

“PHREEQ-N-AMDTreat+REYs” Water-Quality Modeling Tools to Evaluate Acid Mine Drainage Treatment Strategies for Recovery of Rare-Earth Elements

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Hello. My name is Chuck Cravotta. I am a research hydrologist at the U.S. Geological Survey Pennsylvania Water Science Center. Today, I am going to introduce new software that I developed: “PHREEQ-N-AMDTreat+REYs” Water-Quality Modeling Tools to Evaluate Acid Mine Drainage Treatment Strategies for Recovery of Rare-Earth Elements.

Many studies have identified elevated concentrations of rare-earth elements plus yttrium (REYs) in acid mine drainage (AMD) and in solids formed in the treatment of these waters. Routine treatment methods plus additional steps may be applicable for the efficient recovery of REYs, depending on the AMD composition, volume, location, and economic considerations. The PHREEQ-N-AMDTreat+REYs geochemical modeling tools have the fundamental capability to simulate and predict key reactions during the routine treatment of AMD and the formation of treatment solids, including the precipitation of REYs compounds and the adsorption of REYs onto hydrous Fe, Al, and Mn oxides. The new tools were expanded from the PHREEQ-N-AMDTreat tools to include trace-element attenuation. Additions include a caustic titration model that indicates equilibrium surface and aqueous speciation of REYs as functions of pH and caustic agents, and a sequential kinetics+adsorption model that simulates progressive changes in pH, major ions, and REYs in water and solids during passive and/or active treatment. A goal of such modeling is to identify strategies that could produce a concentrated REYs extract from AMD or mine waste leachate that could be highly valuable. For example, if REYs could be concentrated after first removing substantial Fe and Al, the final REYs-bearing phase(s) could be more efficiently processed for REYs recovery and, therefore, may represent a more valuable commodity. Preliminary modeling supports the hypothesis that Fe and Al can be removed at pH >5.5 using conventional sequential oxidation and neutralization treatment processes without removing REYs, and that further increasing pH can promote the adsorption of REYs by hydrous Mn oxides. Alternatively, chemicals such as oxalate or phosphate may be added to precipitate REYs compounds following steps to decrease Fe and Al concentrations. Field and lab studies may be helpful to demonstrate REYs attenuation from AMD during specific treatment steps and to corroborate, refine, and constrain modeling parameters.

“AMDTreat 6.0”

AMDTreat 6.0 (2022) is a newly updated computer application for estimating costs and sizing of facilities to abate AMD (acidic or alkaline mine drainage) that is maintained by the Office of Surface Mining Reclamation and Enforcement (OSMRE).

The PHREEQ-N-AMDTreat water-quality modeling tool, developed by the USGS with support from OSMRE, was recently incorporated with AMDTreat 6.0 (beta version shown here).

<https://www.osmre.gov/programs/reclaiming-abandoned-mine-lands/amdtreat>

Module	Capital Cost	Annual Cost	Net Present Value
Ponds	\$36,018.22	\$0.00	\$39,357.70
Vertical Flow Pond	\$619,390.98	\$12,587.82	\$1,114,016.18
Vertical Flow Pond	\$619,390.98	\$12,587.82	\$1,114,016.18
Vertical Flow Pond	\$619,390.98	\$12,587.82	\$1,114,016.18
Decarbonation	\$58,873.72	\$12,954.71	\$392,131.45
Ponds	\$15,907.11	\$348,465.03	\$10,792,229.54
Conveyance Ditch	\$6,337.58	\$221.82	\$13,776.04
Wetland	\$144,792.10	\$7,235.11	\$12,537.81
Conveyance Ditch	\$6,337.58	\$221.82	\$13,776.04
Manganese Removal Bed	\$19,633.69	\$392.77	\$25,291.79
Conveyance Ditch	\$11,651.36	\$44.60	\$24,992.36

AMD Treat 6.0 Beta | Total Capital Cost: \$2,225,164.14 | Total Annual Cost: \$400,635.85 | Total Net Present Value Cost: \$15,119,649.19 | Project Footprint in Acres: 14.28

AMDTreat 6.0 (2022) is a newly updated computer application for estimating costs and sizing of facilities to abate AMD (acidic or alkaline mine drainage) that is maintained by the Office of Surface Mining Reclamation and Enforcement (OSMRE).

The PHREEQ-N-AMDTreat water-quality modeling tool, developed by the USGS with support from OSMRE, was recently incorporated with the newly recoded AMDTreat 6.0 (beta version shown here).

“PHREEQ-N-AMDTreat”

- ❖ Kinetics models simulate effects on water quality by treatment system components/size; used for costs/benefits analysis.
- ✓ CO₂ outgassing and O₂ ingassing;
- ✓ Iron and manganese oxidation;
- ✓ Limestone dissolution;
- ✓ Oxidation of organic carbon coupled with reduction of Fe^{III}, sulfate, and nitrate.
- ✓ Active treatment with H₂O₂ and/or caustic chemicals.
- ✓ Mass and composition of solids formed, including Fe, Mn, and Al adsorbed by hydrous metal oxides (HMeO = HFO + HMO + HAO).
- ❖ A newly expanded stand-alone model includes REYs attenuation by precipitation and by adsorption.

Annual Cost: \$400,635.65 Total Net Present Value Cost: \$15,119,649.19 Project Footprint in Acres: 14.28

The embedded PHREEQ-N-AMDTreat tool and the stand-alone TreatTrainMix2 tool reported by Cravotta (2020, 2021) simulate effects on water quality by various treatment components, involving different technologies and retention times. The model results may be used to optimize treatment system configuration or size and, also, for costs/benefits analysis.

Kinetics processes such as CO₂ outgassing and O₂ ingassing, FeII and MnII oxidation, limestone dissolution, and oxidation of organic matter are simulated, all of which may affect the pH and equilibrium speciation.

Active treatment with hydrogen peroxide and caustic chemicals also may be simulated. The potential for formation of solids from dissolved constituents and the corresponding mass of solids is computed, including amounts of Fe, Mn, and Al adsorbed by hydrous metal oxides (HMeO = HFO + HMO + HAO).

A newly expanded stand-alone model includes rare-earth elements attenuation by adsorption and precipitation.

Element Groups (Families)

Alkali Earth Metals	Alkaline Earth Metals	Transition Metals
Rare Earth Metals	Other Metals	Metalloids
Non-Metals	Halogens	Noble Gases

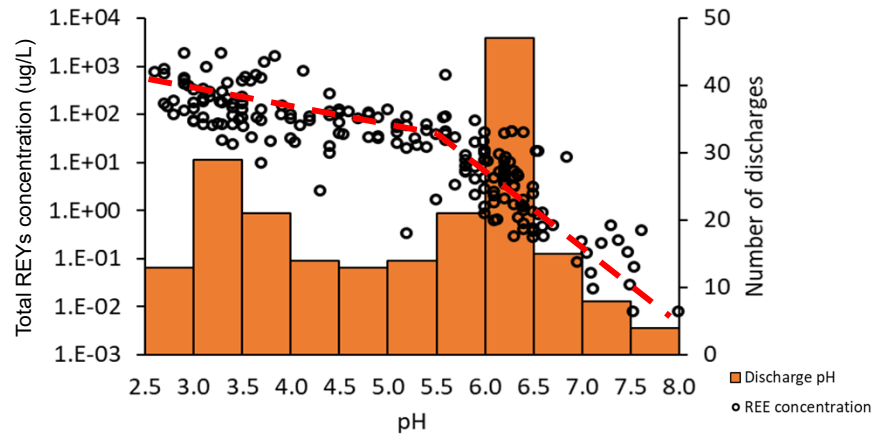
	I A	II A	III A	IV A	V A	VI A	VII A	VIII A	VIII A	VIII A	I B	II B	III B	IV B	V B	VI B	VII B	VIII
1	1 H																	
2														6 C	7 N	8 O	9 F	
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl
4	19 K	20 Ca	21 Sc						24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn		33 As	34 Se
5		38 Sr	39 Y											48 Cd				
6		56 Ba	*													82 Pb		
7			**															
	Lanthanide Rare Earth Elements (REE)	*	57 La	58 Ce	59 Pr	60 Nd		62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			**															

Elements included in the
 PHREEQ-N-AMDTreat+REYs models
 are shown here in their respective positions
 on the periodic table:

 REYs = Lanthanide rare-earth
 elements (REE) plus yttrium
 and scandium

The elements included in the PHREEQ-N-AMDTreat+REYs models are shown here in their respective positions on the periodic table. The lanthanide rare-earth elements plus yttrium and scandium are referred to as “REYs”. REYs are in great demand for clean energy and other modern technologies.

