fire Clay coal)	[38,39]
93951	Plant I, unit 1 (Kentucky)	Silo fly ash	App (Fire Clay coal)	[38,40]
93964	Plant H, unit 3 (Kentucky)	ESP fly ash	ILB	[41,42]
94012	Plant I, unit 1 (Kentucky)	ESP fly ash	Арр	[41,42]

Table 1. CFA characteristics.

Note: CCP: Coal Combustion Products; ESP: electrostatic precipitator; App: Appalachian; ILB: Illinois basin; PRB: Powder River basin.

Information on the REE contents and compositions of major and trace elements in these ashes was provided by related literature and compiled in Tables 2 and 3. A total of 33 elements were investigated in this study: 15 REEs, two actinides that were commonly found in CFA, six bulk elements, and 10 trace elements of concern. Elemental composition will be discussed in detail in Section 3.1.

Element	93927	92801	93932	93951	93964	94012
Sc	22.13	60.2	-	-	34.65	28
Y	31.52	253	110	124	81.8	61
La	46.72	237	108	141	75.01	84
Ce	91.09	496	224	304	158.97	180
Pr	9.4	58.1	79	66	19.13	20
Nd	33.65	204	111	121	77.3	81
Sm	6.52	48.3	28	34	16.42	17
Eu	2.52	4.7	7	5	3.52	3.4
Gd	6.75	26.9	15	29	19.02	17
Tb	0.97	6.3	12	8	2.62	2.5
Dy	5.52	41.3	20	24	14.66	16
Ho	1.11	8.5	15	5	2.96	3.1
Er	3.15	26.2	22	14	8.32	8.7
Yb	2.81	23.3	11	15	7.43	8
Lu	0.43	-	6	5	1.14	1.1
ΣREE	264	1494	768	895	523	531
U	21.35	52.6	-	-	16.46	-
Th	6.6	101	-	-	24.05	-

Table 2. REEs, Th, and U concentrations (ppm) of CFAs in this study.

Note: a "-" indicated the original mass concentration of the element was unknown for the CFA.

# 2.2. CFA Alkaline Pretreatment

Alkaline pretreatment was performed for the five Class F CFAs following procedures as described in previous work [30]. In general, a 5.0 M NaOH solution was added to Class F CFA samples in a 10:1 mL/g ratio, and the mixture was heated to 85 °C and magnetically stirred at 300 rpm for five hours. After the mixture was cooled to room temperature, the supernatant was removed for inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis to quantify elemental losses from the solids by the pretreatment. The

CFA solids were rinsed with DI water, filtered, and dried at approximately 80 °C in an oven overnight before the leaching and stripping processes.

	Element	93927	92801	93932	93951	93964	94012
Major Oxides (wt %)	Mg	6.98	0.95	1.07	0.82	0.99	1.16
	AĬ	16.56	29.5	28.43	29.91	23.08	29.89
	Si	29.49	50.1	54.21	53.47	48.51	52.64
	Ca	31.1	2.3	4.01	1.5	1.89	2.04
	Ti	1.12	2	1.6	1.72	1.22	1.59
	Fe	4.8	9.9	7.6	8.46	22.22	8.41
	V	192	359	486	516	401	496
Trace Elements (ppm)	Cr	26	254	156	168	165	182
	Mn	80	134	223	114	280	149
	Ni	39	209	137	110	152	142
	Cu	181	254	181	204	134	190
	Zn	96	250	177	113	174	206
	As	2	549	73	124	83	320
	Se	-	239	-	-	-	-
	Cd	2	2	1	<1	4	<1
	Pb	63	186	81	100	69	183

Table 3. Composition of major and trace elements of CFAs in this study.

Note: a "-" indicated the original mass concentration of the element was unknown for the CFA.

# 2.3. Leaching and Stripping Experiments

The leaching and stripping experiments followed optimized conditions selected from prior studies [30,35] and are depicted in Figure 2.



Figure 2. Optimized scheme of REE-CFA recovery using [Hbet][Tf<sub>2</sub>N].

# 2.3.1. Leaching

Dry pre-treated CFA, water-saturated IL, and 1.0 M NaCl aqueous solution (AQ) were added to a vial to achieve a liquid-liquid (IL:AQ) mass ratio of 1:1 and a solid-total liquid ratio of 15:1 (mg/g). The vial was heated in an oil bath at 85 °C with magnetic stirring at 300 rpm for three hours. After the vial was cooled to room temperature, the solid and liquid phases were separated through vacuum filtration. The filtered CFA was rinsed with DI water, dried at approximately 80 °C in an oven overnight, and stored. The liquid (AQ and IL phases) was collected in a new vial, and concentrated betaine monohydrate and ascorbic acid (AA) solutions were added to the liquid, resulting in 10 mg betaine/g AQ phase and 25 mM AA in the AQ phase. The new IL-AQ mixture was heated under the same conditions for 1.5 h, cooled to room temperature, and kept at 4 °C overnight. Then,

the AQ phase was removed and prepared for ICP-OES analysis. The IL phase was saved for the stripping process.

# 2.3.2. Stripping

HCl solution (1.5 M) was added to the vial from the leaching process, containing the IL phase and a magnetic stir bar, to achieve a liquid-liquid (IL:HCl) mass ratio of 1:1. The vial was heated in an oil bath at 85 °C with stirring at 300 rpm for 1.5 h. After cooling to room temperature, the vial was kept at 4 °C overnight. Then, the HCl phase was removed and prepared for ICP-OES analysis.

