

CONCENTRATION OF RARE EARTH MINERALS FROM COAL BY FROTH FLOTATION

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ABSTRACT

Rare earth elements (REEs) found in coal are in the form of minerals, ion-substitution with clays and organically bound. Rare earth minerals (REMs) such as monazite exist in coal and have a grain size less than 5 microns. Froth flotation was successful in concentrating REMs existing in a thickener underflow material derived from Fire Clay seam coal which contained around 300 ppm of rare earth elements (REEs). Conditioning with fatty acid followed by processing using multiple stages of conventional flotation produced a final concentrate containing 2300 ppm REEs. Using a laboratory flotation column, a concentrate containing around 4700 ppm of total REEs was produced equating to an enrichment ratio of 10:1.

INTRODUCTION

Rare earth elements (REEs) are becoming increasingly important and have been widely used as raw materials for the production of phosphor, metal catalysts, magnets, and batteries [1, 2]. REE recovery from alternative sources such as coal and coal by-products has the potential to stabilize the economic viability of coal mining operations while providing a dependable supply of critical materials.

The average REE content of the world coal is around 60-70 ppm [2]. There are many well-known coal beds with high contents of REEs such as those in the Far East coalfields in Russia (300-1000 ppm), the Fire Clay coal seam in eastern Kentucky (500 ppm), and the Sydney Basin in Nova Scotia, Canada (72-483 ppm) [3-6]. The occurrence of REEs in coal and coal by-products can be classified into three types, i.e., rare earth minerals such as monazite and xenotime, ion exchangeable REEs in clays, and REEs associated with organic matrix. The particle size of the rare earth (RE) minerals in coal and coal by-products is very small and normally in the micron and/or nanometer scales. The flotation technique, which is based on the surface chemistry difference, has been widely used to treat fine rare earth industrial minerals such as monazite, xenotime, and bastnaesite [7-11]. As such, flotation is a promising method for the concentration of REEs from coal and coal by-products.

In the current study, rare earth flotation was conducted using the fine coal refuse generated at an operating coal preparation plant treating coal from the Fire Clay seam. REE concentration by flotation required an appropriate amount of grinding and control of the pH value while using typical collectors. Prior to RE concentration, release tests were conducted to evaluate the floatability of the recoverable coal and the REE distribution in the flotation fractions in the fine refuse. Mineralogy of the REE was studied using SEM-EDX.

MATERIALS AND EXPERIMENTS

Representative samples of fine coal refuse were collected from the thickener underflow of an eastern Kentucky coal preparation plant which utilizes the Fire Clay coal as feed stock. Ash content and rare earth analysis of the collected material are shown in Table 1. The sample contained 256 ppm of REE on a whole mass basis with a heavy rare earth (HREE) to light rare earth (LREE) ratio of 0.18. The ash content of the sample was about 60% which indicated the potential for coal recovery. In addition to adding additional revenue, coal recovery prior to REE concentration benefits the separation process by eliminating a component that would compete for collector adsorption.

Flotation release tests were conducted to evaluate the floatability of the coal while also providing information about the association characteristics of REEs within the ash-bearing components of the coal.

Table 1. Ash content and REE analysis (ppm, whole mass basis) of Fire Clay coal fine refuse.

Ash (%)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
59.32	34.42	120.94	10.24	30.53	9.46	1.03	6.18	0.30
Dy	Ho	Er	Tm	Yb	Sc	Y	Lu	HREE/LREE*
5.18	2.20	3.08	0.68	2.09	11.71	17.84	0.01	0.18

*Notes: HREE = Eu + Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu + Y;
LREE = La + Ce + Sc + Pr + Nd + Sm

Due to the fine grain size of the RE minerals present in the coal, feed samples were ground for different lengths of time in a series of tests using a stirred ball mill. The particle size of the material after grinding was measured using a CILAS laser particle size analyzer.

