Laboratory and Field Observations Inform Geochemical Models of Treatment Strategies to Recover Rare-Earth Elements from Acid Mine Drainage

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Extended Abstract

Discharges from coal mines that have low pH, hereinafter identified as acid mine drainage (AMD), commonly have elevated dissolved concentrations of sulfate (SO_4), transition metals (Fe > Mn > Zn > Ni > Co > Cu > Cr > Cd), other metals (Al > Pb > Ga > Tl > In), and the lanthanide rare-earth elements, yttrium, and scandium (REYs: Y > Ce > Sc > Nd > La > Gd > Dy > Sm > Pr > Er > Yb > Eu > Ho > Tb > Tm > Lu) (Cravotta, 2008a). The REYs and many of these associated metals are among more than 50 "critical minerals" that are in great demand for clean energy and other modern technologies and for which global supply chains are vulnerable to disruption (Schulz et al. 2017; Nassar et al. 2020). The REYs occur as trace cations having predominant 3+ oxidation state (Me^{3+}) in AMD and associated waters, with tendency to form aqueous and surface complexes (Verplanck et al. 2004; Pourret and Davranche, 2013; Liu et al. 2017; Lozano et al. 2019). Dissolved REYs concentrations in AMD generally decrease as the pH increases, especially at pH > 5, accumulating with Fe, Al, and Mn that precipitate as hydrous metal oxides (HMeO) (Verplanck et al. 2004; Cravotta, 2008a; Vass et al. 2019a, 2019b; Hedin et al. 2020, 2024) (Fig. 1). In contrast, the concentration of dissolved SO_4, the predominant anion in AMD, tends to remain elevated and largely uncomplexed across a wide range of pH, despite limited precipitation with Fe and Al hydroxysulfate compounds (e.g. jarosite, schwertmannite, basaluminite) (Cravotta, 2008a, 2008b; Nordstrom, 2020) and/or adsorption by hydrous Fe, Al, and/or Mn oxides (Dzombak and Morel, 1990; Yao and Millero, 1996; Karamalidis and Dzombak, 2010; Lozano et al. 2019).
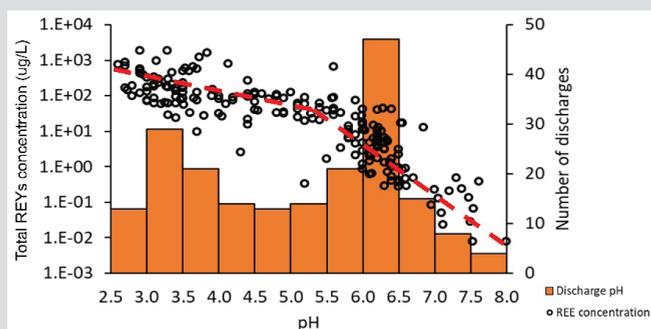
Figure 1 Rare-earth elements (REYs) are elevated in AMD from coal mines in Pennsylvania (adapted from Cravotta, 2008a; Hedin et al. 2020). Dissolved REYs concentrations decrease with increased pH, exhibiting a break in slope at pH ≈5. The REYs accumulate with Fe, Mn, and Al in AMD treatment solids

An economically sustainable approach for recovery of REYs and other associated critical minerals from AMD could offset treatment costs, depending on environmental and economic factors for extraction and transport (Fritz et al. 2021). Various AMD treatment strategies may be effective for concentrating REYs with AMD treatment solids through adsorption and/or precipitation with hydroxide, phosphate, or oxalate compounds (Ayora et al. 2016; Zhang and Honaker, 2018; Josso et al. 2018; Edahbi et al. 2018; Royer-Lavallée et al. 2020; Wang et al. 2021; Leon et al. 2021; Mwewa et al. 2022; Hermassi et al. 2022). Nevertheless, impurities such as Fe, Al, Mn, Ca, and Mg, which are major components in typical AMD treatment solids (Hedin et al. 2020, 2024; Wang et al. 2021), tend to dilute the concentrations of more valuable trace components, increasing costs for transportation and processing. If REYs could be concentrated after first removing Fe and Al, without addition or precipitation of Mg and Ca, subsequent REYs-bearing fluids or solid(s) may have greater value for REYs recovery.