# 2.4. Quantification of Extraction and Separation

Elements leached from the CFA are distributed by mass (M) among three phases: the alkaline pretreatment phase ( $M_{PT}$ ), the AQ phase ( $M_{AQ}$ ), and the IL phase ( $M_{IL}$ ).  $M_{IL}$  was determined by ICP-OES analysis on the HCl phase after stripping. Three parameters were calculated based on the mass of leached elements to quantify the extraction and separation of elements from CFA: the leaching efficiency (L), the distribution coefficient (D), and the recovery efficiency (R).

*L* represents the amounts of total leached element from the three phases compared to the total mass concentration of the element ( $M_{Total}$ ) in the untreated CFA.

$$L(\%) = \frac{M_{\text{PT}} + M_{\text{AQ}} + M_{\text{IL}}}{M_{\text{Total}}}$$
(2)

*D* reflects the preference of an element for the IL phase over the AQ phase using Equation (3):

$$D = \frac{M_{IL}}{M_{AQ}}$$
(3)

*R* represents the amounts of an element recovered from the IL phase by acid stripping as a percentage of the total concentration.

$$R(\%) = \frac{M_{\rm IL}}{M_{\rm Total}} \tag{4}$$

A high *R* value implied that the element was strongly leached from the solids and preferred the IL phase.

All pretreatment, leaching, and stripping experiments were performed in duplicate. *D*, *L*, and *R* were calculated for elements in each experimental trial, and the averages were presented. A zero value implied that the elemental concentration was below the detection limit of ICP-OES.

#### 3. Results

#### 3.1. Elemental Compositions

As given in Table 2, CFA derived from the Fire Clay coals (92801, 93951, and 93932) showed high total REE contents (1494 ppm, 895 ppm, and 768 ppm, respectively), with sample 92801 being remarkably high due to the exclusive burn of a single Fire Clay coal from a single mine [20]. Fly ash 93927 obtained from burning Powder River coals had the lowest REE contents of 264 ppm. CFA samples from the Illinois (93964) and Central Appalachian basins (94012) showed similar total REE content (523 ppm and 531 ppm, respectively). Among all the samples, Y, La, Ce, and Nd were the most abundant elements, comprising over 70% of the total REE contents. Notably, Y and Nd are listed as critical REEs that are vital in technology development [43,44].

For the six major oxides shown in Table 3, the four Appalachian fly ashes (92801, 93951, 93932, and 94012), regardless of the coal source, had high  $Al_2O_3$  and  $SiO_2$  contents (29.4 wt % and 52.6 wt % on average, respectively). The Illinois ash 93964 had a high  $Fe_2O_3$  content of 22.2 wt % compared to an average of 7.8 wt % for the other five fly ashes. The

Powder River sample 93927 had a significantly higher CaO content of 31.1 wt % and a relatively high MgO content of 7.0 wt % compared to an average of 2.3 wt % and 1.0 wt % from the rest, respectively. Most of the investigated trace metals, except Cd, had an average concentration exceeding 100 ppm, and the average concentration of vanadium was the highest (408.3 ppm). High As and Se concentrations of fly ash 92801 were discussed in the original publication [20]. Fly ash 92801 also showed high concentrations of radioactive U and Th that could present risks for waste disposal [13,14,45–47].

#### 3.2. Elemental Behaviors

The leaching and partitioning behaviors of each group of elements (REEs, actinides, trace elements, and bulk elements) during the processes of alkaline pretreatment, IL leaching, and acid stripping were studied based on the three quantification parameters, L (%), D, and R (%), and the mass distribution of an element detected in the alkaline solution after pretreatment (PT%), in the NaCl AQ solution after leaching (AQ%), in the HCl solution after stripping (IL%), and in the residual solids (residual%). Residual% was determined by subtracting the PT%, AQ%, and IL% from a total of 100%, assuming complete stripping of leached elements from IL to HCl [34,48].

### 3.2.1. REEs

The overall leaching behavior was measured by *L*. In Figure 3A, six REEs (Y, Nd, Sm, Gd, and Yb) exhibited high *L* values, with the average of six samples greater than 91.9% (Table S2). All the remaining REEs, except Tb, had a moderate average *L* ranging from 62.6% to 80.6%. It should be noted that the *L* values of fly ash 93927 were zero for Pr, Tb, and Ho, indicating negligible amounts of such elements were leached from the CFA solids during any process. Potential reasons for the zero values are the low elemental contents and entrapment in the CFA matrix. Terbium had the lowest average *L* of 27.0%, but sample 92801 showed a moderate *L* of 63.9%.

Since the *L* value only implied the overall leaching efficiency, the mass distribution was introduced to visualize each component of L. In Figure 4, no PT% was presented for the Class C ash 93927 because the alkaline pretreatment was only performed for recalcitrant Class F ashes. The calcium oxide-rich Class C ashes would leach abundant Ca and Si in alkaline solutions and form calcium silicates that could hinder the upcoming REE extraction [28]. Our previous study confirmed a lower average leaching efficiency of REEs for Class C ash samples after alkaline pretreatment [30]. For REEs, the alkaline pretreatment resulted in negligible losses in Sc, Y, La, Ce, and Dy (average PT% < 2%, Table S2). A minor elemental loss with an average PT% ranging from 2% to 12.7% was found in 8 REEs (Pr, Nd, Sm, Eu, Gd, Tb, Er, and Yb). For Ho and Lu, the average PT% was 19.6% and 20.0%, respectively. The individual PT% of Ho and Lu for samples 93964 and 94012 was relatively high (30.6–37.8%), which could be attributed to their low initial concentrations (1.1–3.1 ppm). In general, the REE mass distribution demonstrated that PT% was not the dominant component of L, and a high L indicated that the leaching process effectively extracted REEs from CFA solids into the IL/AQ mixture. A low L value, such as Tb, could be correlated to a high residual percentage in the mass distribution.