Rare-earth elements are elevated in low-pH AMD from coal mines in Pennsylvania

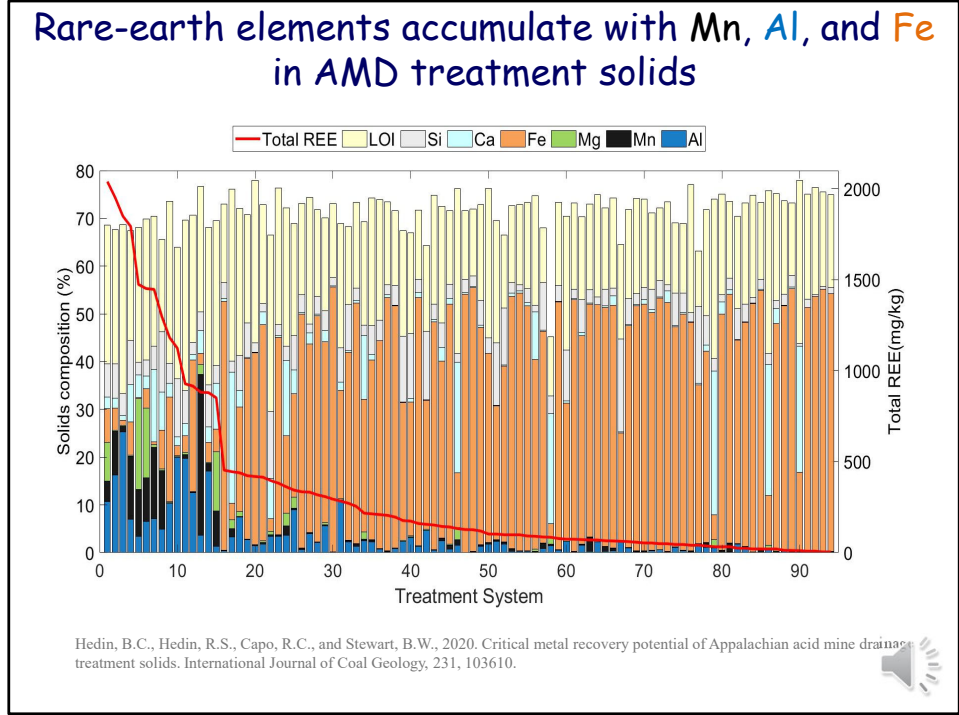


The PHREEQ-N-AMDTreat+REYs water-quality modeling tool set emphasizes adsorption of trace elements by hydrous metal oxides

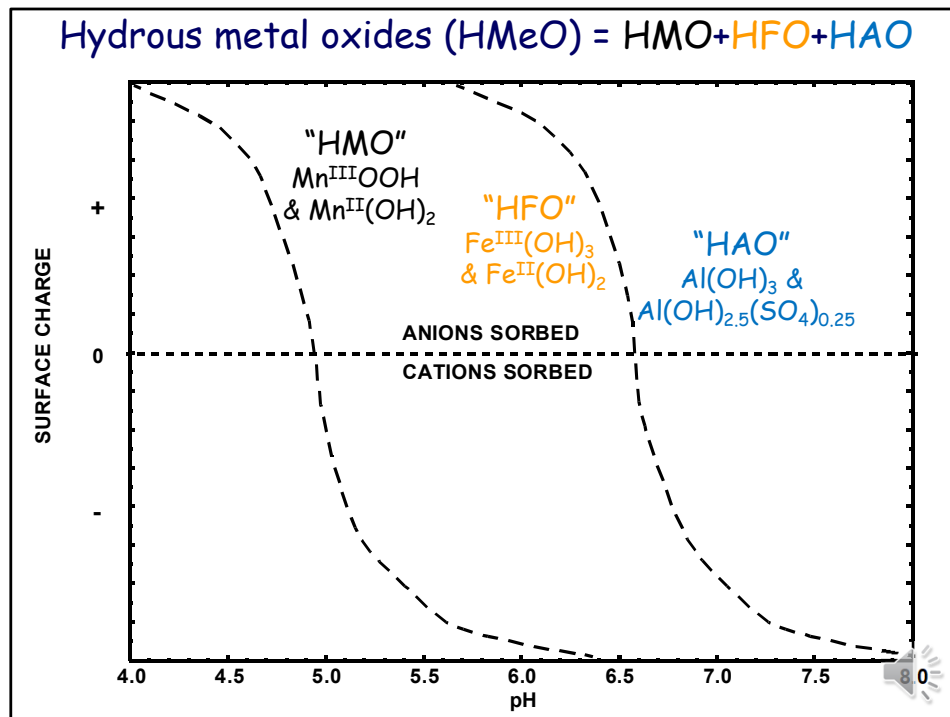
Cravotta, C.A. III (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA: 1. Constituent concentrations and correlations: Applied Geochemistry, 23, 166-202.



The pH of coal-mine drainage in Pennsylvania has a bimodal frequency distribution. Roughly half of the discharges have pH less than 5.5. Dissolved concentrations of rare-earth elements and other trace metals generally decrease with increased pH, with a break in slope at pH 5.5. Cravotta (2008) showed that trace-element minerals tend to be undersaturated in AMD and suggested adsorption as the primary mechanism to explain the relations among trace elements and pH. Thus, the PHREEQ-N-AMDTreat+REYs tool set, which consists of the TreatTrainMix2REYS and CausticTitrationMix2REYs models, emphasizes the adsorption of REYs and other trace elements by hydrous metal oxides.



Rare-earth elements accumulate with manganese, aluminum, and iron that precipitate with other major elements in AMD treatment solids. The highest rare-earth element concentrations generally occur in solids with mixed compositions where manganese and aluminum are abundant. Such solids are typically produced by treatment of low-pH AMD. Solids dominated by iron can be produced by treatment of net-alkaline, near-neutral pH AMD that has relatively low dissolved concentrations of the rare earths to begin with.

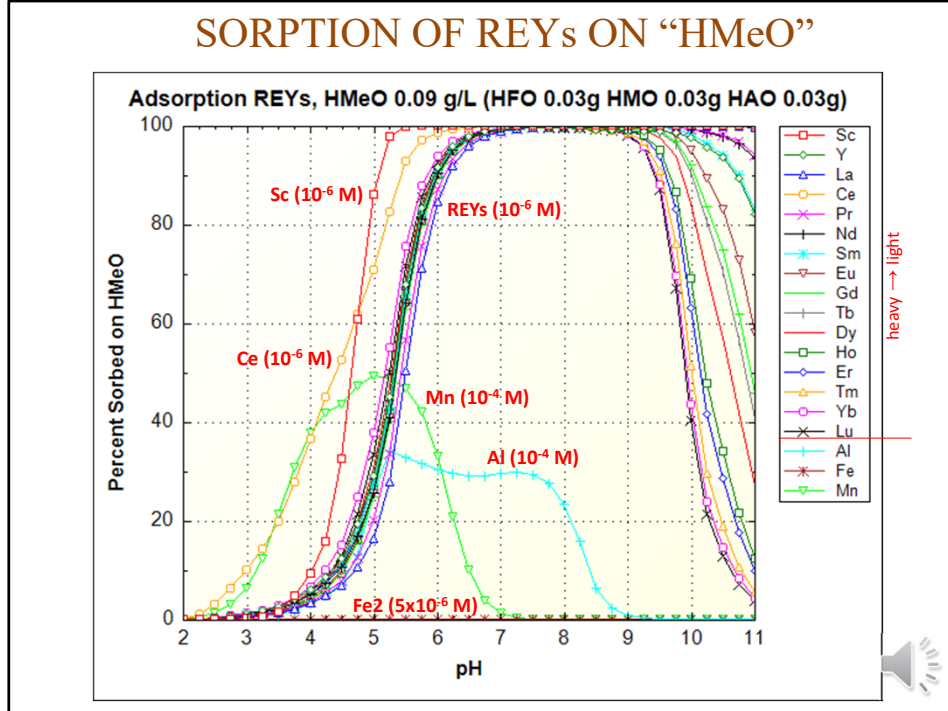


At low pH, hydrous metal oxides tend to have positively charged surfaces that adsorb anions. As pH increases past the “zero point of charge”, the surfaces become negatively charged and then adsorb cations.

