Water-Quality Modeling Tools to Evaluate Attenuation of Dissolved Constituents by Precipitation and Adsorption Reactions During Treatment of Acid Mine Drainage

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Abstract

An understanding of geochemical reactions and environmental factors that control water quality is required for management and mitigation of environmental effects from acid mine drainage (AMD). This paper describes water-quality modeling tools that were developed to aid in the evaluation of key hydrogeochemical processes and their relative importance in controlling concentrations of dissolved metals and associated constituents in AMD and the effluents from treatment systems.

Keywords: Critical minerals, rare earth elements, equilibrium, kinetics, speciation, AMDTreat, PHREEQC

Introduction

Knowledge of the interactive processes that account for variations in pH and attenuation of dissolved metals is essential for the prediction of aquatic toxicological effects (e.g. Smith and Huyck, 1999) and the identification of strategies for treatment of acid mine drainage (AMD) to minimize impacts and control costs (e.g. Cravotta et al., 2015; Cravotta, 2021). To address aquatic toxicity concerns from excessive concentrations of metals, treatment of AMD is widely practiced to increase pH (> 6) and remove Fe (< 7 mg/L), Al (<1.5 mg/L), Mn (< 5 mg/L) and associated trace elements before discharging the effluent to receiving water bodies (e.g. Cravotta and Brady, 2015; Skousen et al., 2019; Nordstrom, 2020). Untreated, net-acidic AMD having pH < 5 frequently has elevated concentrations of rare-earth elements, yttrium, and scandium (REYs) plus various other trace elements, including cobalt (Co), copper (Cu), chromium (Cr), nickel (Ni), and zinc (Zn) that generally decrease as pH is increased through typical AMD treatment steps (Cravotta, 2008b; Cravotta and Brady, 2015; Vass et al., 2019a, 2019b; Hedin et al., 2020). The REYs and trace metals tend to be attenuated by adsorption to hydrous ferric oxides (HFO), hydrous aluminum oxides (HAO), and/or hydrous manganese (III–IV) oxides (HMO) that precipitate as the AMD is neutralized, forming AMD treatment solids (Smith et al., 1999; Cravotta, 2008b; Pourret and Davranche, 2013; Ayora et al., 2016; Cravotta et al., 2024; Hedin et al., 2024).

The REYs, Co, Cu, Cr, Ni, and Zn are among more than 50 “critical minerals” that are essential for modern industrial, transportation, energy, and electronics products and for which global supplies are vulnerable to disruption (Schulz et al., 2017; Nassar et al., 2020; White et al., 2024). Recovery of major metals plus REYs and other potentially valuable constituents from AMD could offset some treatment costs while addressing domestic supply concerns (Fritz et al., 2021). Nevertheless, the determination of optimal conditions for economic recovery of valuable trace components tends to be complicated because major components in typical AMD solutions and associated treatment solids tend to interact with and dilute the concentrations of more valuable trace components, particularly REYs. Although adsorption is the primary mechanism for REYs attenuation in passive systems and freshwater environments (Ayora et al., 2016; Hedin et al., 2024), precipitation of REYs with hydroxide, phosphate, carbonate, or oxalate compounds may also be feasible, especially through active chemical treatment (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).

Methods

This study employs the interactive PHREEQ-N-AMDTreat (v.1.4.5) and PHREEQ-N-AMDTreat+REYs (v.1.0.5) water-quality modeling tool sets (Cravotta, 2021, 2022) that use PHREEQC (Parkhurst and Appelo, 2013) with a customized thermodynamic database including new adsorption constants (Tasker et al., 2025). These models simulate changes in pH, dissolved metals, and associated solutes resulting from passive and active treatment of AMD. In addition to Fe, Al, Mn, and major elements, the PHREEQ-N-AMDTreat+REYs tools consider various trace elements and REYs. Each tool set consists of a caustic titration model and a sequential reaction model. Stand-alone models are available from the U.S. Geological Survey (Cravotta, 2020, 2022), and modified versions will be accessible as "new" tools through radio buttons in the final version of the AMDTreat 6.0 cost-analysis model, now available as a beta release (Office of Surface Mining Reclamation and Enforcement, 2022).