The *D* coefficient specifies the partitioning behavior of an element by identifying the distribution between the IL and AQ phases during the leaching process. In Figure 5A, most REEs among the six CFAs displayed a preference for the IL phase with *D* greater than one. Exceptions from sample 93927 included:  $D_{Pr}$ ,  $D_{Tb}$ , and  $D_{Ho}$  were zero as no amount was detected in either the AQ or IL phases;  $D_{Gd}$  equaling 0.8 (Table S3) suggested a higher partitioning into the AQ phase. Possible explanations could be that the 93927 ashes had the lowest initial Gd concentration (6.75 ppm compared to an average of 18.9 ppm), and the total concentrations detected in the AQ and IL phases exceeded 100%. On an average basis, extremely high *D* values were observed for Sc and Tb.



**Figure 3.** Average leaching efficiency, *L*, of REEs and two actinides (**A**) and bulk/trace elements (**B**) after the IL extraction process for six CFA samples. Error bars represent the standard deviation of duplicate samples. A  $\bigtriangledown$  indicated that the total mass concentration of the element was unknown for the CFA sample. Columns marked with \* indicated that the *L* value exceeded the scale of 120%. Note: *L* > 100% may be the result of a low initial concentration in solids or potential enrichment in the CFA because of alkaline pretreatment.



**Figure 4.** Mass distribution of detected REEs following alkaline pretreatment and IL leaching/stripping processes of six CFA samples (from left to right correspond to samples 93927, 92801, 93932, 93951, 93964, and 94012). A  $\bigtriangledown$  indicated that the total mass concentration of the element was unknown for the CFA sample. Note: a total distribution >100% may be the result of low initial concentrations in solids or potential enrichment in the CFA because of alkaline pretreatment.



**Figure 5.** Average distribution, *D*, of REEs and two actinides (**A**) and bulk/trace elements (**B**) after the IL extraction process for six different CFA samples. Error bars represent the standard deviation of duplicate samples. A + indicated an extremely large *D* value because no elements were found in the AQ phase. A × indicated that the element was not detected in the AQ phase but had minor amounts in the IL phase. Note: Selenium was not presented because only sample 92801 had a known original concentration and  $D_{Se} = 0$ .

*R* depends on the *L* and *D* of an element and determines the eventual amounts recovered from the entire procedure. In Figure 6A, four REEs (Sc, Nd, Sm, and Gd) showed a high average *R* (>61.0%, Table S4).  $R_{Sc}$  and  $L_{Sc}$  were the same for all the CFAs with provided Sc contents and in accordance with the results of mass distribution and *D*, indicating a negligible Sc loss in the alkaline pretreatment and a high preference for the IL phase in the leaching process. Six REEs (Y, La, Ce, Pr, Dy, and Yb) showed a medium average *R* (47.6% to 58.1%). Similar to the results of *L* and *D*,  $R_{Pr}$ ,  $R_{Tb}$ , and  $R_{Ho}$  were zero for sample 93927. The average  $R_{Tb}$  was at its lowest of 18.8%, but fly ash 92801 showed a medium recovery of 51.6%.

## 3.2.2. Actinides and Trace Elements

The two actinides in this study exhibited different leaching and partitioning behaviors.  $L_U$ ,  $D_U$ , and  $R_U$  were zero for all the CFAs and confirmed with each other that U remained in the ash solids. The main reason could be that uranium typically exists in anionic forms, but the carboxylic acid group of [Hbet][Tf<sub>2</sub>N] needs to complex with cations for metal extraction [49]. In contrast, Th was detected in three phases: PT%, AQ%, and IL% (Figure 7). The average  $D_{\text{Th}}$  of 3.2 (Table S3) was comparable to the values for most REEs, indicating Th's strong tendency to partition into the IL phase.



**Figure 6.** Average recovery efficiency, *R*, of REEs and two actinides (**A**) and bulk/trace elements (**B**) after the IL extraction process for six CFA samples. Error bars represent the standard deviation of duplicate samples. A  $\bigtriangledown$  indicated that the total mass concentration of the element was unknown for the CFA sample. Columns marked with \* indicate that *R* exceeded the scale of 100%. Note: Selenium was not presented because only sample 92801 had a known original concentration and  $R_{Se} = 0\%$ .

For the 10 trace elements investigated, five (Mn, Ni, Cu, Zn, and As) showed an average *L* greater than 52.0%, and the remaining had a low overall leaching from 10.1% to 39.7% on average (Figure 3B and Table S5). Regarding the five trace metals with high *L* values, all of them showed a strong preference for the AQ phase ( $D \le 0.5$ , Figure 5B and Table S7); Cu, Zn, and As had a major portion leached during alkaline pretreatment (average PT% = 55.0%, 33.8%, and 62.4%, respectively, Figure 7 and Table S6). Combining the *L* with the *D* and mass distribution, the average *R* of each trace element was low ( $\le 30.8\%$ , Figure 6B and Table S8) compared to the fact that most REEs had a *R* greater than 50%. Chromium had the highest *R* and showed a consistent preference for the IL phase over different CFAs, but Figure 7 revealed that for all the samples other than 93927, the residual solids preserved the highest amounts of Cr. Arsenic, Se, and Cd showed *R* = 0% and were not detected in the AQ or IL phases, so all the leached amounts were from the pretreatment.