In the PHREEQ-N-AMDTreat model, more than one compound may precipitate to form fresh sorbent: HMO consists of oxidized and reduced manganese hydroxide; HFO consists of oxidized and reduced iron hydroxide; and HAO consists of aluminum hydroxide and basaluminite.

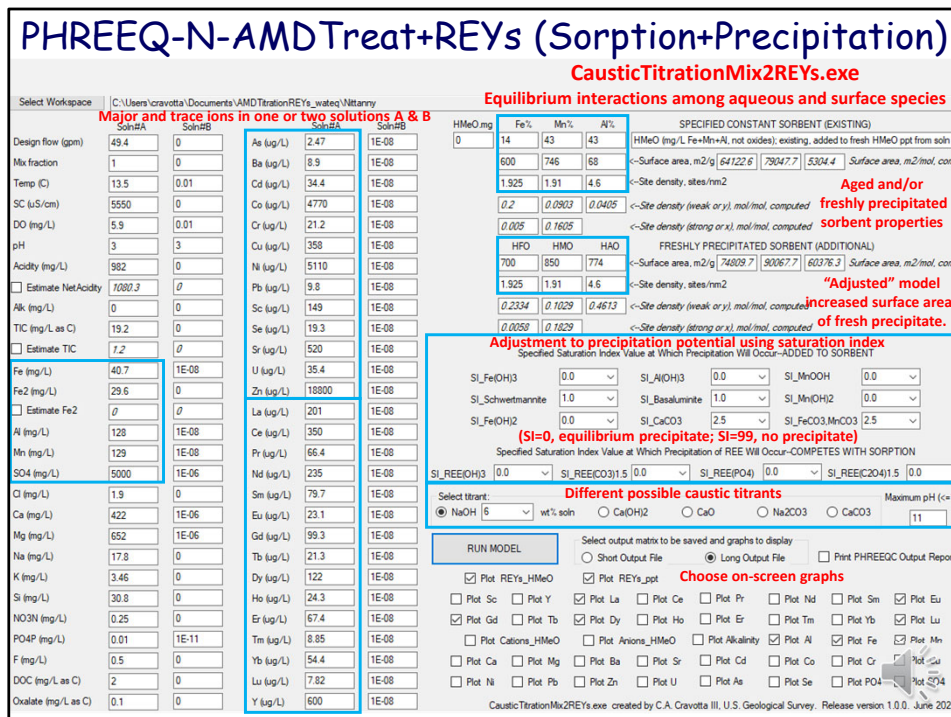
In the PHREEQ-N-AMDTreat model, more than one compound may precipitate to form fresh sorbent: HMO consists of MnOOH (manganite) and $\text{Mn}(\text{OH})_2$ (pyrochroite); HFO consists of $\text{Fe}(\text{OH})_3$ (ferrihydrite) and $\text{Fe}(\text{OH})_2$; and HAO consists of $\text{Al}(\text{OH})_3$ and basaluminite.

SORPTION OF REYs ON "HMeO"



This slide shows an example simulation of the adsorption of REYs (10^{-6} M each) as a function of pH, given a specified total mass of HMeO consisting of 0.03 g each of HFO, HMO, and HAO. The area below curve indicates the fraction that is adsorbed. Except for Sc and Ce, individual REYs have similar sorption behavior, with a majority sorbed by about pH 5.5, consistent with field observations.

Simulations were conducted using the CausticTitrationMix2REYsMoles.exe tool.

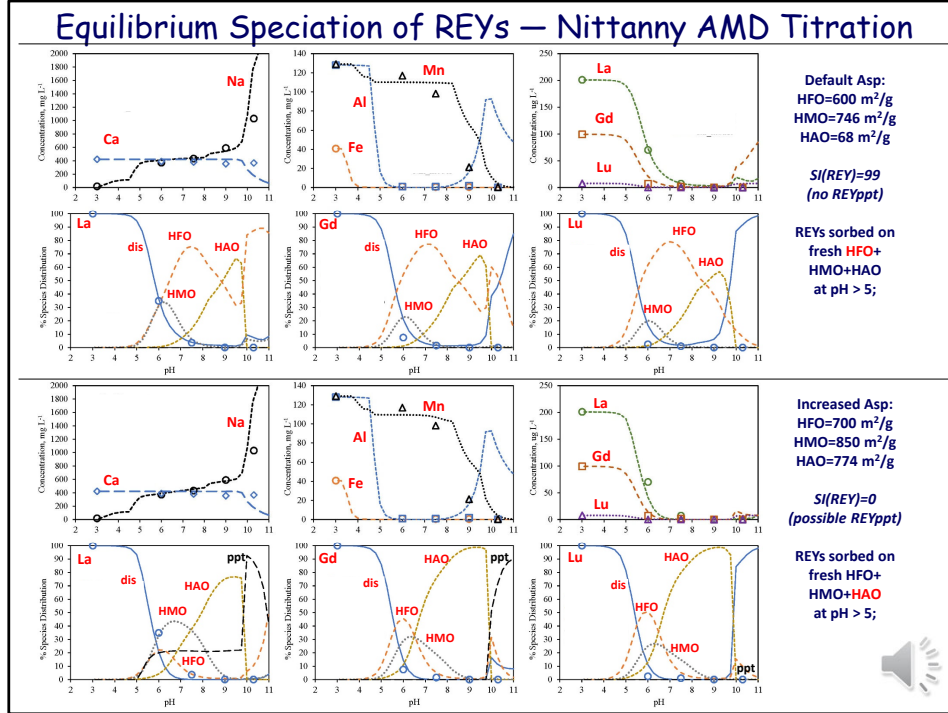


This slide shows the user interface (UI) for the “CausticTitrationMix2REYs” tool. Redox and speciation reactions are modeled as instantaneous, equilibrium processes in response to changes in pH and sorbent availability. The model simulates the addition of a selected caustic agent (NaOH, Ca(OH)₂, CaO, Na₂CO₃, or CaCO₃) and the consequent attenuation of REYs, Fe, Mn, Al, and other elements by precipitation as solid compounds *and* by adsorption to hydrous metal oxide (HFO, HMO, and HAO).

The hydrous metal oxide sorbent can be a combination of fresh precipitate that forms during titration plus specified pre-existing solids. The freshly precipitated and existing sorbent can have different surface properties.

This particular image shows input values for untreated AMD at the Nittanny mine, which had low pH (3.0) with elevated concentrations of major and trace elements. The Nittanny AMD was titrated in the field with NaOH to pH 6.0, 7.5, 9.0, and 10.3. Measured concentrations of dissolved Fe, Al, Mn, and REYs decreased with increased pH.

Mg (652 mg L⁻¹), Ca (422 mg L⁻¹), Al (128 mg L⁻¹), Mn (129 mg L⁻¹), Fe (40.7 mg L⁻¹), and REYs (2.0 mg L⁻¹). Corresponding precipitated solids and sorbent properties were not characterized.



This slide shows graphs for the simulation results of the Nittanny AMD titration with NaOH, shown as curves, compared to measured values, shown as point symbols. Measurement errors are roughly the size of symbols.

The upper set of six graphs indicates results for default values of the specific surface area (Asp) of the “fresh” HFO, HMO, and HAO; REYs minerals were not allowed to precipitate. Decreases in the concentrations of Fe, Al, and Mn correspond to their precipitation as HFO, HAO, and HMO. The REYs begin to sorb at pH ~5 and are effectively sequestered to the freshly precipitated solids by pH 7.5. The individual graphs for La, Gd, and Lu indicate differences in the sorption affinities for different elements. HFO was the predominant sorbent of each of the REYs to about pH 8.5. Adsorption by HMO and HAO is indicated to be more important for La, which is considered a light REY, compared to Gd and Lu.

