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

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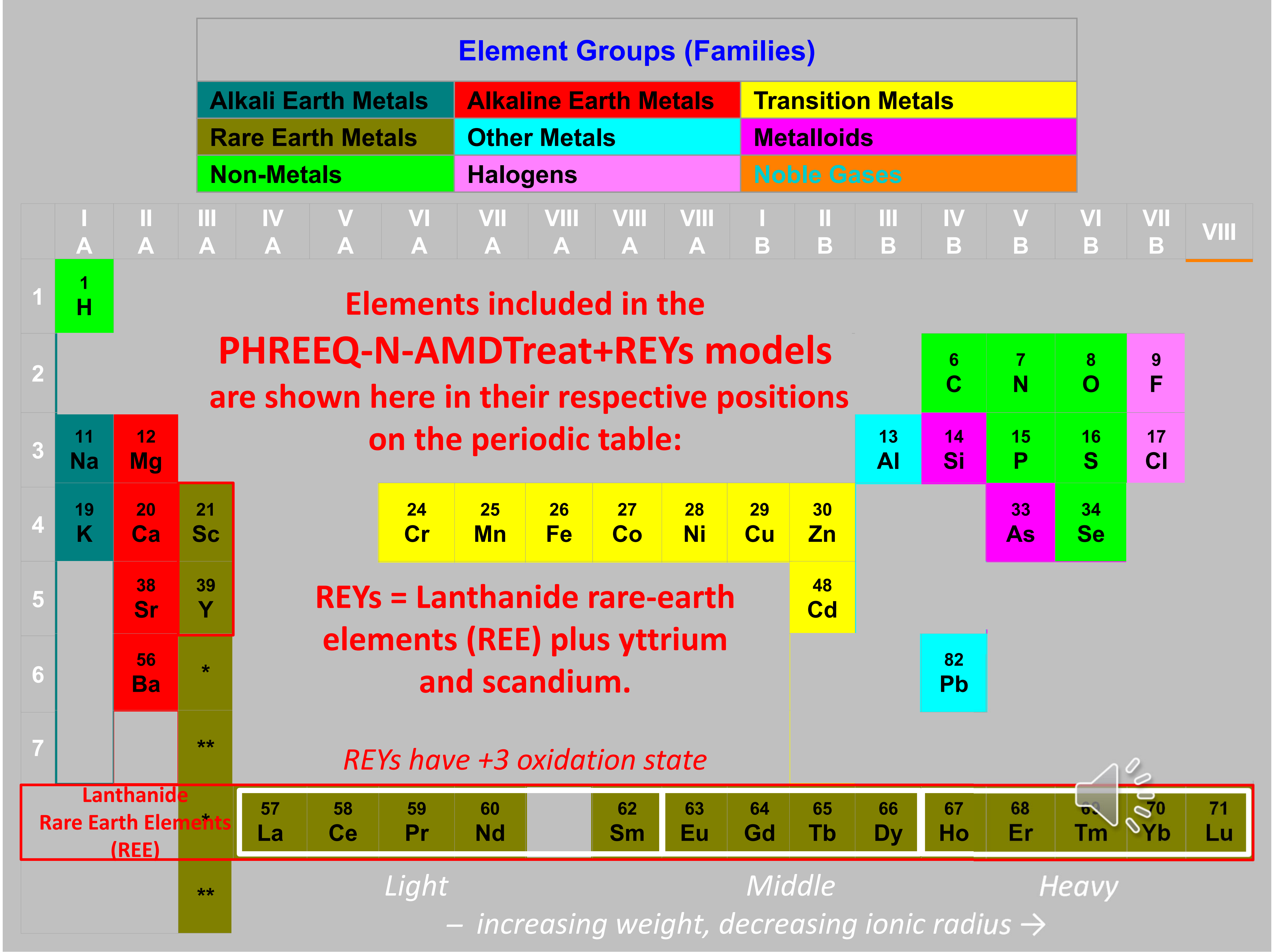
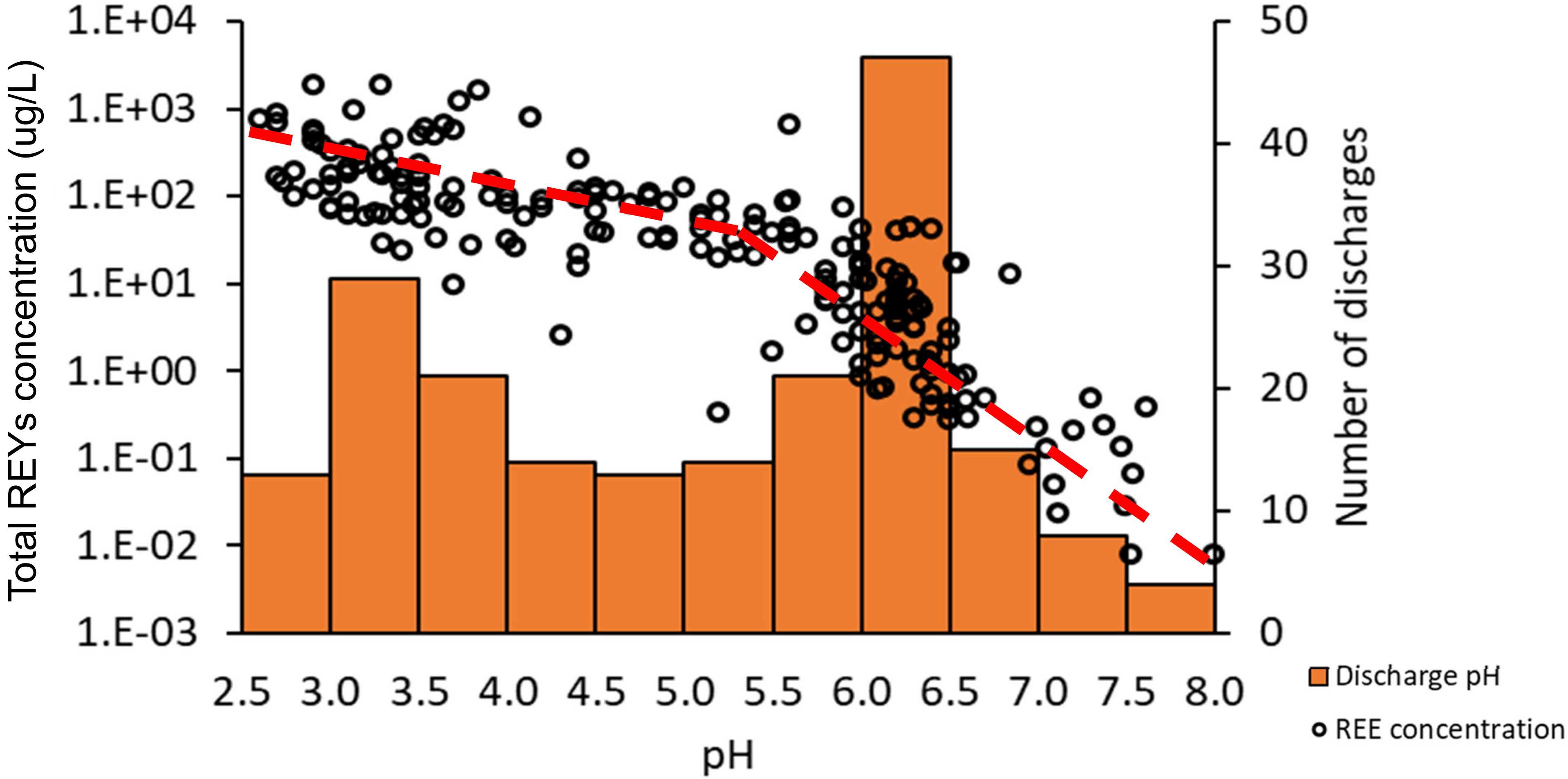
West Virginia Mine Drainage Task Force Symposium and
15th International Mine Water Association Congress
April 21–26, 2024, Morgantown Event Center, WV, USA

USGS science for a changing world

cravotta geochemical consulting


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
2
3
4
5
6
7
1 H
Elements included in the
PHREEQ-N-AMDTreat+REYs models
are shown here in their respective positions
on the periodic table:
6 C
7 N
8 O
9 F
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
19 K
20 Ca
21 Sc
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
33 As
34 Se
38 Sr
39 Y
48 Cd
REYs = Lanthanide rare-earth
elements (REE) plus yttrium
and scandium.
56 Ba
*
82 Pb
**
REYs have +3 oxidation state
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
Tm
70 Yb
71 Lu
**
Light
Middle
Heavy
– increasing weight, decreasing ionic radius →

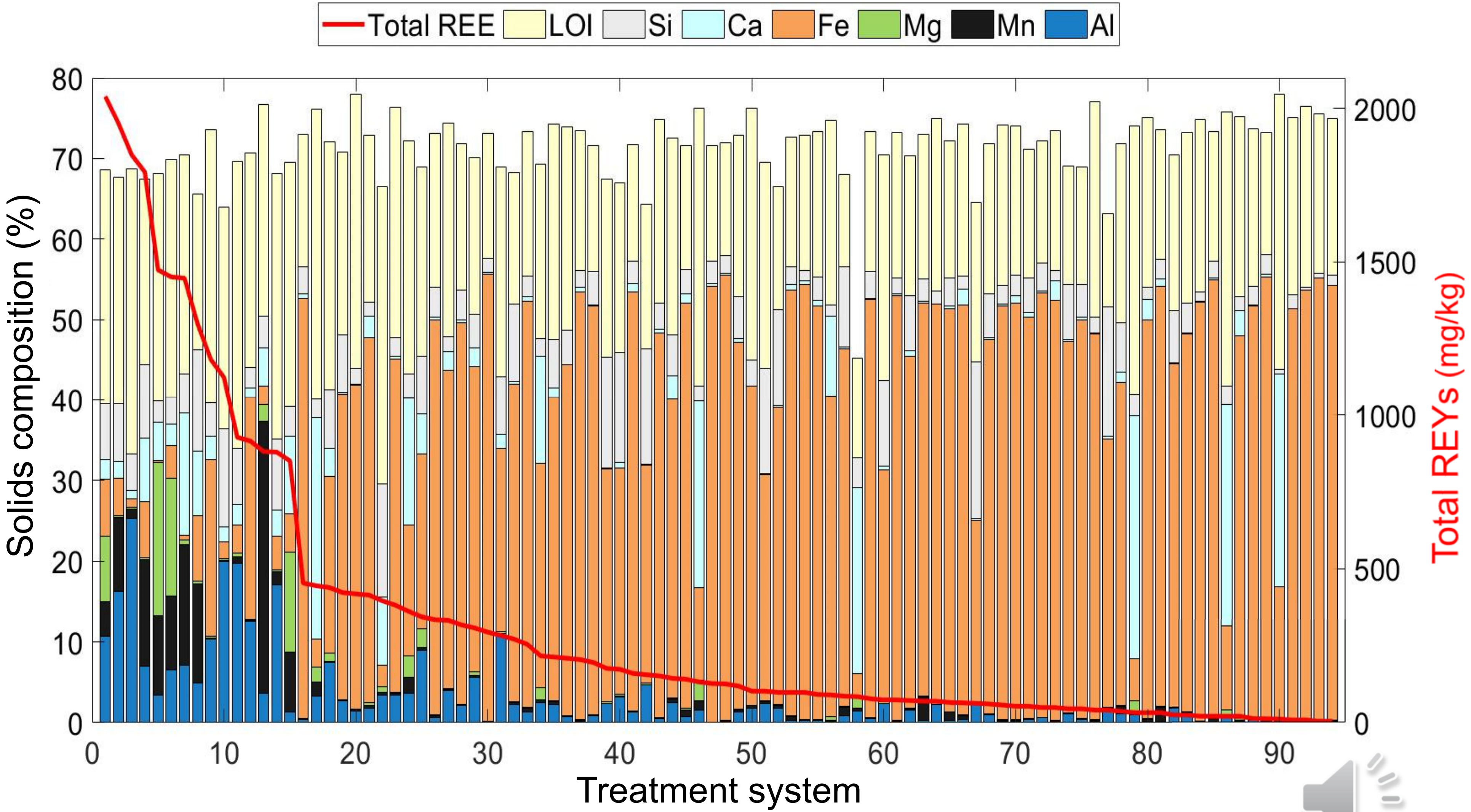
Rare-earth elements are elevated in low-pH AMD from coal mines in Pennsylvania



Generally, REYs concentrations decrease with increased pH, with a break in slope at pH ~5.

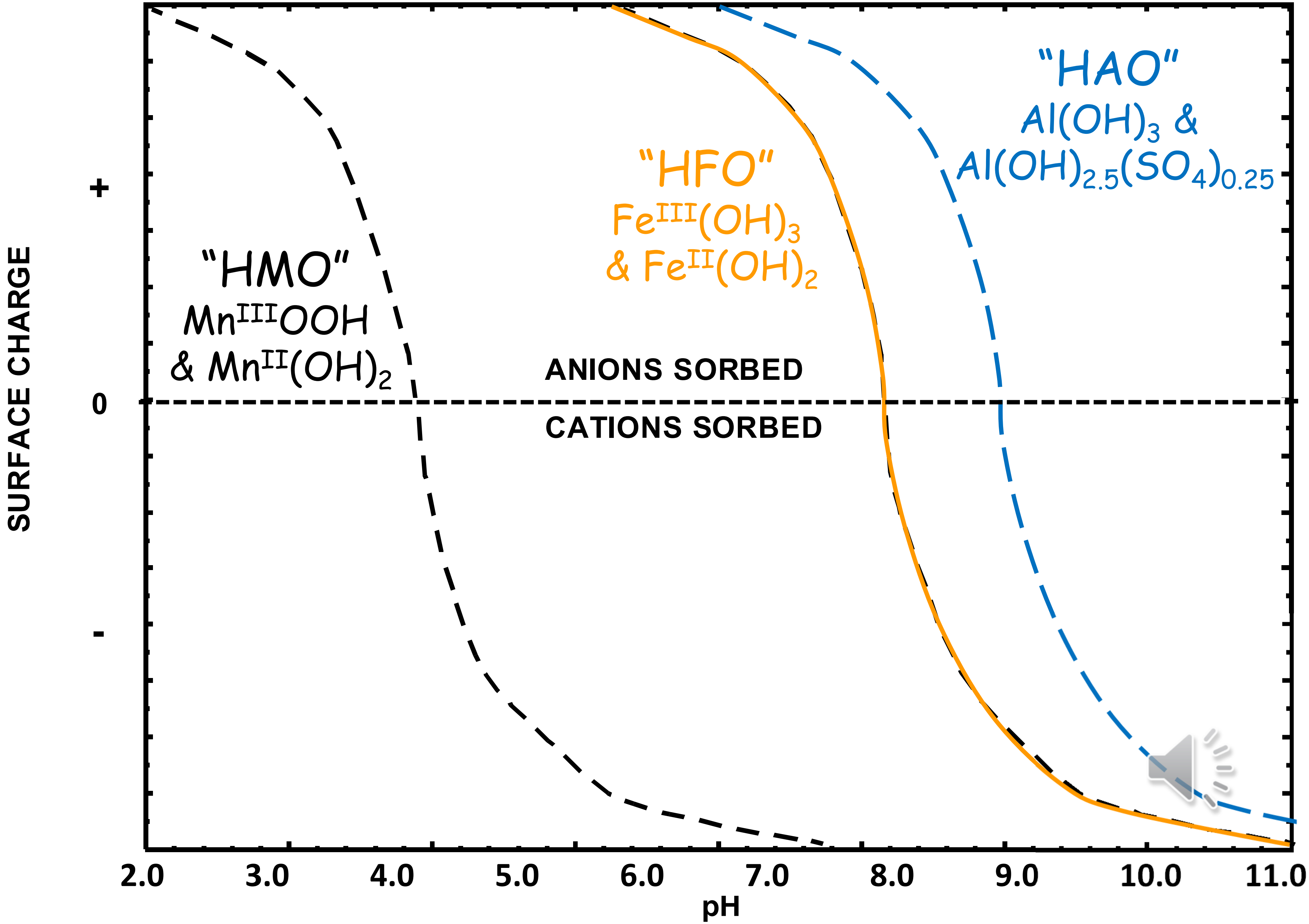
Cravotta, C.A. III (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA: 1. Constituent concentrations and correlations: Applied Geochemistry, 23, 166-202.

Rare-earth elements accumulate with Fe, Mn, and Al in AMD treatment solids



Hedin, B.C., Hedin, R.S., Capo, R.C., and Stewart, B.W., 2020. Critical metal recovery potential of Appalachian acid mine drainage treatment solids. International Journal of Coal Geology, 231, 103610.

