

Distributions of Rare Earth Elements in Coal Mine Drainages

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Abstract

In the U.S., rare earth elements (REEs) are reported to be closely associated with coal deposits, especially in the Appalachian Basins. Historical coal mining in the Northern Appalachian Coal field of the United States has produced significant amount of coal drainage (CMD). In this study, we investigated 29 abandoned CMDs in eastern Ohio, USA. The main objective of this study is to understand the geochemical behaviour of REEs in CMD. Results obtained from this study provide the knowledge that will form the basis of a reactive transport model, which can be used to predict REE retention and recovery.

Keywords: Coal Mine Drainage, Rare Earth Elements, Abandoned Coal Mine, Mine Drainage Chemistry

Introduction

In response to increasing global demand and supply dominance of China, finding alternative sources of rare earth elements (REEs) has become a critical national security issue for other countries, including the United States. Coal and coal ash are considered as important alternative sources for REEs. In the U.S., high concentrations of rare earths have been reported to be closely associated with coal deposits (Hatch 2012), especially in the Appalachian Basins. In addition to coal and coal ash, another potential important alternative REE source is coal mine drainage (CMD). CMD occurs during and after coal mining. When surface and/or groundwater comes in contact with geologic strata and ore bodies containing sulfide minerals, such as pyrite (FeS₂), exposed by coal mining, the accelerated oxidation of sulfide minerals in the presence of natural oxidants (e.g., ferric iron and oxygen) or induced by certain micro-organisms can produce sulfuric acid (Evangelou 1998, Johnson 2003). It promotes the weathering of REE-bearing rocks and minerals in the host geologic strata (Jennings *et al.* 2000, Lottermoser 2007).

Historical coal mining in the Northern Appalachian Coal field produces significant amount of mine drainage, which causes widespread degradation of water resources. According to Ohio Department of Natural

Resources, CMD have degraded more than 2000 km of streams in Ohio. Currently, state, and federal funds for abandoned mine land reclamation are raised through taxes on coal extraction in the region, but these funding sources are limited.

In this study, we investigated CMD discharges from abandoned coal mines and refuse piles in eastern Ohio. The main objective of this study is to understand the geochemical behavior of REEs in CMD. A multivariate statistical analysis technique, principal component analysis, was used to correlate the hydrogeochemical characteristics of CMD and the concentrations of REEs.

Study and Methods

A total of 29 CMD discharges were studied. These CMD discharges are from historic underground mines at different coal seams, abandoned surface mines, and minespoil/refuse piles. Refuse/slurry piles disposed from mines and coal preparation plants are also major sources of acid drainage.

We used PHREEQC, an aqueous geochemical modeling code developed by the United States Geological Survey (USGS) (Charlton and Parkurst 2002), to calculate the speciation distribution of REEs in CMD. The thermodynamic dataset compiled by the Lawrence Livermore National Laboratory is used, which includes stability constants of the

REE sulfate, chloride, phosphate, hydroxide, and carbonate complexes.

To simplify the analysis of complex chemical correlations between REEs and other monitoring parameters, we used a principal components analysis (PCA) to extract information from the water quality dataset. PCA is a statistical technique that quantifies the relationship among water quality parameters, such as pH, acidity, and concentrations of major and rare earth elements, and finds a new set of independent and uncorrelated variables, i.e., principal components (PCs), to represent the original water quality data. Each PC is a linear combination of the original water quality parameters. No pre-treatment of the original data was performed as the PCA was carried out on a correlation matrix. Left-censored data were replaced by the values equal one-half of the detection limits. A commercially available statistical program, JMP, developed by SAS Institute was used to carry out PCA.