Diesel and MIBC were used as the collector and frother, respectively, for the release test and coal flotation recovery tests. For the REE flotation tests, sodium oleate was added as the collector. The chemicals used in the study were of analytical grade and purchased from Fisher Scientific.

Conventional flotation tests were conducted using a bench-top Denver flotation machine equipped with cells of different volumes. Column flotation tests were conducted using a lab-scale column that was 2.5 m length and 5cm in diameter (see Figure 1). To produce concentrates with high REE content, multi-stages of flotation were tested using the flowsheet shown in Figure 2.

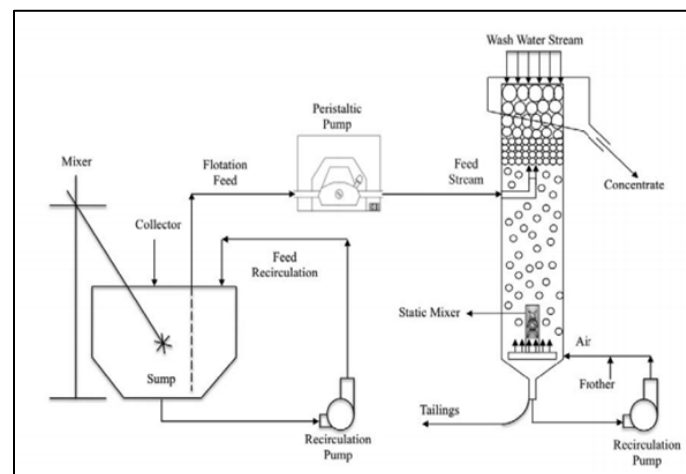


Figure 1. Schematic diagram of the flotation column used for REE recovery from Fire Clay fine refuse.

Feed and test product samples were digested using a combination of aqua regia and hydrofluoric acid. REE content of the digested liquid was analyzed using ICP-OES. Sample characterization was conducted using the X-ray diffraction (XRD) and scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX).

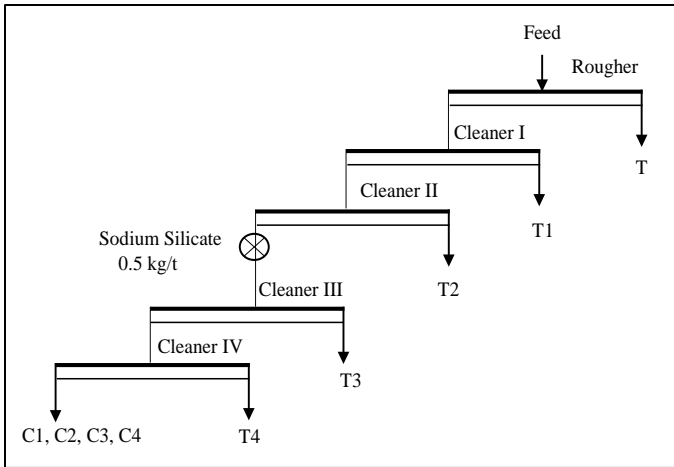


Figure 2. Multi-stages column flotation test flowsheet for REE recovery from the Fire Clay fine refuse.

RESULTS AND DISCUSSION

Release Tests

Flotation release tests provided an estimate of the ultimate separation performance achievable under a given set of conditions for the Fire Clay thickener underflow material. As shown in Figure 3, the selectivity achieved by flotation of the sample was excellent which produced a clean coal concentrate containing 10% ash-forming minerals while recovering 85% of the combustible material. The result indicated the potential of significant economic gains from the recovery of coal prior to the concentration stages needed for REE recovery.