Hydrous metal oxides (HMeO) = HMO+HFO+HAO

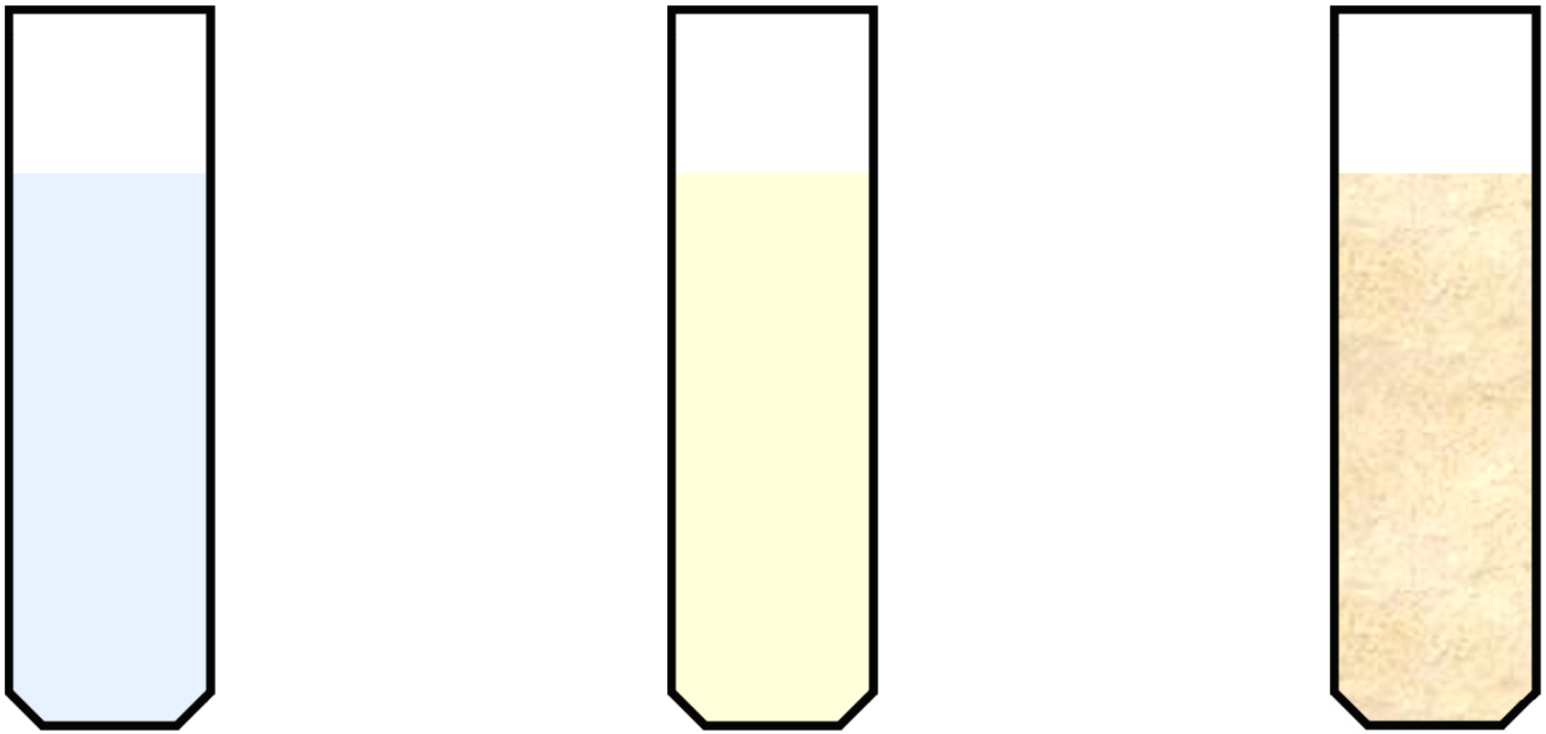


REYs Sorption by HFO, HAO, (HMO)—Empirical Titration Data

50 μg/L REYs
1 mmol/L Fe^{+3}, Al^{+3}, or Mn^{+3}
HCl matrix (no SO_4)

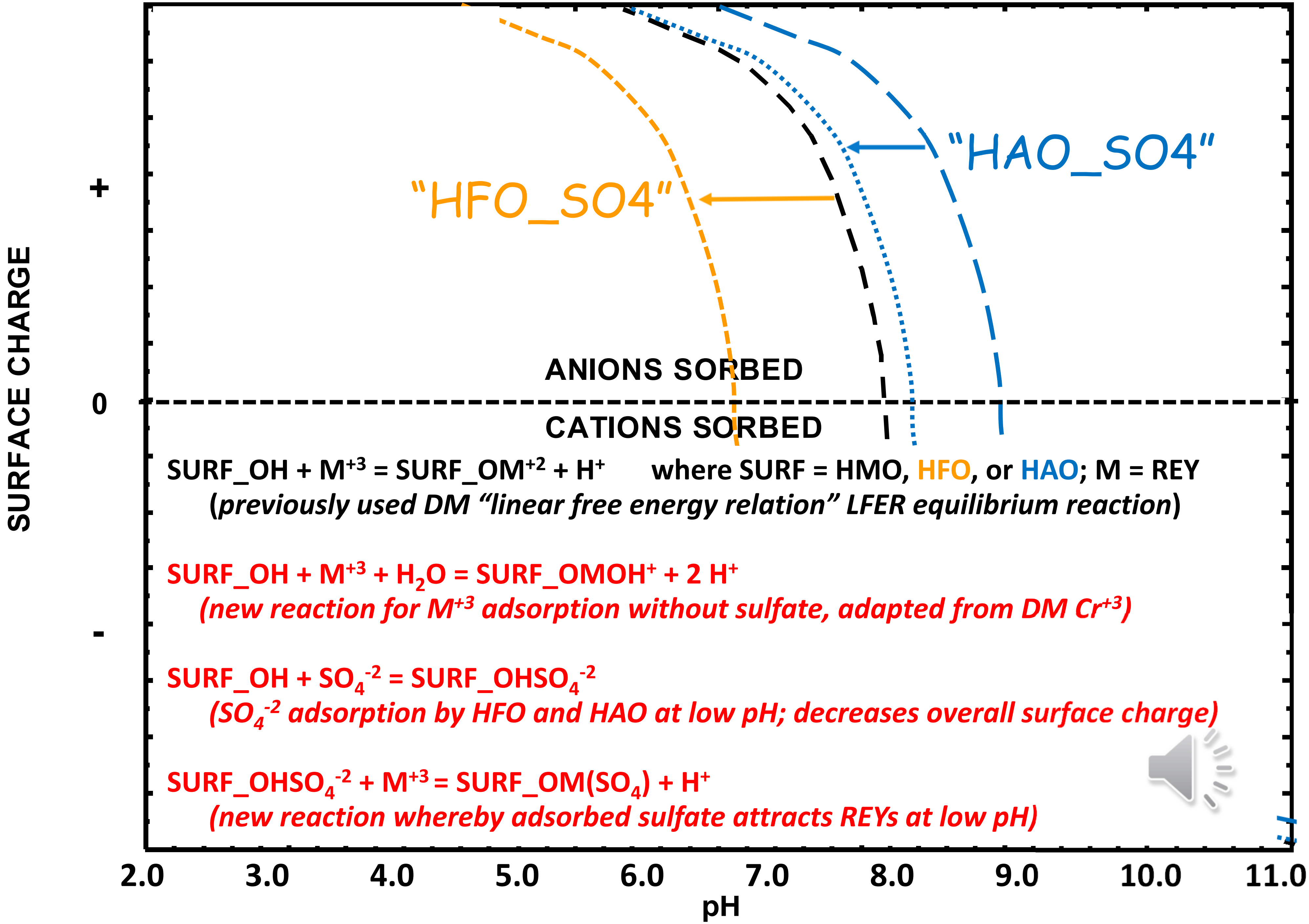
50 μg/L REYs
1 mmol/L Fe^{+3}, Al^{+3}, or Mn^{+3}
H_2SO_4 matrix

50 μg/L REYs
1 mmol/L HFO, HAO, or HMO
H_2SO_4 matrix



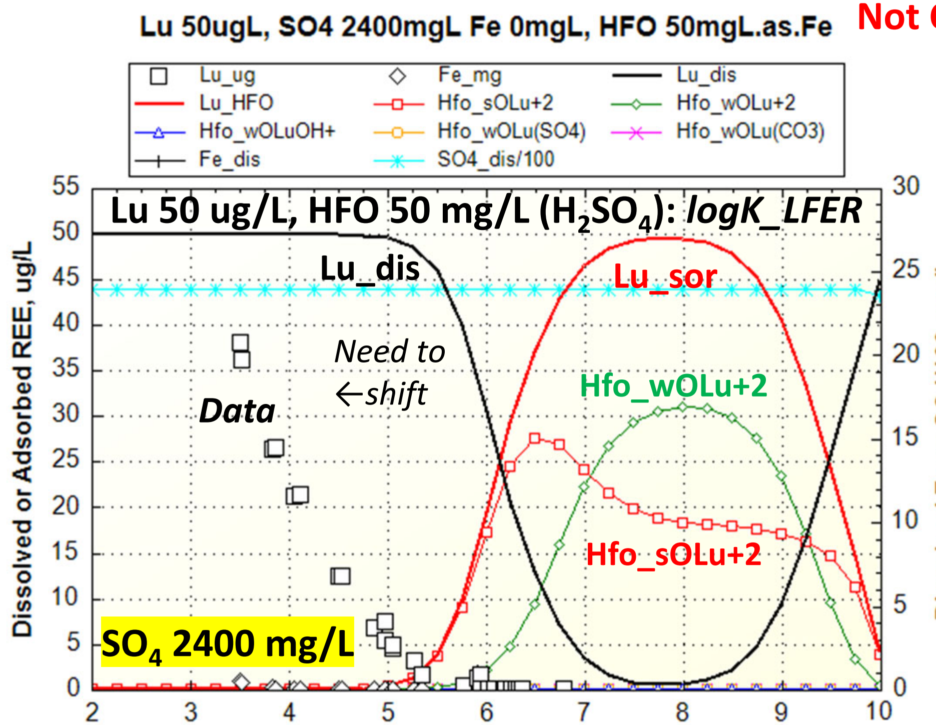
- ✓ 50 ml polyethylene centrifuge tube
- ✓ 40 ml solution of REYs plus Fe, Al, or Mn sorbent in HCl or H_2SO_4 matrix
- ✓ titrate with 0.1 to 5 N NaOH to multiple target pH values (3-10)
- ✓ mix on shaker table for 24 hours
- ✓ remeasure pH
- ✓ centrifuge, filter (0.45 μm) supernatant, acidify, and analyze by ICP-MS and ICP-OES

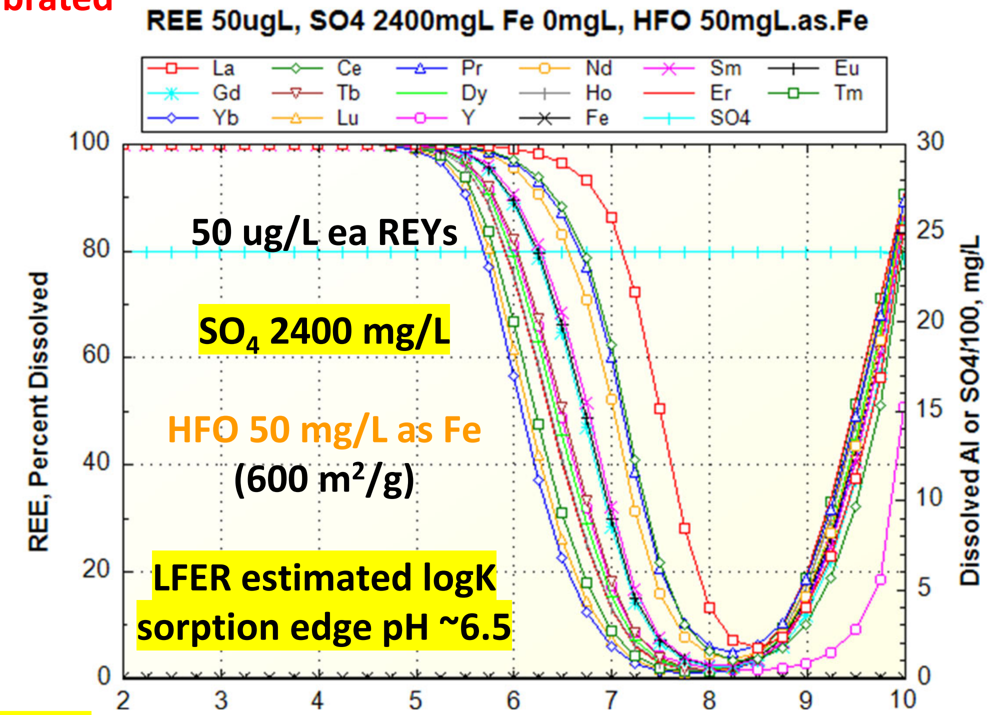
Effect of Sulfate on REYs Adsorption(?)



REYs Sorption by "HFO"- Model Calibration to Empirical Data

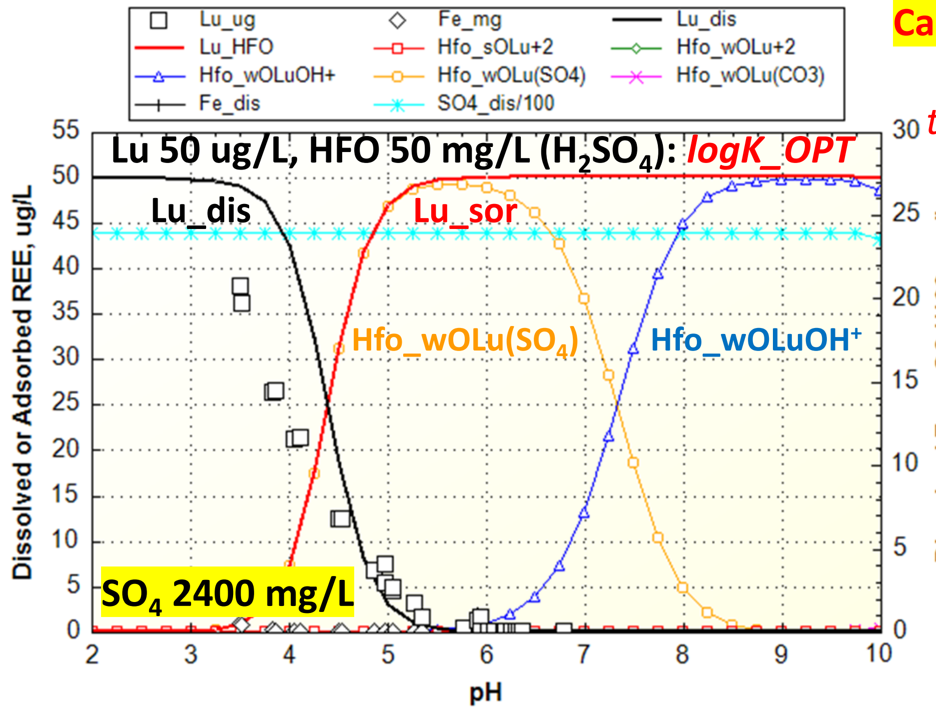
Not Calibrated

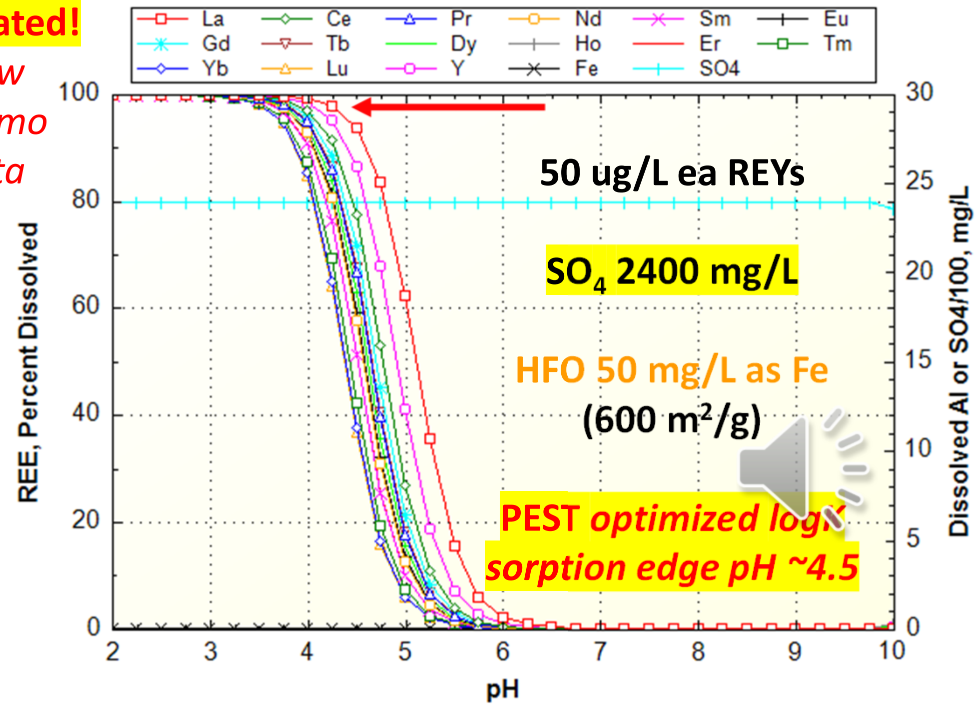




Calibrated!

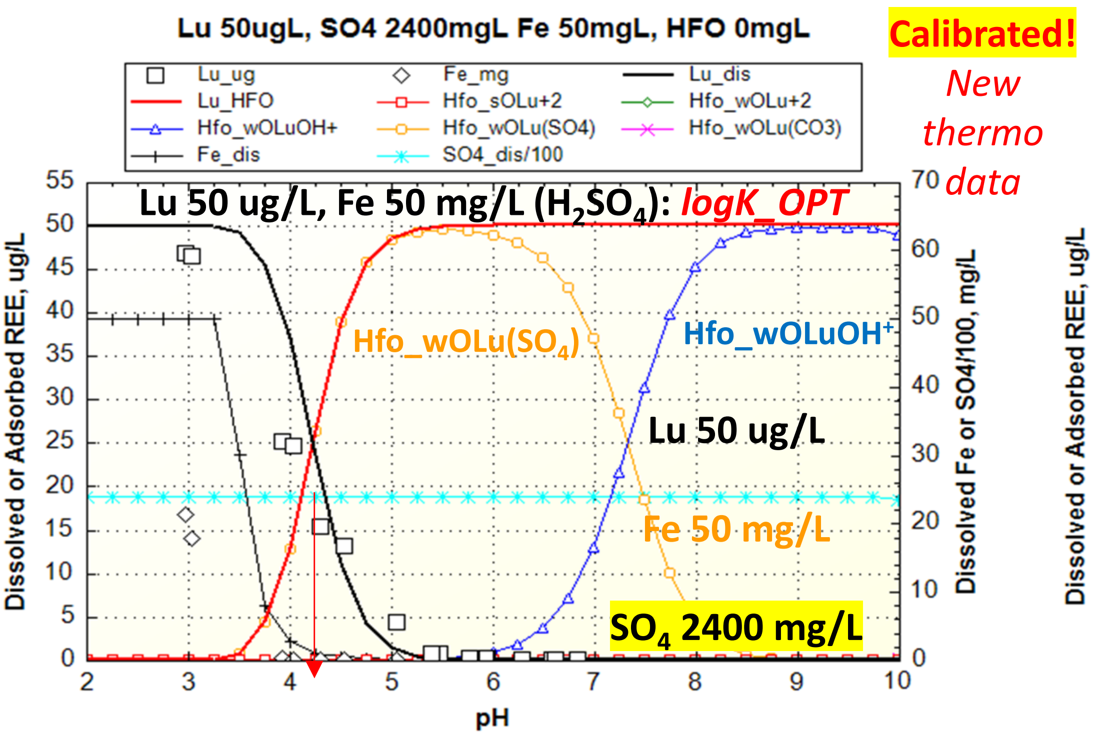
New thermo data



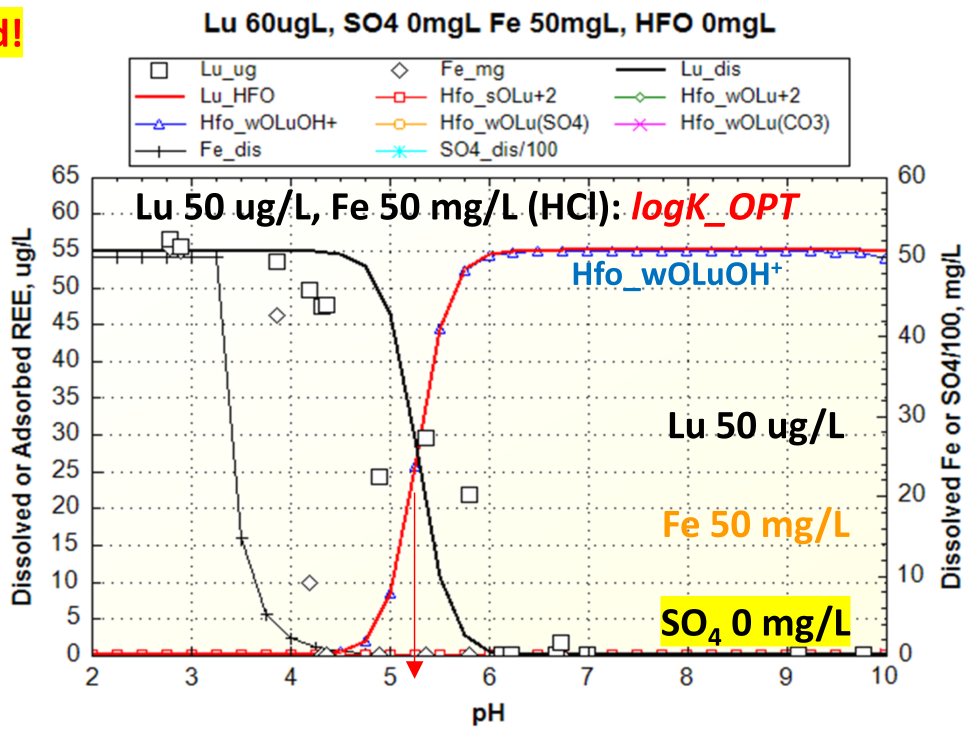


REYs Sorption by "HFO"- Model Calibration to Empirical Data

With Sulfate



Without Sulfate



PHREEQ-N-AMDTreat+REYs Models

Goal: Simulate water-quality changes during passive/active treatment; evaluate design/performance of alternatives for cost/benefit analysis.