#### 3.2.3. Bulk Elements

Magnesium and Ca displayed a high average L (90.2% and 91.0%, respectively, Figure 3B and Table S5). Previous studies found that Mg was slightly soluble in acidic solutions, and the amounts of leachable Mg increased as more dissolved Ca was leached from the solids [22]. As given in Figure 5B and Table S7, Mg, Si, Ca, and Fe had a strong preference for the AQ phase ( $D \le 0.5$ ), Al distributed evenly between the AQ and IL phases with a slight preference for the IL phase (average D = 1.5), and Ti displayed a strong prefer-

ence for the IL phase (average D = 6.1). However, Ti had poor overall leaching (average L = 4.5%), and Figure 8 revealed that more than 95% of Ti was in the CFA residuals. Similar to the behaviors of trace elements, the average *R* of each bulk element was low ( $\leq 25.9\%$ , Figure 6B and Table S8) compared to that of most REEs.



**Figure 7.** Mass distribution of detected trace elements and actinides following alkaline pretreatment and IL leaching/stripping processes of six CFA samples (from left to right correspond to samples 93927, 92801, 93932, 93951, 93964, and 94012). A  $\bigtriangledown$  indicated that the total mass concentration of the element was unknown for the CFA sample. Note: a total distribution >100% may be the result of low initial concentrations in solids or potential enrichment in the CFA because of alkaline pretreatment. Arsenic, Se, Cd, and U were not presented because they were not detected in the AQ or IL phases.



**Figure 8.** Mass distribution of detected bulk elements following alkaline pretreatment and IL leaching/stripping processes of six CFA samples (from left to right correspond to samples 93927, 92801, 93932, 93951, 93964, and 94012). Note: a total distribution >100% may be the result of low initial concentrations in solids or potential enrichment in the CFA because of alkaline pretreatment.

# 4. Discussion

# 4.1. Class F vs. Class C CFAs

As previously mentioned, the Class C CFA from Powder River basin (93927) contained the lowest REE concentration compared to the other five Class F CFA samples. The sum of overall REE leaching,  $L_{\Sigma REE}$ , for the Class F CFAs had an average of 89.1%, but the Class C sample had a  $L_{\Sigma REE}$  equal to 59.6% (Table S1). The main reason was that no Pr, Tb, or Ho were leached from the 93927 ash during any process. Our previous study analyzed seven REEs (Sc, Y, La, Ce, Nd, Eu, and Dy), and the Class C CFA in that study was found to have comparable L to the other two Class-F ashes [30]. Regarding the seven REEs, the Class C 93927 ashes showed an even lower  $L_{\Sigma REE}$  (57.2%) than the Class F ashes (91.6% on average). Meanwhile, the  $R_{\Sigma REE}$  of sample 93927 (48.5%, Table S4) wa close to that of the average of Class F ashes (54.0%) and higher than Class F sample 93951 (44.6%). This observation provided another explanation for the low  $L_{\Sigma REE}$  of Class C ashes; that is, the leached REEs in the PT and AQ contributed to the high L values of Class F ashes. Figure 5A also reflected that, for most REEs, the Class C ashes showed a higher D than the Class F ashes, so REEs leached to the IL phase and accounted for the major portion of L. In addition, sample 93927 displayed extremely high D values for La and Dy (D >> 1000), while  $D_{La}$ and  $D_{\rm Dv}$  for the rest of the samples were slightly greater than one. The increased  $D_{\rm REEs}$ in the Class C ashes may be caused by the abundance of soluble Ca minerals, which will dissolve during the acidic IL leaching and consequently release more REEs available for complexation [17,28,30].

The leaching behaviors for most non-REEs were similar between Class C and Class F ashes. For fly ash 93927, Cu, Zn, and As were not leached to the AQ or IL phases (L = 0), but  $L_V$  (71.4%),  $L_{Cr}$  (137.9%), and  $L_{Mn}$  (144.4%) were significantly higher than the average of Class F ashes (33.4%, 15.0% and 65.6%, correspondingly). Along with high  $D_{REEs}$ , the Class C ashes showed a higher D for most bulk and trace elements compared to the Class F ashes, likely for the same reason for higher  $D_{REEs}$ . D = 0 was observed for Si, Cu, and Zn only in the 93927 fly ashes. Combining the effects of L and D, the Class C ashes exhibited notably high R values for Al, V, Cr, and Mn, which resulted in higher  $R_{\Sigma bulk}$  and  $R_{\Sigma trace}$  (22.1% and 28.3%, respectively) compared to the average of Class F ashes (8.2% and 7.3%, respectively).

