Geochemical Modeling to Understand and Mitigate Aquatic Contamination by Abandoned Mine Drainage

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15th International Mine Water Association Congress
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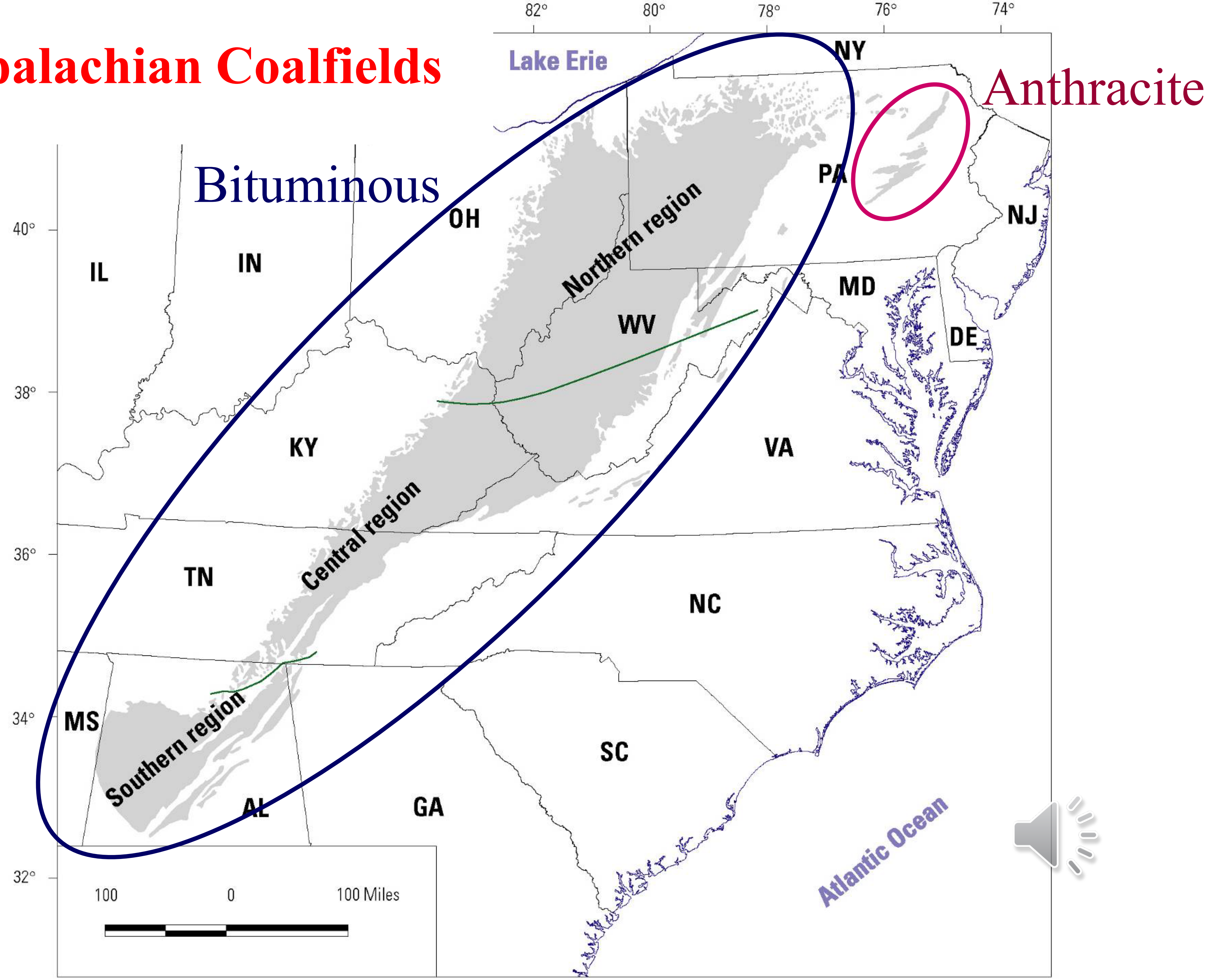
Appalachian Coalfields



ANTHRACITE – COMPLEX STRUCTURE

USGS science for a changing world

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BITUMINOUS – SIMPLE STRUCTURE