Three complementary tools, each with user interface, employ the same expanded thermodynamic database (wateq4fREYsKinetics.dat):

- ✓ CausticTitrationMix2REYs.exe *(equilibrium precipitation/sorption)*
  CausticTitrationMix2REYsMoles.exe
- ✓ TreatTrainMix2REYs.exe *(kinetics plus precipitation/sorption)*

Graphical and tabular output indicates changes in pH, concentrations of solutes, TDS, and specific conductance plus cumulative quantity of elements in solids as a function of pH or retention time.

CausticTitrationMix2REYs (Sorption+Precipitation)

uses updated wateq4fREYsKinetics.dat thermodynamic database

CausticTitrationMix2REYsMoles.exe

Equilibrium interactions among aqueous and surface species

Major and trace ions in one or two solutions A & B

	Soln#A	Soln#B
Design flow (gpm)	690	0
Mix fraction	1	0
Temp (C)	11.63	0.01
DO (mol/L)	0.00031	0.000001
pH	2.0	2.0
Acidity (mol/L)	0	0
☐ Estimate NetAcidity	0	0
Alk (mol/L)	0	0
TIC (mol/L as C)	0.0001	0
☐ Estimate TIC	0	0
Fe (mol/L)	0.0005	1E-13
Fe2 (mol/L)	0.0003	0
☐ Estimate Fe2	0	0
Al (mol/L)	0.0005	1E-13
Mn (mol/L)	0.0005	1E-13
SO4 (mol/L)	0.005	1E-10
S-2 (mol/L)	0	0
Cl (mol/L)	0.0001	0
Ca (mol/L)	0.0025	1E-10
Mg (mol/L)	0.005	1E-10
Na (mol/L)	0.001	0
K (mol/L)	0.0001	0
Si (mol/L)	0.0003	0
NO3N (mol/L)	0.0000001	0
PO4P (mol/L)	0.000001	1E-13
F (mol/L)	0.000001	0
DOC (mol/L as C)	0.0001	0
Oxalate (mol/L as C)	1E-06	1E-16

	Soln#A	Soln#B
As (mol/L)	0.000001	1E-13
Ba (mol/L)	0.000001	1E-13
Cd (mol/L)	0.000001	1E-13
Co (mol/L)	0.000001	1E-13
Cr (mol/L)	0.000001	1E-13
Cu (mol/L)	0.000001	1E-13
Ni (mol/L)	0.000001	1E-13
Pb (mol/L)	0.000001	1E-13
Sc (mol/L)	0.000001	1E-13
Se (mol/L)	0.000001	1E-13
Sr (mol/L)	0.000001	1E-13
U (mol/L)	0.000001	1E-13
Zn (mol/L)	0.000001	1E-13
La (mol/L)	0.000001	1E-13
Ce (mol/L)	0.000001	1E-13
Pr (mol/L)	0.000001	1E-13
Nd (mol/L)	0.000001	1E-13
Sm (mol/L)	0.000001	1E-13
Eu (mol/L)	0.000001	1E-13
Gd (mol/L)	0.000001	1E-13
Tb (mol/L)	0.000001	1E-13
Dy (mol/L)	0.000001	1E-13
Ho (mol/L)	0.000001	1E-13
Er (mol/L)	0.000001	1E-13
Tm (mol/L)	0.000001	1E-13
Yb (mol/L)	0.000001	1E-13
Lu (mol/L)	0.000001	1E-13
Y (mol/L)	0.000001	1E-13

SPECIFIED CONSTANT SORBENT (EXISTING)

HMeO.g	HFO.g	HMO.g	HAO.g					
0.09	0.03	0.03	0.03	HFO + HMO + HAO g/L				
	600	746	68	<--Surface area, m2/g	*64122.6*	*79047.7*	*5304.4*	*Surface area, m2/mol, comp.*
	1.925	1.91	4.6	<--Site density, sites/nm2				
	0.2	*0.0903*	*0.0405*	*<--Site density (weak or y), mol/mol, computed*				
	0.005	*0.1605*		*<--Site density (strong or x), mol/mol, computed*				

Aged and/or freshly precipitated sorbent properties

FRESHLY PRECIPITATED SORBENT (ADDITIONAL)

HFO	HMO	HAO					
600	746	68	<--Surface area, m2/g	*64122.6*	*79047.7*	*5304.4*	*Surface area, m2/mol, comp.*
1.925	1.91	4.6	<--Site density, sites/nm2				
0.2	*0.0903*	*0.0405*	*<--Site density (weak or y), mol/mol, computed*				
0.005	*0.1605*		*<--Site density (strong or x), mol/mol, computed*				

Specified Saturation Index Value at Which Precipitation of Fe, Al, Mn, or Ca Will Occur--ADDED TO FRESH SORBENT

SI_Fe(OH)3	0.0	SI_Al(OH)3	0.0	SI_MnOOH	0.0		
SI_Schwertmannite	1.0	SI_Basaluminite	1.0	SI_Mn(OH)2	0.0		
SI_CaCO3	1.0	SI_Fe-Mn(CO3)	1.0	SI_Fe(OH)2	0.0	SI_Fe-Al-Mn-Ca(PO4)	99

Specified Saturation Index Value at Which Precipitation of REE Will Occur--COMPETES WITH SORPTION

SI_REE(OH)3	99	SI_REE(CO3)1.5	99	SI_REE(C2O4)1.5*	99	SI_REE(PO4)	99

(SI=0, precipitate; SI=99, no precipitate) *Also applies to Fe(C2O4), Al(C2O4), Mn(C2O4), Ca(C2O4), Mg(C2O4)

Select titrant: ◉ NaOH 20 wt% soln ○ Ca(OH)2 ○ CaO ○ Na2CO3 ○ CaCO3

Maximum pH (<=11): 11

Different possible caustic titrants

RUN MODEL

Select output matrix to be saved and graphs to display: ○ Short Output File ◉ Long Output File ☐ Print PHREEQC Output Report

Choose on-screen graphs

☑ Plot REYs_HMeO ☑ Plot REYs_ppt

☐ Plot Sc ☐ Plot Y ☑ Plot La ☐ Plot Ce ☐ Plot Pr ☐ Plot Nd ☐ Plot Sm ☑ Plot Eu

☑ Plot Gd ☐ Plot Tb ☐ Plot Dy ☐ Plot Ho ☐ Plot Er ☐ Plot Tm ☐ Plot Yb ☑ Plot Lu

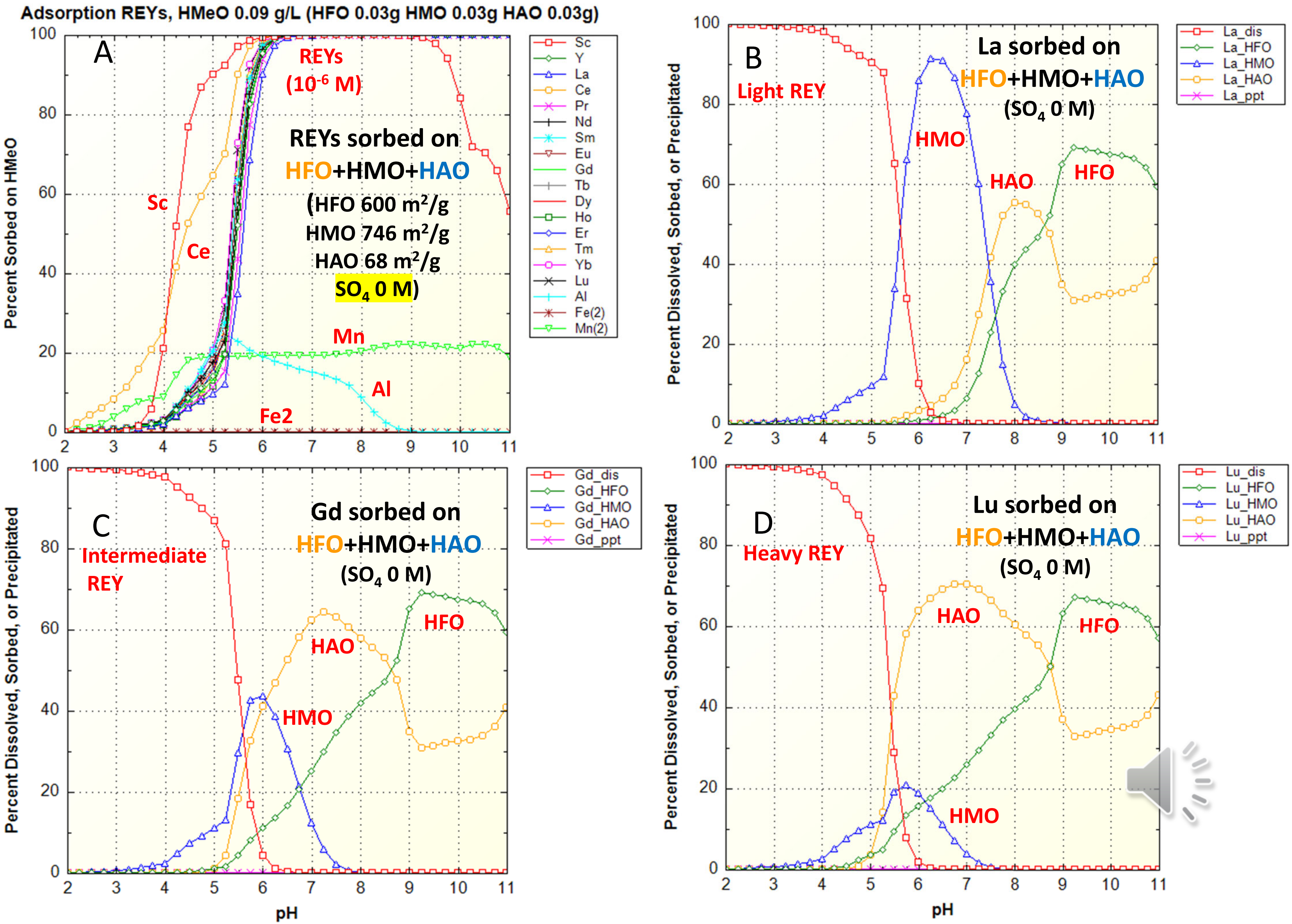
☑ Plot Cations_HMeO ☑ Plot Anions_HMeO ☑ Plot Alkalinity ☑ Plot Al ☑ Plot Fe ☑ Plot Mn

☐ Plot Ca ☐ Plot Mg ☐ Plot Ba ☐ Plot Sr ☐ Plot Cd ☐ Plot Co ☐ Plot Cr ☐ Plot Cu

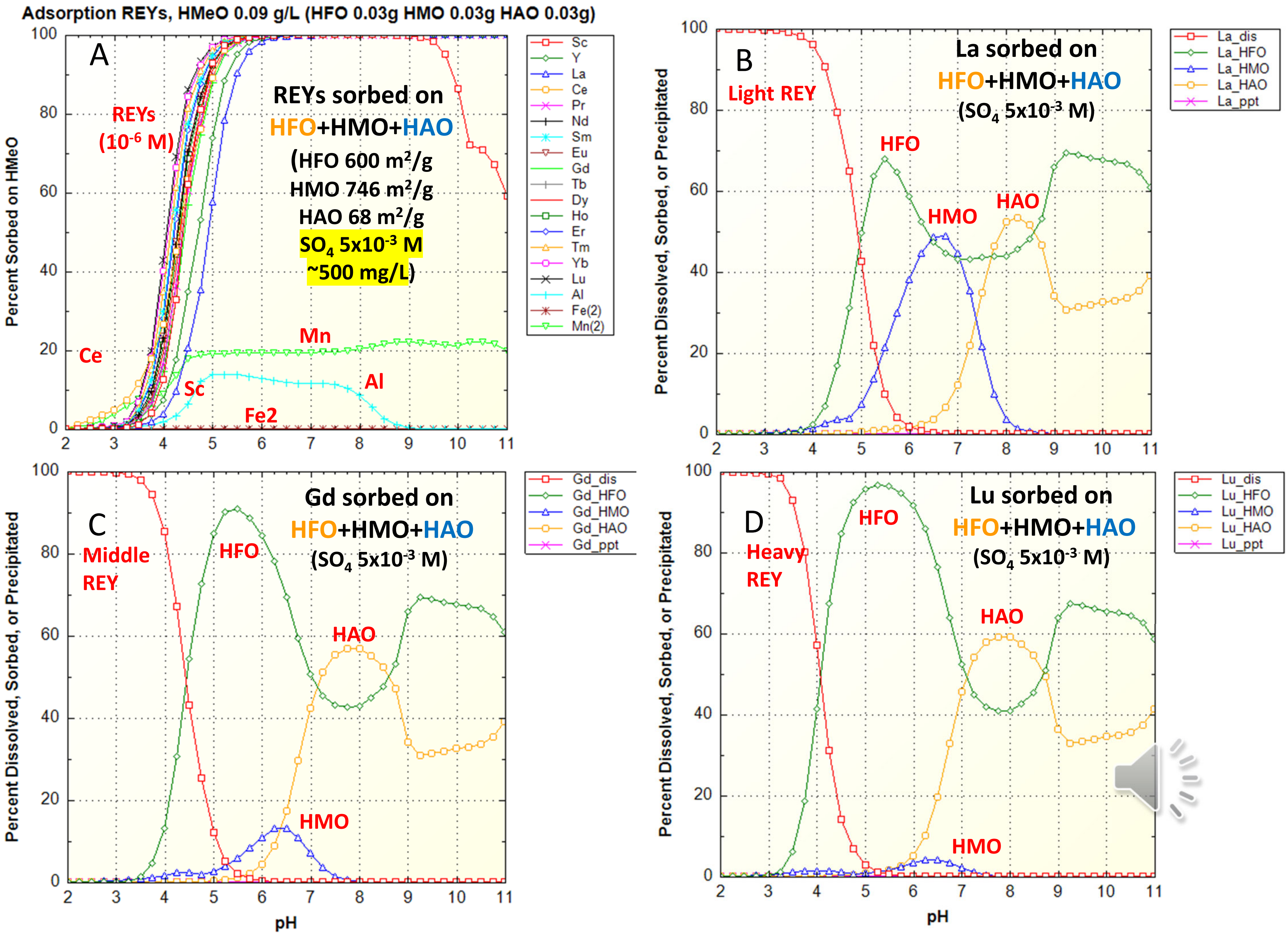
☐ Plot Ni ☐ Plot Pb ☐ Plot Zn ☐ Plot U ☐ Plot As ☐ Plot Se ☐ Plot PO4 ☐ Plot SO4

CausticTitrationMix2REYsMoles.exe created by C.A. Cravotta III, U.S. Geological Survey. Release version 1.0.3. July 2023