The lower set of graphs shows results after increasing the specific surface area of all three sorbents, especially that of HAO. The lower set also allows the precipitation of REYs compounds. For this scenario, adsorption by HMO and HAO are enhanced compared to the default simulation. Furthermore, precipitation of La and Gd as phosphate and carbonate compounds competes with sorption.

Both simulations provide reasonable fits to the empirical data in the pH range 3 to 9, with some improvement at high pH by the second simulation with greater surface area and REY precipitation.

These graphs were created using the selected output file imported to Excel.

PHREEQ-N-AMD Treat+REYs Sequential Model

Treatment Simulation: Pine Forest ALD+Pond+Wetlands

TreatTrainMix2REYs.exe

Select Workspace: C:\Users\craovita\Documents\AMD Treat Train REYs_watex\PineFor151212_REYs

Design flow (gpm)	Sub-A	Sub-B	Sub-A	Sub-B	factr-kCO2	factr-kO2	EXProc	Sorbent	Surface Area (m ² /g)	Site Density (sites/m ²)
600	0	0	As (ug/L)	5.1	1E-06	factr-kFeHMT	1	HFO, HMeO	600	1.925
Mx fraction	1	0	Ba (ug/L)	11	1E-06	factr-kFeH2O2	1	HFO, equipart	600	1.925
Temp (C)	11.63	0.01	Cd (ug/L)	0.03	1E-06	factr-kMnHFO	1	HMO, HMeO	746	1.91
SC (uS/cm)	700	0	Co (ug/L)	32	1E-06	factr-kSHFO	1	HMO, equipart	746	1.91
DO (mg/L)	0.4	0.01	Cr (ug/L)	0.67	1E-06			HMO, HMeO	68	4.6
pH	5.79	0	Cu (ug/L)	8.1	1E-06	SI_FeOH3	0.0	HMO, equipart	68	4.6
Acidity (mg/L)	0	0	Ni (ug/L)	42	1E-06	SI_Schweitzerite	1.0			
Estimate Net Acidity	5.3	0	Pb (ug/L)	0.01	1E-06	SI_FeOH2	0.0			
Al (mg/L)	26	0	Se (ug/L)	1E-06	1E-06	SI_NDH3	0.0			
TIC (mg/L as C)	39.2	0	Si (ug/L)	1E-06	1E-06	SI_Basulimite	1.0			
Estimate TIC	30.9	0	Sr (ug/L)	370	1E-06	SI_FeOH2	0.0			
Fe (mg/L)	14	1E-08	U (ug/L)	0.03	1E-06					
Fe2 (mg/L)	14	1E-08	Zn (ug/L)	37	1E-06					
Estimate Fe2	0	0	La (ug/L)	0.91	1E-06					
Al (mg/L)	0.09	1E-08	Ce (ug/L)	1.6	1E-06					
Mn (mg/L)	3.1	1E-08	Pr (ug/L)	0.18	1E-06					
SO4 (mg/L)	330	1E-06	Nd (ug/L)	0.72	1E-06					
Cl (mg/L)	4	0	Sm (ug/L)	0.11	1E-06					
Ca (mg/L)	56	1E-06	Eu (ug/L)	0.038	1E-06					
Mg (mg/L)	51	1E-06	Gd (ug/L)	0.21	1E-06					
Na (mg/L)	7.4	1E-06	Tb (ug/L)	0.018	1E-06					
K (mg/L)	0.54	0	Dy (ug/L)	0.073	1E-06					
S (mg/L)	5.4	0	Ho (ug/L)	0.015	1E-06					
NO3 (mg/L)	1.5	0	Er (ug/L)	0.024	1E-06					
PO4 (mg/L)	0.03	1E-11	Tm (ug/L)	0.025	1E-06					
F (mg/L)	0.1	0	Yb (ug/L)	0.015	1E-06					
DOC (mg/L as C)	3.67	0	Lu (ug/L)	0.45	1E-06					
Quabie (mg/L as C)	1.3	1E-11	Y (ug/L)	0.59	1E-06					

Step	Caustic (mg/L)	pH	Time (hrs)	Temp (C)	H2O2 (mol)	LaCO2 (1/g)	PCO2 (atm)	S (acc. org) (mol)	10/MOx	SOC (mg)	HMeO (mg)	Fe (mg)	Mn (mg)	Al (mg)	Description
1	2.5	4	11.63	0	0.0001	3.4	72	1	0	75	80.3	10.5	19.2	0	ALD w/ 0.22-m coating
2	2.5	0.0003	11.6	0	0.02	3.4	13	1	0	1	97.8	11.0	19.2	0	Aeration ramp
3	2.5	13	12.16	0	0.0002	3.4	0	1	0	3	95	15	0	0	Oxidation wetting pond
4	2.5	0.0028	12.16	0	0.005	3.4	0	1	0	1	95	15	0	0	Aeration cascade
5	2.5	0	12.15	0	0.0005	3.4	0	1	0.1	3	60	140	0	0	Herbic wetland
6		0.0028	12.15	0	0.005	3.4	0	1	0	1	60	140	0	0	Aeration ramp
7		5.1	12.04	0	0.0005	3.4	0	1	0.1	2	140	160	0	0	Herbic wetland
8		0.0028	12.04	0	0.005	3.4	0	1	0	1	140	160	0	0	Aeration ramp
9		1.1	11.88	0	0.0001	3.4	0	1	0.1	2	20	80	0	0	Herbic wetland
10		0.0042	11.88	0	0.005	3.4	0	1	0	1	20	80	0	0	Aeration ramp
11		0	11.88	0	0	3.4	0	1	0	0	100	10	0	0	NULL

TreatTrainMix2REYs.exe created by C.A. CRAVITA III, U.S. Geological Survey, Release version 1.0.0., June 2022

Pine Forest Mine (Dec. 2015):
 moderate Fe & Mn, low Al, and low REYs (~5 ug/L)
 "validation data" for comparison to simulations

The TreatTrainMix2REYs.exe tool simulates water-quality changes through sequential steps in passive or active AMD treatment systems. Kinetics processes such as CO₂ outgassing, O₂ ingassing, Fe^{II} and Mn^{II} oxidation, SO₄ reduction, and limestone dissolution, all of which affect pH, are coupled with the same equilibrium speciation and precipitation reactions as the CausticTitrationMix2REYs tool. Unlike the titration tool, the pH may decrease or increase in response to dynamic, kinetically limited processes. A total of 11 treatment steps may be considered, with each having a specified reaction time, CO₂ outgassing rate, availability of limestone, organic matter, H₂O₂, sorbent, and other variables. A target pH may be specified for the addition of a caustic agent (NaOH, Ca(OH)₂, CaO, Na₂CO₃, or CaCO₃) to begin steps 1 to 5, possibly after aeration (decarbonation) or other pre-treatment steps. The solution composition at the end of each step is passed to the next step.

This slide shows the UI with input values for simulation of passive treatment of net-acidic coal mine discharge at the Pine Forest Mine in Pennsylvania. Sequential treatment involves an anoxic limestone drain at step 1; aeration pond at step 3; and aerobic wetlands at steps 5, 7, and 9, with aeration at intermediate and final steps (2, 4, 6, 8, 10).

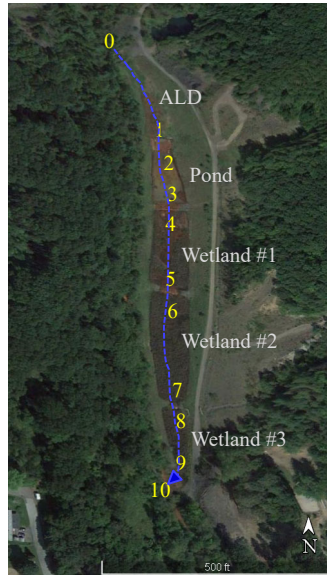
For the reported simulations, retention time, CO₂ outgassing rate, available limestone, and pre-existing HMeO mass and composition were varied at each step. The fractions of Fe, Al, and Mn in the pre-existing sorbent were estimated from measured sediment composition at the inflow and points downstream of the ALD.