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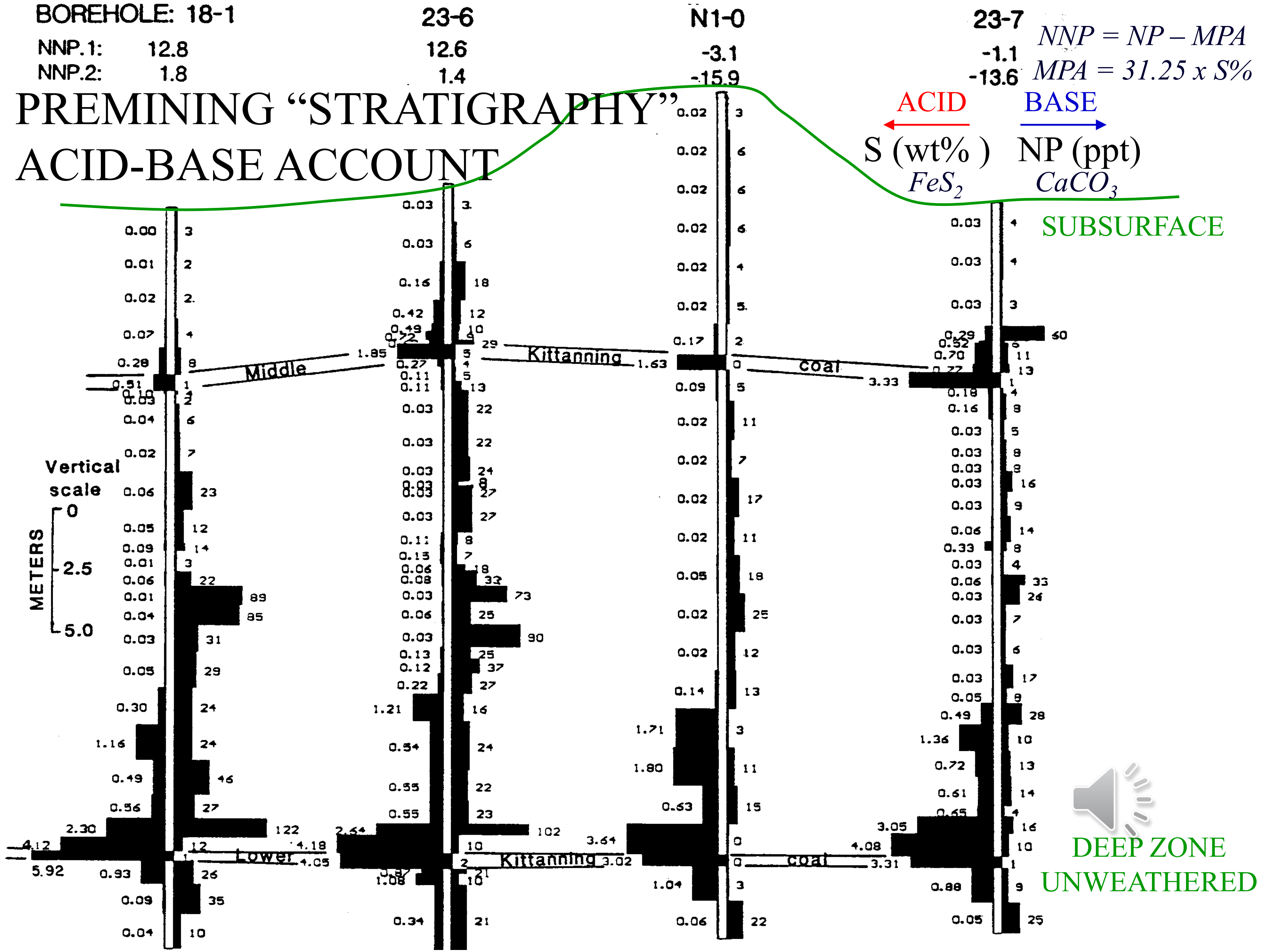
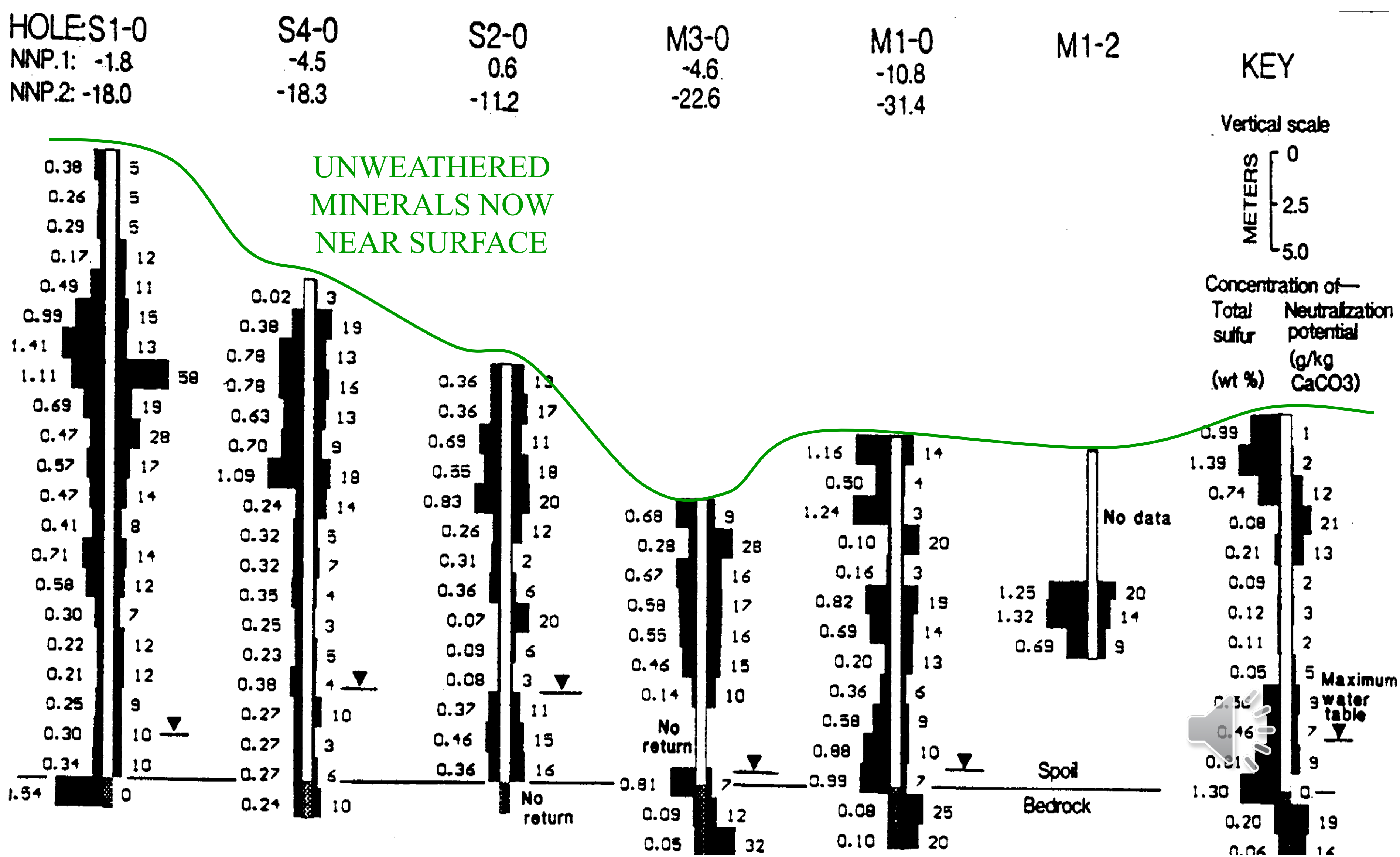
MINING IMPACTS