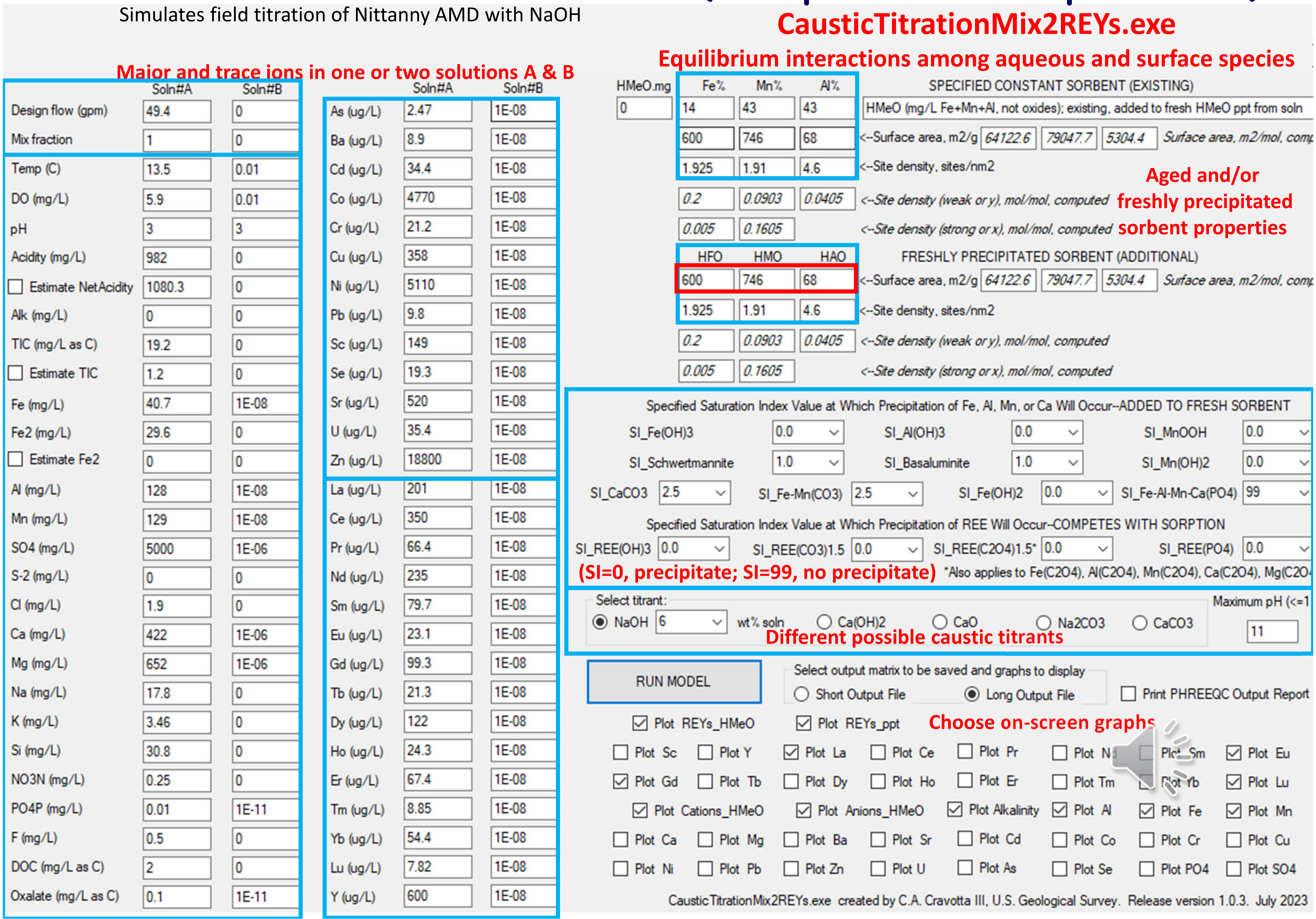
Sorption of REYs on “HMeO“ (0.03 g ea HFO, HMO, HAO) – No Sulfate



Sorption of REYs on "HMeO+Sulfate" (0.03 g ea HFO, HMO, HAO)



CausticTitrationMix2REYs (Sorption+Precipitation)



Simulates field titration of Nittanny AMD with NaOH

CausticTitrationMix2REYs.exe

Equilibrium interactions among aqueous and surface species

Major and trace ions in one or two solutions A & B

	Soln#A	Soln#B
Design flow (gpm)	49.4	0
Mix fraction	1	0
Temp (C)	13.5	0.01
DO (mg/L)	5.9	0.01
pH	3	3
Acidity (mg/L)	982	0
☐ Estimate NetAcidity	1080.3	0
Alk (mg/L)	0	0
TIC (mg/L as C)	19.2	0
☐ Estimate TIC	1.2	0
Fe (mg/L)	40.7	1E-08
Fe2 (mg/L)	29.6	0
☐ Estimate Fe2	0	0
Al (mg/L)	128	1E-08
Mn (mg/L)	129	1E-08
SO4 (mg/L)	5000	1E-06
S-2 (mg/L)	0	0
Cl (mg/L)	1.9	0
Ca (mg/L)	422	1E-06
Mg (mg/L)	652	1E-06
Na (mg/L)	17.8	0
K (mg/L)	3.46	0
Si (mg/L)	30.8	0
NO3N (mg/L)	0.25	0
PO4P (mg/L)	0.01	1E-11
F (mg/L)	0.5	0
DOC (mg/L as C)	2	0
Oxalate (mg/L as C)	0.1	1E-11

	Soln#A	Soln#B
As (ug/L)	2.47	1E-08
Ba (ug/L)	8.9	1E-08
Cd (ug/L)	34.4	1E-08
Co (ug/L)	4770	1E-08
Cr (ug/L)	21.2	1E-08
Cu (ug/L)	358	1E-08
Ni (ug/L)	5110	1E-08
Pb (ug/L)	9.8	1E-08
Sc (ug/L)	149	1E-08
Se (ug/L)	19.3	1E-08
Sr (ug/L)	520	1E-08
U (ug/L)	35.4	1E-08
Zn (ug/L)	18800	1E-08
La (ug/L)	201	1E-08
Ce (ug/L)	350	1E-08
Pr (ug/L)	66.4	1E-08
Nd (ug/L)	235	1E-08
Sm (ug/L)	79.7	1E-08
Eu (ug/L)	23.1	1E-08
Gd (ug/L)	99.3	1E-08
Tb (ug/L)	21.3	1E-08
Dy (ug/L)	122	1E-08
Ho (ug/L)	24.3	1E-08
Er (ug/L)	67.4	1E-08
Tm (ug/L)	8.85	1E-08
Yb (ug/L)	54.4	1E-08
Lu (ug/L)	7.82	1E-08
Y (ug/L)	600	1E-08

HMeO.mg: 0

SPECIFIED CONSTANT SORBENT (EXISTING)

Fe%	Mn%	Al%	
14	43	43	HMeO (mg/L Fe+Mn+Al, not oxides); existing, added to fresh HMeO ppt from soln
600	746	68	<--Surface area, m2/g 64122.6 79047.7 5304.4 Surface area, m2/mol, comp
1.925	1.91	4.6	<--Site density, sites/nm2
0.2	0.0903	0.0405	<--Site density (weak or y), mol/mol, computed
0.005	0.1605		<--Site density (strong or x), mol/mol, computed

Aged and/or freshly precipitated sorbent properties

FRESHLY PRECIPITATED SORBENT (ADDITIONAL)

HFO	HMO	HAO	
600	746	68	<--Surface area, m2/g 64122.6 79047.7 5304.4 Surface area, m2/mol, comp
1.925	1.91	4.6	<--Site density, sites/nm2
0.2	0.0903	0.0405	<--Site density (weak or y), mol/mol, computed
0.005	0.1605		<--Site density (strong or x), mol/mol, computed

Specified Saturation Index Value at Which Precipitation of Fe, Al, Mn, or Ca Will Occur--ADDED TO FRESH SORBENT

SI_Fe(OH)3 0.0 | SI_Al(OH)3 0.0 | SI_MnOOH 0.0
SI_Schwertmannite 1.0 | SI_Basaluminite 1.0 | SI_Mn(OH)2 0.0
SI_CaCO3 2.5 | SI_Fe-Mn(CO3) 2.5 | SI_Fe(OH)2 0.0 | SI_Fe-Al-Mn-Ca(PO4) 99

Specified Saturation Index Value at Which Precipitation of REE Will Occur--COMPETES WITH SORPTION

SI_REE(OH)3 0.0 | SI_REE(CO3)1.5 0.0 | SI_REE(C2O4)1.5* 0.0 | SI_REE(PO4) 0.0

(SI=0, precipitate; SI=99, no precipitate) *Also applies to Fe(C2O4), Al(C2O4), Mn(C2O4), Ca(C2O4), Mg(C2O4

Select titrant: ◉ NaOH 6 wt% soln ○ Ca(OH)2 ○ CaO ○ Na2CO3 ○ CaCO3 Maximum pH (<=1 11

Different possible caustic titrants

RUN MODEL

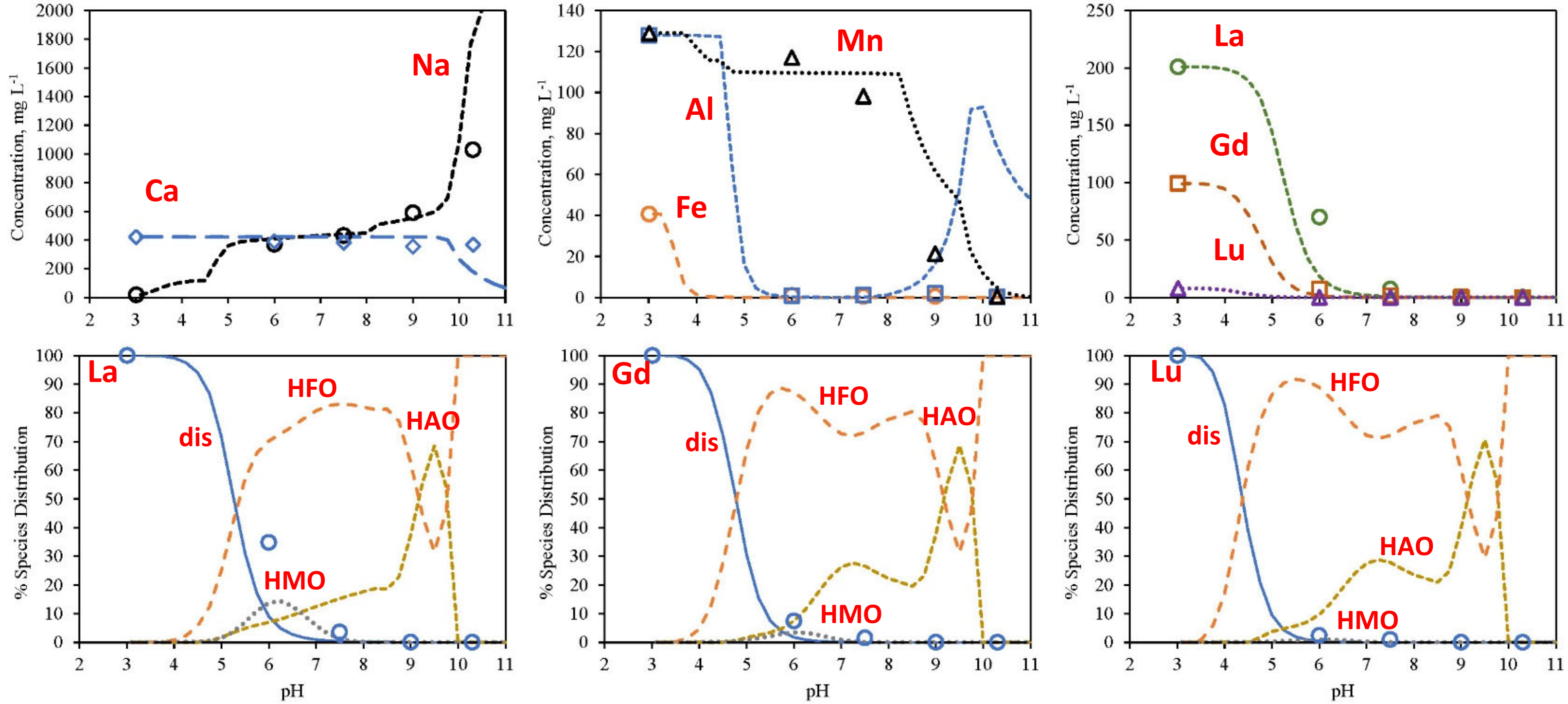
Select output matrix to be saved and graphs to display: ○ Short Output File ◉ Long Output File ☐ Print PHREEQC Output Report

Choose on-screen graphs

☑ Plot REYs_HMeO ☑ Plot REYs_ppt
☐ Plot Sc ☐ Plot Y ☑ Plot La ☐ Plot Ce ☐ Plot Pr ☐ Plot N ☐ Plot Sm ☑ Plot Eu
☑ Plot Gd ☐ Plot Tb ☐ Plot Dy ☐ Plot Ho ☐ Plot Er ☐ Plot Tm ☐ Plot Yb ☑ Plot Lu
☑ Plot Cations_HMeO ☑ Plot Anions_HMeO ☑ Plot Alkalinity ☑ Plot Al ☑ Plot Fe ☑ Plot Mn
☐ Plot Ca ☐ Plot Mg ☐ Plot Ba ☐ Plot Sr ☐ Plot Cd ☐ Plot Co ☐ Plot Cr ☐ Plot Cu
☐ Plot Ni ☐ Plot Pb ☐ Plot Zn ☐ Plot U ☐ Plot As ☐ Plot Se ☐ Plot PO4 ☐ Plot SO4

CausticTitrationMix2REYs.exe created by C.A. Cravotta III, U.S. Geological Survey. Release version 1.0.3. July 2023

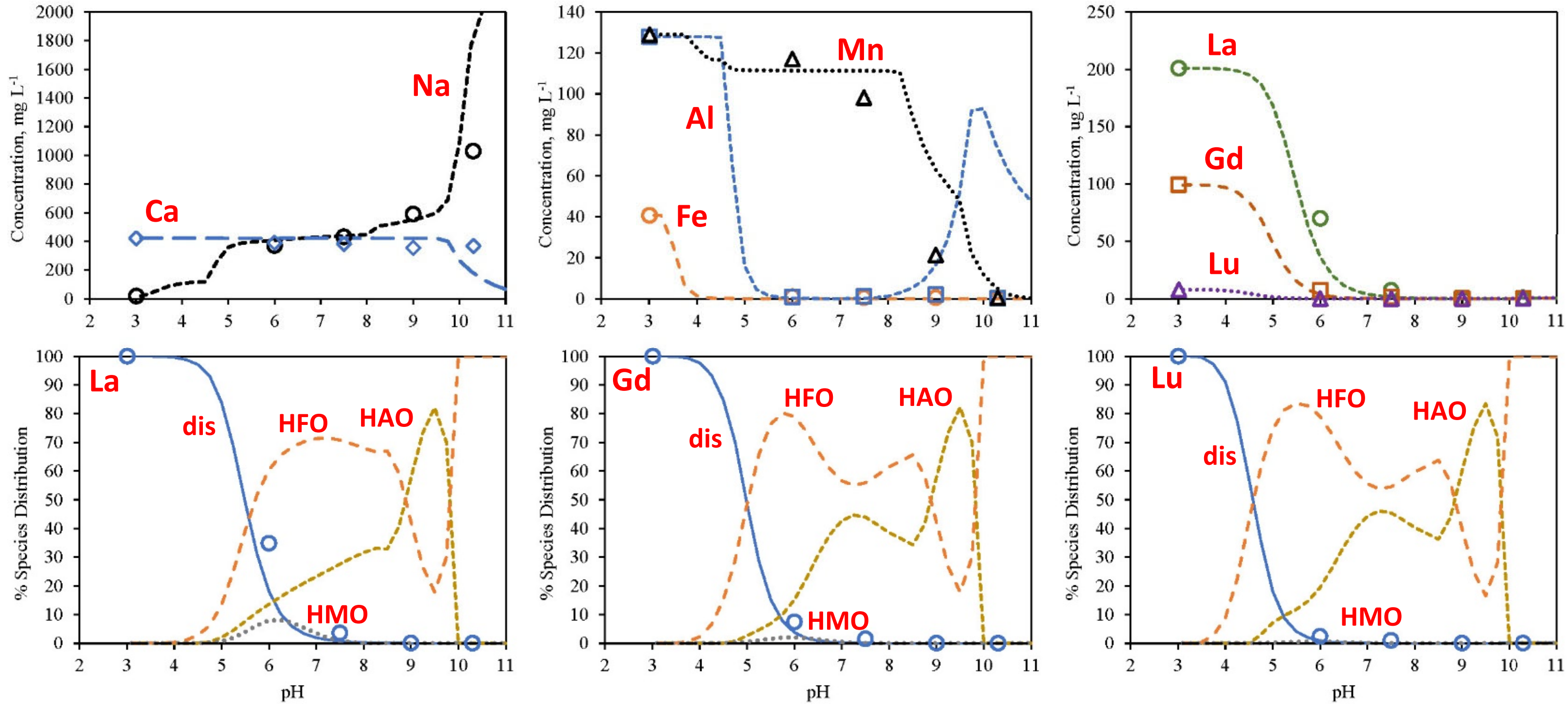
Equilibrium Speciation of REYs — Nittany AMD Titration



Default Asp:
HFO=600 m²/g
HMO=746 m²/g
HAO=68 m²/g

SI(REY)=99
(no REYppt)

REYs sorbed on fresh HFO+ HMO+HAO at pH > 5;



Decreased Asp:
HFO=285 m²/g
HMO=300 m²/g
HAO=68 m²/g

SI(REY)=99
(no REYppt)

REYs sorbed on fresh HFO+ HMO+HAO at pH > 5;