A user interface (UI), which automatically displays a default dataset, facilitates the input of user-defined water-chemistry and flow data for one or two solutions and the adjustment of important system variables, such as reaction rates, mineral solubility, and sorbent characteristics. Adsorption of cations and anions is computed for freshly precipitated HFO, HAO, and HMO having specified surface area, plus previously accumulated sorbent that has known mass of HFO, HAO, and HMO components. Fresh HFO is formed by precipitation of schwertmannite and $Fe(OH)_3$, HAO by hydrobasaluminite and $Al(OH)_3$, and HMO by manganite and $Mn(OH)_2$, at a selected saturation index.

The CausticTitration and CausticTitrationMix2REYs tools compute the equilibrium concentrations of elements among dissolved, precipitated, and sorbed fractions as a function of pH and other solution characteristics. The pH is automatically increased by 0.25-unit intervals from the initial pH to a maximum pH of 11 by the incremental addition of an acid-neutralizing agent (NaOH, $Ca(OH)_2$, CaO, Na_2CO_3, or $CaCO_3$). For both tools, the amount of caustic reacted to achieve the target pH is included in the output with other information such as the concentrations of elements in solution and solids. Graphical and tabular output for each of the water-quality tools indicates the pH, specific conductance, total dissolved solids, alkalinity, net acidity, metals, and other solute concentrations of treated effluent plus the mass and generalized composition of precipitated solids as a function of retention time and/or the amount of caustic (or oxidizing) agent added.

The TreatTrainMix2 and TreatTrainMix2REYs tools incorporate equilibrium aqueous and surface speciation *plus kinetics models* for gas exchange, iron and manganese oxidation and precipitation, limestone dissolution, and organic carbon oxidation combined with reduction of nitrate, sulfate, and ferric iron. Reactions with caustic chemicals or hydrogen peroxide (H_2O_2) coupled with aeration may be simulated separately or combined with additional kinetic steps. Sludge recirculation or reactive coatings on limestone surfaces are modeled by indicating a mass of previously accumulated sorbent.

Results

Equilibrium models using the "CausticTitrationMix2REYs.exe" tool accurately indicated the observed attenuation of REYs over pH ~4.5 to 6 for AMD containing SO_4 (820 mg/L), Fe (103 mg/L), Al (9.5 mg/L), Mn (2.9 mg/L), and individual REE of 58.9 ± 10.3 mg/L titrated with NaOH (Fig. 1). Because of presumed "instantaneous" oxidation, however, the equilibrium model did not accurately simulate observed Fe and Mn concentrations. To better account for redox disequilibrium, a kinetic model was applied to simulate gradual oxidation of FeII and MnII over the 24-hour reaction period. The kinetic model yielded reasonable agreement with observed results for Fe and Mn, but with relatively unchanged results for REYs. In this particular example, almost all the REYs adsorption could be accounted for solely by the precipitation of the initial 3 mg/L Fe^{III} that formed HFO at pH <4, with less than 2% of sorption by more abundant HAO. All the REYs had been attenuated before Mn oxidation and hydrolysis, so none were attenuated by HMO.

Highly acidic leachate (10,500 mg/L as $CaCO_3$) with elevated concentrations of Fe, Al, Mn, and REYs discharged at a coal-refuse facility was considered as a test case to evaluate treatment strategies that could produce a concentrated REYs extract. This facility currently utilizes lime neutralization, which causes precipitation of Fe, Al, and REYs into complex Fe-Al-Ca rich sludge mixture. The lime treatment and two hypothetical strategies that could feasibly concentrate REYs were simulated with the "TreatTrainMix2REYs.exe" tool (Fig. 2). The lime treatment to pH ~8.7 rapidly 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 initial removal of REYs. In one case, NaOH is added to attain pH 3 followed by aeration to precipitate Fe and Al oxyhydroxides while maintaining 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 were 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. Using these results as guidance, bench-scale testing of the modeled treatment steps to concentrate REYs into solids may be considered to test the results and optimize extraction of the REYs from the various solid components (e.g. Rushworth et al., 2023; Boothe et al., 2024).