- Mining disturbs the stratigraphy, topography, and drainage within a watershed.
- Losses of surface water to underground mines can eliminate or reduce streamflow (industrial karst).
- Discharges from legacy (abandoned) and active mines can sustain stream base flow but add contaminants.
- Abandoned (acidic or alkaline) mine drainage (AMD) degrades 5,000 miles of streams in Appalachia.

PREMINING "STRATIGRAPHY" ACID-BASE ACCOUNT

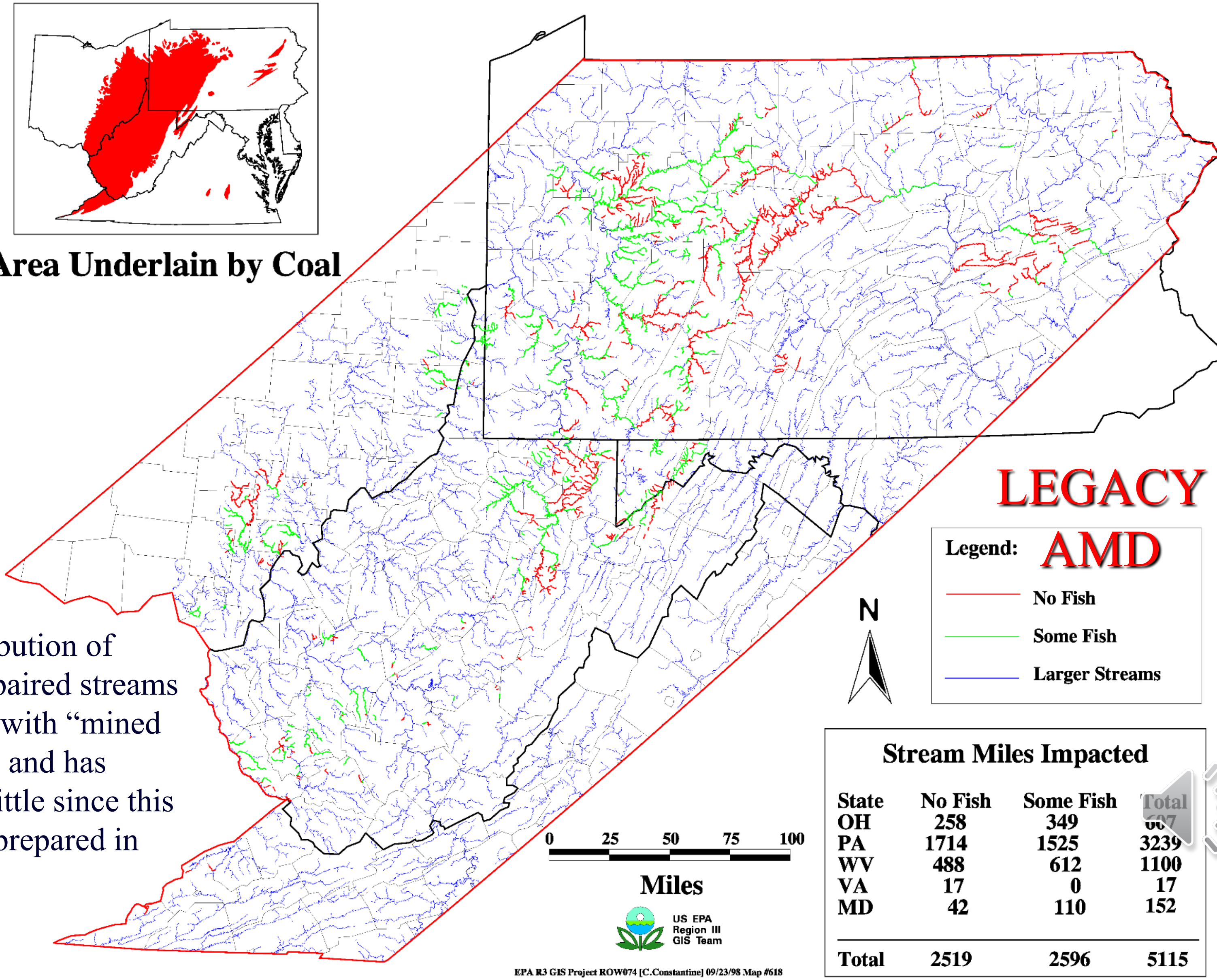


POST-MINING DISTRIBUTION OF SULFUR & NEUTRALIZATION POTENTIAL (STRATA “UPSIDE DOWN”)



