

Recovering Rare Earth Elements from Acid Mine Drainage with Mine Land Reclamation

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Abstract

In this study, we demonstrated a trap-extract-precipitate (TEP) process that effectively recovers rare earth elements (REEs) from coal mine drainage (CMD). This three-stage process uses environmentally benign industrial by-products to retain CMD REEs from CMD. It then applies an extraction/precipitation procedure to produce a concentrate feedstock (>7.5 wt.% of total REEs) that can be economically processed to produce marketable rare earth oxides. We envision the TEP process can be integrated with abandoned mine land reclamation to create a commercially viable approach to mitigate CMD and restore lands that are adversely impacted by historical mining.

Keywords: Rare Earth Elements, Acid Mine Drainage, Coal Mine Reclamation, Beneficial Use Of Coal Combustion Residues, Flue Gas Desulfurization By-products

Introduction

Rare earth elements (REEs) (including scandium, yttrium and a group of 15 lanthanides) are often considered to be critical components in the productions of renewable energy hardware, electric vehicles, health care and military equipment, and consumer electronic products. The demand of REEs has been projected to be growing at an annual rate of 5-9% in the next 25 years (Alonso *et al.* 2012). China overwhelmingly dominates the current worldwide rare earth productions (over 95%) (Hatch 2012), causing significant instability for the global market. Finding alternative sources has become a critical issue for the US and other countries.

Recovering REEs from the sludge of coal mine drainage (CMD) remediation system has been suggested as an environmentally beneficial and economically feasible alternative (Ayora *et al.* 2016). CMD remediation systems are normally operated at active mine sites. In the United States, CMD discharging from an active mine is mitigated to meet federal effluent limits based on the quality of the receiving water bodies by the coal mining operator. However, there are many CMDs discharging from abandoned

mines, where mining activities occurred prior to current state and federal mining regulations, and therefore, remain untreated. In the state of Ohio, approximately 2000 kilometres streams are currently impaired by CMD. Implementing adequate treatment systems for these abandoned CMDs is limited by funds available for the state and federal reclamation agencies, local conservation organizers, and watershed associates.

In this study, we tested a three-stage process that first retains REEs from CMD using alkaline industrial by-products and then concentrates the retained REEs using a non-acid based organic ligand extraction procedure. The lixiviant is then oxidized to form REE precipitates. This trap-extract-precipitate (TEP) process can be integrated with abandoned mine land (AML) reclamation to create an approach that provides economic incentives to AML reclamation and remediates CMD discharges. It provides a long-term, high-volume beneficial use for coal combustion residuals, which otherwise needs to be disposed of in a landfill and eliminates public safety hazards and threats to local environment and ecological systems posed by AMLs.

Experimental

Materials

The alkaline industrial by-products used in this study to retain CMD REEs include two stabilized flue gas desulfurization materials (sFGDs) and a lime sludge produced from the softening process of a drinking water treatment plant. sFGD is a mixture of lime (CaO), coal ash, and calcium sulfite FGD by-product, which is produced from the wet scrubber for removing sulfur dioxide (SO₂) from the coal flue gas. We obtained the sFGDs from two pulverized-coal power generating facilities burning bituminous coal located in east and southeast Ohio. sFGD 1 was obtained from the wet scrubbers at Plant C that used limestone slurry as the desulfurization reagent. sFGD 2 was produced from the lime slurry used at Plant G. Magnesium hydroxide was added to the lime slurry to enhance SO₂ removal. Both wet scrubber systems are natural oxidation systems. All materials were dried in an oven at 60 °C before being crushed and sieved using a No.60 sieve.

The CMD used in this study was periodically collected from the Flint Run, a perennial CMD stream from the seepage discharge of a reclaimed abandoned surface mine, located at 36.06170–82.51139. Each batch of CMD was preserved at 4 °C before use and purged with nitrogen to minimize oxidation during test.

Retaining REEs

A series of column tests were carried out to simulate the percolation condition that occurs when using a passive treatment unit for CMD mitigation and REE recovery. The tests were carried out under various percolation rates ranging from 0.5 to 2 liquid-to-solid per day (L-S-1-day⁻¹). In addition, the retention of REEs was also investigated by a series of batch experiments, which simulates the retention of REEs under a completely mixed condition. These tests were carried out by adding predetermined amounts of sFGD 1 or WTP sludge (DRWP) to bottles. CMD was then added to each bottle to achieve a specific liquid-to-solid (L/S) ratio, which ranged from 5 to 1000.