HMeO mass of 75 mg L⁻¹ specified for the ALD represents accumulated coatings on

limestone particles. For subsequent steps, the specified sorbent mass was only 1 to 3 mg, representing suspended particles or coatings on rock or plant surfaces. Consistent values for retention time, kinetics variables, and sorbent properties were used for different model scenarios whereby the only values varied were the rate factor for iron-oxidizing bacteria (FeOB) and/or potential for REYs solids to precipitate. For the simulated “biofouling” scenario, the FeOB rate factor (factr.kbact) was increased from the default value of 1 to 2; for the abiotic scenario, that factor is 0.

HMeO mass of 75 mg L^{-1} specified for the ALD is consistent with a 0.22-mm thick coating on limestone particles ($72 \text{ cm}^2 \text{ mol}^{-1}$) in contact with 1 L water volume, assuming 35 % bed porosity and sorbent density of 1.92 g cm^{-3} .

PHREEQ-N-AMDTreat+REYs Sequential Model
 (Kinetics plus Equilibrium Sorption+Precipitation)
 Pine Forest Anoxic Limestone Drain + Aerobic Pond + Aerobic Wetlands



TreatTrainMix2REYs.exe

<u>Step</u>	<u>Treatment</u>
0	Untreated
1	ALD*
2	Riprap
3	Pond
4	Riprap
5	Wetland
6	Cascade
7	Wetland
8	Cascade
9	Wetland
10	Riprap
11	NULL

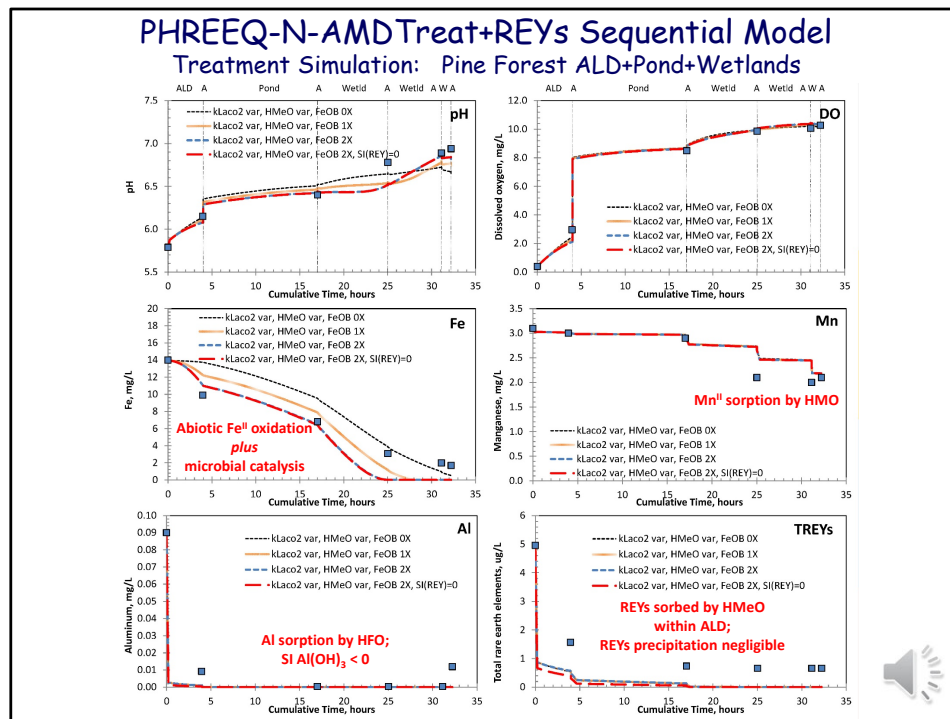
*Biofouled "Anoxic" Limestone Drain



This Google Earth image from 2012 shows sampling points along flow path through the Pine Forest passive treatment system. The first step is an underground "biofouled" anoxic limestone drain that had gelatinous orange precipitate coating limestone particles and clogging porosity. Water started to upwell to the surface along the length of the bed because of accumulated solids.

A settling tank near the inflow permitted initially anoxic AMD to become partly oxygenated before entering the buried limestone bed.

Subsequent treatment steps involve aerobic ponds and wetlands with aeration steps in between. Total retention time in the system is approximately 30-40 hours, depending on inflow rate.



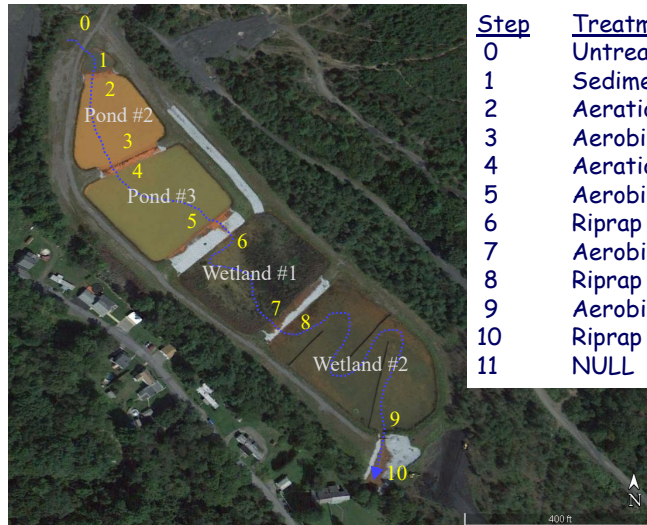
The TreatTrainMix2REYs results shown as a function of retention time generally reproduce the longitudinal trends for measured water quality at the Pine Forest treatment system. The pH and DO increased within the ALD and, subsequently, in response to aeration steps. The Fe concentration decreased by 30% within the ALD, simulated to result from abiotic plus microbial oxidation of Fe^{II}, which led to the precipitation and accumulation of HFO with lesser quantities of HAO and HMO on limestone surfaces. Concentrations of Mn were relatively unchanged through the ALD but decreased by about 30% within wetlands where the pH and DO were greatest and the Mn content of accumulated sorbent was highest. Initial concentrations of Al were very low and were simulated to decrease by adsorption to accumulated sorbent within the ALD. Simulated attenuation of REYs also took place within the ALD because of adsorption. Despite less mass of HMeO within wetlands downstream of the ALD, greater Mn content of sorbent and increased pH in wetlands promoted attenuation of dissolved Mn^{II} and remaining REYs.

Compared to adsorption, REYs precipitation has only a small effect as indicated by the difference between red-dashed (REY precipitation) and blue-dashed curves (no REY precipitation), both simulating the biofouling scenario where the FeOB rate factor was doubled. Simulation results for the two reference scenarios (orange solid or black dotted curves) demonstrate that abiotic, homogeneous Fe^{II} oxidation may explain observations in aerobic ponds and wetlands, but does not explain observed Fe removal within and immediately below the ALD. Thus, microbial and abiotic oxidation, combined with

adsorption account for the attenuation of Fe, REYs, and associated metals within the limestone bed. However, in downstream zones where pH and DO are greater, abiotic Fe^{II} oxidation is sufficient to explain observed trends.

PHREEQ-N-AMDTreat+REYs Sequential Model (Kinetics plus Equilibrium Sorption+Precipitation) Silver Creek Aerobic Ponds + Aerobic Wetlands

TreatTrainMix2REYs.exe



Step	Treatment
0	Untreated
1	Sedimentation Pond 1
2	Aeration Cascade
3	Aerobic Pond 2
4	Aeration Cascade
5	Aerobic Pond 3
6	Riprap Cascade
7	Aerobic Wetland 1
8	Riprap Cascade
9	Aerobic Wetland 2
10	Riprap
11	NULL

The TreatTrainMix2REYs tool is also used to simulate decreasing concentrations of dissolved metals and REYs within the Silver Creek passive treatment system. This Google Earth image from 2012 shows sampling points along conceptual flow path through the passive treatment system, which consists of a sedimentation pond at step 1, two large oxidation/settling ponds at steps 3 and 5, followed by two aerobic wetlands at steps 7 and 9, with wide, shallow aeration cascades in between. The second and third ponds account for 4/5 of the total retention time for the system, which is approximately 250-450 hours, depending on inflow rate. When sampled in 2015 and 2016, the Silver Creek AMD was anoxic, marginally net alkaline with pH 5.9-6.0. Rapid outgassing of CO₂ during aeration steps caused large increases in pH, which facilitated Fe^{II} oxidation in subsequent steps.