Fisheries Impacted by Acid Mine Drainage in MD, OH, PA, VA, WV

(Based on EPA Fisheries Survey - 1995)



Stream Miles Impacted

State	No Fish	Some Fish	Total
OH	258	349	607
PA	1714	1525	3239
WV	488	612	1100
VA	17	0	17
MD	42	110	152
Total	2519	2596	5115

The distribution of AMD-impaired streams coincides with "mined out areas" and has changed little since this map was prepared in 1995.

STREAMFLOW LOST TO UNDERGROUND MINES

Photos by Dan Koury, PaDEP, 3/25/1999

VERTICAL SHAFT

DRAINAGE BOREHOLE

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DRAINAGE TUNNEL

BANK SEEPAGE

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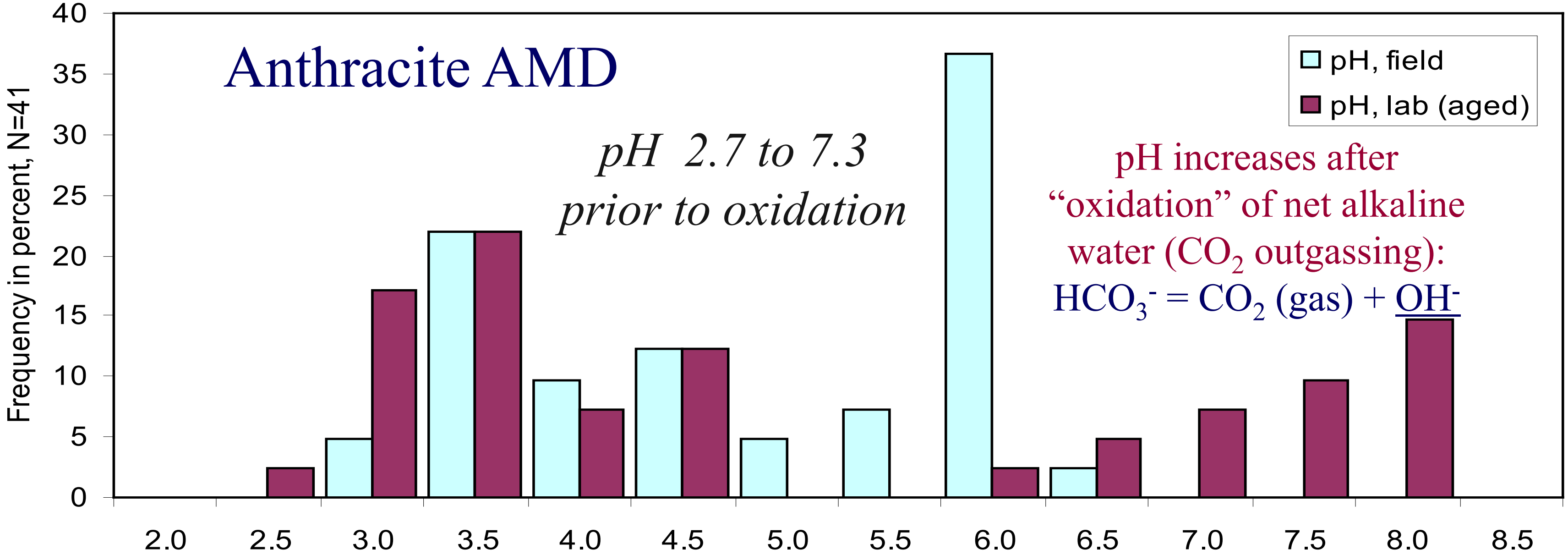
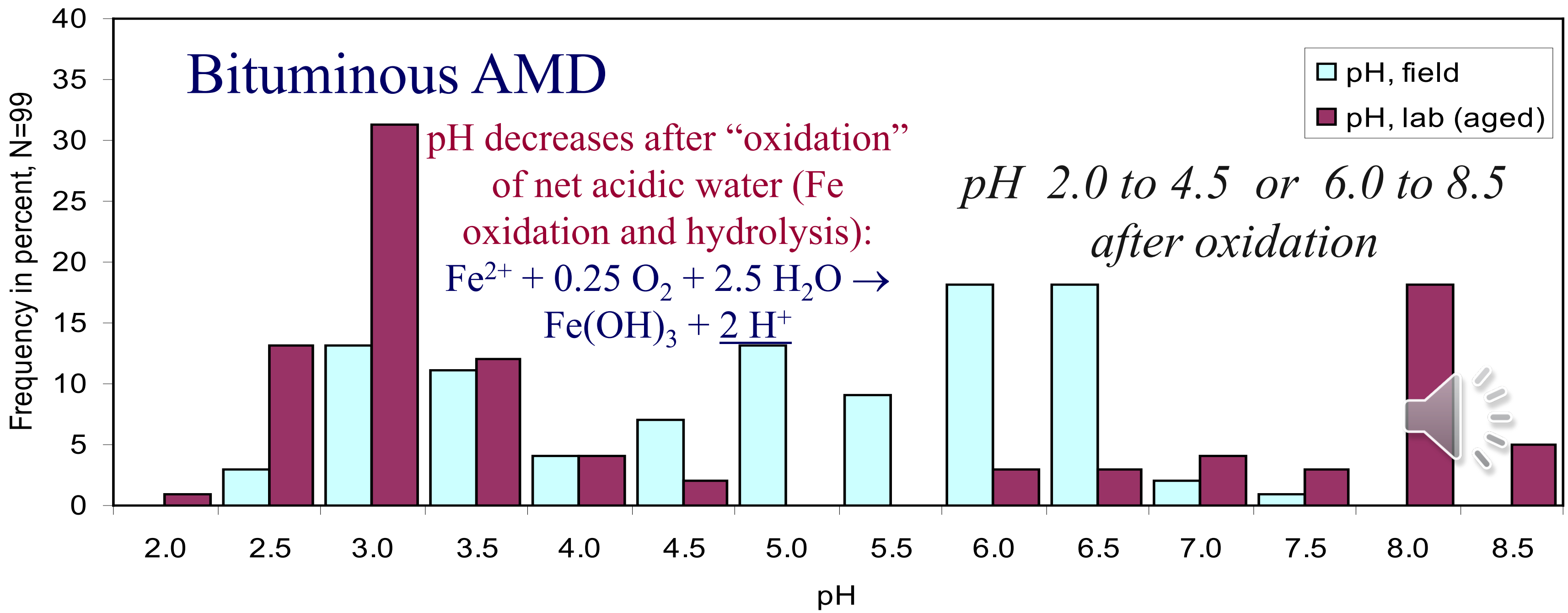
GEOCHEMISTRY OF AMD

