



Full Length Article

Application of sequential extraction and hydrothermal treatment for characterization and enrichment of rare earth elements from coal fly ash



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GRAPHICAL ABSTRACT



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ABSTRACT

Rare earth elements (REE) play a critical role in the global economy. The concern about the REE supply challenge has stimulated global interest in recovering REE from alternative non-conventional REE sources such as coal fly ash. In this paper, sequential extraction, physical separations and hydrothermal alkaline treatment were explored for characterization and enrichment of REE from coal fly ash. Seven-step sequential extraction of coal fly ash has demonstrated that 86.1% of total REE were associated with the glassy phase of the fly ash, with the remaining REE mainly distributed in the organic and sulfides phase (8.3%), the exchangeable phase (3.7%), and the carbonates phase (1.5%). A process combining physical separations, namely, particle size separation and magnetic separation, and hydrothermal alkaline treatment was proposed for enrichment of REE from coal fly ash. The optimal hydrothermal alkaline treatment condition was determined. It was demonstrated that NaOH concentration, solid-to-liquid ratio, temperature, and reaction duration had significant influence on ash dissolution in NaOH solution. Grinding could also enhance ash dissolution during subsequent hydrothermal alkaline treatment. REE were enriched from coal fly ash from 325 mg/kg to 877 mg/kg via the proposed process under optimal hydrothermal alkaline treatment conditions.

1. Introduction

Rare earth elements (REE) play a critical role in the global economy. They are increasingly needed in numerous applications, such as phosphors for lighting, batteries for electrical vehicles, magnets for wind turbines, catalysts for petroleum refining and many others [1,2]. However, supplies of REE are controlled by a limited number of sources [3]. The concern about the REE supply challenge has thus stimulated global interests in investing in scientific research and technological development for extracting REE from new alternative sources,

particularly from coal and coal by-products [3–10].

Fly ash is a coal combustion product. It is a highly heterogeneous material, largely spherical in shape. These spherical particles are known to be associated with aggregates of polycrystalline, amorphous and glassy material [11], mainly composed of complex iron oxides, calcium, sodium and potassium aluminosilicates, quartz and mullite [12]. During coal combustion, trace elements including REE will be concentrated in fly ash due to their organic affinity (elements associated with organic coaly matter) or mineral affinity (elements associated with sulfides, aluminosilicates, carbonates and other minerals in coal)

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Table 1
Extraction reagents and conditions used in 7-step sequential extraction.

Step #	Targeted Fraction	Reagents	L:S ratio	L (cm ³)	S (g)	Temp (°C)	Duration (h)	pH
S1	Water soluble	MilliQ water	10:1	40	4	25	24	
S2	Exchangeable	1 M ammonium sulfate	10:1	40	4	25	24	5.0
S3	Bound to carbonate	0.11 M acetic acid	10:1	35	3.5	25	24	3.0
S4	Bound to Mn oxides	0.1 M hydroxylammonium chloride	50:3	50	3	25	0.5	3.5
S5	Bound to amorphous Fe oxides	0.2 M ammonium oxalate + 0.2 M oxalic acid in dark	20:1	50	2.5	25	4	3.0
S6	Bound to crystalline Fe oxides	0.2 M ammonium oxalate + 0.2 M oxalic acid + 0.1 M ascorbic acid	20:1	40	2	80	0.5	2.3
S7	Bound to organics and sulfides [*]	1) 30% H ₂ O ₂	10:1	10	1.0	25/85	1 + 1	2–3
		2) 30% H ₂ O ₂	10:1	10	1.0	85	1	2–3
		3) 1 M ammonium acetate wash	50:1	50	1.0	25	16	2.0
S8	Residual	LiBO ₂ digestion	–	–	0.1	–	–	–

* Extraction step S7 followed the BCR step to extract organics and sulfides [24].

[5,13]. Franus et al. [14] studied different coal fly ashes from ten Polish power plants for their REE content and concluded that most of the samples have REE content relatively high and can be considered promising REE raw materials. A recent study by Taggart et al. [7] showed that generic coal burned in the U.S. could produce fly ashes with greater than 500 mg/kg total REYSc (the sum of the lanthanides, yttrium, and scandium). They further concluded that coal fly ash production in the U.S. could provide a substantial domestic supply of REYSc, but the feasibility of recovery depends on the development of extraction technologies [7]. Blissett et al. [15] studied six European coal fly ash for their REY (lanthanides and yttrium) content and evaluated a simply processing scheme for REY enrichment. They found that REY were slightly enriched in the finer non-magnetic inorganic fraction of the ashes. Our previous study showed that REE in coal fly ash could be enriched by simple physical separation methods, namely, particle size separation, density or float-sink separation, and magnetic separation [4], but the enrichment factor was relatively low due to the fact that REE mainly disperse in minerals within the glassy phases in the fly ash [16,17].