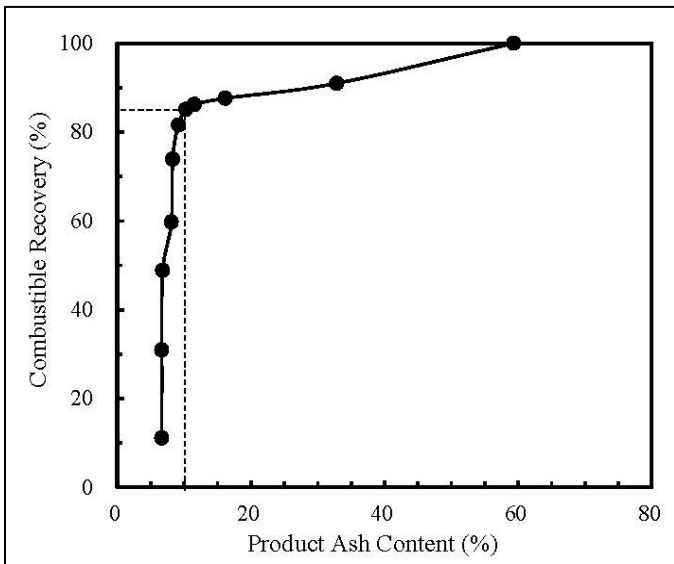


Figure 3. Release test results of Fire Clay coal fine refuse.

The release analysis samples were analyzed for REE content and the result plotted in Figure 4 on a dry whole mass basis and dry ash basis. Products with low ash contents contained higher REE values on an ash basis but lower values on whole coal basis. The low REE content on a whole sample basis in the low ash content samples occurred as a result of organic dilution. After the organic matter was burned, the REE associated with the organic matter reported to the residual ash. As such, a higher REE content in the residual ash is expected as a result of organic matter through an organic affinity with humic acids or micro-dispersed as minerals or mineral associations. However, the amount of total REEs (TREEs) in the organic matrix is relatively small in total weight.

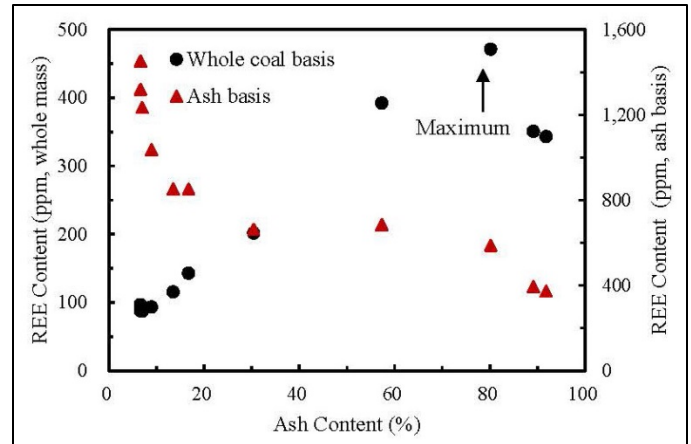


Figure 4. REE content on both whole mass basis and ash basis as a function of the ash content.

The maximum REE content on a whole sample basis occurred in flotation products containing 80% ash. Above this value, the TREE content was reduced to the dilution effect caused by the presence of low TREE content rock.

The more valuable heavy REEs was found to be concentrated in the low ash content products as shown by the increase in the HREE/LREE ratio in Figure 5. The affinity of the HREEs may be associated with their 3+ valence and high ionic charge density. After transfer of the REEs into the coal bed by geothermal fluids and/or exposure to volcanic ash, it is hypothesized that humic acid chelates with the HREEs and, as the humic acid content decreases, associates with the clays that fill the micro-cracks existing within the coal [6, 12].

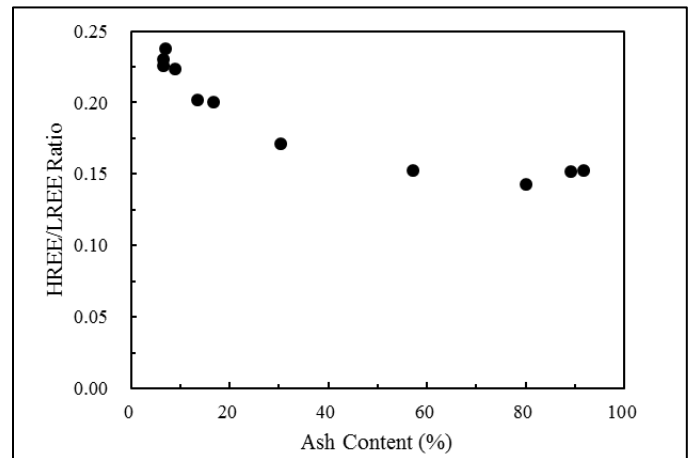


Figure 5. HREE/LREE ratio as a function of the ash content.