TreatTrainMix2REYs Sequential Model

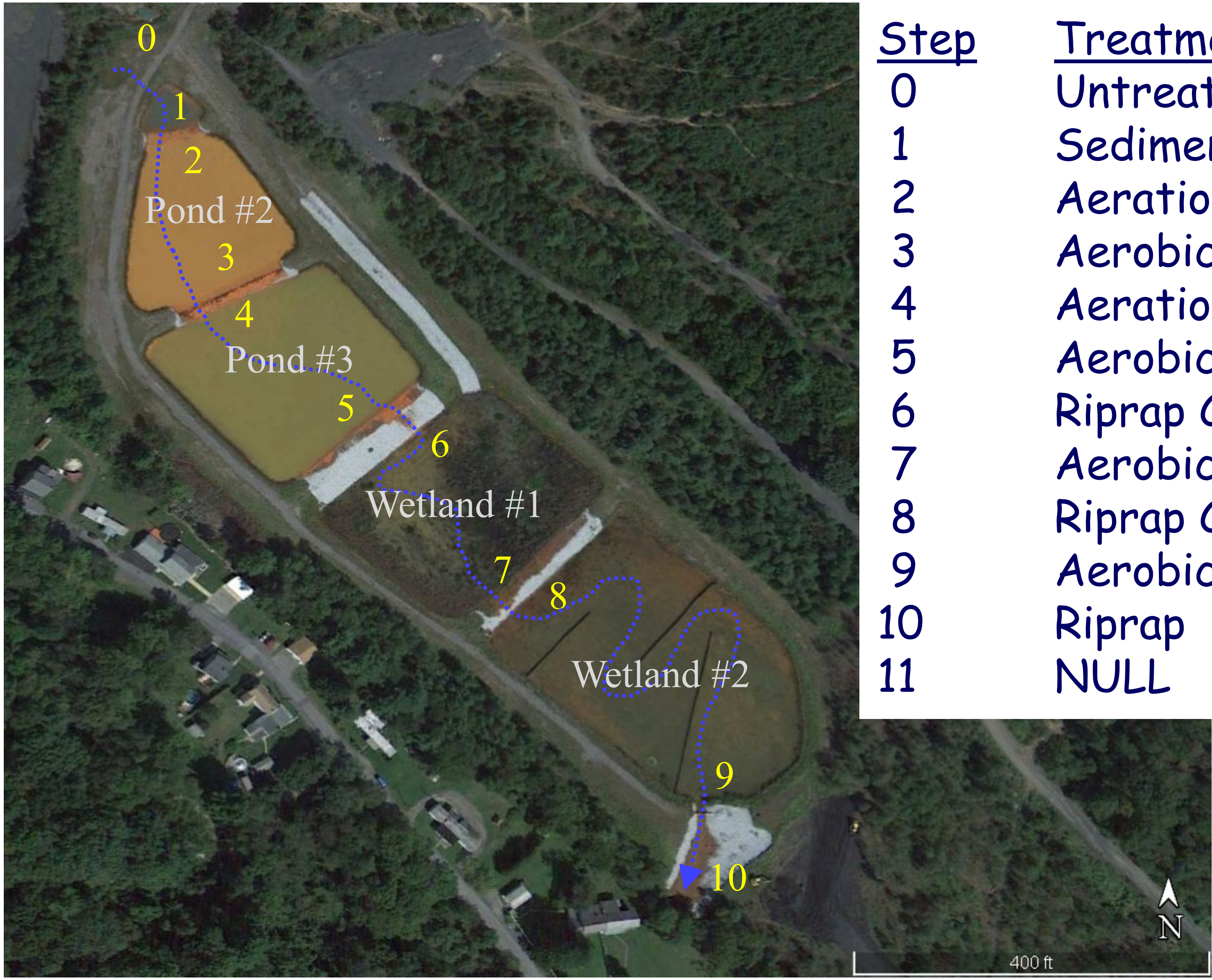
Simulate sequential changes through treatment--equilibrium aqueous and surface (sorption) speciation combined with kinetics models:

- ✓ Atmospheric exchange--CO_2 outgassing and O_2 ingassing.
- ✓ Iron and manganese oxidation--pH-dependent homogeneous and heterogeneous rate laws (pH, pO_2, sorption) plus catalysis by acidophilic and neutrophilic iron-oxidizing bacteria.
- ✓ Organic-carbon oxidation--reduction of sulfate and nitrate by carbon, plus Fe^{III} by adsorbed sulfide (from sulfate reduction).
- ✓ Limestone dissolution--considers solution chemistry (pH, pCO_2) plus surface area of limestone fragments (particle size).
- ❖ *Adsorption and precipitation of REYs and other trace elements.*

TreatTrainMix2REYs Sequential Model
(Kinetics plus Equilibrium Sorption+Precipitation)

Silver Creek AMD: Passive Treatment Aerobic Ponds + Aerobic Wetlands

TreatTrainMix2REYs.exe

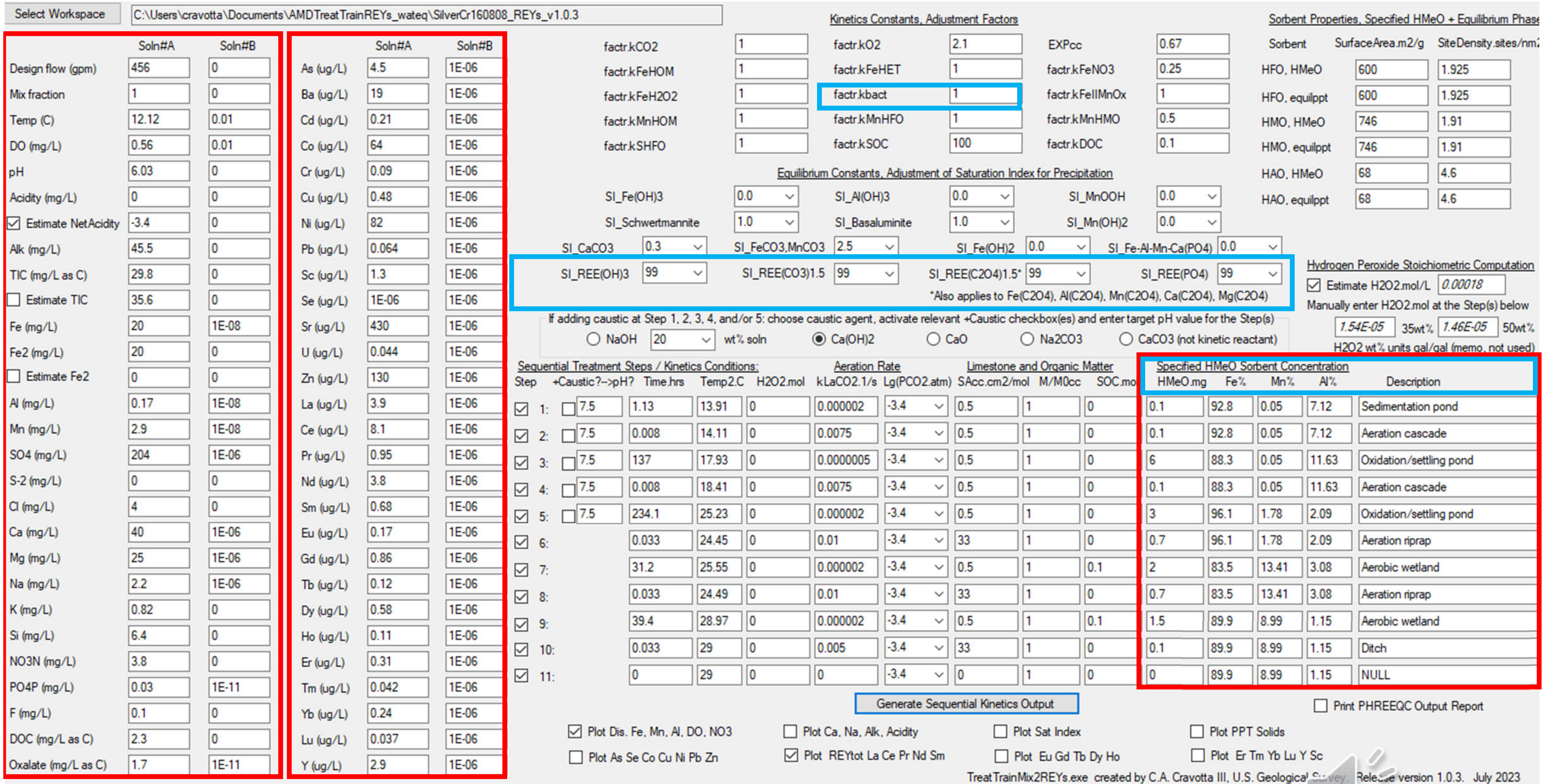


Step	Treatment
0	Untreated
1	Sedimentation Pond 1
2	Aeration Cascade
3	Aerobic Pond 2
4	Aeration Cascade
5	Aerobic Pond 3
6	Riprap Cascade
7	Aerobic Wetland 1
8	Riprap Cascade
9	Aerobic Wetland 2
10	Riprap
11	NULL

TreatTrainMix2REYs Sequential Model

Treatment Simulation: Silver Creek AMD, Aerobic Ponds+Wetlands

TreatTrainMix2REYs.exe

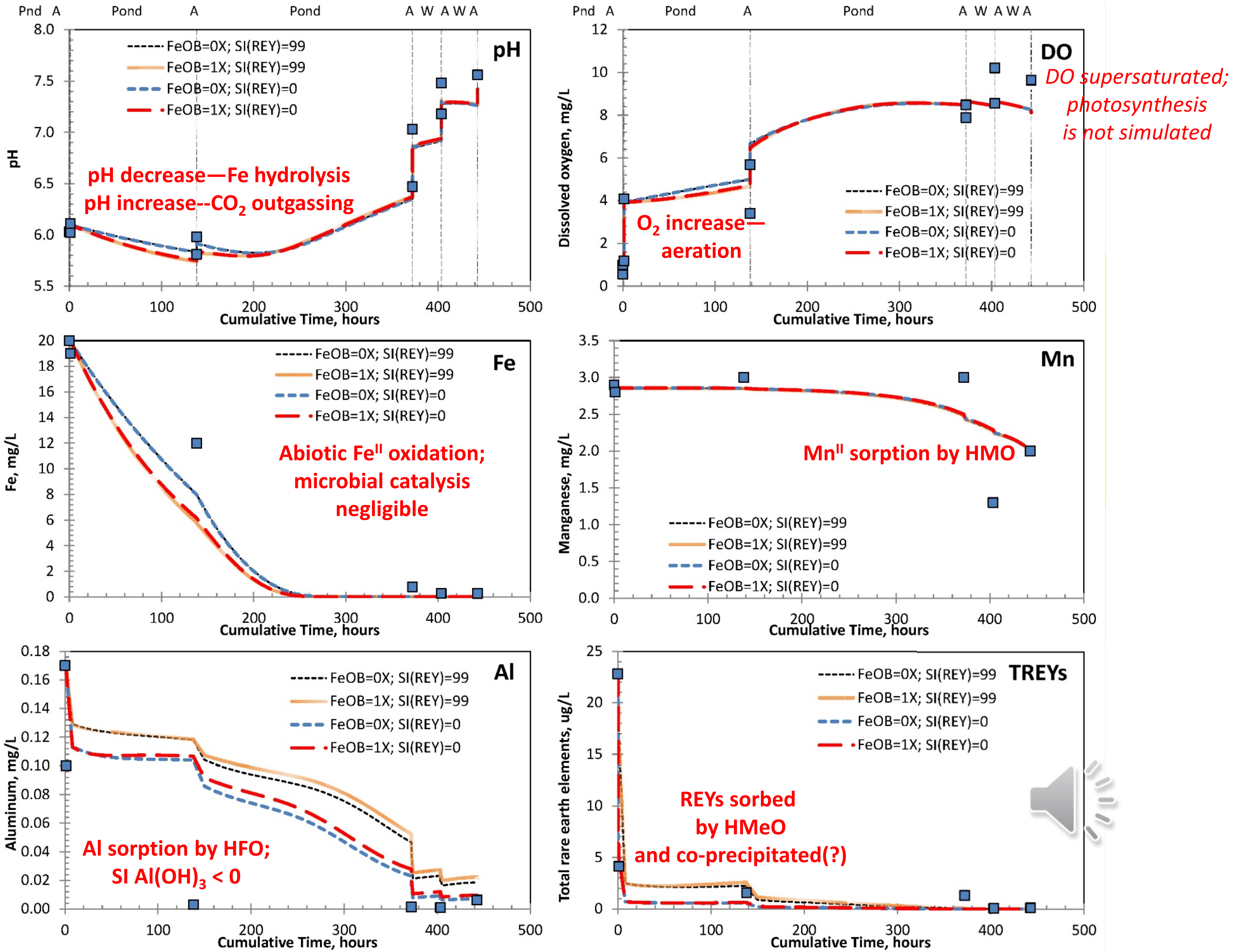


Silver Creek Mine (Aug. 2016):

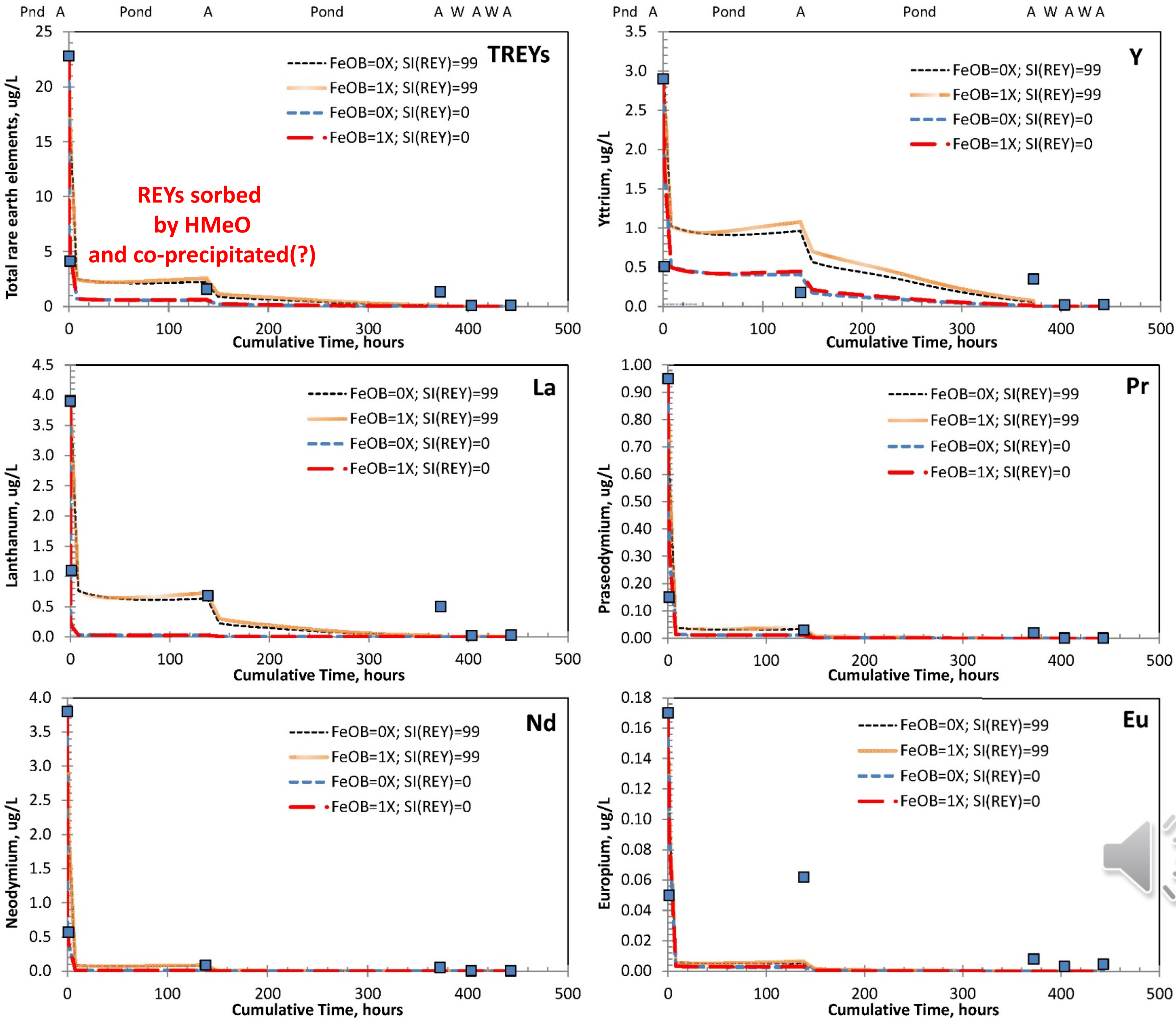
moderate Fe & Mn, moderate REYs (~23 ug/L)

"validation data" from Ashby (2017) for comparison to simulations

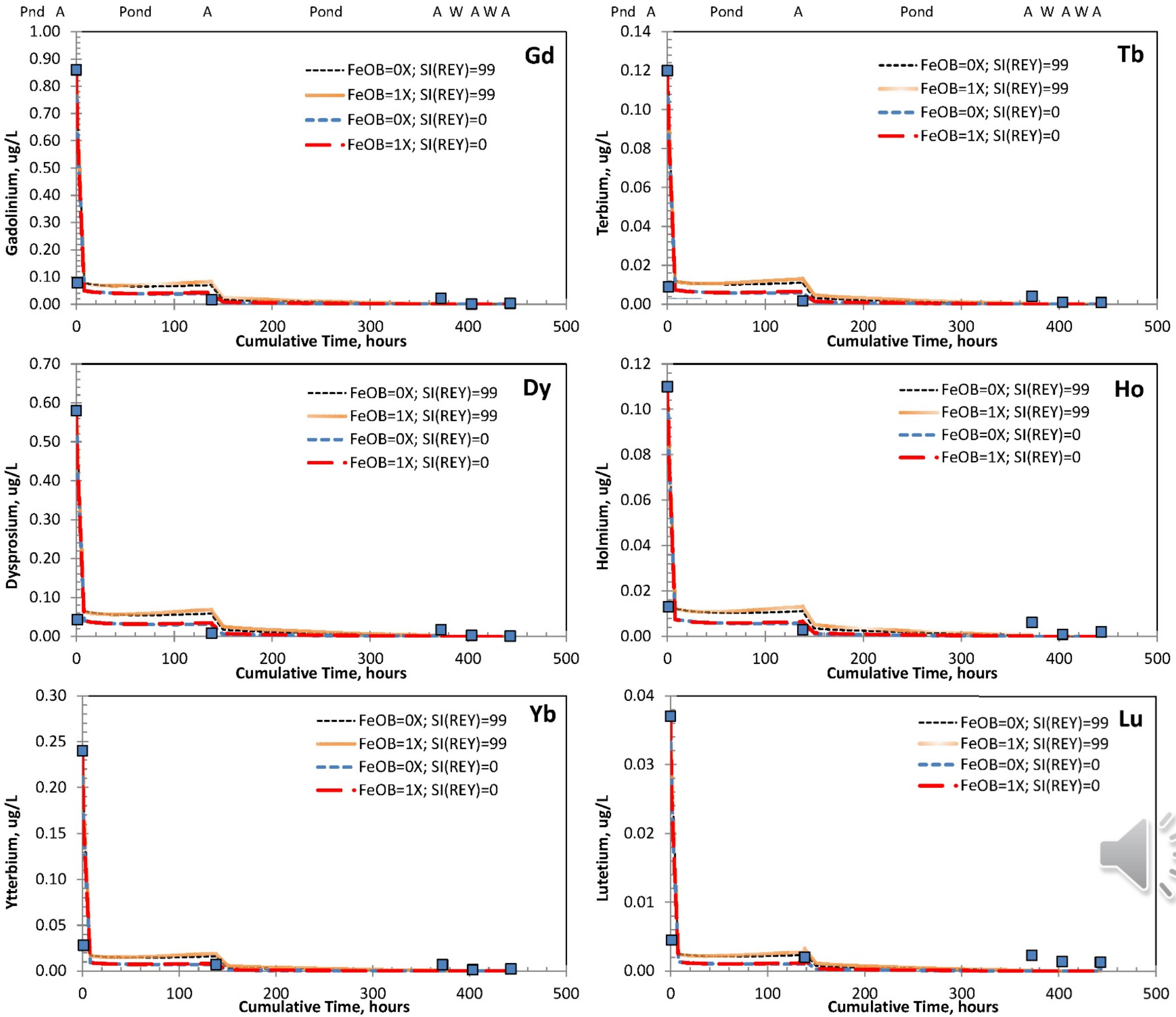
Treatment Simulation: Silver Creek Aerobic Ponds+Wetlands (160808)