This study employs version 1.0.3 of the PHREEQ-N-AMDTreat+REYs water-quality modeling tools (Cravotta, 2022), which were expanded from the original PHREEQ-N-AMDTreat tools (Cravotta, 2021) to simulate changes in the concentrations of REYs, Fe, Al, Mn, SO_4, and other solutes plus the formation of solids containing REYs. The models simulate the evolution of AMD in response to treatment, considering the composition and availability of HMeO sorbent and the potential for REYs compounds and other solids to precipitate. The models utilize the wateq4fREYsKinetics.dat database, which was expanded from wateq4f.dat (Ball and Nordstrom, 1991) provided with PHREEQC (Parkhurst and Appelo, 2013) to include thermodynamics data on REYs aqueous and surface species plus relevant REYs solid phases (hydroxide, carbonate, phosphate, and oxalate compounds). Surface species for REYs plus other cations and anions were added for hydrous ferric oxide (HFO: Dzombak and Morel, 1990), hydrous aluminum oxide (HAO: Karamalidis and Dzombak, 2010; Lozano et al. 2019), and hydrous manganese oxide (HMO: Tonkin et al. 2004; Pourret and Davranche, 2013), which constitute the total HMeO sorbent mass.

To investigate potential effects of sorbent composition, pH, and SO_4, a series of titration experiments was recently conducted in the laboratory during summer 2022. Each experiment used a solution with starting pH less than 2 that contained 50 μg/L of each of the 16 REYs plus 1 mmol/L of sorbent metal (Fe, Al, or Mn). To evaluate if REYs attenuation resulted by co-precipitation with Fe, Al, or Mn versus adsorption by HFO, HAO, or HMO, replicate experiments were conducted in parallel using the same REYs concentrations with initially aqueous (Fe^{3+}, Al^{3+}, or Mn^{3+}) or solid (HFO, HAO, or HMO) forms. A hydrochloric acid (HCl) solution matrix was used for the first set of experiments, whereas a sulfuric acid (H_2SO_4) solution was used for the other sets of experiments. For all experiments, the pH was increased to pH values ranging from about 3 to 10 by titration with sodium hydroxide (NaOH). The dissolved concentrations of REYs and major metals were measured after 24 hours reaction time, centrifuging, and filtration (0.45-μm).

To model the empirical titration results, new adsorption reactions and equilibrium constants were estimated using PEST version 17.5 (Doherty, 2015) in combination with PHREEQC (Parkhurst and Appelo, 2013). Instead of using estimates from linear free energy relations (LFER) for divalent cations, we (1) adapted the adsorption expression for Cr^{3+}, the only trivalent cation reported by Dzombak and Morel (1990) (eq. 5), and also (2) determined new equilibrium constants for reactions where the uncomplexed cation is bound by adsorbed SO_4 (eq. 7) (Table 1).

Speciation models using PHREEQC with the new adsorption expressions (eqs. 5 and 7) accurately describe the observed adsorption of REYs to HFO (Fig. 2, bottom graphs). In contrast, modeled adsorption using equilibrium constants estimated by LFER (eq. 4)

Table 1 Aqueous and surface speciation reactions considered in PHREEQ-N-AMDTreat+REYs models

Aqueous speciation reactions (Me^{+n} is divalent (n=2) or trivalent (n=3) cation):		
$Me^{+n} + H_2O = MeOH^{(n-1)} + H^+$	$LogK_{OH}$ $MeOH_1$	(eq. 1)
$Me^{+n} + SO_4^{-2} = Me(SO_4)^{(n-2)}$	$LogK_S$ $MeSO_4$	(eq. 2)
Surface speciation reactions (SURF is HFO, HAO, or HMO):		
$SURF\_OH + SO_4^{-2} = SURF\_OHSO_4^{-2} + H^+$	$Log\ K_1$ $SURF\_OHSO_4^{-2}$	(eq. 3)
$SURF\_OH + Me^{+n} = SURF\_OMe^{(n-1)} + H^+$ (LFER)	$Log\ K_2$ $SURF\_OMe^{(n-1)}$	(eq. 4)
$SURF\_OH + Me^{+n} + H_2O = SURF\_OMeOH^{(n-2)} + 2H^+$	$Log\ K_3$ $SURF\_OHMe^{(n-2)}$	(eq. 5)
$SURF\_OH + Me(SO_4)^{(n-2)} = SURF\_OMe(SO_4)^{(n-3)} + H^+$	$Log\ K_4$ $SURF\_OMe(SO_4)^{(n-3)}$	(eq. 6)
$SURF\_OHSO_4^{-2} + Me^{+n} = SURF\_OMe(SO_4)^{(n-3)} + H^+$	$Log\ K_5$ $SURF\_OMe(SO_4)^{(n-3)}$	(eq. 7)