REE contents in solid samples are usually normalized using the concentration of REEs in North American Shale (NAS), chondrite, Upper Continental Crust (UCC), etc., to characterize the sample and study the geochemistry effects on the movement of REEs. For example, Ce is the only REEs that can exist as Ce⁴⁺ in certain re-dox environments which likely precipitates in-situ instead of moving with ground water flow. As such, a cerium anomaly may occur relative to other REEs such as La and Pr. The cerium anomaly (Ce_N/Ce_N^*) can be calculated using the following equation:

$$Ce_N/Ce_N^* = Ce_N / (0.5 * La_N + 0.5 * La_N)$$

where the footnote *N* represents the normalized concentration, i.e., the REE concentration divided by the REE content in chondrite [12]. As shown in Figure 6, the chondrite normalized REE pattern was similar for all the products, which may indicate that the REEs in ash material in the organic matrix, partings, roof and floor are of the same source.

Furthermore, positive cerium was observed for all the products including coal. However, in previous studies, a positive cerium anomaly was rarely observed in coal including those with associated intra-seam partings and host rocks [7]. As such, the REE association with the Fire Clay coal seam is unique relative to other coal sources [6, 7]. Figure 7 shows changes of the cerium anomaly as a function of ash content. The cerium is preferentially enriched in the low ash organic and high ash inorganic fractions. However, it is difficult to correlate the result to the core sample data published previously due to the fact that different coal benches are mixed in the fine refuse as well as partings and roof rocks [6].

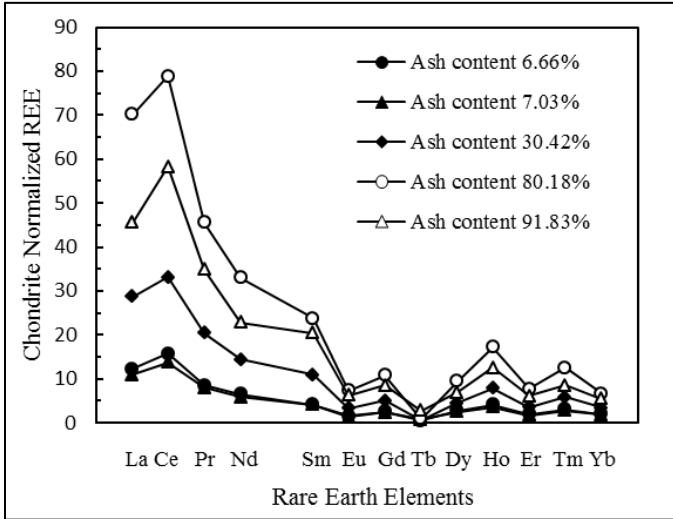


Figure 6. Chondrite normalized REEs in different release test products.

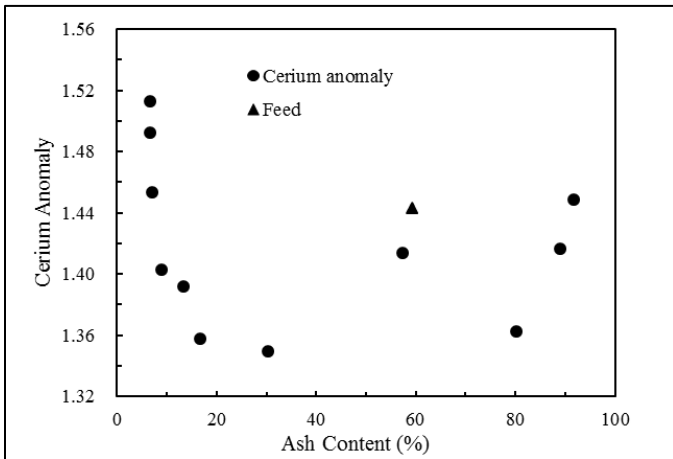


Figure 7. The cerium anomaly in release test products as a function of ash content.