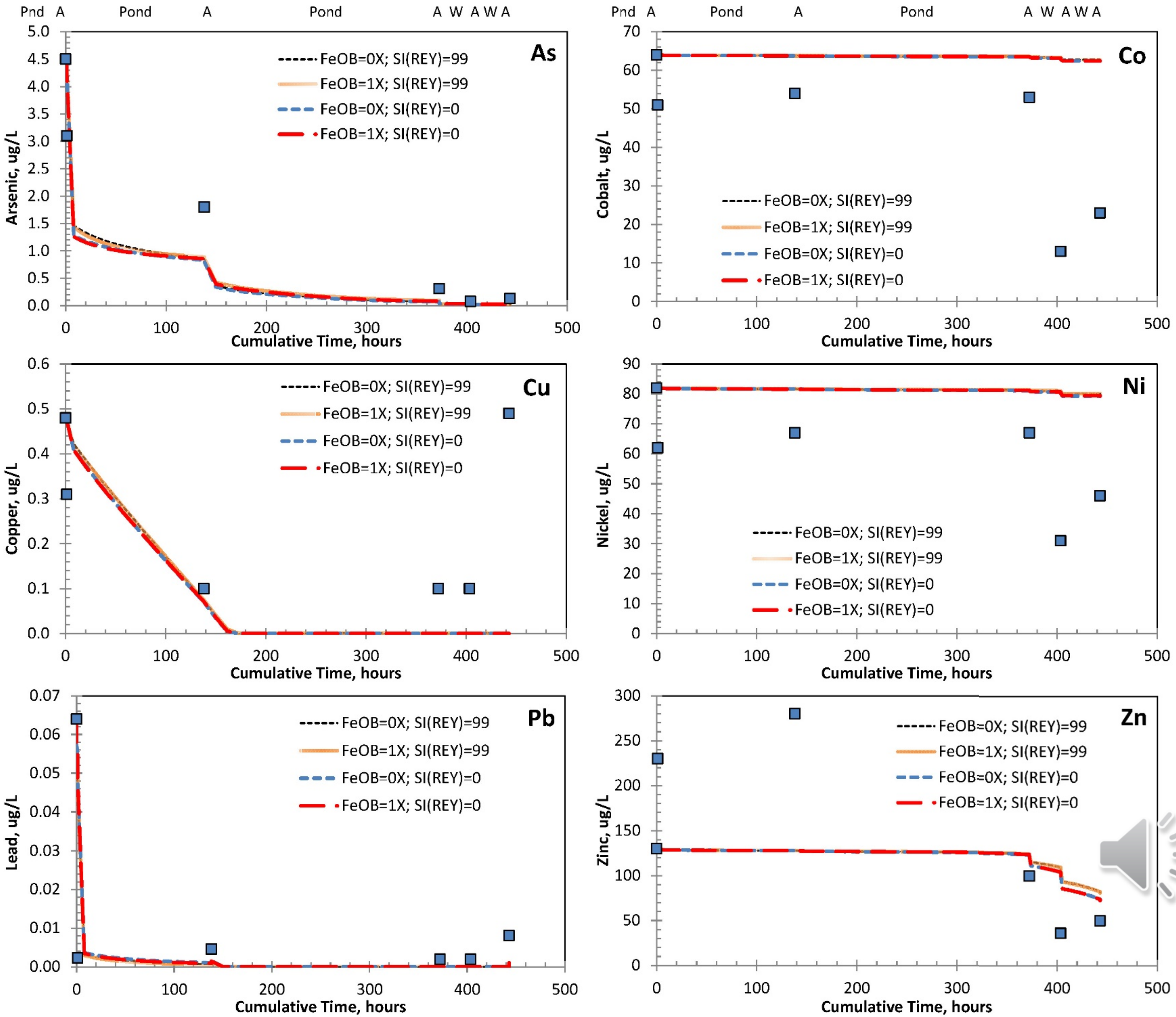
Treatment Simulation: Silver Creek Aerobic Ponds+Wetlands (160808)



Treatment Simulation: Silver Creek Aerobic Ponds+Wetlands (160808)

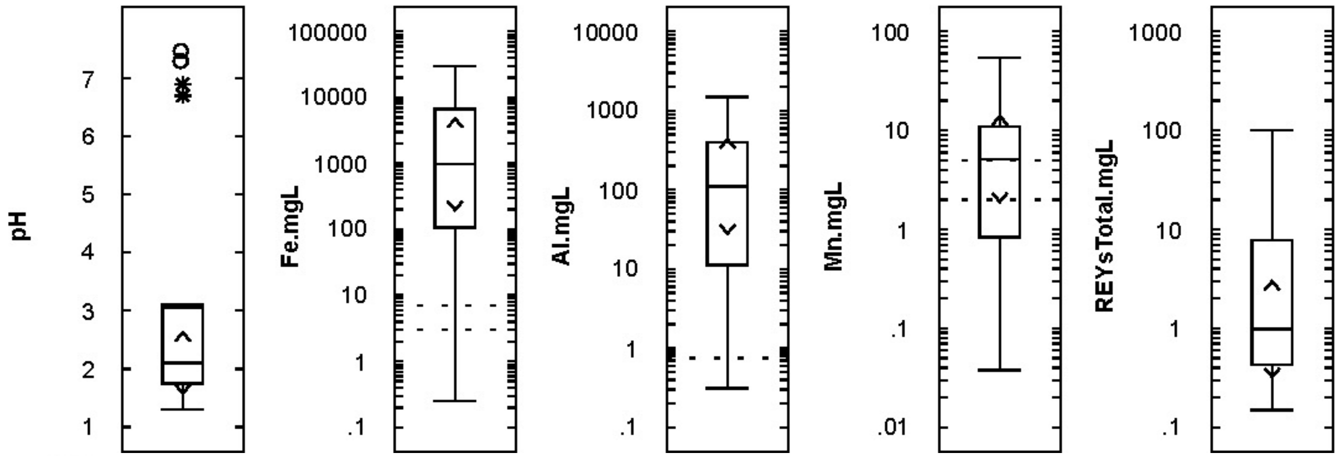


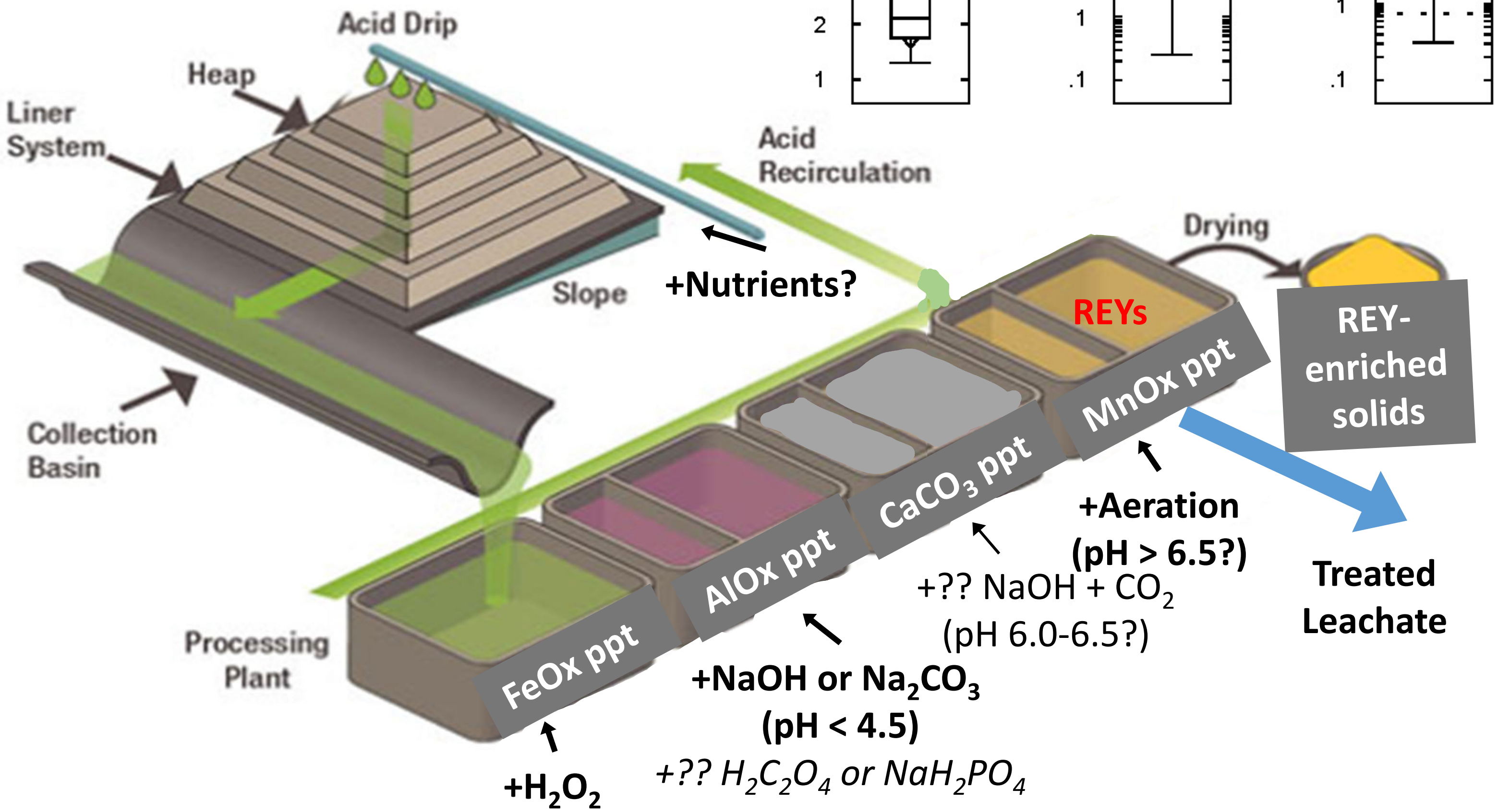
Treatment Simulation: Silver Creek Aerobic Ponds+Wetlands (160808)



Simulated Treatment of Coal Refuse 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.





The 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.

TreatTrainMix2REYs Sequential Model

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

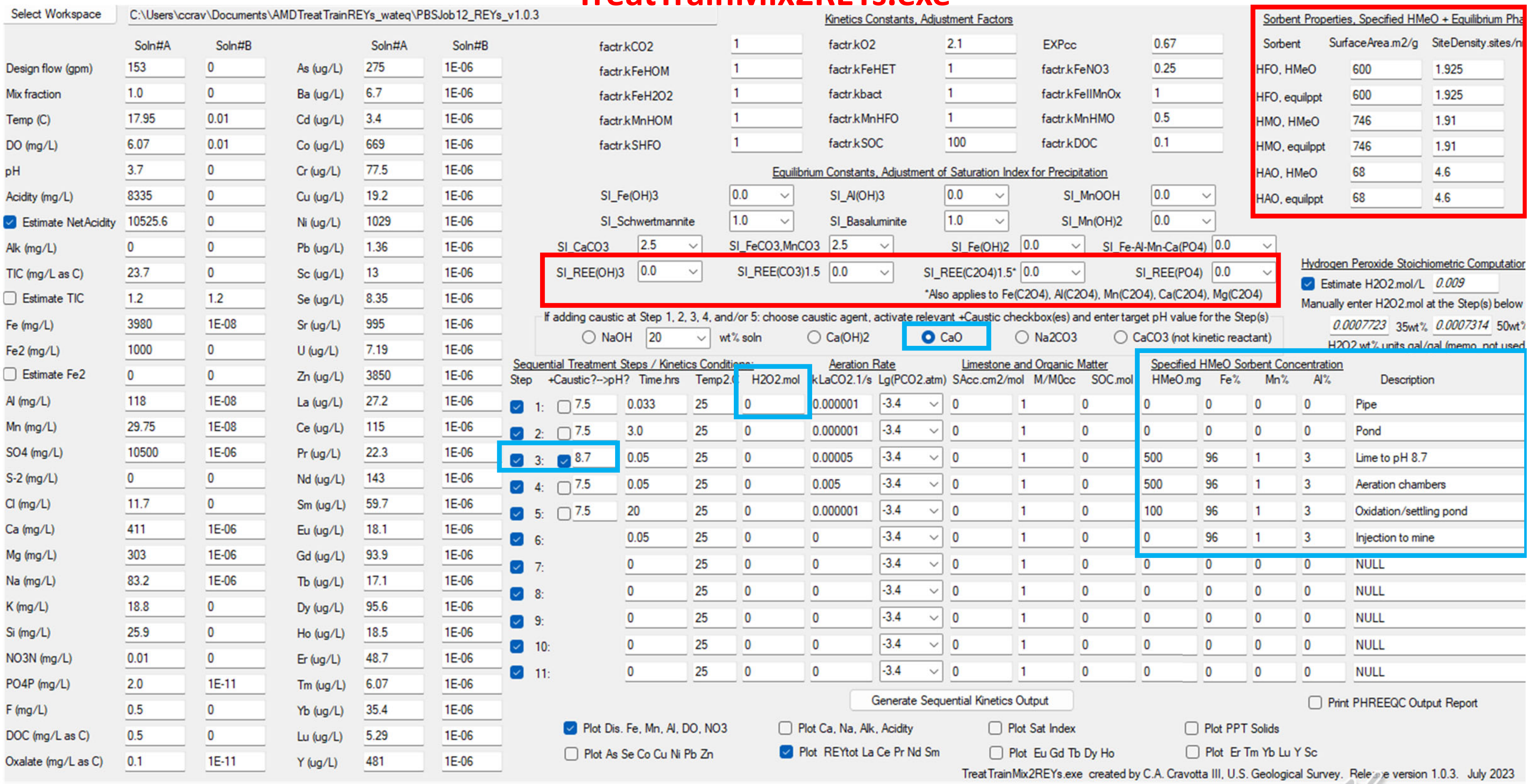
TreatTrainMix2REYs.exe

Step	Currently Lime Treatment
0	Untreated
1	Sedimentation Pond
2	Lime to pH ~8.5-9.0
3	Aerobic chambers
4	Oxidation/setting pond(s)
5	Injection to mine
6	NULL
7	NULL
8	NULL
9	NULL
10	NULL
11	NULL

TreatTrainMix2REYs Sequential Model

Current Treatment of Coal Refuse Leachate with Lime

TreatTrainMix2REYs.exe



PBS Job 12:

Lime to pH ≥ 8.7

High acidity and REYs

Current treatment produces sludge containing Ca, Fe, Al, Mn, and REYs

TreatTrainMix2REYs Sequential Model

Hypothetical Sequential Treatment of Leachate with H_2O_2+NaOH

TreatTrainMix2REYs.exe

Select Workspace: C:\Users\ccrav\Documents\AMDTreatTrainREYs_wateq\PBSJob12_REYs_v1.0.3

	Soln#A	Soln#B		Soln#A	Soln#B
Design flow (gpm)	153	0	As (ug/L)	275	1E-06
Mix fraction	1.0	0	Ba (ug/L)	6.7	1E-06
Temp (C)	17.95	0.01	Cd (ug/L)	3.4	1E-06
DO (mg/L)	6.07	0.01	Co (ug/L)	669	1E-06
pH	3.7	0	Cr (ug/L)	77.5	1E-06
Acidity (mg/L)	8335	0	Cu (ug/L)	19.2	1E-06
☑ Estimate NetAcidity	10525.6	0	Ni (ug/L)	1029	1E-06
Alk (mg/L)	0	0	Pb (ug/L)	1.36	1E-06
TIC (mg/L as C)	23.7	0	Sc (ug/L)	13	1E-06
☐ Estimate TIC	1.2	1.2	Se (ug/L)	8.35	1E-06
Fe (mg/L)	3980	1E-08	Sr (ug/L)	995	1E-06
Fe2 (mg/L)	1000	0	U (ug/L)	7.19	1E-06
☐ Estimate Fe2	0	0	Zn (ug/L)	3850	1E-06
Al (mg/L)	118	1E-08	La (ug/L)	27.2	1E-06
Mn (mg/L)	29.75	1E-08	Ce (ug/L)	115	1E-06
SO4 (mg/L)	10500	1E-06	Pr (ug/L)	22.3	1E-06
S-2 (mg/L)	0	0	Nd (ug/L)	143	1E-06
Cl (mg/L)	11.7	0	Sm (ug/L)	59.7	1E-06
Ca (mg/L)	411	1E-06	Eu (ug/L)	18.1	1E-06
Mg (mg/L)	303	1E-06	Gd (ug/L)	93.9	1E-06
Na (mg/L)	83.2	1E-06	Tb (ug/L)	17.1	1E-06
K (mg/L)	18.8	0	Dy (ug/L)	95.6	1E-06
Si (mg/L)	25.9	0	Ho (ug/L)	18.5	1E-06
NO3N (mg/L)	0.01	0	Er (ug/L)	48.7	1E-06
PO4P (mg/L)	2.0	1E-11	Tm (ug/L)	6.07	1E-06
F (mg/L)	0.5	0	Yb (ug/L)	35.4	1E-06
DOC (mg/L as C)	0.5	0	Lu (ug/L)	5.29	1E-06
Oxalate (mg/L as C)	0.1	1E-11	Y (ug/L)	481	1E-06

Kinetics Constants, Adjustment Factors

factr.kCO2	1	factr.kO2	2.1	EXPcc	0.67
factr.kFeHOM	1	factr.kFeHET	1	factr.kFeNO3	0.25
factr.kFeH2O2	1	factr.kbact	1	factr.kFeIIMnOx	1
factr.kMnHOM	1	factr.kMnHFO	1	factr.kMnHMO	0.5
factr.kSHFO	1	factr.kSOC	100	factr.kDOC	0.1