PHREEQ-N-AMD Treat+REYs Sequential Model

Treatment Simulation: Silver Creek Mine, Aerobic Ponds+Wetlands

TreatTrainMix2REYs.exe

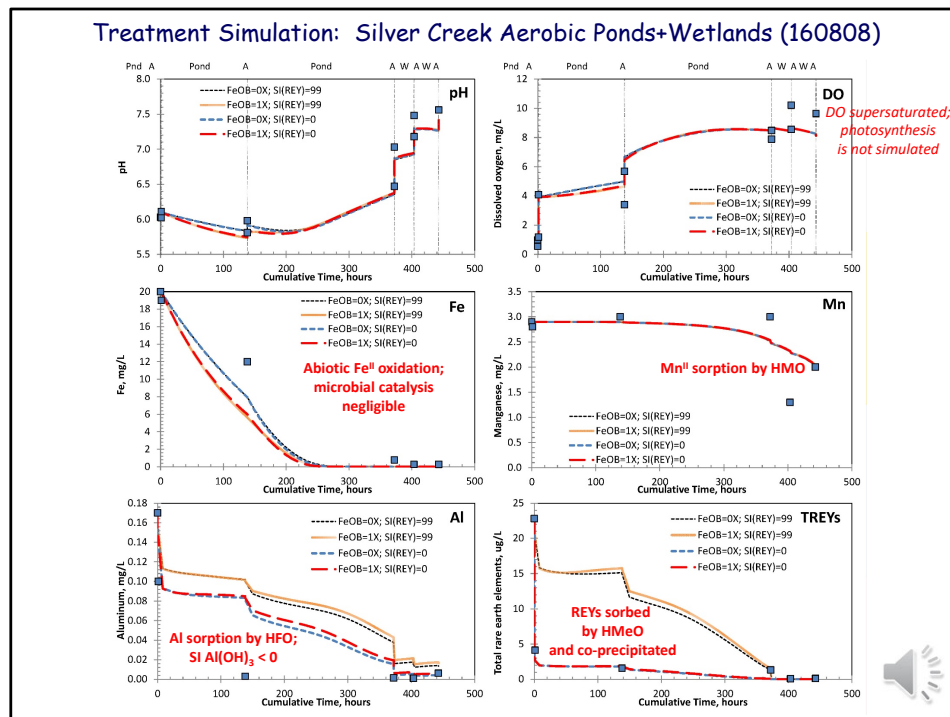
The screenshot displays the PHREEQ-N-AMD software interface with several key sections highlighted in red boxes:

- Design Parameters:** A table of input values for design flow, temperature, and various ion concentrations (e.g., SO4, Ca, Mg, Fe, Mn, Al, Ni, Pb, Zn, Cu, Cd, Cr, Sr, U, Th, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y).
- Chemical Reactions:** A list of reactions such as factr-KFeHOM, factr-KFeHOO2, factr-KMnHOM, factr-KSHFO, and various equilibrium constants (SI_FeOH3, SI_Schwertmannite, SI_FeOH2, SI_NiOH3, SI_Basakunitite, SI_MnOOH, SI_MnOH2).
- Sequential Treatment Steps / Kinetics Conditions:** A table with 11 steps, each with a caustic agent (NaOH, Ca(OH)2, Na2CO3, CaCO3), a kinetic rate constant (k), and a description of the step (e.g., Sedimentation pond, Aeration cascade, Oxidation/wetting pond, Aeration cascade, Oxidation/wetting pond, Aeration riprap, Aerobic wetland, Aeration riprap, Aerobic wetland, Ditch).
- Soil Sorption Parameters:** A table of parameters for various sorbents (HFO, HMeO, HMO, HMO2, HMO3, HMO4, HMO5) including surface area, density, and distribution coefficients.

Silver Creek Mine (Aug. 2016):
 moderate Fe & Mn, moderate REYs (~23 ug/L)
 "validation data" for comparison to simulations



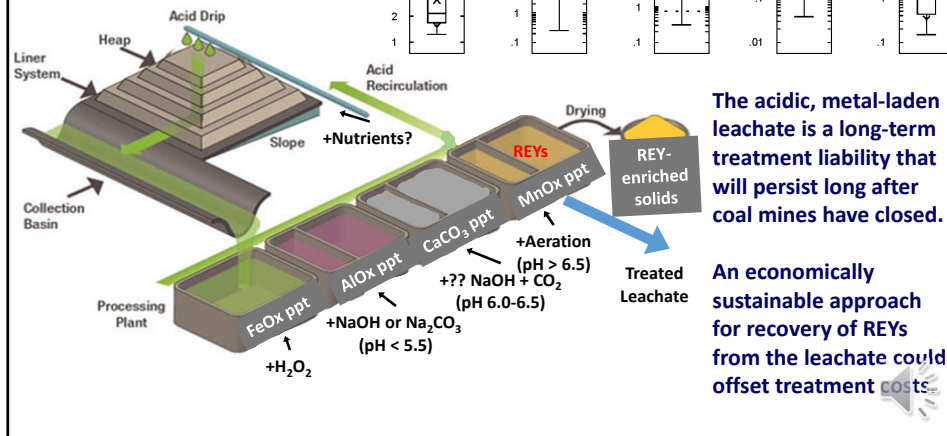
For initial simulations, HMeO composition was varied on the basis of values reported by Ashby (2017) for sampled sediments at Silver Creek. The HMeO mass at each step was assumed to be less than or equal to the difference between immediately upstream and downstream samples for the combined mass of Fe, Al, and Mn. Only the CO₂ outgassing rate and sorbent mass and composition (HMeO.mg, Fe%, Mn%, Al%) at each step were adjusted to achieve a reasonable match between empirical and simulated values for longitudinal changes in pH, Fe, Mn, Al, and associated major solute concentrations. Eventual removal of Mn^{II} in the wetland treatment steps were simulated by HMeO sorbent having greater HMO content, as observed for the sampled sediment.



Abiotic oxidation of Fe combined with adsorption and precipitation of solids explains observed attenuation of Fe, Al, Mn, and associated REYs at the Silver Creek treatment system; microbial Fe oxidation had little effect (FeOB=1X). Although the results for initial simulations effectively reproduced the longitudinal trends for measured pH, DO, Fe, Mn, and Al (black dashed or orange curves), without REYs mineral precipitation, the corresponding modeled concentrations of total dissolved REYs (and individual REYs, not shown) remaining in solution were at least five times greater than observed values for all but the last stages of the treatment system (black dashed curves). Simply permitting the precipitation of REYs (SI_REEPO4=0) resulted in substantial decrease in the concentration of total REYs (blue or red curves), consistent with observations. Nevertheless, simulated attenuation was not consistently effective for individual REYs, many of which remained undersaturated (e.g. Y, Eu, Gd, Tb, Dy, Ho, Yb, and Lu). As explained by Liu and Byrne (1997), formation of REEPO₄ in the environment generally involves co-precipitation of phases which incorporate multiple REYs, in which case the overall trend may be expected.

PHREEQ-N-AMDTreat+REYs Sequential Model Simulated Treatment of Leachate for Recovery of REYs

Leachate from pyritic shale and coal waste (coal refuse) at a centralized processing facility has low pH and elevated concentrations of metals.



A goal of modeling with the PHREEQ-N-AMDTreat+REYs tools is to identify strategies that could feasibly produce a concentrated REYs extract from AMD or mine waste leachate that could be highly valuable.

For example, leachate from pyritic shale and coal waste (coal refuse) at a centralized processing facility has low pH and elevated concentrations of metals. The acidic, metal-laden leachate is a long-term treatment liability that will persist long after coal mines have closed. An economically sustainable approach for recovery of REYs from the leachate could offset treatment costs.

If Fe and Al can be removed sequentially, at pH < 5.5, REYs may be retained in solution and recovered at pH > 6.5 with manganese in later steps.