Mineralogical Studies

SEM-EDX scanning was conducted to characterize the particles with high REE content. A particle with high REE content is shown in Figure 8 (a). A small portion of the particle was enriched in REEs, which means the REE mineral was not liberated thereby indicating the need for grinding to liberate the mineral for an effective REE recovery process. A focused ion beam (FIB) unit was used to mill out the high REE content grain which measured to be around 2 μm. Figure 8 (b) shows the SEM image of one lamella together with the TEM-FFT image. The fraction with a high REE content had an irregular shape and was embedded into the parent particle. The TEM-FFT images shows that the fraction was well crystallized and the composition of the grain was pure rare earth phosphate ((La, Ce, Nd, Sm, Th)PO₄) thereby indicating that the REEs were present in the form of monazite.

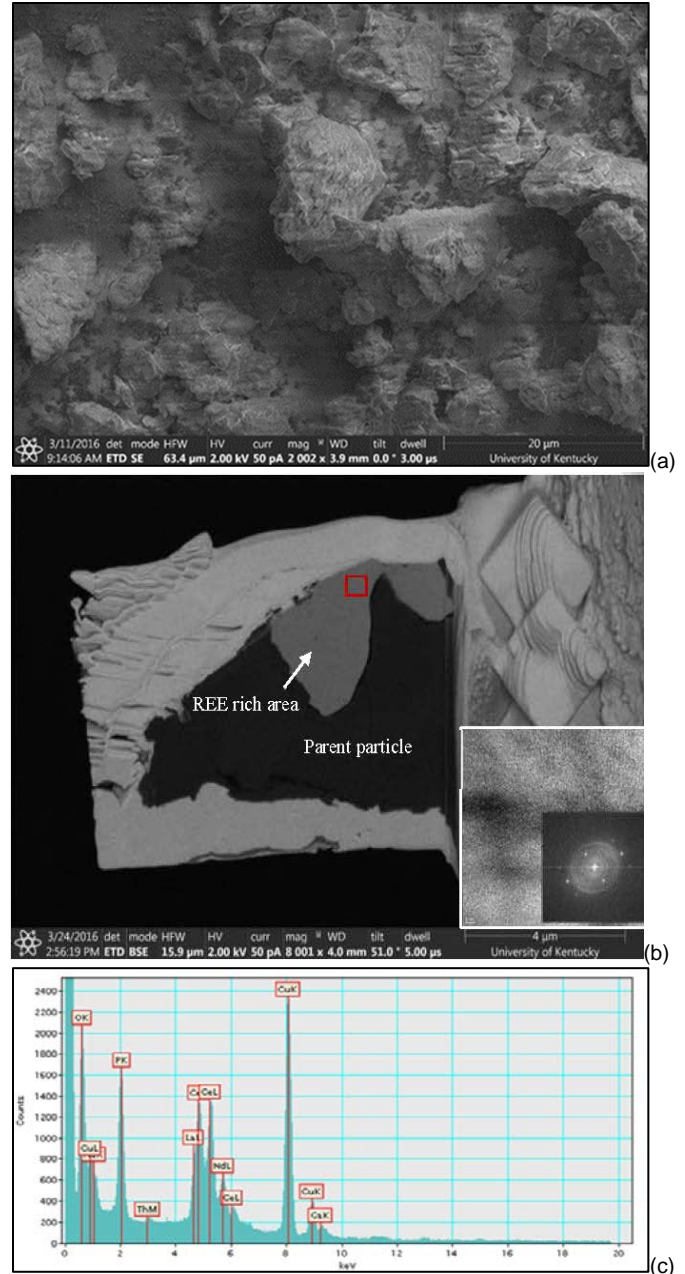


Figure 8. SED, TEM, EDX analysis of rare earth minerals in Fire Clay fine coal refuse: (a) SEM-EDX map; (b) lamella with high REE concentration milled using focused ion beam (FIB) and the TEM-FFT images of specific area with high REE concentration; (c) EDX images of the area selected from (b).