Results and discussion

General Hydrochemical Property of CMDs

All water samples are highly mineralized with total dissolved solids (TDS) concentration ranging from 247 to 7364 mg/L. The pH value ranged from acidic (2.3) to circumneutral (6.89). The major ions in the CMD samples include sulfate, Ca, Mg, Fe, Al, Na, Si, Mn, Cl, and K (Figure 1(a)). By comparing the relative concentrations of major cations and anions in the CMD samples, the waters are categorized as CaSO_4 and MgSO_4 type. In addition to these aforementioned major elements, the waters also contain a number of trace constituents (Figure 1(b)), such as Tl, Co, P, Cr, and V. However, not all of the samples contain detectable levels of trace constituents. As shown in Figure 1(c), the concentration levels of REEs vary significantly among these CMD discharges. The concentration of total REEs (ΣREEs) ranges from 2212 to 5 $\mu\text{g/L}$. Y, Nd, and Ce are the most abundant REEs. The heavy (Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and critical REEs (i.e., Y, Dy, Eu, Dy, and Tb) account for

approximately 34% and 48% of total REEs, respectively (Figure 1(c)).

Geochemical Property of REEs in CMDs

It has been suggested that the concentrations of rare earth elements in CMD are strongly correlated with pH (Grawunder *et al.* 2018). However, this correlation was not observed in this study. As shown in Figure 2, the pH of four CMD discharges with the highest total and critical REEs concentrations are less than 4.0. However, not all CMD discharges with low pH values contain high REE concentrations. No significant correlation between the pH and concentration of total ($r=-0.366$) was observed. Similar ΣREEs -pH correlation was also reported by Stewart *et al.* (2017).

The correlations among ΣREEs , critical REEs, and other hydrochemical parameters in CMDs were analyzed using a principal component analysis (PCA). The loadings of the considered parameters for the first three principal components (PCs), which explain 70.9% of the observed variance in the hydrochemical properties, are shown in the table embedded in Figure 3. In addition, the eigenvalue for each component and cumulative percent of variance explained by these three PCs are shown. The first PC (PC1) explaining approximately 34.7% of the variance shows that the CMD samples with high acidity also contain relatively higher ΣREEs , critical REEs, and a number of major constituents, i.e., Al, Ca, Fe, Mg, and Mn. It demonstrates the significance of the oxidation process by the acidity forming minerals. PC2 explaining 23.5% the variances has relatively strong loadings from B, K, and Na suggests some of the CMD samples were affected by fresh streams or surface runoff. As shown in Figure 3, CMD samples with higher pH normally contain higher concentrations of Na, Cl, and B. PC3, explaining approximately 12.7% of the variance, suggests acidity was mostly contributed from Fe for these CMD samples. Acidity was measured using the standard “hot peroxide treatment” method, mainly results from the potential for hydrolysis of dissolve ferric iron (Fe^{3+}), ferrous iron (Fe^{2+}), Al, and Mn^{2+} , as well as the precipitation of associated hydroxide solids.