Extraction

The spent solids obtained from the column and batch tests were air dried before extraction. The spent solids were mixed with an extraction solution prepared from sodium citrate at a ratio ranging from 1:10 to 1:40. The mixture was then heated in a hot block at 80 °C under different doses of sodium dithionite, a strong reductant. After heating for 15 minutes, the extract was separated from the suspension by filtering through a 0.45-µm filter and collected for chemical analysis. The extraction residues were then air dried for chemical analysis.

Precipitation

After extraction, we separated REEs from the lixiviants by promoting the formation of Na-REE-double sulfate precipitates (REE concentrate) through an oxidation process.

Results and Discussion

Retaining CMD REEs

Results obtained from the column tests (Figure 1 (a)) demonstrate that all three tested solids were able to recover over 98% of REEs under a wide range of percolation conditions before the materials exhausted neutralization capacities. In one of the tests (Column D with sFGD 1), only approximately 90% of REEs passing through the column was retained, which was due to a breakthrough.

The recovery of CMD REEs was also evaluated under a completely mixed condition. As shown in Figure 1 (b), when sFGD 1 was used, the retaining efficiency remained above 95% at an L/S ratio 50 or lower. At a higher L/S ratio of 100, although the retaining efficiency decreased to 83.8%, the concentration of total REEs (T-REEe) in the spent solids reached 94.2 µg/g (dry basis), which is the highest among the sFGD1 batches.

In the batches using the WTP sludge, over 98% of the total REEs mass in CMD partitioned to the solids under an L/S ratio less than 250. The retaining efficiency decreased at higher L/S ratios. The highest concentration of T-REEe in the spent solid after the reaction reached approximately 230 µg/g.

Extracting Retained REEs from Spent Solids

To optimize the extraction process, different sodium dithionite doses, pH buffering conditions, and liquid-to-solid ratios were tested. Results obtained from the extraction tests are shown in Figure 2. The extraction efficiency shown in the figure was calculated using the following equation.

$$\text{Extraction Efficiency, \%} = \frac{C_{lx,i} \times V_{lx}}{C_{ss,i} \times m_{ss}} \times 100 \quad \text{eq.1}$$

where $C_{ss,i}$ and $C_{lx,i}$ are the concentrations of REE, i , in the spent solids and lixiviant, respectively; m_{ss} is the amount of spent solids used in the extraction process; and V_{lx} is the volume of lixiviant.