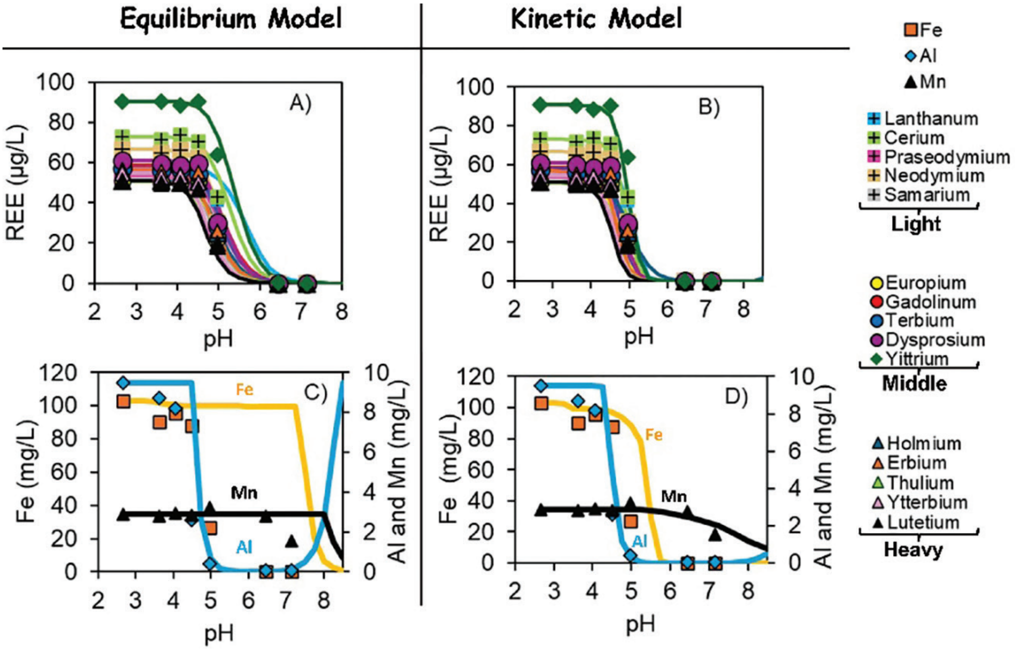

Figure 1 *Comparison of measured (symbols) and PHREEQ-N-AMDTreat+REYs simulation results (curves) for pH and concentrations of dissolved Fe, Al, Mn, and REYs in AMD from the Hughes Borehole (after Tasker et al., 2025). Oxidation of FeII and MnII is instantaneous for the equilibrium model but varies with pH for kinetic model.*

Considering the design flow with the modeled reaction time estimates for each of the treatment system components in the TreatTrainMix2 or TreatTrainMix2REYs model, the size (land area, pond volume, limestone bed volume, etc.) of a treatment component can be estimated (Cravotta, 2021). Now, a user may use these reaction times in the AMDTreat 6.0 cost-analysis model (Office of Surface Mining Reclamation and Enforcement, 2022) to readily (1) estimate the sizing and quantities of reactive materials for specific treatment steps; (2) compute the land-area and costs for installation and operation of relevant components; and (3) evaluate the cost-effectiveness of alternatives for AMD treatment that could meet effluent discharge limits and also result in effective recovery of Fe, Al, Mn, and various critical minerals.