# 4.2. Effect of Fire Clay Coals

Within the three Class F CFAs derived from Fire Clay coals, fly ash 92801 displayed the highest  $L_{\Sigma REE}$  (85.6%) and  $R_{\Sigma REE}$  (51.2%), fly ash 93932 displayed medium  $L_{\Sigma REE}$  (81.8%) and  $R_{\Sigma REE}$  (50.4%), and fly ash 93951 displayed the lowest for both ( $L_{\Sigma REE}$  = 76.7% and  $R_{\Sigma R E E}$  = 44.6%). The L and R values of Pr and Tb were distinctively high in sample 92801. No significant difference in other REEs was found. For bulk elements, fly ash 93932, 92801, and 93951 displayed the highest to lowest  $L_{\Sigma bulk}$  (43.4%, 38.8%, and 30.0%, respectively) and  $R_{\Sigma bulk}$  (11.9%, 8.2%, and 6.8%, respectively). The same trend was found for trace elements ( $L_{\Sigma trace} = 81.3\%$ , 71.8%, and 41.4%, respectively;  $R_{\Sigma trace} = 13.0\%$ , 5.9%, and 5.1%, respectively). The distinctively high leaching behavior of Ni in sample 93932 (L = 157.5%) contributed to the overall high leaching and recovery efficiency of trace elements. A desirable REE recovery process is expected to have high REE contents with limited contaminants. Therefore, fly ash 92801, with a high REE recovery and a relatively low bulk and trace element extraction, demonstrated a promising performance among the three Fire Clay coal-derived ashes. Overall, while there were some variabilities, the performance in L, D, and R of elements did not vary greatly among these Class F ashes, possibly because of their related properties.

For the other two Class F ashes, both 93964 and 94012 samples showed higher  $L_{\Sigma REE}$  (110.7% and 90.8%, respectively) and  $R_{\Sigma REE}$  (66.3% and 57.7%, respectively) than all the Fire Clay coal-derived CFAs. It should be noted that the majority of REEs detected in the 93964 ashes and more than half of REEs detected in the 94012 ashes exceeded L = 100%. One possible explanation is that the actual REE contents of the samples may be higher than what had been determined by HF digestion. For bulk and trace elements, 93964 ashes were

higher in all *L* and *R* than 94012 ashes ( $L_{\Sigma bulk} = 36.3\%$  and 20.3%,  $R_{\Sigma bulk} = 9.1\%$  and 4.9%,  $L_{\Sigma trace} = 54.2\%$  and 32.1%,  $R_{\Sigma trace} = 9.4\%$  and 3.2%, respectively). For all the Class F CFAs, sample 94012, derived from a power plant burning App feed coals, showed a high REE recovery and the lowest bulk and trace element coextraction.

# 4.3. Evaluation of Scandium and Critical REEs

As noted above, for the four CFA samples with given Sc contents,  $R_{Sc}$  was the same as  $L_{Sc}$ , and 93964 and 94012 ashes had high  $R_{Sc}$  (73.9% and 78.4%, respectively, Table S4). Figure 9A showed that  $R_{Sc}$  and  $L_{Sc}$  were linearly correlated, and all the fly ashes had  $R_{Sc}$ similar to or higher than  $R_{\Sigma REE}$  in spite of lower  $L_{Sc}$  values. Onghena and Binnemans [50] also found that [Hbet][Tf<sub>2</sub>N] had higher selectivity for Sc compared to Y and other trivalent lanthanide ions appearing in red mud. One main reason is that Sc has a smaller ionic radius and forms more stable complexes with the carboxylic group than the rest of the REEs [50]. Considering other observations that Sc loss during the alkaline pretreatment was negligible and Sc had a strong preference for the IL phase during the leaching process, this method holds promising potential for preferential Sc recovery.



**Figure 9.** (A) The leaching efficiency, *L*, in comparison with the recovery efficiency, *R*, of scandium, total REEs, and critical REEs. (B) The outlook coefficient,  $K_{outl}$ , in comparison with the percentage of critical REYs in total REY contents, REY<sub>def</sub>, for six CFA samples in this study.

Seredin [43] classified the lanthanides and yttrium (REY) as critical (Y, Nd, Eu, Tb, Dy, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu) elements according to the forecasted relationship between global demand and supply of each element. A new criterion, the outlook coefficient ( $K_{outl}$ ), was introduced to evaluate the potential of coal ash as an REY raw material.  $K_{outl}$  was calculated as the ratio of the relative amounts of critical REYs in total REY contents to the relative amounts of excessive REYs:

$$K_{\text{outl}} = \frac{Y + \text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er}/\Sigma\text{REY}}{\text{Ce} + \text{Ho} + \text{Tm} + \text{Tb} + \text{Lu}/\Sigma\text{REY}}$$
(5)

A REY<sub>def</sub>– $K_{outl}$  graph (Figure 9B) was plotted, where REY<sub>def</sub> was the percentage of critical REYs in total REY contents. The cluster of six CFA samples in this study was located at 32%  $\leq$  REY<sub>def</sub>  $\leq$  38% and 0.8  $\leq$   $K_{outl} \leq$  1.1 and was considered promising for REY recovery [16,43].

In terms of overall leaching behavior, five critical REEs (Y, Nd, Eu, Dy, and Er) exhibited a moderate to high average *L* (>69%). All the Class-F ashes had a high  $L_{\Sigma critical}$  (>91%, Table S1), and fly ash 93927 has a moderate  $L_{\Sigma critical}$  of 76.0% due to  $L_{Tb} = 0$ . The average *L* of Tb was low (23.0%), but fly ash 92801 showed a relatively high  $L_{Tb}$  of 63.9%. The combined leaching and partitioning behavior, in terms of *R*, followed the same tendency as *L*: Y, Nd, Eu, Dy, and Er exhibited a medium to high average *R* ranging from 40% to 66.2%.