Sorbent Properties, Specified HMeO + Equilibrium Phas

Sorbent	SurfaceArea.m2/g	SiteDensity.sites/nm
HFO, HMeO	600	1.925
HFO, equilppt	600	1.925
HMO, HMeO	746	1.91
HMO, equilppt	746	1.91
HAO, HMeO	68	4.6
HAO, equilppt	68	4.6

Equilibrium Constants, Adjustment of Saturation Index for Precipitation

SI_Fe(OH)3	0.0	SI_Al(OH)3	0.0	SI_MnOOH	0.0		
SI_Schwertmannite	0.0	SI_Basaluminite	0.0	SI_Mn(OH)2	0.0		
SI_CaCO3	0.3	SI_FeCO3,MnCO3	0.3	SI_Fe(OH)2	0.0	SI_Fe-Al-Mn-Ca(PO4)	0.0
SI_REE(OH)3	0.0	SI_REE(CO3)1.5	0.0	SI_REE(C2O4)1.5*	0.0	SI_REE(PO4)	0.0

*Also applies to Fe(C2O4), Al(C2O4), Mn(C2O4), Ca(C2O4), Mg(C2O4)

Hydrogen Peroxide Stoichiometric Computation

☑ Estimate H2O2.mol/L 0.009

Manually enter H2O2.mol at the Step(s) below

0.0007723 35wt% 0.0007314 50wt%

H2O2 wt% units gal/gal (memo, not used)

If adding caustic at Step 1, 2, 3, 4, and/or 5: choose caustic agent, activate relevant +Caustic checkbox(es) and enter target pH value for the Step(s)

◉ NaOH 30 wt% soln ○ Ca(OH)2 ○ CaO ○ Na2CO3 ○ CaCO3 (not kinetic reactant)

Sequential Treatment Steps / Kinetics Conditions; Aeration Rate; Limestone and Organic Matter; Specified HMeO Sorbent Concentration

Step	+Caustic?-->pH?	Time.hrs	Temp2.C	H2O2.mol	kLaCO2.1/s	Lg(PCO2.atm)	SAcc.cm2/mol	M/M0cc	SOC.mol	HMeO.mg	Fe%	Mn%	Al%	Description
☑ 1:	☐	0.033	25	0.0092	0.000001	-3.4	0	1	0	0	0	0	0	Hydrogen peroxide
☑ 2:	☐	3.0	25	0	0.00005	-3.4	0	1	0	500	100	0	0	Oxidation/mixing pond
☑ 3:	☑ 3.0	0.05	25	0	0.0005	-3.4	0	1	0	500	95	0	5	Sodium hydroxide pH 3.0
☑ 4:	☐	0.0833	25	0	0.005	-3.4	0	1	0	500	95	0	5	Aeration/mixing
☑ 5:	☐	6.0	25	0	0.000001	-3.4	0	1	0	100	95	0	5	Oxidation/settling pond
☑ 6:		0.05	25	0	0.01	-3.4	0	1	0	0.1	90	0	10	Aeration cascades
☑ 7:		6.0	25	0	0.000001	-3.4	0	1	0	100	70	0	30	Oxidation/settling pond
☑ 8:		0.05	25	0	0.01	-3.4	0	1	0	0.1	60	5	35	Aeration cascades
☑ 9:		12.0	25	0	0.0000001	-3.4	72	1	0	100	0	5	95	Oxic limestone bed
☑ 10:		16.0	25	0	0.0000001	-3.4	72	1	0	100	0	95	5	Mn sorption bed
☑ 11:		0.033	25	0	0.005	-3.4	0	1	0	0.1	10	85	5	Ditch

Generate Sequential Kinetics Output

☑ Print PHREEQC Output Report

☑ Plot Dis. Fe, Mn, Al, DO, NO3 ☐ Plot Ca, Na, Alk, Acidity ☐ Plot Sat Index ☐ Plot PPT Solids

☐ Plot As Se Co Cu Ni Pb Zn ☑ Plot REYtot La Ce Pr Nd Sm ☐ Plot Eu Gd Tb Dy Ho ☐ Plot Er Tm Yb Lu Y Sc

TreatTrainMix2REYs.exe created by C.A. Cravotta III, U.S. Geological Survey. Release version 1.0.3. July 2023

PBS Job 12:

High acidity and REYs

Alternative treatment to segregate Fe, Al, and Mn, concentrating REYs

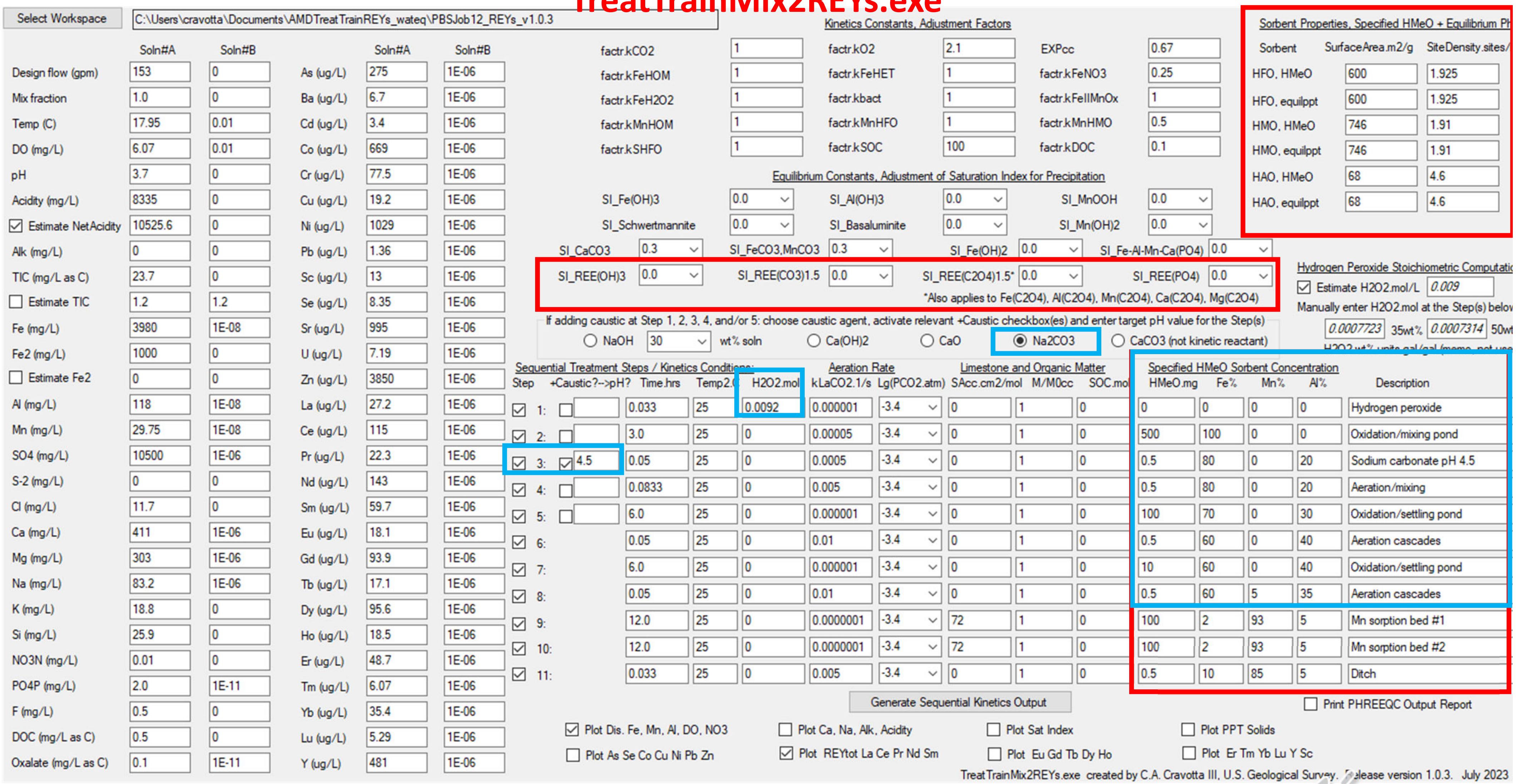
H_2O_2 + NaOH to pH ~3.0

(up to 4.5?)

TreatTrainMix2REYs Sequential Model

Hypothetical Sequential Treatment of Leachate with H_2O_2+Na_2CO_3

TreatTrainMix2REYs.exe



PBS Job 12:

High acidity and REYs

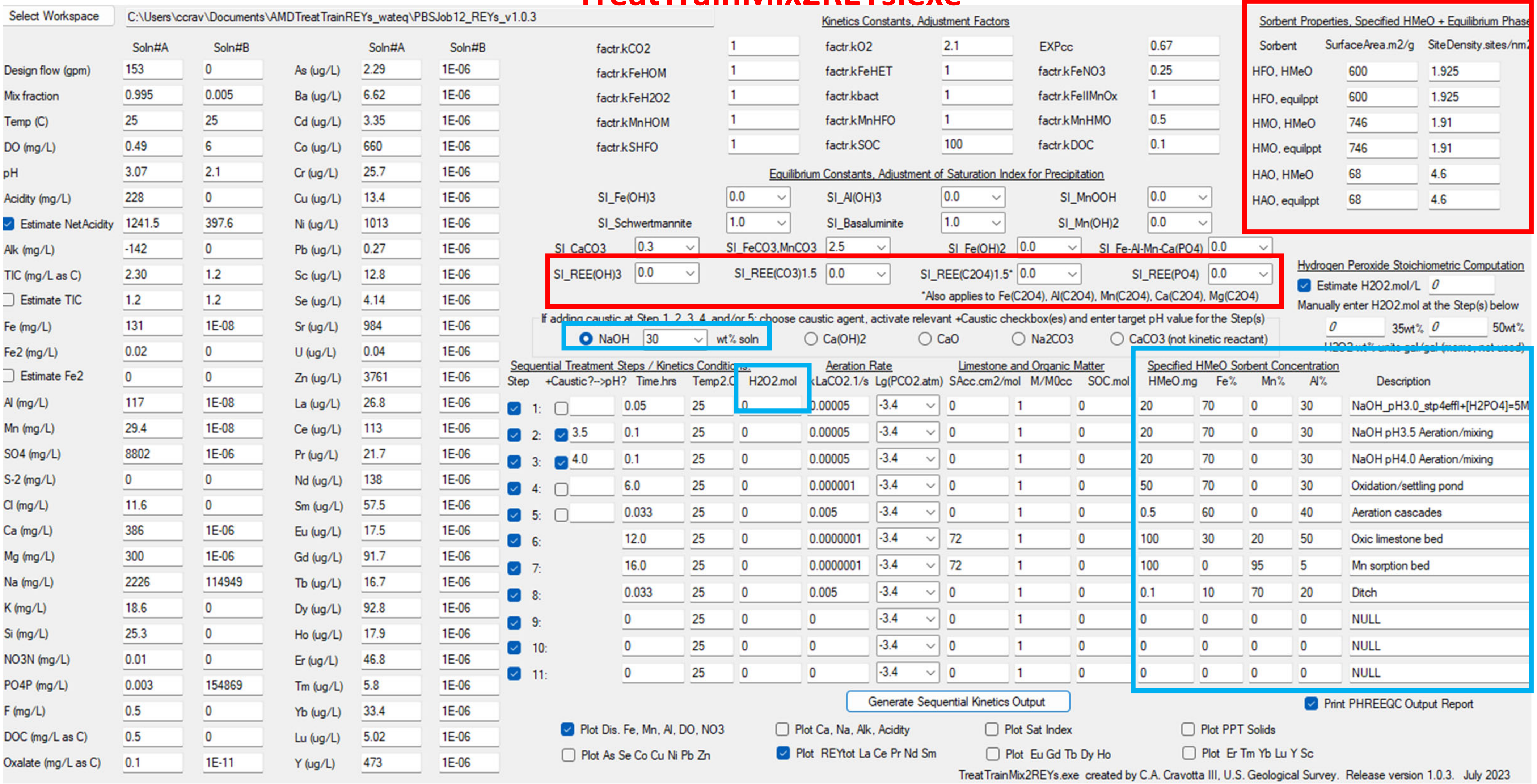
Alternative treatment to segregate Fe, Al, and Mn, concentrating REYs

H_2O_2 + Na_2CO_3 to pH ~4.5

TreatTrainMix2REYs Sequential Model

Hypothetical Sequential Treatment of Leachate with H_2O_2+NaOH+NaH_2PO_4

TreatTrainMix2REYs.exe



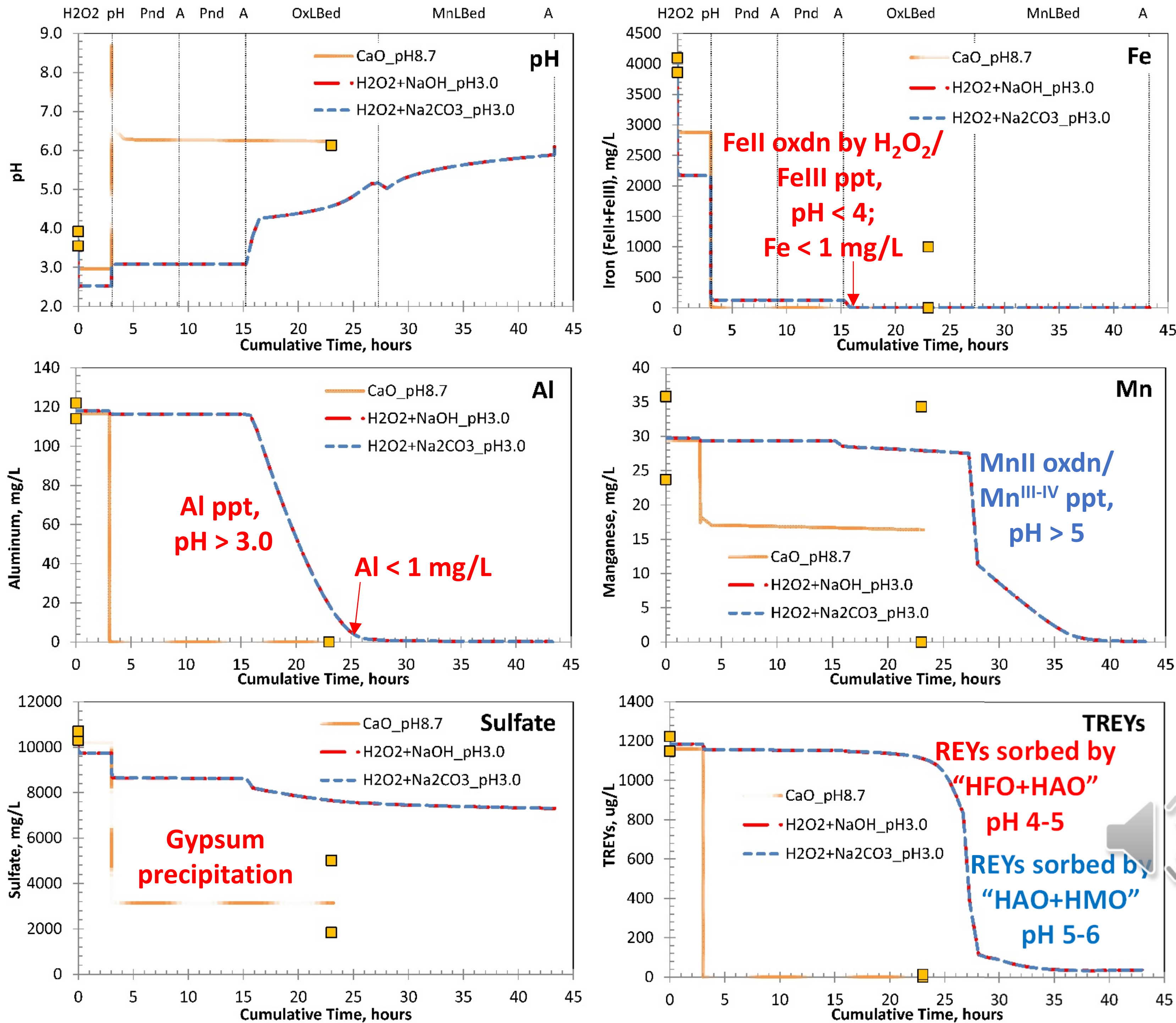
PBS Job 12: **H_2O_2 + NaOH to pH 3.0 (previous model to step #3)**

High acidity and REYs **_THEN ADDING_ NaH_2PO_4 (as solution B, step #1 here)**

Alternative treatment to segregate Fe, Al, and Mn, concentrating REYs

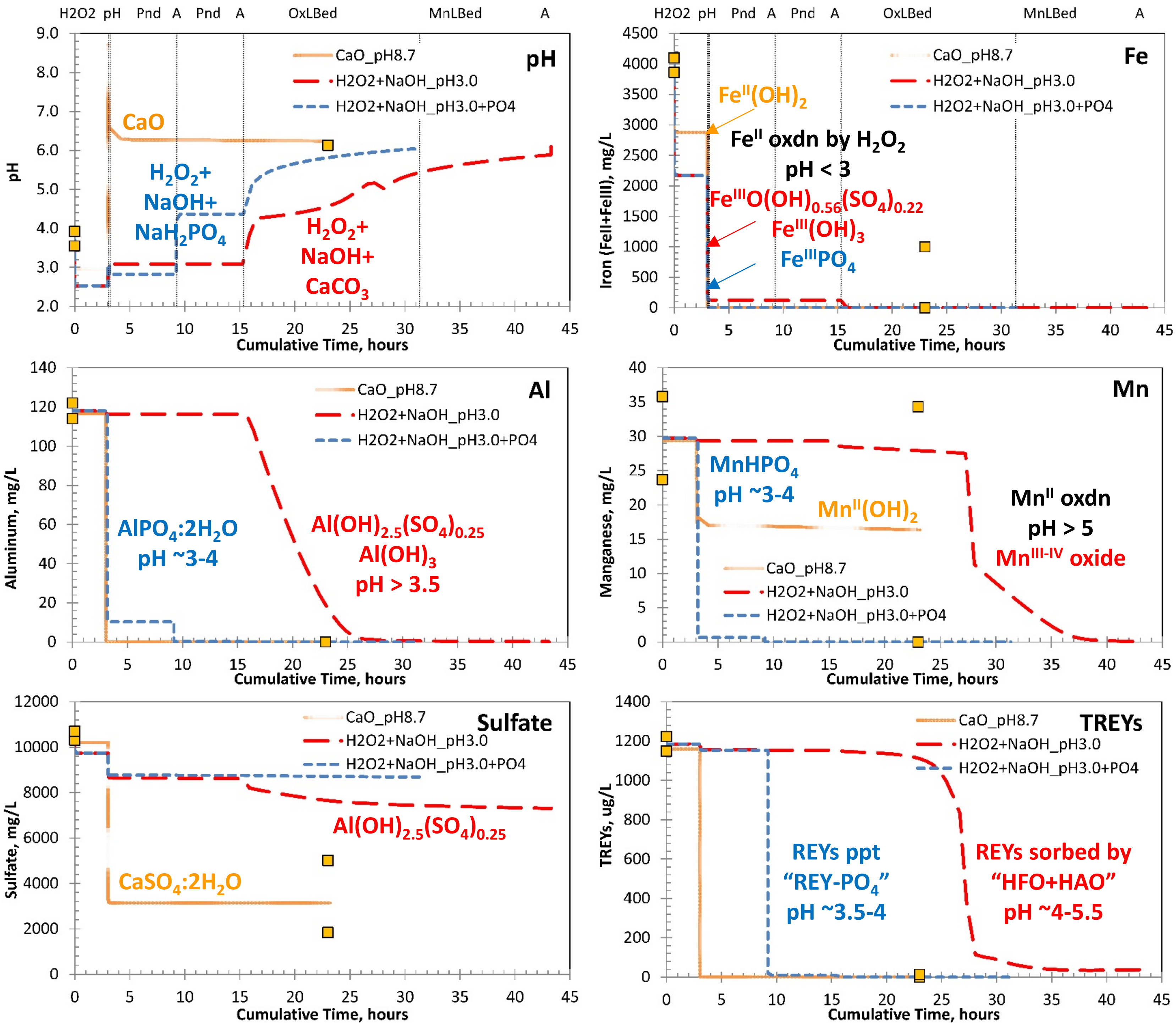
TreatTrainMix2REYs Model Results:

