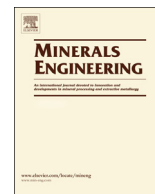




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# Conception of an integrated flowsheet for rare earth elements recovery from coal coarse refuse

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## ARTICLE INFO

## Keywords:

Rare earth elements  
Coal  
Coarse refuse  
Heap leaching  
Selective leaching  
Selective precipitation

## ABSTRACT

The majority of rare earth elements (REEs) existing in the feed to coal preparation plants report to the coarse refuse streams which are transported for permanent storage in contained piles. In this study, an integrated flowsheet was developed based on laboratory test data which combines physical separation, pyrite bio-oxidation, heap leaching, selective precipitation and solvent extraction processes. The test data was obtained from (1) characterization of a number of natural leachate and solid samples collected from different preparation plants which process coals from a number of coal seams and (2) laboratory acid leaching and selective precipitation tests results. The highly-valued critical REEs (i.e., Y, Nd, Eu, Tb and Dy) were selectively leached from the refuse samples in the natural environment due to the acid generated by pyrite oxidation. The leachate samples were evaporated to remove water and obtain residual solids (i.e., dissolved solids in the leachates). The total REE content in the dissolved solids from a given leachate sample was 380 ppm, which was higher than the REE content of the coarse refuse material that generated the leachate (322 ppm). Acid leaching tests recovered as much as 80% of the total REEs from the coarse refuse samples using a 1.2 M sulfuric acid solution. Afterwards, the pH of the leachate was increased in a step-wise fashion which resulted in the production of precipitates containing 0.3–1.1% total REEs. A significant amount of contaminants, such as Fe, Al, and Ca, were eliminated in the sequential precipitation process, which allowed further upgrading using oxalic acid precipitation and/or solvent extraction. In the proposed flowsheet, the coarse refuse is arranged in heap leach pads and the acid needed for REE leaching is primarily produced from pyrite bio-oxidation, which enhances the selectivity of REE recovery and significantly reduces the cost. The successful application of the flowsheet would result in significant benefits to both the coal and rare earth industries.

## 1. Introduction

Rare earth elements (REEs) are a group of 17 elements consisting of the 15 lanthanides plus scandium and yttrium. The supply of REEs is an international concern due to: (1) the uneven distribution of economically recoverable REE reserves worldwide, (2) environmental and social issues associated with current REEs mining operations, and (3) the increasing demands from the manufacturing of modern technologies (Alonso et al., 2012). The world demand for REEs in 2011 was approximately 105,000 tonnes ( $\pm 15\%$ ) and predicted to grow at a rate between 5% and 9% due to their use in the manufacturing of advanced military and renewable energy technologies, as well as other items used by the general public (Alonso et al., 2012; Hatch, 2012). An increase in demand of more than 700% for Nd and 2600% for Dy over the next 25 years was projected due to the development of the electronic vehicles and wind energy industries (Alonso et al., 2012; Bauer et al.,

2010). Based on this anticipated rise in demand, the U.S. Department of Energy included Nd and Dy among five REEs (i.e., Nd, Dy, Y, Tb and Eu) identified as critical for future supply.

Previous researchers reported that elevated concentrations of REEs exist in various coal sources worldwide (Seredin et al., 2013; Seredin and Dai, 2012). Dai et al. (2010) reported a new type of Nb(Ta)-Zr(Hf)-REE-Ga rare-metal deposit of volcanic origin in a coal bearing strata of eastern Yunnan, southwestern China. The ore beds are highly enriched in (Nb, Ta)<sub>2</sub>O<sub>5</sub> (302–627 ppm), (Zr, Hf)O<sub>2</sub> (3805–8468 ppm), REO (rare earth oxide, 1216–1358 ppm), and Ga (52–81 ppm). Coals with higher REE contents than the world average level (60–70 ppm), such as the Fire Clay coal seam in eastern Kentucky in United States (500 ppm), the Far East coalfield in Russia (300–1000 ppm), and the Sydney Basin in Canada (72–483 ppm), have previously been reported (Blissett et al., 2014; Birk and White, 1991; Hower et al., 1999; Seredin, 1996).

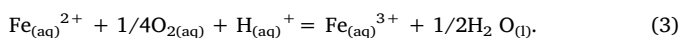
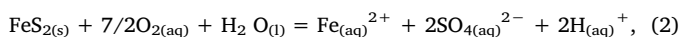
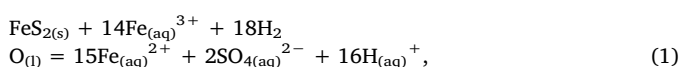
Recent studies have been conducted to investigate the potential of

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recovering REEs from coal and its byproducts (Ayora et al., 2016; Honaker et al., 2017, 2016a, 2016b, 2014; Huang et al., 2018; Lin et al., 2017; Rozelle et al., 2016; Zhang et al., 2018, 2017, 2015; Zhang and Honaker, submitted for publication; Ziemkiewicz et al., 2016). Due to ultrafine dispersion and complicated mineralogy of the REEs in coal, physical separation methods via density, magnetism, and surface hydrophobicity differences are limited in their ability to concentrate the REEs (Honaker et al., 2016b; Lin et al., 2017). An investigation of samples collected from 20 coal preparation plants indicated that the majority of the REEs by weight reported to the coal refuse streams, which provided a target for maximizing REE recovery from pre-combustion coal sources (Honaker et al., 2014).