Flotation Tests

Solution pH values and grinding time were the two critical parameters evaluated to improve the selectivity of the REE flotation tests. Figure 9 shows the effects of pH and particle size on the enrichment ratio, i.e., the REE concentration in the concentrate divided by the concentration in the feed. As shown in Figure 9 (a), maximum enrichment ratio occurred at pH 9, which agrees with previous findings reported on pure monazite flotation using sodium oleate [7-9]. Maximum surface active sites (REE(OH)⁺ and REE(OH)²⁺) exist on monazite surfaces at pH 9.0 and, as such, higher adsorption kinetic rates and maximum adsorption capacity occurs. Figure 9 (b) shows that a particle size of 2.76 μm (D50) produced by 60 minutes of grinding in an attrition mill provided the highest enrichment ratio.

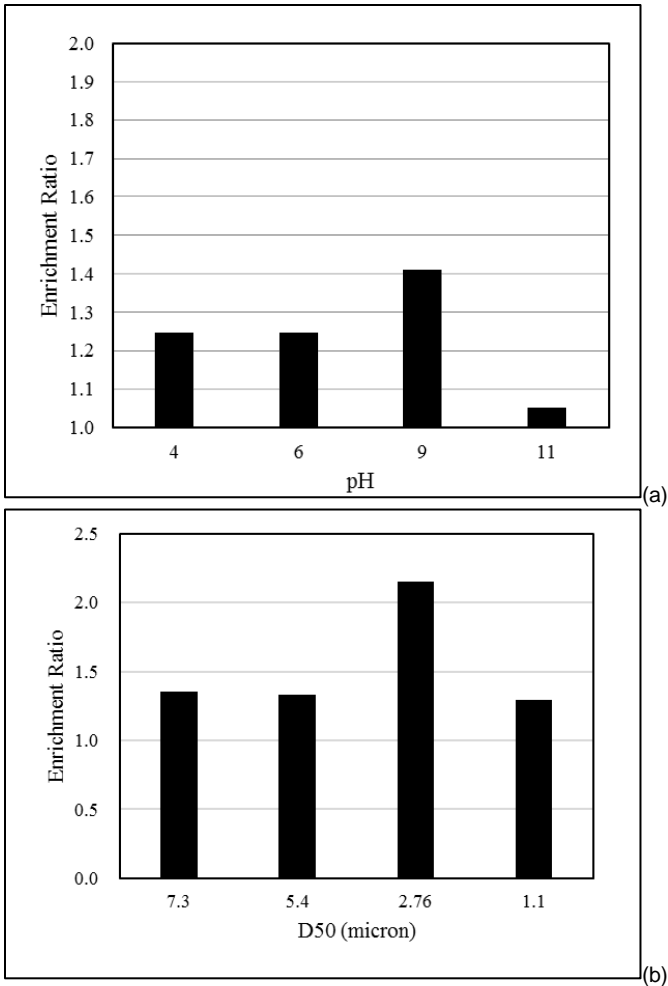


Figure 9. Effects of pH and particle size on the rare earth flotation separation: (a) pH effects; (b) particle size effects.

Multiple stages of flotation was conducted using a batch-type conventional cell and continuous flotation column in separate test programs. Figure 10 (a) shows the cumulative REE content in the products as a function the cumulative REE recovery. For recovery values below 20%, column flotation was more efficient than the conventional flotation, i.e., the REE contents in the column flotation products were two times higher than the products obtained using conventional flotation. Column flotation produced a concentrate containing around 4700 ppm of TREES from a feed containing 431 ppm of TREES on an ash basis which equates to an enrichment ratio of over 10:1. The improved selectivity provided by column flotation was due to the ability to minimize hydraulic entrainment and maximize recovery of the ultrafine REE containing particles as a result of the plug-flow environment. As shown in Figure 10 (b), LREEs were preferentially recovered using flotation methods based a decrease in the HREE/LREE ratio with an increase in product REE content, which agrees with the fact that RE minerals such as monazite is more enriched in LREEs.