Sequential Treatment of Leachate with H_2O_2+Caustic to Concentrate REYs



TreatTrainMix2REYs Model Results:

Sequential Treatment of Leachate with H_2O_2+Caustic to Concentrate REYs



ACS Sustainable Chemistry & Engineering

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Research Article

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

Cite This: *ACS Sustainable Chem. Eng.* 2021, 9, 9308–9316

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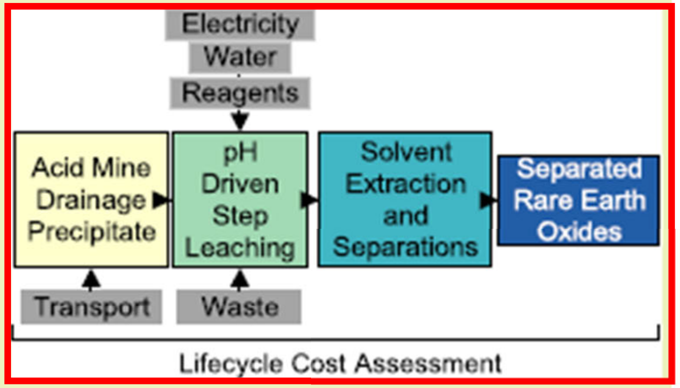


ABSTRACT: Coal waste products have been studied as a new source of rare earth elements (REEs) and other critical minerals (CM) essential for the development of renewable energy technologies, but the economic viability of these source materials is not well understood. This paper examines the technoeconomic 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 5900 \$/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*

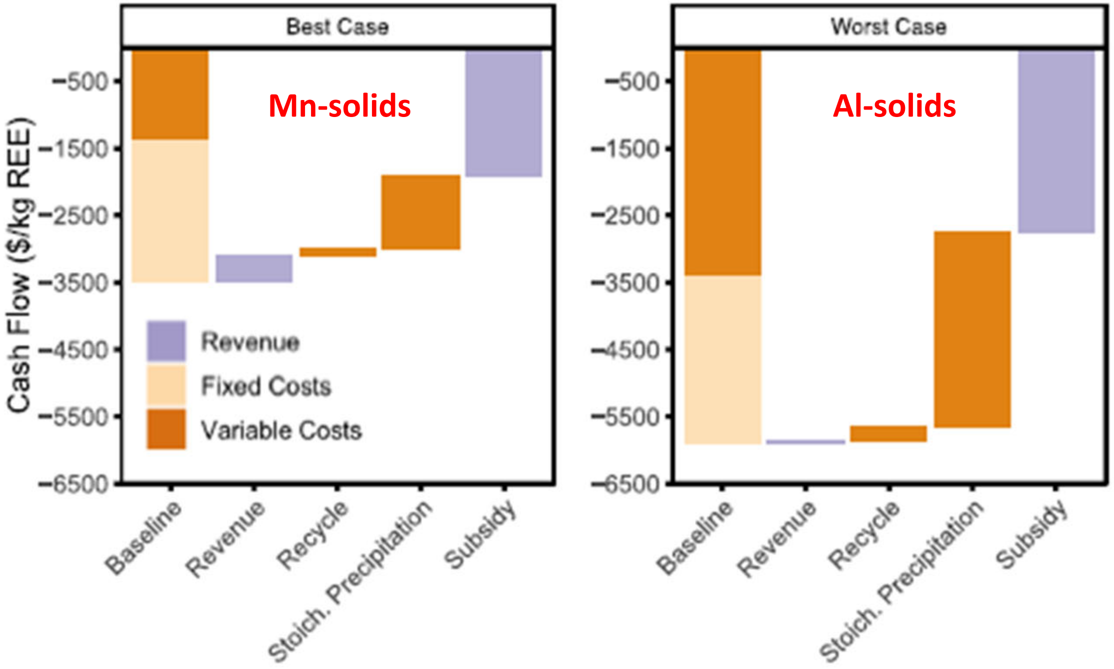


Figure 4. Changes in cash flow from process improvements and market changes to achieve break-even net profit for the best-case [Mn-rich] and worst-case [Al-rich] scenarios.

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.

Summary/Conclusions

- ✓ The PHREEQ-N-AMDTreat+REYs tools incorporate equilibrium aqueous and surface speciation *plus* kinetics models for CO_2 outgassing, oxidation/reduction processes, and limestone dissolution.
- ✓ Field and laboratory studies that demonstrate attenuation of REYs and corresponding aqueous/solid interactions can be accurately simulated.
- ✓ By adjusting kinetics variables or chemical dosing, effects on effluent chemistry resulting from various passive and/or active treatment strategies can be modeled.
- ✓ Potential treatment steps may be indicated that concentrate REYs with sorbing solids, increasing potential for recovery and value of the extract.
- ❖ *AMDTreat software can be used to evaluate the construction footprint and costs for installation and operation of system(s) that produce the desired composition of effluent and associated solids.*

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

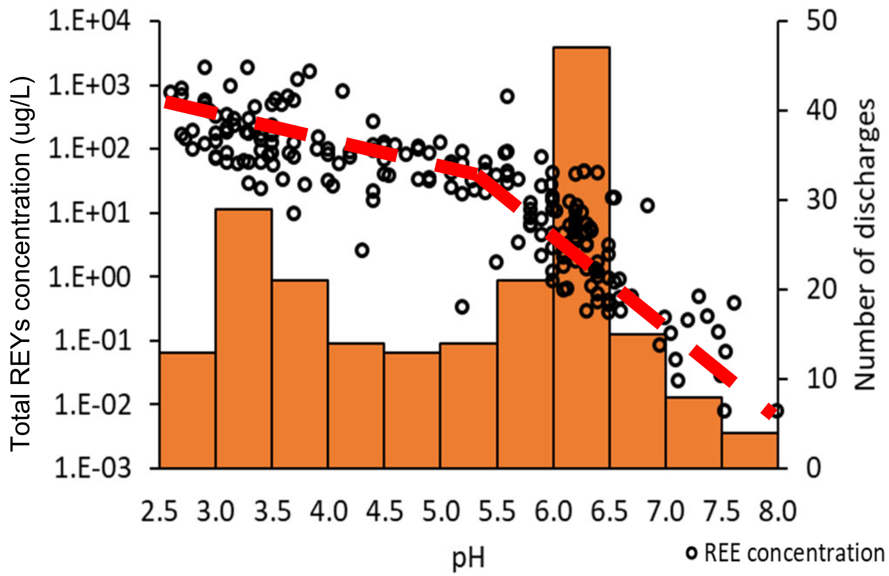
https://water.usgs.gov/water-resources/software/PHREEQC/IPhreeqcCOM-3.7.3-15968-x64.msi

Questions can be addressed to Chuck Cravotta cravottageochemical@gmail.com.

T10. Characterization of Critical Metals in Unconventional Ores to Inform Recovery Potential—

Empirical Observations and Geochemical Modeling to Evaluate Treatment Strategies for Recovery of Rare-Earth Elements from Acid Mine Drainage

Chuck Cravotta (USGS PAWSC), Travis Tasker (St. Francis U.), Ben Hedin (Hedin Environmental)

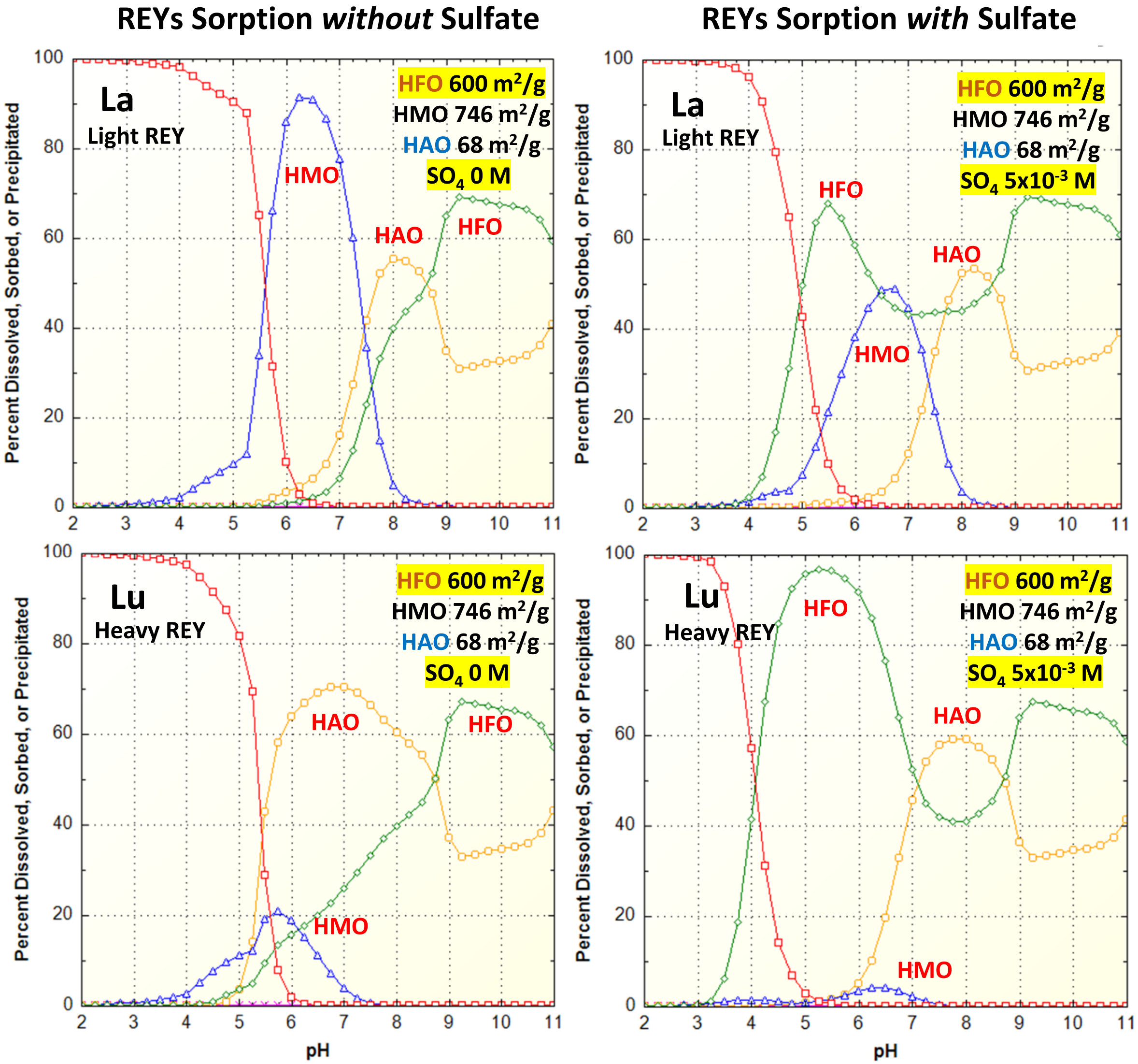


"AMD" in Pennsylvania has a bimodal pH distribution. Roughly half the coal-mine discharges have pH < 5.

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-element concentrations and pH.

Summary:

- Rare-earth elements plus yttrium and scandium (REYs) and other trace metals have elevated concentrations in AMD that generally decrease with increased pH.
- Surface speciation (adsorption) involving hydrous ferric oxide (HFO), hydrous aluminum oxide (HAO), and hydrous manganese oxide (HMO) may explain the notable break in slope at pH ~5.
- PHREEQ-N-AMDTreat+REYs models consider *equilibrium* aqueous and surface speciation plus solids precipitation combined with *kinetics* of gas exchange; Fe, Mn, and organic carbon oxidation; and limestone dissolution, all of which affect pH.



SURF_OH + M+3 + H2O = SURF_OMOH+ + 2 H+
SURF_OHSO4-2 + M+3 = SURF_OM(SO4) + H+

SURF = HFO or HAO
M+3 = Free REY cation

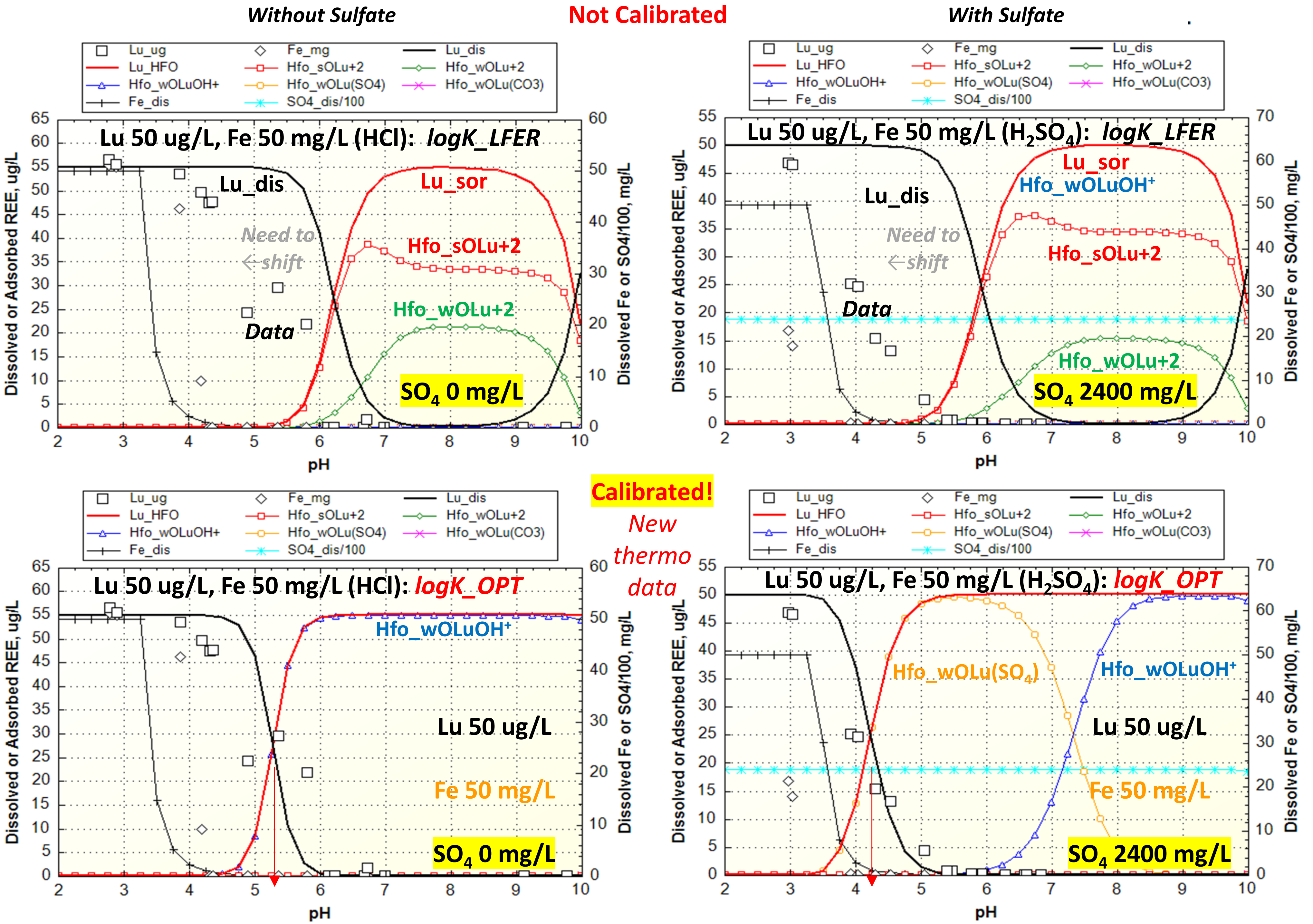
SURF_OH + M(SO4)+ = SURF_OM(SO4) + H+ (indicated by Lozano and others)
rewritten/recomputed considering:
SURF_OH + SO4-2 = SURF_OHSO4-2 (subtract adsorption of SO4-2))
M+3 + SO4-2 = M(SO4)+ (add sulfate complex formation)

Goal -- Predict the attenuation of dissolved REYs and other trace elements to metal-rich solids formed during passive and active treatment of mining affected water.

Status:

- Titration experiments quantify changes in REYs concentrations with pH in Fe or Al systems, without or with SO_4.
- PHREEQC used with PEST to obtain "best-fit" adsorption coefficients (log K) for equilibrium speciation models.
- Updated PHREEQ-N-AMDTreat+REYs models simulate data for selected treatment systems and may be used to indicate strategies for recovery of REYs.
- Journal articles in progress to document the new adsorption equilibrium constants and models.

REYs Sorption by “HFO“- Model Calibration to Empirical Data



REYs Sorption by "HFO"- Model Calibration to Empirical Data