14 of 16

Similarly, the average *R* of Tb was low (18.8%), but fly ash 92801 showed a relatively high  $L_{\text{Tb}}$  of 51.6%. Figure 9A indicated that  $R_{\Sigma \text{critical}}$  for all the investigated CFAs (ranging from 52.1% to 67.6%, Table S4) was higher than the corresponding  $R_{\Sigma \text{REE}}$  (ranging from 44.6% to 66.3%).

#### 5. Conclusions

This IL-based REE-CFA recovery method combined the extraction of REEs from CFA solids and the separation of REEs from bulk and trace elements into one step. [Hbet][ $Tf_2N$ ] had a high solubility of metal oxides and preferred to form complexes with trivalent REE cations during the leaching process. In general, REEs performed high leaching and strong partitioning into the IL phase among different types of CFA. Uranium, bulk, and the trace elements exhibited minor or poor leaching and preferred the AQ phase. The trace and bulk elements that remained in the AQ phase after IL leaching should be investigated further for treatment and purification, aiming to improve water recycling and process sustainability. The co-extraction of some Al and Th with REEs was the issue of most concern. The Illinois basin CFA 93964 and the Appalachian CFA 94012 demonstrated the highest recovery efficiency of total REEs and critical REEs. The Appalachian CFA 92801 contained the highest REE contents and had the highest REE recovery within the Fire Clay coals. For the Class C ashes, most elements, regardless of REEs or non-REEs, tended to have a higher D than the Class F ashes. The specific mechanisms of metal complexation and separation need to be studied in detail to understand the different elemental behaviors between various CFAs. Further work will be conducted to improve the purity of the recovered REE solution and to extract individual REE from the existing REE-enriched mixture.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/min13070952/s1, Text S1: Chemicals; Text S2: IL Synthesis; Table S1: Leaching efficiency, L (%), of REEs, Th, and U; Table S2: Mass distribution of REEs, Th, and U in the alkaline solution after pretreatment (PT%); Table S3: Distribution coefficient, D, of REEs, Th, and U; Table S4: Recovery efficiency, R (%), of REEs, Th, and U; Table S5: Leaching efficiency, L (%), of major oxides and trace elements; Table S6: Mass distribution of major oxides and trace elements in the alkaline solution after pre-treatment (PT%); Table S7: Distribution coefficient, D, of major oxides and trace elements; Table S8: Recovery efficiency, R (%), of major oxides and trace elements.

Author Contributions: Conceptualization and methodology, C.-H.H. and J.C.H.; experiments and data curation, T.L.; writing—original draft preparation, T.L.; writing—review and editing, C.-H.H. and J.C.H.; funding acquisition, C.-H.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Georgia Research Alliance and Georgia Power.

Data Availability Statement: Not applicable.

**Acknowledgments:** Laboratory assistance from Kaylin Cross, Jiale Xu, Andrew Sharkey, and Chaoyang Huang is also gratefully acknowledged.

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

#### References

- 1. Damhus, T.; Hartshorn, R.; Hutton, A. Nomenclature of Inorganic Chemistry: IUPAC Recommendations 2005; Royal Society of Chemistry: Cambridge, UK, 2005.
- Massari, S.; Ruberti, M. Rare earth elements as critical raw materials: Focus on international markets and future strategies. *Resour. Policy* 2013, 38, 36–43. [CrossRef]
- 3. Balaram, V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geosci. Front.* **2019**, *10*, 1285–1303. [CrossRef]
- 4. Dutta, T.; Kim, K.-H.; Uchimiya, M.; Kwon, E.E.; Jeon, B.-H.; Deep, A.; Yun, S.-T. Global demand for rare earth resources and strategies for green mining. *Environ. Res.* 2016, 150, 182–190. [CrossRef] [PubMed]
- 5. Humphries, M. Rare Earth Elements: The Global Supply Chain; DIANE Publishing Company: Collingdale, PA, USA, 2010.
- 6. Atwood, D.A. The Rare Earth Elements: Fundamentals and Applications; Wiley: Hoboken, NJ, USA, 2013.