- Not all coal-mine drainage is acidic.
- Oxidation of pyrite (FeS_2) and dissolution of oxidation products release iron, sulfate, and acid.
- Dissolution of carbonate and silicate minerals neutralizes acid and releases calcium, magnesium, manganese, aluminum, and other solutes to groundwater.
- CO_2 outgassing after discharge causes pH to increase.
- Increased pH promotes iron and manganese oxidation and precipitation, plus adsorption of trace metals.

BIMODAL pH FREQUENCY DISTRIBUTION





Production of Acidity

Pyrite: $FeS_2(s) + 3.75\ O_2 + 3.5\ H_2O \rightarrow$

$Fe(OH)_3(s) + 2\ SO_4^{2-} + \underline{4\ H^+}$

1) $FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + \underline{2\ H^+}$

2) $Fe^{2+} + 0.25\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3 + \underline{2\ H^+}$

- ✓ *Pyrite oxidation can be rapid in humid air or aerated water.*
- ✓ *Iron and sulfur oxidizing bacteria catalyze the low-pH oxidation of Fe and S.*
- ✓ *pH may decline when H^+(protons) are released. Half the H^+ is from oxidation of S^- (Eq.1); half is from oxidation of Fe^{2+} and hydrolysis of Fe^{3+} (Eq.2).*
- ❖ *Abiotic oxidation of Fe^{2+} (Eq. 2) increases 100x for each unit increase of pH.*

Secondary Iron-Sulfate Minerals

(*intermediate products of pyrite oxidation*)

Melanterite	$FeSO_4 \cdot 7H_2O$
Rozenite	$FeSO_4 \cdot 4H_2O$
Szomolnikite	$FeSO_4 \cdot H_2O$
Röemerite	$Fe^{II}Fe^{III}_2(SO_4)_4 \cdot 14H_2O$
Copiapite	$Fe^{II}Fe^{III}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Coquimbite	$Fe^{III}_2(SO_4)_3 \cdot 9H_2O$
Jarosite	$(K,Na,H_3O)Fe^{III}_3(SO_4)_2(OH)_6$
Halotrichite	$Fe^{II}Al_2(SO_4)_4 \cdot 22H_2O$
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O$

Release of Stored Acidity

(dissolution of pyrite oxidation products)

Coquimbite:

$$Fe_2(SO_4)_3 \cdot 9H_2O \rightarrow \underline{2\ Fe(OH)_3} + 3\ SO_4^{2-} + \underline{6\ H^+} + 3\ H_2O$$

Halotrichite:

$$Fe^{II}Al_2(SO_4)_4 \cdot 22H_2O + 0.25\ O_2 \rightarrow$$

$$\underline{Fe(OH)_3} + \underline{2\ Al(OH)_3} + 4\ SO_4^{2-} + \underline{8\ H^+} + 13.5\ H_2O$$

- ✓ *Dissolution of secondary sulfates by runoff, infiltration, or rising groundwater results in the rapid release of the "stored acidity"*

Neutralization of Acidity

Calcite: $CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$

Dolomite: $CaMg(CO_3)_2 + 2\,H^+ \leftrightarrow$
$Ca^{2+} + Mg^{2+} + 2\,HCO_3^-$

1) $CaCO_3 + 2\,H^+ \leftrightarrow Ca^{2+} + H_2O + CO_2\,(aq)$ *pH < 6*

2) $CaCO_3 + CO_2(aq) + H_2O \leftrightarrow Ca^{2+} + 2\,HCO_3^-$ *pH > 6*

3) $HCO_3^- \leftrightarrow CO_2(g)\uparrow + OH^-$ *(CO_2 outgassing increases pH)*