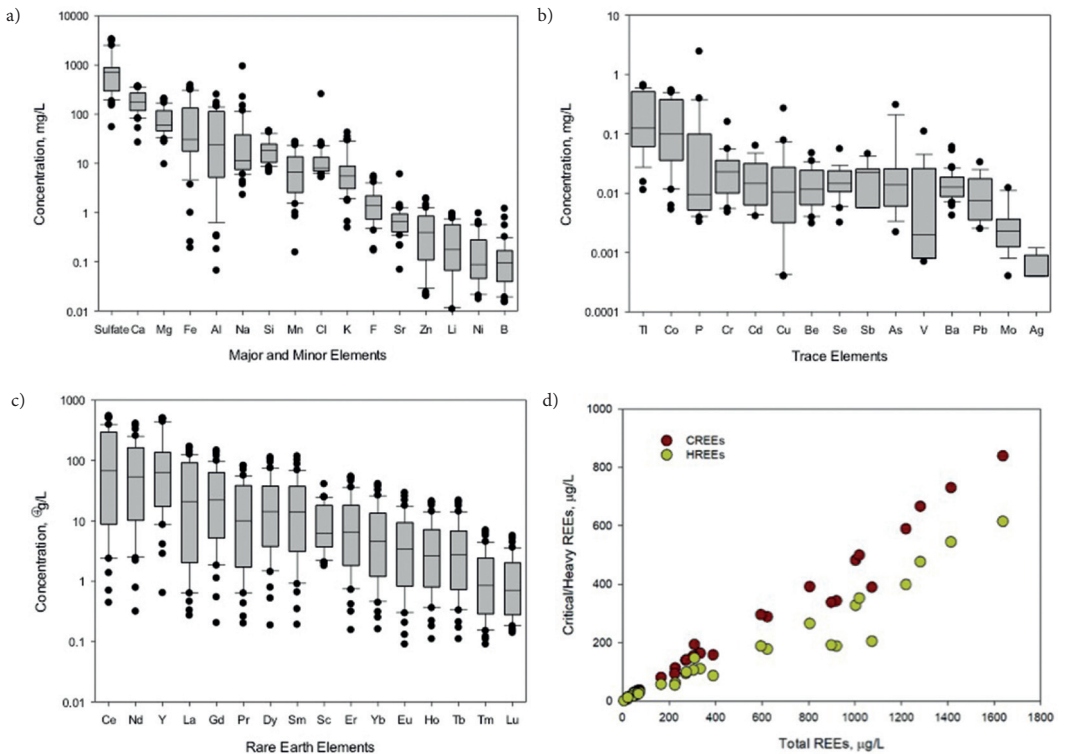


Figure 1 Concentrations of (a) major and minor, (b) trace, and (c) rare earth elements in CMD discharges. Only detectable data are included in the plots. (d) Concentrations of total heavy (Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and total critical REEs (i.e., Y, Dy, Eu, Dy, and Tb) as a function of total REEs.

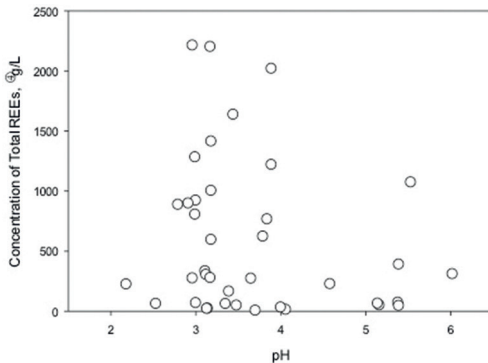


Figure 2 Correlations between pH and concentrations of total REEs.

As demonstrated in Figure 3, instead of pH, Σ REEs and critical REEs showed better correlations with acidity. In fact, among the three acidity-related cations, Mn has the strongest correlation with Σ REEs and critical REEs, followed by Al (Table 1). In addition to Mn and Al, Mg also shows high correlation.

Enrichment of REEs

The concentrations of REEs were normalized with North American Shale Composite (NASC, Taylor and McLennan, 1985) to detect REE enrichment. The REE enrichment patterns are described using [La/Gd]_N, [La/Sm]_N, and [La/Yb]_N to compare relative levels of light REEs (LREEs) (i.e., La, Ce, Pr, Nd, and Sm) to middle REEs (MREEs) (i.e., Eu, Gd, Tb, Dy) and heavy REEs (HREEs) (i.e., Ho, Er, Tm, Yb, and Lu). As shown in Figure 4, the CMD samples showed a clear MREE enrichment compared with LREEs and HREEs, which has been a typical feature of REEs in acidic environments (Johannesson and Lyons 1995).

In addition, mostly positive Ce anomalies were shown in the studied CMDs, indicating the immobilization of Ce^{3+} by oxidation to Ce^{4+} played an insignificant role in the migration of Ce. The strong correlation between Mn and REEs indicates the