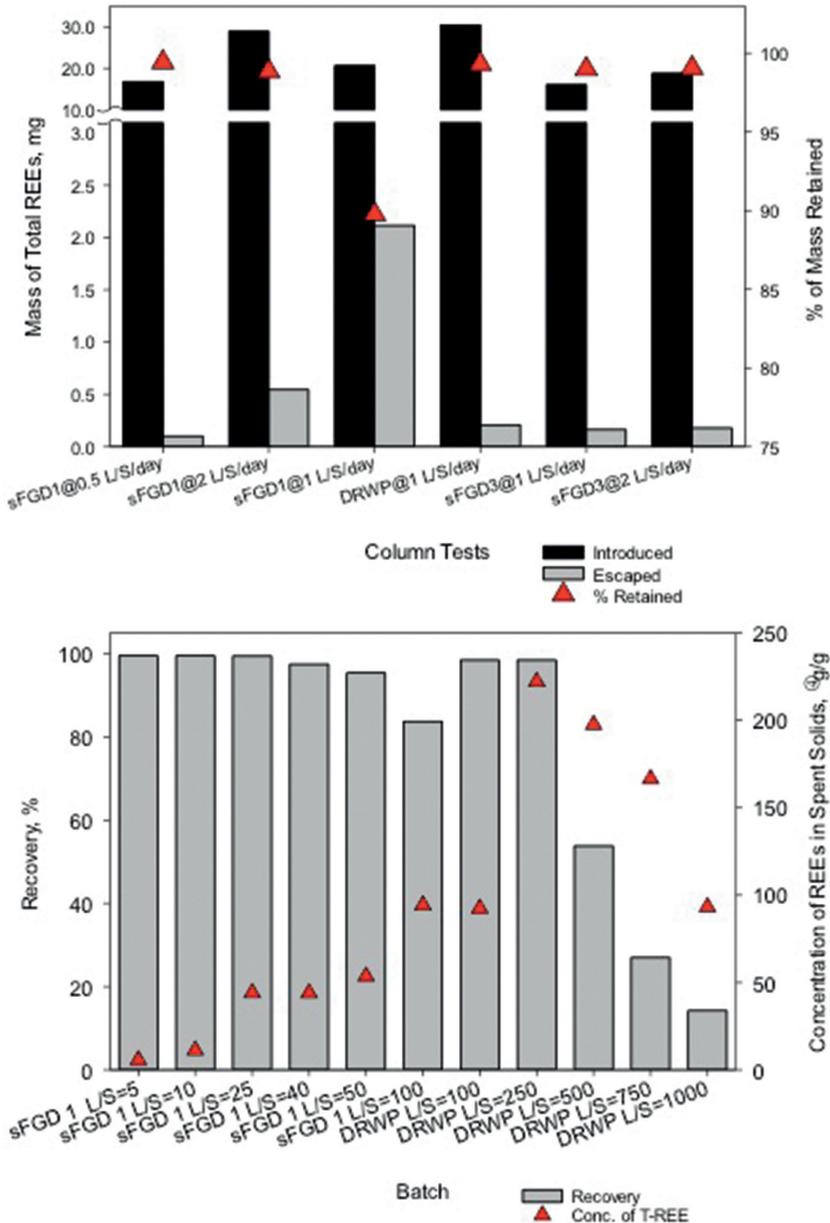


Figure 1 Retaining AMD REEs under (a) percolation and (b) completely mixed conditions.

As shown in Figure 2, the extraction efficiency was not affected when we decreased the dose strength to 1/3 of the original strength (columns shaded in light grey in Figure 2). To test the effect of buffering, we carried out the extraction process with and without a buffering solution and obtained slightly better extraction efficiency (columns shaded in light red in Figure 2). It was demonstrated that the effect of pH change during the extraction process is insignificant.

To optimize the use of the extraction solution, we conducted a series of extraction process using different solid-to-extractant (S/L) ratios ranging from (1/40 to 1/10) and evaluated the extraction efficiency (columns shaded in dark grey in Figure 2). It was found that no observable change in extraction efficiency when the S/L ratio was increased from 1/40 to 1/30. The extraction efficiency significantly decreased with higher ratios.

Producing REE Concentrate

The extracts produced from two of the selected extraction procedures of E1 and E8 were purged with air under various flow rates

and duration to observe the effects on the formation of REE concentrates. Formation of precipitates was observed during purging (Figure 3). After purging, precipitate was recovered by filtrating the extract using a 0.45µm filter and dried in an oven at 105°C. The amounts of precipitates formed during the purging process were determined gravimetrically and the results are shown in Figure 4 (a). Also shown in the figure are the amounts of REEs in the extract before and after purging.

Since the amounts of precipitate formed during the purging process are limited, the concentration of T-REEs in the solids was determined based on the principal of mass balance. As shown in Figure 4(b), we are able to precipitate over 90% of the extracted REEs and form a REE concentrate with the T-REEe concentration of approximately 7.5%wt.

Full-Scale Application

The TEP process can be integrated with AML reclamation to create an AML reclamation approach, which is illustrated in Figure 5. In a full-scale application, sFGD (fresh