- ✓ *Limestone is composed of calcite and dolomite*
- ✓ *dissolved CO_2 and HCO_3^- (alkalinity) are produced by carbonate dissolution*
- ❖ *outgassing of CO_2 increases pH without affecting acid-neutralizing capacity*

Manganese, Magnesium, Aluminum, & Other Solutes

Siderite:

$$Fe_{1-x}Mn_xCO_3 + 2\ H^+ \rightarrow$$
$$(1\text{-}x)\ Fe^{2+} + x\ \underline{Mn^{2+}} + H_2CO_3,\ \ (0 \leq x \leq 0.1)$$

Chlorite:

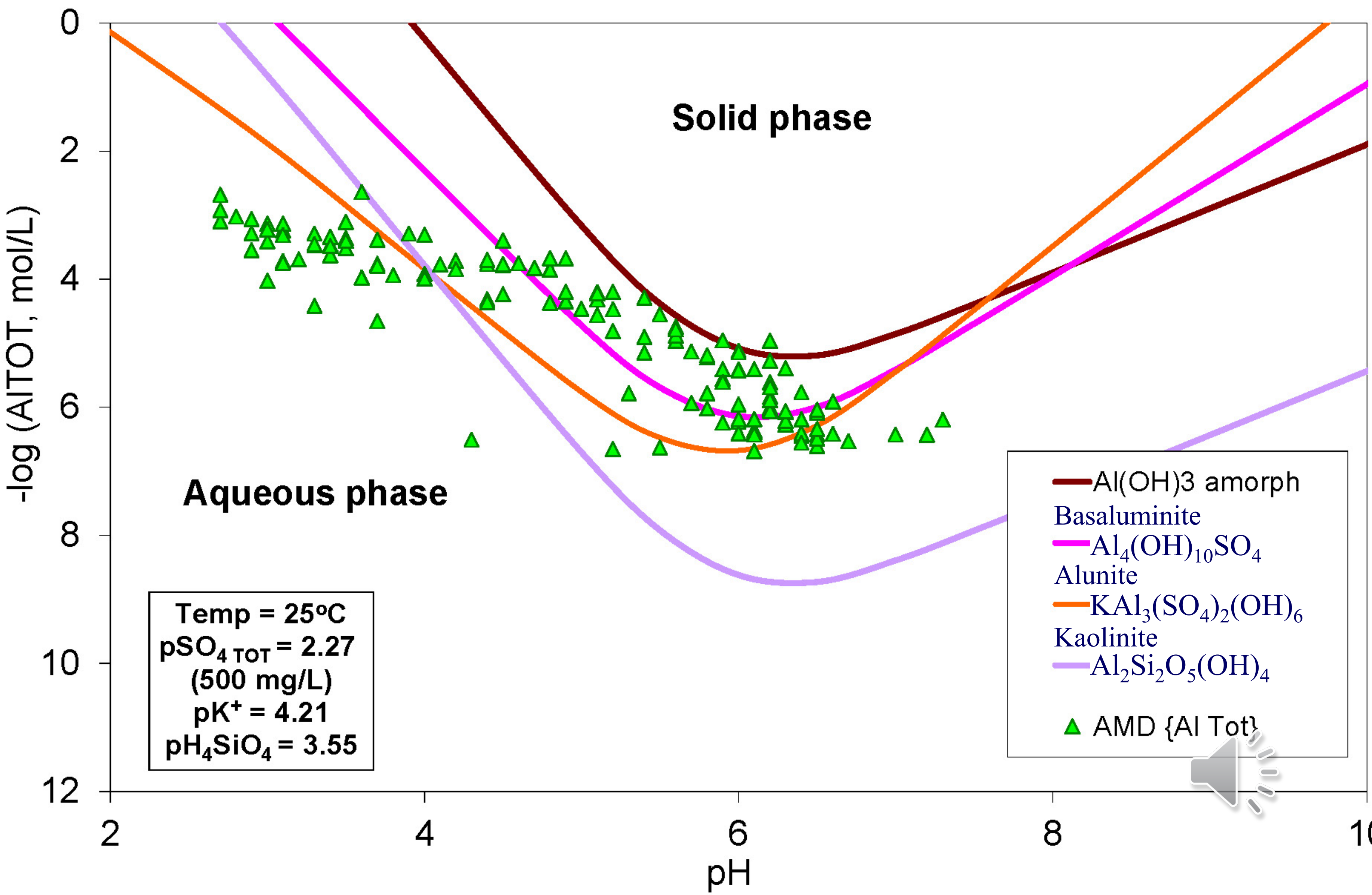
$$Mg_5Al_2Si_3O_{10}(OH)_8 + 10\ H^+ \rightarrow$$
$$5\ \underline{Mg^{2+}} + 2\ Al(OH)_3 + 3\ SiO_2 + 6\ H_2O$$

Kaolinite:

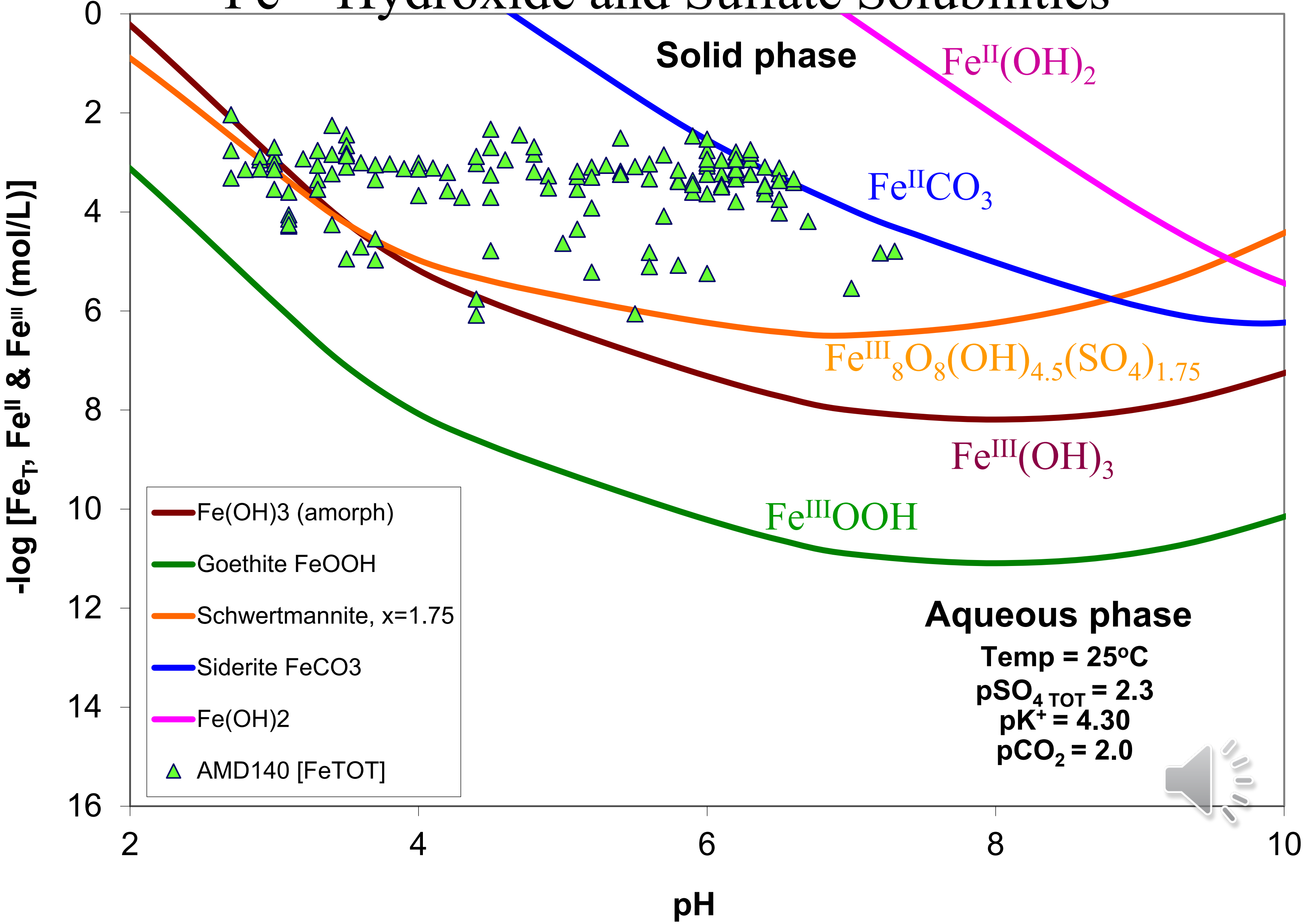
$$Al_2Si_2O_5(OH)_4 + 6\ H^+ \rightarrow 2\ \underline{Al^{3+}} + 2\ SiO_2 + 5\ H_2O$$

✓ *Siderite and aluminosilicate minerals are important sources of manganese, magnesium, aluminum, and silica.*