The design of processes for the enrichment and recovery of REE from coal fly ashes with desired performance and efficiency would require a thorough understanding of the distribution and modes of occurrence of REE in coal fly ashes. However, the knowledge about the quantitative REE association with different solid fractions in fly ash samples is still lacking, and thus additional research in this area becomes very necessary.

Sequential extraction has been widely used to determine the geochemical association of trace elements in fly ash and geological materials [17,18] and also to evaluate trace metal availability under environmental relevant conditions [19]. This study used sequential extraction modified from a previous fly ash extraction study by Jegadeesan et al. [17] to semi-quantify REE affinity to different solid fractions (e.g., water soluble, exchangeable, carbonates, Fe/Mn oxides, sulfides and organic phases) for the studied fly ash sample to determine potential REE-bearing phases for efficient REE recovery.

As revealed by previous studies [11,16] as well as the current study, REE are mainly associated with the glassy phase of coal fly ashes. In order to recover REE from coal fly ashes, it is necessary to first break the amorphous aluminosilicate glass matrix to liberate REE or rare earth minerals. Hydrothermal alkaline conversion is a conventional method for zeolite synthesis from fly ashes. The methodology is based on the dissolution of aluminosilicate phases with alkaline solutions and the subsequent precipitation of zeolite crystals [20]. In this work, we studied hydrothermal treatment of coal fly ash using NaOH solutions with the objectives to determine the optimal hydrothermal treatment conditions for dissolution of the glassy phase and to evaluate the feasibility for enriching REE from coal fly ash by a combination of physical separations and hydrothermal alkaline treatment.

2. Experimental

2.1. Materials

The coal fly ash used in this work was collected from a pulverized coal power plant in Ohio, USA. It is a typical class F fly ash, containing more than 85% of SiO₂, Al₂O₃ and Fe₂O₃ in total [4]. The coal seam, type and rank of the feed coal, and the combustion process used to generate the ash were unavailable. Physical separations (particle size, density and magnetic separations) of this fly ash sample for REE characterization and enrichment have been reported in our previous study [4].

The sources and grades of chemicals used in this study follow. Ammonium sulfate (ACS grade), ammonium oxalate (ACS grade), oxalic acid (ACS grade), ascorbic acid (ACS grade), and ammonium acetate (ACS grade) were purchased from Sigma Aldrich, Corp. Acetic acid (glacial grade), hydroxylammonium chloride (ACS grade), hydrogen peroxide (30% w/v), and sodium hydroxide (certified ACS) were purchased from Fisher Scientific, Corp.

2.2. Sequential extraction

The coal fly ash was subjected to a 7-step sequential extraction modified from Jegadeesan et al. [17] in order to identify REE distribution in different solid fractions. The primary targeted fractions extracted in this method (Table 1) were: (1) water soluble, using MilliQ water (18.2mΩ/cm, Millipore Corp.); (2) exchangeable, using 1 mol/dm³(M) ammonium sulfate; (3) bound to carbonate, using 0.11 M acetic acid; (4) bound to amorphous Mn oxides, using 0.1 M hydroxylamine hydrochloride; (5) bound to amorphous iron oxides, using 0.2 M ammonium oxalate and 0.2 M oxalic acid; (6) bound to crystal iron oxides, using 0.2 M ammonium oxalate, 0.2 M oxalic acid and 0.1 M ascorbic acid; (7) bound to organic matter and sulfide bound, using acidified hydrogen peroxide digestion followed by ammonium acetate extraction, and (8) solid residual. The residual phase (silicate bound fraction) was sent to NETL Pittsburgh Analytical Lab (PAL) for LiBO₂ fusion [21] followed by inductively coupled plasma (ICP)-optical emission spectroscopy (OES) and ICP-mass spectroscopy (MS) analysis for major, minor and trace elements. There are lots of sequential extraction literatures that use various extraction reagents to target similar phases. For example, in Lombi et al. [22], arsenic bound to crystalline Fe oxides phases were extracted using 0.2 M ammonium oxalate + 0.1 M ascorbic acid for 30 min at 80 °C, while in Jegadeesan et al. [17], trace metals bound to crystalline Fe oxide phases were extracted using 0.2 M ammonium oxalate for 2 h at room temperature. For the sequential extraction experiments, despite of the differences in extraction procedures, similar phases are usually targeted and the data are deemed reasonably useful to provide information on trace metal partitioning into a certain phase [23].

Specifically, about 5 g of ash was ground to – 100 mesh (< 150 μm) and combined with different extraction reagents (See Table 1) on a

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