Note that equation 4 is widely applied for divalent cations and to estimate adsorption equilibrium constants given the first hydrolysis constant (eq. 1) and linear free energy relation (LFER) expressions. Also, note that equation 7 is derived by subtracting equation 3 from the sum of equations 2 and 6 ($Log\ K_5 = Log\ K_4 + Log\ K_S – Log\ K_1$)
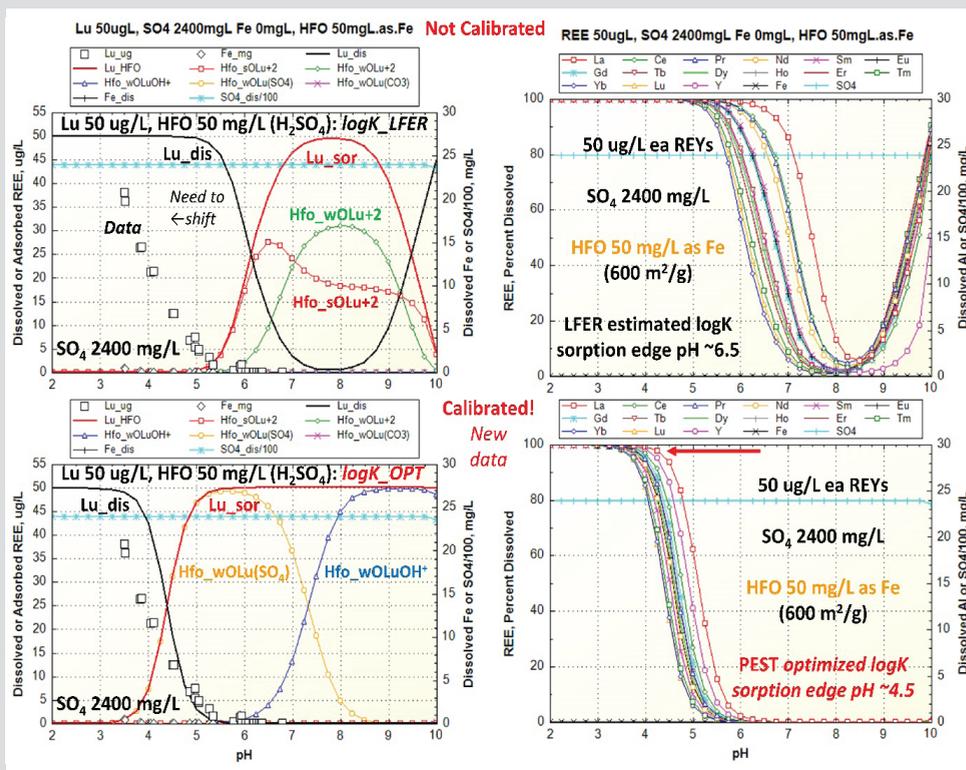

Figure 2 Model calibration to empirical data. Graphs on the left show lutetium attenuation by HFO slurry in sulfuric acid matrix. The top graph shows poor fit of the initial model based on LFER estimated log K values (eq. 3); the lower graph shows results using the "best-fit" adsorption log K values derived using PEST and new equilibrium expressions for trivalent cations that consider effects of pH and SO_4 (eqs. 5, 6, 7). On the right, model curves are shown for all 16 REYs. The upper graph shows initial results using LFER estimates. The lower graph shows results using the new optimized log K values. The empirical data and model results indicate effective pH of adsorption shifted by 2 pH units from approximately 6.5 (LFER) to 4.5 (optimized)

greatly underestimated the observed attenuation of REYs at pH <6, especially in the presence of SO_4 (Fig. 2, top graphs). The new model results are consistent with prior reports for AMD systems where ternary complexes with SO_4 resulted in enhanced adsorption of various divalent cations (Me^{2+}: Cd, Cu, Co, Pb, Ni, Zn) by HFO (Swedlund and Webster, 2001; Swedlund et al. 2003) and trivalent REYs (Me^{3+}) by HAO (Lozano et al. 2019). Therefore, version 1.0.3 of PHREEQ-N-AMDTreat+REYs (Cravotta, 2022) includes the new equilibrium reactions for adsorption of Me^{2+} and Me^{3+} by HFO, HAO, and HMO plus interactions of those cations as with adsorbed SO_4 ($HFO\_SO_4^{-2}$ and $HFO\_SO_4^{-2}$).