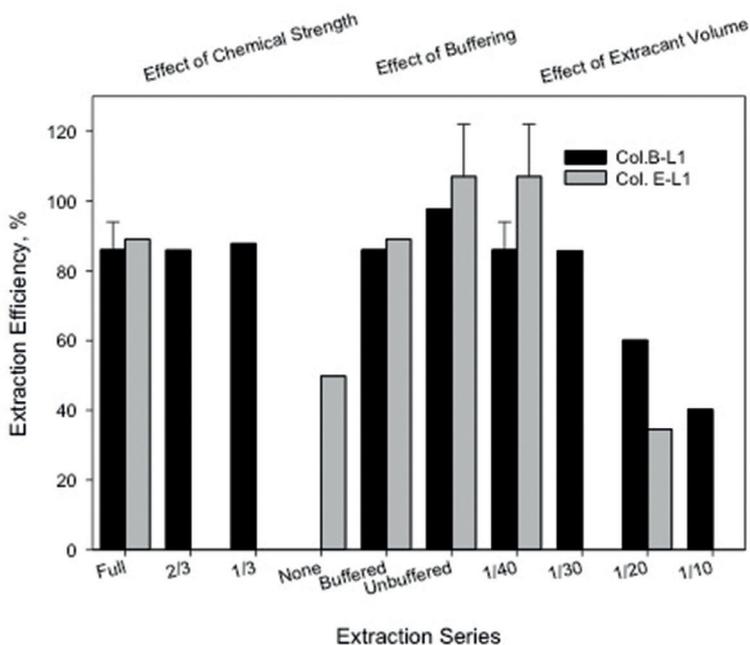


Figure 2 Efficiency of entrapped REEs in sFGD1 (Col. B-L1) and WTP sludge (Col. E-L1) extracted by different extraction conditions. Full strength of sodium dithionite is 3 grams per 1 gram of spent solid. The ratio of spent solid to the volume of citrate extractant ranged from 1/40 to 1/10.

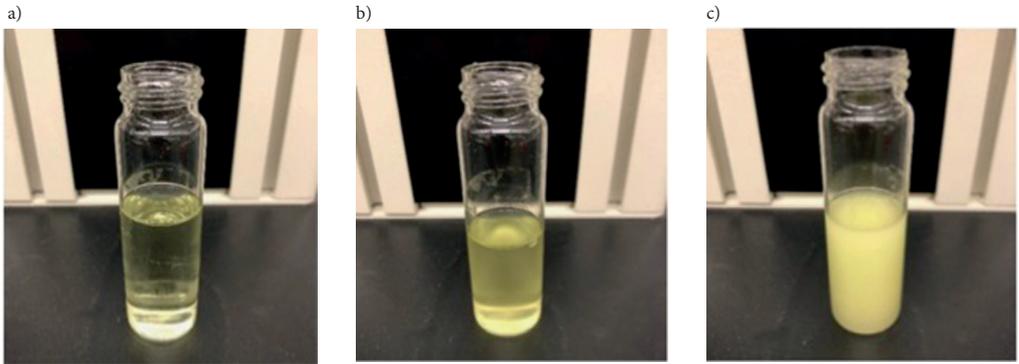


Figure 3 Formation of precipitates during purging. (a) Lixiviant before purging; (b) Lixiviant during purging; (c) Lixiviant after purging.