A means of economically extracting rare earth elements from coal refuse involves leaching using acids that are naturally produced from certain coal sources. Acidic leachates are commonly generated from the coarse refuse produced from coal sources containing pyrite. When exposed to the natural environment, pyrite is oxidized as described by the following reactions (Dold, 2010; Fernando et al., 2018; Ritchie, 1994):



Pyrite oxidization can be accelerated by  $\text{Fe}^{2+}/\text{S}^0$ -oxidizing microorganisms (Casas et al., 1998; Fernando et al., 2018; Mousavi et al., 2006). Using the acid, REEs are leached from the refuse samples, as indicated by the elevated REEs concentration in acidic mine drainage (Sahoo et al., 2012; Stewart et al., 2017; Sun et al., 2012; Zhao et al., 2007; Ziemkiewicz et al., 2016). The natural leachates contain significant concentrations of critical REEs and lower concentrations of the less-valued REEs and contaminants, such as thorium. The production of natural leachates from coarse refuse materials led to the concept of a heap leach system to improve the rate of production. To the authors' knowledge, there are no current applications of heap leaching for coal-based materials.

A preliminary investigation focusing on the development of a low-cost recovery circuit was conducted in the current study. A number of natural leachates and solid refuse samples were collected and characterized to determine the leaching behaviors of REEs under the natural environment. Laboratory acid leaching tests were performed to evaluate the leachability of REEs from coal coarse refuse. Selective precipitation tests investigated the ability to concentrate the REEs from the leachates. The overall study provided a conceptual flow sheet which will provide guidance for future laboratory, pilot and industrial studies of REEs recovery from coal sources.

## 2. Material and methods

### 2.1. Material

Representative samples were collected from six coal preparation plants (WK9-1, WK9-2, WK9/11, WK13, IL6-1, and IL6-2). The plants processed coals from different seams, i.e., West Kentucky No. 9 (WK9-1 and WK9-2), West Kentucky No. 13 (WK13), and Illinois No. 6 (IL6-1 and IL6-2) which are high volatile bituminous coal sources having a relatively high sulfur content. Plant WK9/11 treated a combined material originating from the West Kentucky No. 9 and No. 11 coal seams. The coarse refuse samples were a product of coal cleaning processes which included dense medium cyclones for the material coarser than 1 mm and spiral concentrators for the material having a particle size between 1 mm and 0.15 mm. At each preparation plant, the coarse reject materials were transported by conveyor belt and stored in large refuse piles which were underlined with a clay liner to direct and capture the leachate. Representative leachate samples were collected

from natural leachate streams at a point located upstream of the caustic solution addition. Representative coarse refuse samples were collected using sweep-belt systems every 30 min over three hours of steady-state operation.

Upon delivery of the samples to the laboratory, the coarse refuse solid samples were dried under natural atmospheric conditions before being crushed using a laboratory jaw crusher and ground to finer than 0.15 mm by a hammer mill. To determine the elemental composition, a representative solid sample obtained using a riffler was digested using aqua regia and hydrofluoric acid based on the ASTM D6357-11 standard. A mineralogy analysis of the coarse refuse sample was conducted using X-ray diffraction (XRD).

The natural leachate samples were filtered using 0.45  $\mu\text{m}$  pore size filter papers to remove any suspended particles. The solution pH values were generally in the range from 2.5 to 3.0. Metal ions concentration in solution were quantified using an inductively coupled plasma optical emission spectrometry (ICP-OES) unit. Ion chromatography (IC) was utilized to measure concentrations of major anions in the natural leachate samples.

### 2.2. Methods

Acid leaching experiments were carried out using a 1.2 M sulfuric acid solution heated to 75 °C using a water bath. A solid concentration of 10 g/L was maintained for each experiment. One-liter reactors were employed with a total reflux condenser to maintain a constant volume. Agitation was provided with a magnetic stir bar at 530 rpm. Slurry samples of 25 mL were collected after 1, 3, 5, 10, and 24 h of retention time and centrifuged at 3000 rpm to remove the suspended solids. After the last sample was collected, the remaining slurry in the reactor was filtered, thoroughly washed using deionized water and dried before measuring the dry mass.

Both leachate and solid residue samples along with a representative feed solid sample were analyzed using ICP-OES to determine the contents of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The recovery of each REE represents the amount of REE in the feed that dissolved in the leachate which was determined using the expression:

$$\text{REE recovery (\%)} = 100\% \times (C_L \times V_L) / (C_L \times V_L + C_{SR} \times M_{SR})$$

where  $C_L$  is the REE concentration in the leachate solution ( $\mu\text{g/mL}$ );  $V_L$  the volume of leachate solution (mL);  $C_{SR}$  the REE concentration in solid residue ( $\mu\text{g/g}$ ); and  $M_{SR}$  the weight of solid residue (g).

Sequential precipitation tests were performed on the natural leachate samples using an apparatus consisting of a pH meter, magnetic stirrer and vacuum filter. The pH was gradually increased by the addition of 0.5 mL 2 M sodium hydroxide solution. To eliminate the potential of localized precipitation, the leachate sample was stirred for a period of 2 min during and after the solution addition. A visual observation of changes in the precipitate and solution was used to determine when to stop increasing the pH which led to variable pH ranges when treating the natural leachate samples. The precipitate was filtered using a 0.45  $\mu\text{m}$  pore size filter paper and dried at 100 °C for 12 h. The pH of the filtrate was further increased to obtain a series of precipitates in different pH ranges. The elemental composition of the precipitate was measured using ICP-OES after re-dissolution of the precipitate by digestion using the same method as the coarse refuse samples.

## 3. Results and discussion

### 3.1. Sample characterization

Three coarse refuse samples were collected from different mine sites, i.e., WK13, IL6-1 and IL6-2 to assess the potential of REE recovery. As shown in Table 1, all three refuse samples contained more than 80% ash-bearing mineral matter. Total REE contents on a dry, whole mass basis were 322, 255, and 248 ppm for WK13, IL6-1, and IL6-2,

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