PHREEQ-N-AMDTreat+REYs Sequential Model

Coal-Refuse Leachate—Lime Treatment vs. Alternative Treatment to Recover REYs



TreatTrainMix2REYs.exe

<u>Step</u>	<u>Currently Lime Treatment</u>
0	Untreated
1	Sedimentation Pond
2	Lime to pH ~8.5
3	Aerobic chambers
4	Oxidation/setting pond(s)
5	Injection to mine
6	NULL
7	NULL
8	NULL
9	NULL
10	NULL
11	NULL



Untreated leachate from a coal-refuse disposal facility in Pennsylvania is considered as a proposed test case for REYs recovery. Current treatment utilizes neutralization with lime, which causes precipitation of Fe, Al, and associated REYs into a complex sludge mixture. If REYs could be concentrated after first removing substantial Fe and Al, the final REYs-bearing phase(s) may be efficiently processed for REYs recovery.

The TreatTrainMix2REYs tool was used to simulate the current active treatment with lime to pH 8.5 and two alternative treatments intended to concentrate REYs from the leachate.

PHREEQ-N-AMD Treat+REYs Sequential Model

Current Treatment of Coal Refuse Leachate with Lime

TreatTrainMix2REYs.exe

Select Workspace: C:\Users\Chuck\Documents\AMD\TreatTrainREYs_watreq\PBSJob12_REYs

Design flow (gpm): 153
 Mix fraction: 1.0
 Temp (C): 17.95
 SC (uS/cm): 9740
 DO (mg/L): 6.07
 pH: 3.7
 Acidity (mg/L): 8335
 Estimate NetAcidity: 10526 F
 Alk (mg/L): 0
 TIC (mg/L as C): 23.7
 Estimate TIC: 7.2
 Fe (mg/L): 3980
 Fe2 (mg/L): 1000
 Estimate Fe2: 0
 Al (mg/L): 118
 Mn (mg/L): 29.75
 SO4 (mg/L): 10500
 Cl (mg/L): 11.7
 Ca (mg/L): 411
 Mg (mg/L): 303
 Na (mg/L): 83.2
 K (mg/L): 18.8
 Si (mg/L): 25.9
 NO3 (mg/L): 0.01
 PO4P (mg/L): 2.0
 F (mg/L): 0.5
 DOC (mg/L as C): 0.5
 Dissolve (mg/L as C): 0.1

Kinetics Constants Adjustment Factors

Equilibrium Constants Adjustment of Saturation Index for Precipitation

Substent Properties: Specified HMO = Equilibrium Ph

Sequential Treatment Steps / Kinetics Controls

Reaction Date

Limitations and Organic Matter

Specified HMO Substent Concentration

Generate Sequential Kinetics Output

Print PHREEQC Output Report

TreatTrainMix2REYs.exe created by C.A. Grisvols III, U.S. Geological Survey, Release version 1.0.0, June 2008

PBS Job 12:
 High acidity and REYs
 Current treatment produces sludge containing Ca, Fe, Al, Mn, and REYs

Lime to pH ≥ 8.5

This slide shows the user interface for the lime treatment scenario.

PHREEQ-N-AMD Treat+REYs Sequential Model

Hypothetical Sequential Treatment of Leachate with H₂O₂+NaOH

TreatTrainMix2REYs.exe

The screenshot displays the 'Sequential Treatment Steps / Kinetics Conditions' window. The 'Sequential Treatment Steps' table is highlighted with a red box:

Step	Caustic?	pH?	Time/hrs	Temp2	H2O2/mol	Aeration Rate kLaCO2 1/n (1/pCO2 atm)	Limiting and Organic Matter SAcc:cm2/mol M/MDOc	SDC:mc	Specified H2O2 Subst. Concentrations H2O2/mg Fe% Mn% Al%	Description	
1	<input type="checkbox"/>	<input type="checkbox"/>	0.033	25	0.0092	0.000001	-3.4	0	0	0	Hydrogen peroxide
2	<input type="checkbox"/>	<input type="checkbox"/>	0.05	25	0	0.00005	-3.4	0	0	0	Oxidation/mixing pond
3	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	5.2	25	0	0.00005	-3.4	0	0	0	Sodium hydroxide pH 5.2
4	<input checked="" type="checkbox"/>	<input type="checkbox"/>	0.0833	25	0	0.005	-3.4	0	0	0	Aeration/mixing
5	<input type="checkbox"/>	<input type="checkbox"/>	6.0	25	0	0.000001	-3.4	0	0	0	Oxidation/settling pond
6	<input type="checkbox"/>	<input type="checkbox"/>	0.05	25	0	0.01	-3.4	0	0	0	Aeration cascades
7	<input type="checkbox"/>	<input type="checkbox"/>	6.0	25	0	0.000001	-3.4	0	0	0	Oxidation/settling pond
8	<input type="checkbox"/>	<input type="checkbox"/>	0.05	25	0	0.01	-3.4	0	0	0	Aeration cascades
9	<input type="checkbox"/>	<input type="checkbox"/>	12.0	25	0	0.0000001	-3.4	72	1	0	Mn sorption bed
10	<input type="checkbox"/>	<input type="checkbox"/>	0.033	25	0	0.005	-3.4	0	0	0	Ditch
11	<input type="checkbox"/>	<input type="checkbox"/>	0	25	0	0	-3.4	0	0	0	NULL

PBS Job 12:
High acidity and REYs
Alternative treatment to segregate Fe, Al, and Mn, concentrating REYs

H₂O₂ + NaOH to pH ~5.2
(up to 5.5?)

This slide shows the user interface for the alternative treatment scenario using H₂O₂ followed by NaOH addition and settling and aeration steps.

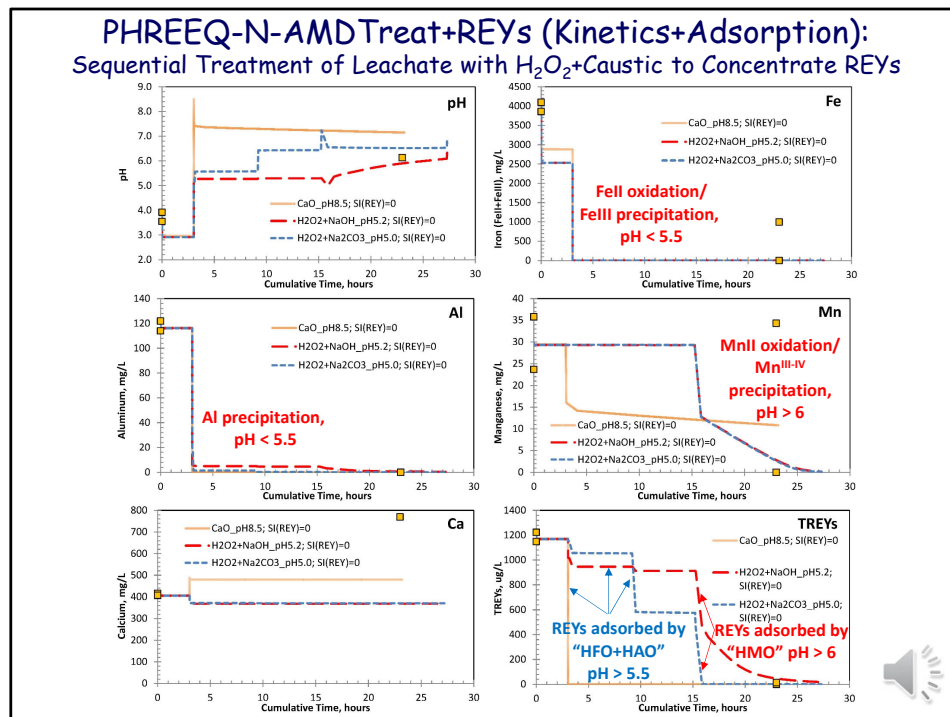
PHREEQ-N-AMD Treat+REYs Sequential Model Hypothetical Sequential Treatment of Leachate with H₂O₂+Na₂CO₃