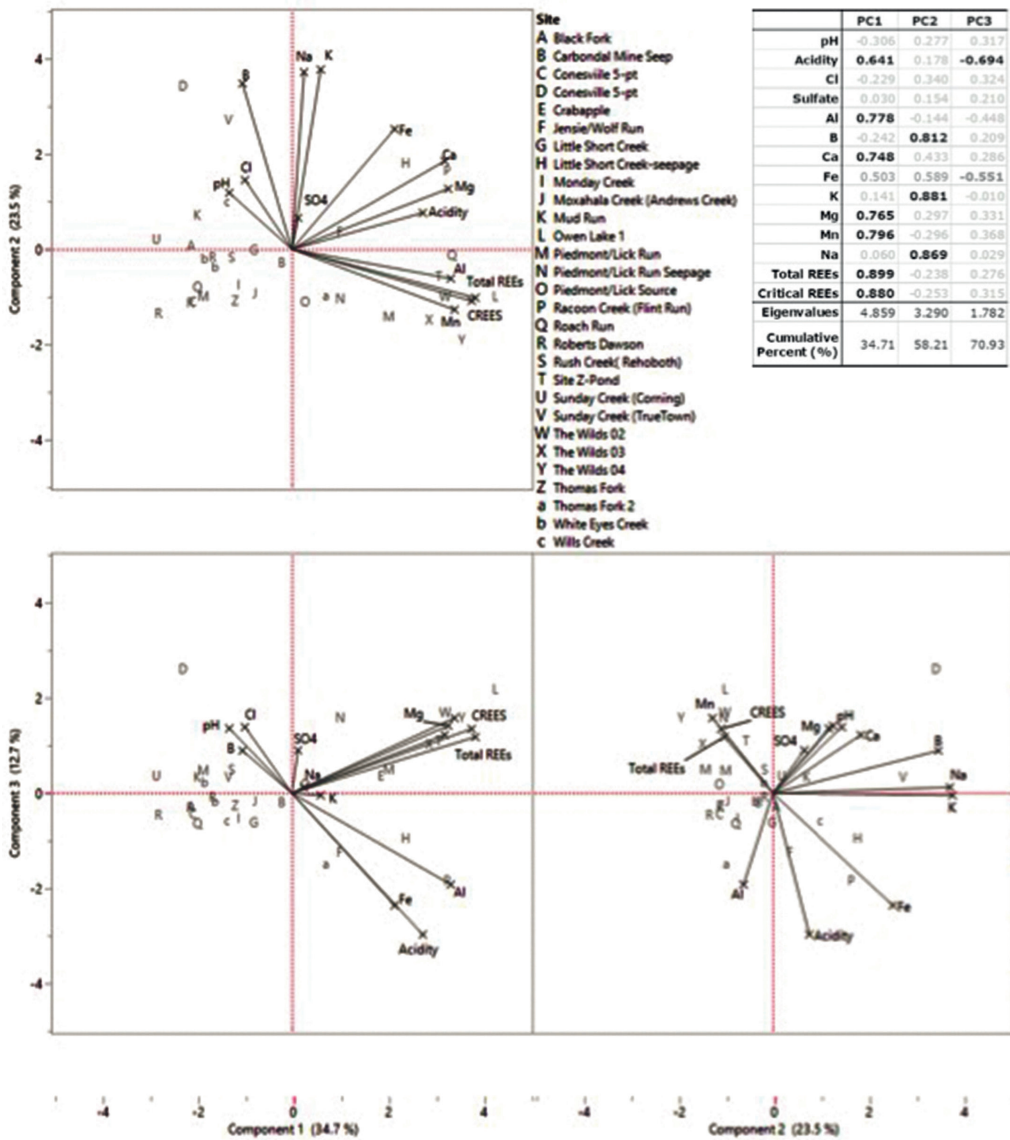


Figure 3 The score and loading plots of REEs and major constituents from principal component analysis.

Table 1 Correlation coefficients between critical REEs and four constituents of interest (Al, Mg, Mn, and Fe).

	Y	Nd	Eu	Tb	Dy
Al	0.6776	0.7692	0.6756	0.6715	0.6841
Mg	0.6845	0.6243	0.628	0.6606	0.6745
Mn	0.8391	0.8331	0.8281	0.8399	0.8452
Fe	0.0252	0.2283	0.1386	0.1093	0.1126

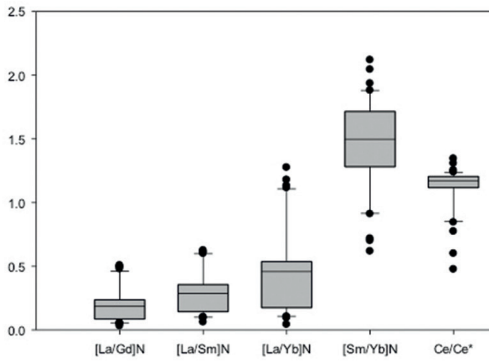


Figure 4 NASC-normalized patterns of the REE concentrations.

dissolution of Mn-bearing minerals led to an enrichment of associated Ce, which resulted in a positive Ce anomaly in the CMDs.