Potential treatment strategies that could feasibly produce a concentrated REYs extract from AMD are evaluated using PHREEQ-N-AMDTreat+REYs models. For a passive treatment case, Hedin et al. (2024) reported REYs accumulated in limestone beds can be accurately simulated using the "CausticTitrationMix2.exe" tool, which indicated attenuation of REYs mainly with HAO and HMO. For an active treatment case, a coal-refuse facility with highly acidic leachate having elevated concentrations of Fe, Al, Mn, and REYs currently utilizes lime neutralization, which causes precipitation of Fe, Al, and REYs into complex Fe-Al-Ca rich sludge mixture. The current treatment and two alternative strategies that could concentrate REYs were simulated with the "TreatTrainMix2REYs.exe" tool (Fig. 3). The lime treatment to pH ≈8.7 removes REYs with the sludge mixture. In contrast, alternative strategies using H_2O_2 to oxidize Fe^{II} demonstrate potential for removal of most Fe and Al without substantial removal of REYs. In one case, NaOH is added to initial pH 3 followed by aeration to precipitate Fe and Al oxyhydroxides at pH <4.5. Subsequent aeration and further increasing pH with limestone promotes adsorption of REYs by HAO and HMO that form thereafter. In another case, NaOH and NaH_2PO_4 are added to precipitate REY-PO_4 after H_2O_2 addition (e.g. Hermassi et al. 2022). In both cases, REYs-enriched solids produced by the alternative treatments contain a small fraction of the initial Fe and Al and most of the REYs. Bench-scale testing of the simulated, sequential treatment steps to concentrate REYs into solids may be considered, guided by modeling, to verify results and evaluate extraction methods to re-mobilize the REYs from the various solid components (e.g. Rushworth et al. 2023; Boothe et al. 2024).
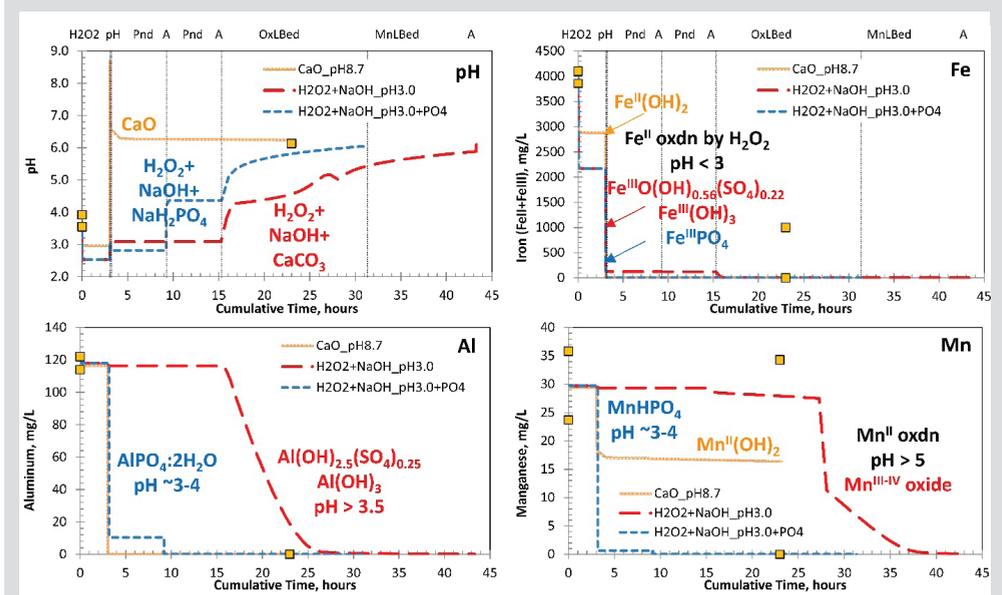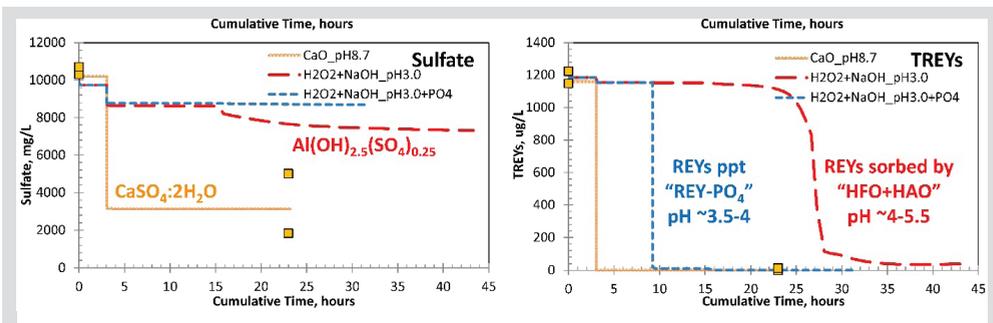
Figure 2 Comparison of measured (symbols) and PHREEQ-N-AMDTreat+REYs simulation results (curves) for pH and dissolved Fe, Al, Mn, SO₄, and total REYs concentrations at a coal-refuse disposal facility. Measured values are for lime treatment without H_2O_2, sampled on two different dates

By combining the PHREEQ-N-AMDTreat+REYs water-quality modeling tools with the AMDTreat 6.0 cost-analysis model (Office of Surface Mining Reclamation and Enforcement, 2022), a user may (1) identify and evaluate strategies for AMD treatment that result in effective REYs recovery and (2) estimate costs for installation and operation of relevant treatment steps.

Keywords: Resource recovery, rare-earth elements, adsorption, aqueous speciation, PHREEQC, AMDTreat

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