- 7. Jowitt, S.M.; Werner, T.T.; Weng, Z.; Mudd, G.M. Recycling of the rare earth elements. *Curr. Opin. Green Sustain. Chem.* 2018, 13, 1–7. [CrossRef]
- Long, K.R.; Van Gosen, B.S.; Foley, N.K.; Cordier, D. The Principal Rare Earth Elements Deposits of the United States: A Summary of Domestic Deposits and a Global Perspective. In *Non-Renewable Resource Issues: Geoscientific and Societal Challenges*; Sinding-Larsen, R., Wellmer, F.-W., Eds.; Springer: Dordrecht, The Netherlands, 2012; pp. 131–155.
- 9. Henderson, P. Chapter 1—General Geochemical Properties and Abundances of the Rare Earth Elements. In *Developments in Geochemistry*; Henderson, P., Ed.; Elsevier: Amsterdam, The Netherlands, 1984; Volume 2, pp. 1–32.
- Dushyantha, N.; Batapola, N.; Ilankoon, I.; Rohitha, S.; Premasiri, R.; Abeysinghe, B.; Ratnayake, N.; Dissanayake, K. The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production. *Ore Geol. Rev.* 2020, 122, 103521. [CrossRef]
- 11. Alonso, E.; Sherman, A.M.; Wallington, T.J.; Everson, M.P.; Field, F.R.; Roth, R.; Kirchain, R.E. Evaluating Rare Earth Element Availability: A Case with Revolutionary Demand from Clean Technologies. *Environ. Sci. Technol.* **2012**, *46*, 3406–3414. [CrossRef]
- 12. Zhou, B.; Li, Z.; Chen, C. Global Potential of Rare Earth Resources and Rare Earth Demand from Clean Technologies. *Minerals* 2017, 7, 203. [CrossRef]
- Haque, N.; Hughes, A.; Lim, S.; Vernon, C. Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact. *Resources* 2014, *3*, 614–635. [CrossRef]
- 14. Huang, X.; Zhang, G.; Pan, A.; Chen, F.; Zheng, C. Protecting the environment and public health from rare earth mining. *Earth's Future* **2016**, *4*, 532–535. [CrossRef]
- 15. American Coal Ash Association. 2021 Coal Combustion Product (CCP) Production & Use Survey Report; American Coal Ash Association: Aurora, CO, USA, 2021.
- 16. Seredin, V.V.; Dai, S.; Sun, Y.; Chekryzhov, I.Y. Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies. *Appl. Geochem.* **2013**, *31*, 1–11. [CrossRef]
- 17. Taggart, R.K.; Hower, J.C.; Dwyer, G.S.; Hsu-Kim, H. Trends in the Rare Earth Element Content of U.S.-Based Coal Combustion Fly Ashes. *Environ. Sci. Technol.* **2016**, *50*, 5919–5926. [CrossRef] [PubMed]
- Hower, J.C.; Dai, S.; Seredin, V.V.; Zhao, L.; Kostova, I.J.; Silva, L.F.O.; Mardon, S.M.; Gurdal, G. A Note on the Occurrence of Yttrium and Rare Earth Elements in Coal Combustion Products. *Coal Combust. Gasif. Prod.* 2013, *5*, 39–47.
- 19. Hower, J.C.; Granite, E.J.; Mayfield, D.B.; Lewis, A.S.; Finkelman, R.B. Notes on Contributions to the Science of Rare Earth Element Enrichment in Coal and Coal Combustion Byproducts. *Minerals* **2016**, *6*, 32. [CrossRef]
- Mardon, S.M.; Hower, J.C. Impact of coal properties on coal combustion by-product quality: Examples from a Kentucky power plant. *Int. J. Coal Geol.* 2004, 59, 153–169. [CrossRef]
- 21. Querol, X.; Fernández-Turiel, J.; López-Soler, A. Trace elements in coal and their behaviour during combustion in a large power station. *Fuel* **1995**, *74*, 331–343. [CrossRef]
- 22. Izquierdo, M.; Querol, X. Leaching behaviour of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* 2012, 94, 54–66. [CrossRef]
- Okeme, I.C.; Crane, R.A.; Nash, W.M.; Ojonimi, T.I.; Scott, T.B. Characterisation of rare earth elements and toxic heavy metals in coal and coal fly ash. RSC Adv. 2022, 12, 19284–19296. [CrossRef]
- Yao, Z.T.; Ji, X.; Sarker, P.; Tang, J.; Ge, L.; Xia, M.; Xi, Y. A comprehensive review on the applications of coal fly ash. *Earth Sci. Rev.* 2015, 141, 105–121. [CrossRef]
- 25. Wang, N.; Sun, X.; Zhao, Q.; Yang, Y.; Wang, P. Leachability and adverse effects of coal fly ash: A review. *J. Hazard. Mater.* **2020**, 396, 122725. [CrossRef]
- 26. Zhang, W.; Noble, A.; Yang, X.; Honaker, R. A Comprehensive Review of Rare Earth Elements Recovery from Coal-Related Materials. *Minerals* **2020**, *10*, 451. [CrossRef]
- 27. Kashiwakura, S.; Kumagai, Y.; Kubo, H.; Wagatsuma, K. Dissolution of Rare Earth Elements from Coal Fly Ash Particles in a Dilute H<sub>2</sub>SO<sub>4</sub> Solvent. *Open J. Phys. Chem.* **2013**, *3*, 69–75. [CrossRef]
- 28. King, J.F.; Taggart, R.K.; Smith, R.C.; Hower, J.C.; Hsu-Kim, H. Aqueous acid and alkaline extraction of rare earth elements from coal combustion ash. *Int. J. Coal Geol.* **2018**, *195*, 75–83. [CrossRef]
- 29. Taggart, R.K.; Hower, J.C.; Hsu-Kim, H. Effects of roasting additives and leaching parameters on the extraction of rare earth elements from coal fly ash. *Int. J. Coal Geol.* 2018, *196*, 106–114. [CrossRef]
- Stoy, L.; Diaz, V.; Huang, C.H. Preferential Recovery of Rare-Earth Elements from Coal Fly Ash Using a Recyclable Ionic Liquid. Environ. Sci. Technol. 2021, 55, 9209–9220. [CrossRef] [PubMed]
- 31. Binnemans, K. Lanthanides and Actinides in Ionic Liquids. Chem. Rev. 2007, 107, 2592–2614. [CrossRef] [PubMed]
- 32. Nockemann, P.; Thijs, B.; Pittois, S.; Thoen, J.; Glorieux, C.; Van Hecke, K.; Van Meervelt, L.; Kirchner, B.; Binnemans, K. Task-Specific Ionic Liquid for Solubilizing Metal Oxides. *J. Phys. Chem. B* **2006**, *110*, 20978–20992. [CrossRef] [PubMed]
- Nockemann, P.; Thijs, B.; Parac-Vogt, T.N.; Van Hecke, K.; Van Meervelt, L.; Tinant, B.; Hartenbach, I.; Schleid, T.; Ngan, V.T.; Nguyen, M.T.; et al. Carboxyl-Functionalized Task-Specific Ionic Liquids for Solubilizing Metal Oxides. *Inorg. Chem.* 2008, 47, 9987–9999. [CrossRef]
- Vander Hoogerstraete, T.; Onghena, B.; Binnemans, K. Homogeneous Liquid–Liquid Extraction of Rare Earths with the Betaine— Betainium Bis(trifluoromethylsulfonyl)imide Ionic Liquid System. *Int. J. Mol. Sci.* 2013, 14, 21353–21377. [CrossRef]