CONCLUSIONS

The mineralogy of REEs in a Fire Clay fine coal refuse sample was studied using the SEM-EDX analysis. Unliberated monazite particles with an REE content of around 60% were discovered having a particle sizes less than two microns. Results from a flotation release analysis found that heavy rare earth elements were likely associated with finely dispersed ash materials within the organic matrix. Furthermore, due to the organic and inorganic dilutions, maximum REE content occurred in particles with an ash content of around 80%.

The TREE content decreased for particles containing greater amounts of ash due to the dilution effect caused by low TREE content rock particles.

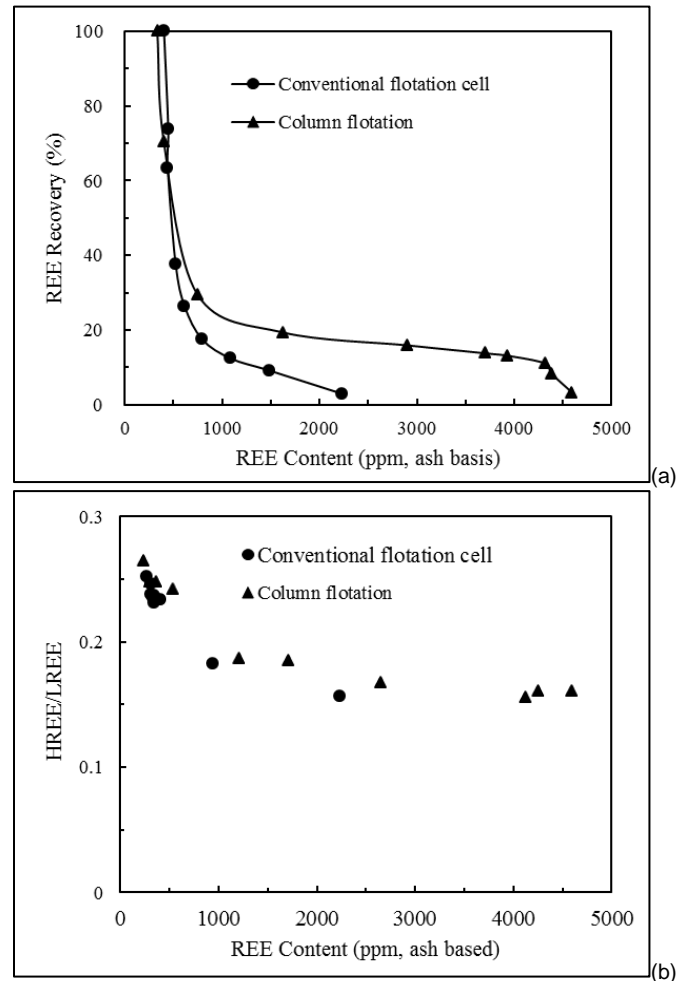


Figure 10. A comparison of the REE recovery performances achieved through multiple cleaning stages using conventional and column flotation cells: (a) REE content on an ash basis as a function of cumulative recovery; (b) HREE/LREE ratio as a function of REE content on an ash basis.

Optimum flotation of rare earth minerals from the coal refuse material occurred using a pH value of 9.0 and grinding time of 60 min. Column flotation was found to be more effective than conventional flotation due to the effects of hydraulic entrainment and hydrodynamic conditions. A final concentrate containing around 4700 ppm of REEs was obtained using column flotation and multiple cleaning stages. Due to the concentration of monazite, the light REEs were preferentially recovered in the flotation product.

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