Speciation of REEs in CMD

Aqueous speciation of REEs in water plays an important role in the migration of REEs in CMD (Grawunder *et al.* 2015). Results from the speciation calculation are summarized in Figure 5. As demonstrated, $\text{Ln}(\text{SO}_4)^+$ is the most dominant species, except for Sc, Gd, and Ce. Free trivalent ion species are the primary forms for Sc, Ce, and Gd. Except for naturally occurring Ce^{4+} and Eu^{2+} , REE are usually trivalent. Both Eu^{2+} and Ce^{4+} are

negligible. $\text{Gd}(\text{SO}_4)^{2-}$ is more abundant than the mono-sulfate complex. The observation, in general, agrees with other studies (Zhao *et al.* 2007)

Conclusions

The concentrations of total REEs (ΣREEs) in the 29 CMDs discharging from abandoned coal mines and refuse piles in eastern Ohio varied significantly, ranging from 2212 to 5 $\mu\text{g/L}$. Y, Nd, and Ce are the most abundant REEs. Instead of pH, ΣREEs and critical REEs show better correlations with acidity. Based on results from the multivariate statistical analysis of the geochemical parameters, among the three acidity-related cations (i.e., Fe, Al, and Mn), Mn has the strongest correlation followed by Al. Mg also shows high correlation. The NASC-normalized REEs patterns suggest there is an obvious enrichment of MREEs than the LREEs and HREEs in the CMD. Calculation of REEs speciation demonstrates that sulfate complexes ($\text{Ln}(\text{SO}_4)^+$) are predominate species. However, for Ce and Gd, trivalent free ions are the major forms. Results obtained from this study provide the knowledge that will form the basis of a reactive transport model that can be used for REE retention and recovery.

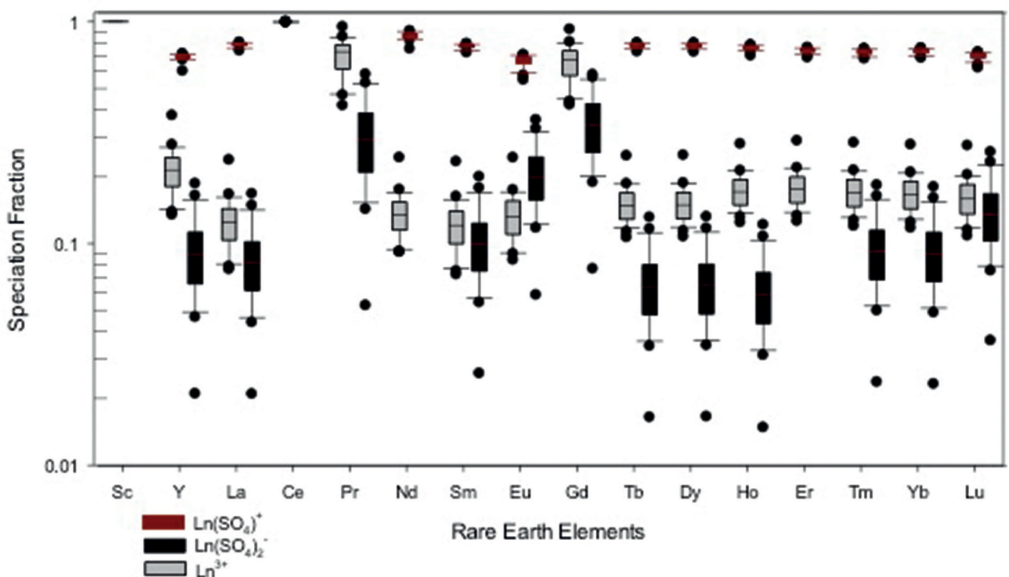


Figure 5 Speciation fractions of REEs in CMDs.

Acknowledgements

The authors thank the U.S. Department of Energy, Ohio Coal Development Office of the Ohio Development Service Agency, and The Ohio State University for funding support. We also thank the technical supports provided by Ohio Department of Natural Resources and National Energy Technology Laboratory.

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