Conclusions

Water-quality modeling tools are now freely available to aid in the evaluation of key hydrogeochemical processes and their relative importance for controlling concentrations of dissolved metals and associated constituents in AMD through sequential steps in treatment systems. By adjusting the modeled chemical dosing or kinetic variables, such as aeration rate and duration, the effects of independent and sequential treatment steps that have different retention times or quantities of reactive solids, such as limestone or sorbing substrates, can be simulated. The reaction

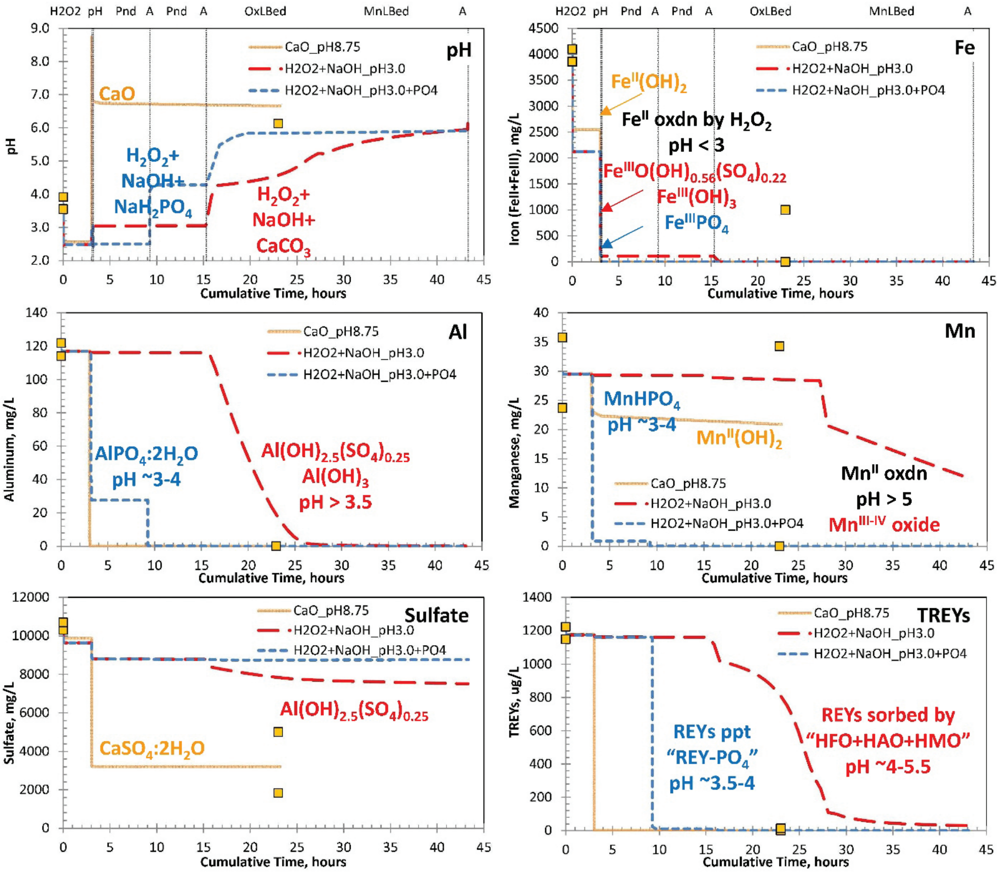

Figure 2 Comparison of measured (symbols) and PHREEQ-N-AMDTreat+REYs simulation results (curves) for pH and dissolved Fe, Al, Mn, SO4, and total REYs concentrations at a coal-refuse disposal facility. Measured values are for lime treatment without H2O2, sampled on two different dates (adapted from Cravotta et al., 2024).

times considered for the kinetics models correspond to retention times for the modeled treatment steps. The retention times can be used with known or anticipated AMD flow rates to estimate the dimensions of the system components, such as a limestone bed or pond, the quantities of reactive materials consumed or sludge generated, and corresponding installation and operation costs for individual components and the overall treatment system.

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