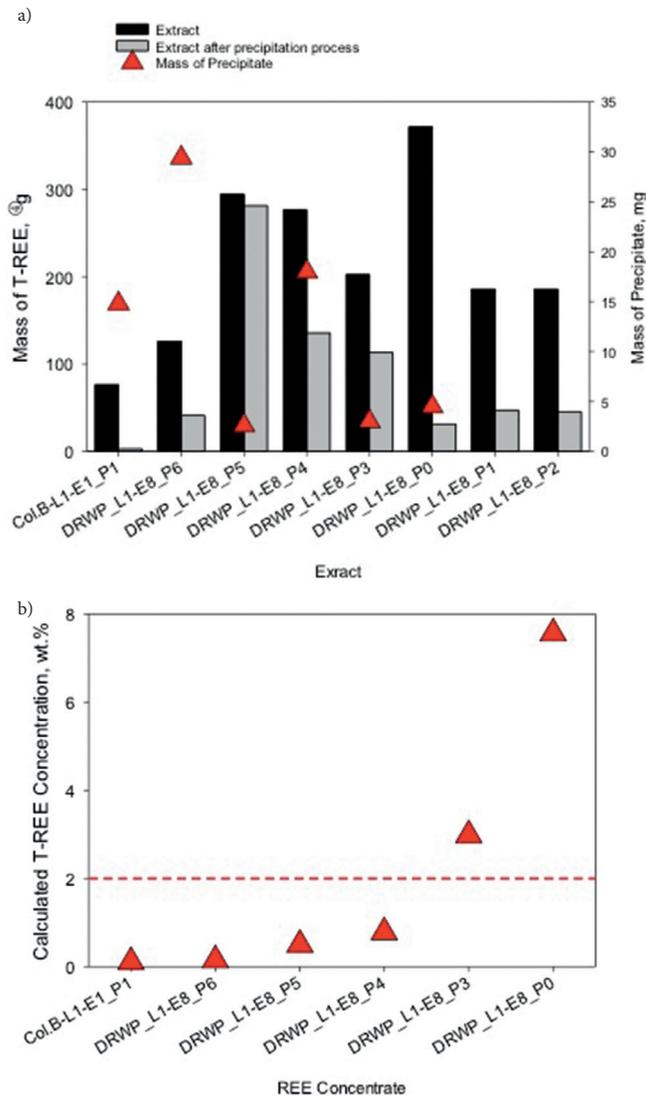


Figure 4 (a) Precipitation of REE concentrate and (b) calculated T-REE concentration in REE concentrates from selected aeration batches.

or landfilled), WTP sludge, and/or other environmentally benign alkaline industrial by-products are used to backfill and reclaim the AML (Figure 5(a)). With proper engineering design, CMD seeping out of the abandoned mine is collected by a drainage system and directed to nearby treatment cells (Figure 5(b)).

In the remediation cells, filled with suitable alkaline materials (e.g., sFGD and WTP sludge), a CMD dispensing system (e.g., geotextile material) is placed within the fill to facilitate the percolation of CMD, and consequently accelerate the mitigation process (Figure 5(c)). After the material exhausts its neutralization capacity, the spent solids are removed from the treatment cells for the following extraction and precipitation processes (Figure 5(d)). The operation is renewable by placing another batch of the alkaline material in the treatment cells.

Acknowledgements

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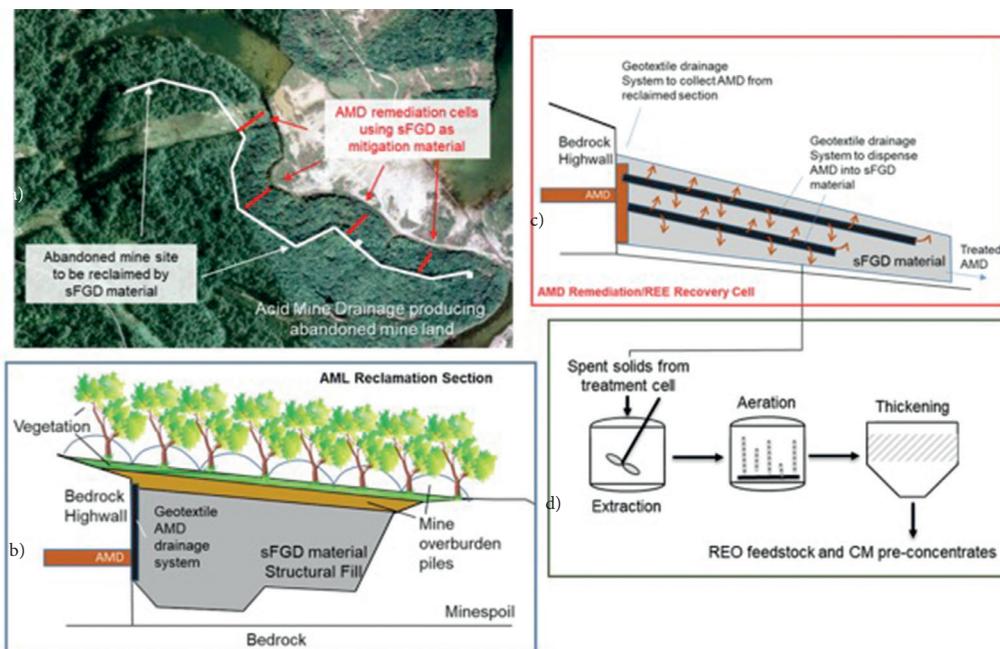


Figure 5 Schematic description of concept that integrates TEP process and AML reclamation.