- 35. Stoy, L.; Kulkarni, Y.; Huang, C.H. Optimization of Iron Removal in the Recovery of Rare-Earth Elements from Coal Fly Ash Using a Recyclable Ionic Liquid. *Environ. Sci. Technol.* **2022**, *56*, 5150–5160. [CrossRef]
- Stoy, L.; Xu, J.; Kulkarni, Y.; Huang, C.-H. Ionic Liquid Recovery of Rare-Earth Elements from Coal fly Ash: Process Efficiency and Sustainability Evaluations. ACS Sustain. Chem. Eng. 2022, 10, 11824–11834. [CrossRef]
- Hower, J.C.; Berti, D.; Winkler, C.R.; Qian, D.; Briot, N.J. High-Resolution Transmission Electron Microscopy Study of a Powder River Basin Coal-Derived Fly Ash. *Minerals* 2022, 12, 975. [CrossRef]
- 38. Hower, J.; Groppo, J.; Henke, K.; Hood, M.; Eble, C.; Honaker, R.; Zhang, W.; Qian, D. Notes on the Potential for the Concentration of Rare Earth Elements and Yttrium in Coal Combustion Fly Ash. *Minerals* **2015**, *5*, 356–366. [CrossRef]
- 39. Hower, J.; Qian, D.; Briot, N.; Santillan-Jimenez, E.; Hood, M.; Taggart, R.; Hsu-Kim, H. Nano-Scale Rare Earth Distribution in Fly Ash Derived from the Combustion of the Fire Clay Coal, Kentucky. *Minerals* **2019**, *9*, 206. [CrossRef]
- 40. Hood, M.M.; Taggart, R.K.; Smith, R.C.; Hsu-Kim, H.; Henke, K.R.; Graham, U.; Groppo, J.G.; Unrine, J.M.; Hower, J.C. Rare Earth Element Distribution in Fly Ash Derived from the Fire Clay Coal, Kentucky. *Coal Combust. Gasif. Prod.* 2017, *9*, 22–33. [CrossRef]
- Taggart, R.K.; Rivera, N.A.; Levard, C.; Ambrosi, J.P.; Borschneck, D.; Hower, J.C.; Hsu-Kim, H. Differences in bulk and microscale yttrium speciation in coal combustion fly ash. *Environ. Sci. Process. Impacts* 2018, 20, 1390–1403. [CrossRef]
- 42. Hower, J.C.; Groppo, J.G.; Hopps, S.D.; Morgan, T.D.; Hsu-Kim, H.; Taggart, R.K. Coal Feed-Dependent Variation in Fly Ash Chemistry in a Single Pulverized-Combustion Unit. *Minerals* **2022**, *12*, 1071. [CrossRef]
- Seredin, V.V. A new method for primary evaluation of the outlook for rare earth element ores. *Geol. Ore Depos.* 2010, 52, 428–433.
  [CrossRef]
- 44. United States Department of Energy. *Report on Rare Earth Elements from Coal and Coal Byproducts*; United States Department of Energy: Washington, DC, USA, 2017.
- Senior, C.; Granite, E.; Linak, W.; Seames, W. Chemistry of Trace Inorganic Elements in Coal Combustion Systems: A Century of Discovery. *Energy Fuels* 2020, 34, 15141–15168. [CrossRef]
- Findeiß, M.; Schäffer, A. Fate and environmental impact of thorium residues during rare earth processing. J. Sustain. Metall. 2017, 3, 179–189. [CrossRef]
- 47. Zhu, Z.; Pranolo, Y.; Cheng, C.Y. Separation of uranium and thorium from rare earths for rare earth production—A review. *Miner. Eng.* **2015**, 77, 185–196. [CrossRef]
- 48. Vander Hoogerstraete, T.; Onghena, B.; Binnemans, K. Homogeneous Liquid–Liquid Extraction of Metal Ions with a Functionalized Ionic Liquid. J. Phys. Chem. Lett. 2013, 4, 1659–1663. [CrossRef] [PubMed]
- Mochizuki, A.; Murata, T.; Hosoda, K.; Katano, T.; Tanaka, Y.; Mimura, T.; Mitamura, O.; Nakano, S.-I.; Okazaki, Y.; Sugiyama, Y.; et al. Distributions and geochemical behaviors of oxyanion-forming trace elements and uranium in the Hövsgöl–Baikal–Yenisei water system of Mongolia and Russia. *J. Geochem. Explor.* 2018, 188, 123–136. [CrossRef]
- 50. Onghena, B.; Binnemans, K. Recovery of Scandium(III) from Aqueous Solutions by Solvent Extraction with the Functionalized Ionic Liquid Betainium Bis(trifluoromethylsulfonyl)imide. *Ind. Eng. Chem. Res.* **2015**, *54*, 1887–1898. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.