TreatTrainMix2REYs.exe

Step	Caustic (mol/L)	Time (hr)	Temp (C)	H2O2 (mol)	K1 (CO2 l/s)	LiP (CO2 atm)	LiAc (mol)	M (Mol/L)	SOC (mol)	Unitname and Diapic Matter	Specified H2O2 Concentration (H2O2 mol/L)	Fe (%)	Al (%)	Description
1	0.033	25	0	0.0002	0.000001	3.4	0	0	0	0	0	0	0	Hydrogen peroxide
2	0	0	0	0	0.00005	3.4	0	0	0	0	500	100	0	Oxidation/setting pond
3	0	0	0	0	0.0005	3.4	0	0	0	0	50	70	0	Sodium carbonate pH 5.0
4	0	0.0833	25	0	0.005	3.4	0	0	0	0	0.5	70	0	Aeration/mixing
5	0	0.000001	3.4	0	0	0	0	0	0	0	20	70	0	Oxidation/setting pond
6	0	0.05	25	0	0.01	3.4	0	0	0	0	0.5	60	0	Aeration cascades
7	0	0.05	25	0	0.000001	3.4	0	0	0	0	10	60	0	Oxidation/setting pond
8	0	0.05	25	0	0.01	3.4	0	0	0	0	0.5	90	5	Aeration cascades
9	12.0	25	0	0.0000001	3.4	72	1	0	0	0	100	2	90	Mn exception bed
10	0.033	25	0	0.005	3.4	0	0	0	0	0	0.5	110	85	Ditch
11	0	25	0	0	0	3.4	0	0	0	0	0	0	0	NULL

PBS Job 12: H₂O₂ + Na₂CO₃ to pH ~5.0
 High acidity and REYs
 Alternative treatment to segregate Fe, Al, and Mn, concentrating REYs

This slide shows the user interface for the alternative treatment scenario using H₂O₂ followed by Na₂CO₃ addition and settling and aeration steps.



The active lime treatment to pH 8.5 results in nearly complete removal of REYs with Fe-Al-Ca rich sludge. REYs, which are adsorbed primarily by HFO and HAO, are diluted by the major metals and other impurities in the sludge.

By comparison, alternative treatment strategies using H₂O₂ to oxidize Fe^{II}, followed by metered addition of Na-caustic agents (NaOH or Na₂CO₃) to achieve a target pH < 5.5 sequentially remove Fe and Al from solution. Subsequent aeration of the effluent over extended time results in the oxidation of Mn which adsorbs and concentrates REYs in final steps. The scenario using NaOH instead of Na₂CO₃ maintains pH < 5.5 until most Fe and Al have been removed and, consequently, results in greater concentrations of REYs with Mn-rich solids.

Alternatively, chemicals such as oxalate or phosphate may be added to the effluent to precipitate REYs compounds, following initial steps to remove Fe and Al

Technoeconomic Assessment of a Sequential Step-Leaching Process for Rare Earth Element Extraction from Acid Mine Drainage Precipitates

Alison G. Fritz, Thomas J. Tarka, and Meagan S. Mauter* **NETL Authors**

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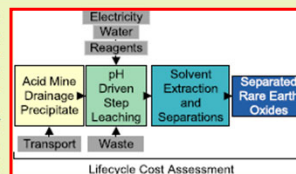
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ABSTRACT: Coal waste products have been studied as a new source of rare earth elements (REEs) and other critical minerals (CM) essential for the development of renewable energy technologies, but the economic viability of these source materials is not well understood. This paper examines the technoeconomic performance of a novel process for REE extraction from acid mine drainage precipitates (AMDp) from passive treatment beds in the Appalachian coal basin. The three-phase extraction process includes the excavation and transportation of AMDp, multi-phase pH-driven step-leaching of REEs under ambient conditions, and commercial solvent extraction to produce a saleable-grade rare earth oxide material that can be reduced to a pure metal. Using bench-scale data, we estimate the life-cycle cost of extraction of REEs from two representative Appalachian AMDp feedstock chemistries between 3400 and \$900 \$/kg of the mixed REE concentrate produced. Both the AMDp composition and process parameters affect the profitability of REE extraction, with the REE concentration and distribution of REEs in the feedstock, extraction and precipitation reagent consumption rates, and the potential for reagent recycling as the key variables. Economically profitable valorization of REEs from AMDp will require a combination of continued process innovation and sizable financial incentives to substantially influence the domestic supply of REEs.

KEYWORDS: rare earth elements, technoeconomic assessment, remediation, acid mine drainage, beneficial reuse



The PHREEQ-N-AMDTreat+REYs models suggest that conventional treatment technology to recover REYs and other critical minerals may be feasible. Nevertheless, economic benefits warrant further evaluation. In this 2021 paper by Fritz and others, chemical costs plus additional factors such as purification and transportation costs were considered in their technoeconomic assessment of REYs recovery from AMD.

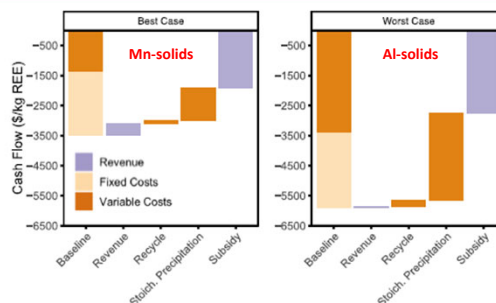


Figure 4. Changes in cash flow from process improvements and market changes to achieve break-even net profit for the best-case [Mn-rich] and worst-case [Al-rich] scenarios.

Precipitation costs could also be excluded completely by eliminating the direct-to-precipitation stage by incorporating alternative separation technologies, such as sorbents. Oxalic acid consumption could be minimized through oxalic acid recycling using cation exchange resins after the REE-enriched solid precipitate is dried on the belt filter.⁴⁶ Future work can experimentally determine the bench-scale reagent and energy use of these opportunities for reduction of precipitant cost in order to calculate the reagent, water, electricity, and waste management cost savings.

Subsequent efforts could also quantify the effect of other process optimizations for the step-leaching process by examining the impact of AMD feedstock composition on extraction costs in different limestone treatment bed configurations. Following work could also evaluate alternative counter-current leaching techniques that require lower acid

significantly reduce the environmental damages of REE mining and extraction. Recovering REEs from REE-enriched AMDp also has the potential to offset the costs of AMD treatment that hinder compliance with environmental remediation efforts. Therefore, it is important to consider the range of regulatory changes and quantify the magnitude of incentives needed to develop a viable alternative supply chain from AMDp sources. This study suggests that the subsidy required for the best-case scenario with the current process design is \$1900/kg REEs. Further cost reduction is constrained by the process performance associated with the selected processing approach and the assumptions made about plant size and feedstock availability. A different extraction technique or a different AMD setting may substantially change the economic viability of REO recovery. Cooperation between the public and private sectors will be necessary to develop a framework for these subsidies.

As suggested by Fritz et al., use of sorbents may be economically favorable over methods involving REYs precipitation. Thus, the alternative treatment strategies simulated previously, involving sorption by HMO, could be advantageous over other methods. The HMO sorbent may possibly be re-used after recovery of REYs. Additional research on specific treatment strategies and associated economic factors REEs would be needed for any given site-specific design.

Conclusions

- ✓ Geochemical tools using PHREEQC that incorporate equilibrium aqueous and surface speciation *plus* kinetics models for oxidation processes and limestone dissolution have been developed to evaluate mine effluent treatment options.
- ✓ The user interface for the PHREEQ-N-AMDTreat tools facilitates adjustment to input concentrations and system variables.
- ✓ Graphical and tabular output indicates changes in the pH, solute concentrations, and element distributions in effluent and associated solids.
- ✓ By adjusting kinetics variables or chemical dosing, various passive and/or active treatment strategies can be simulated.
- ✓ AMDTreat cost-analysis software can be used to evaluate the feasibility for installation and operation of treatments that produce the desired effluent quality.



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Instructions for Access, Installation, and Use

The executable software, instructions, required input files, and examples of input/output presented today are accessible to the public at the link below.

Cravotta, C.A. III (2022) Interactive PHREEQ-N-AMDTreat+REYs water-quality modeling tools to evaluate potential attenuation of rare-earth elements and associated dissolved constituents by aqueous-solid equilibrium processes: U.S. Geological Survey Software Release (software download). <https://doi.org/10.5066/P9M5QVK0>

To use the executable models, IPhreeqcCOM for Windows (Charlton and Parkhurst, 2011) must be installed on the user's computer. That software is accessible for download at:

<https://water.usgs.gov/water-resources/software/PHREEQC/IPhreeqcCOM-3.7.3-15968-win32.msi>

<https://water.usgs.gov/water-resources/software/PHREEQC/IPhreeqcCOM-3.7.3-15968-x64.msi>

Questions can be addressed to Chuck Cravotta cravotta@usgs.gov.



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