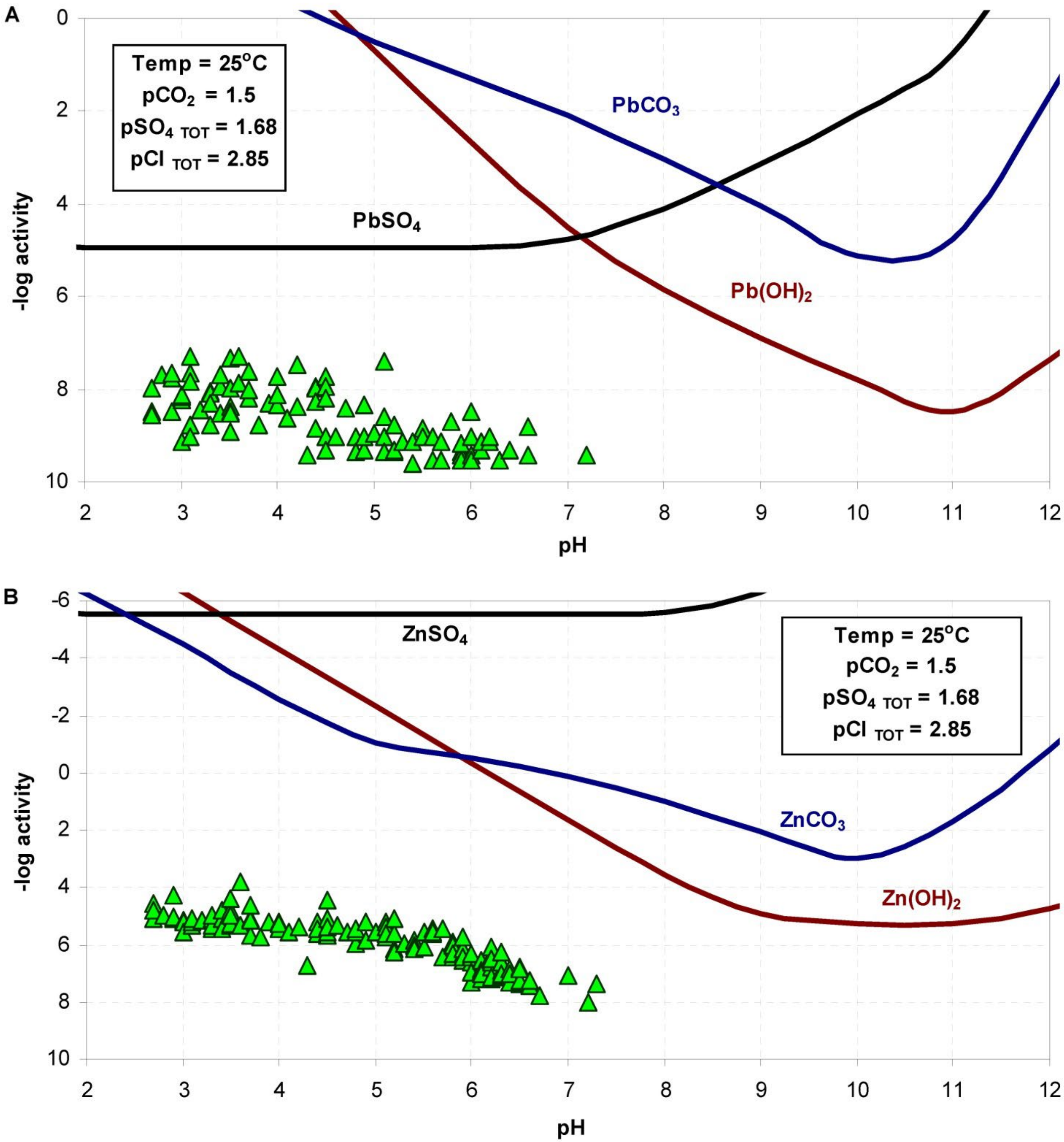
Aluminum Limited by Al-Hydroxide and Sulfate Solubilities



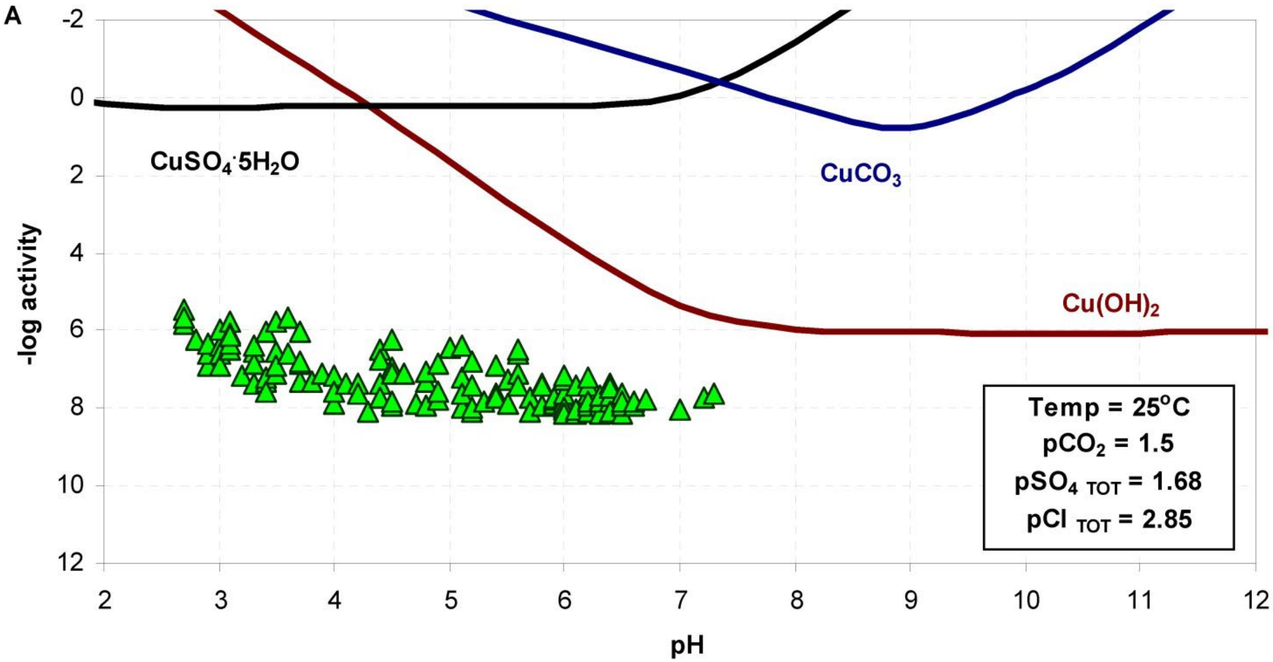
Fe Limited by Fe^{II}-Carbonate and Fe^{III}-Hydroxide and Sulfate Solubilities

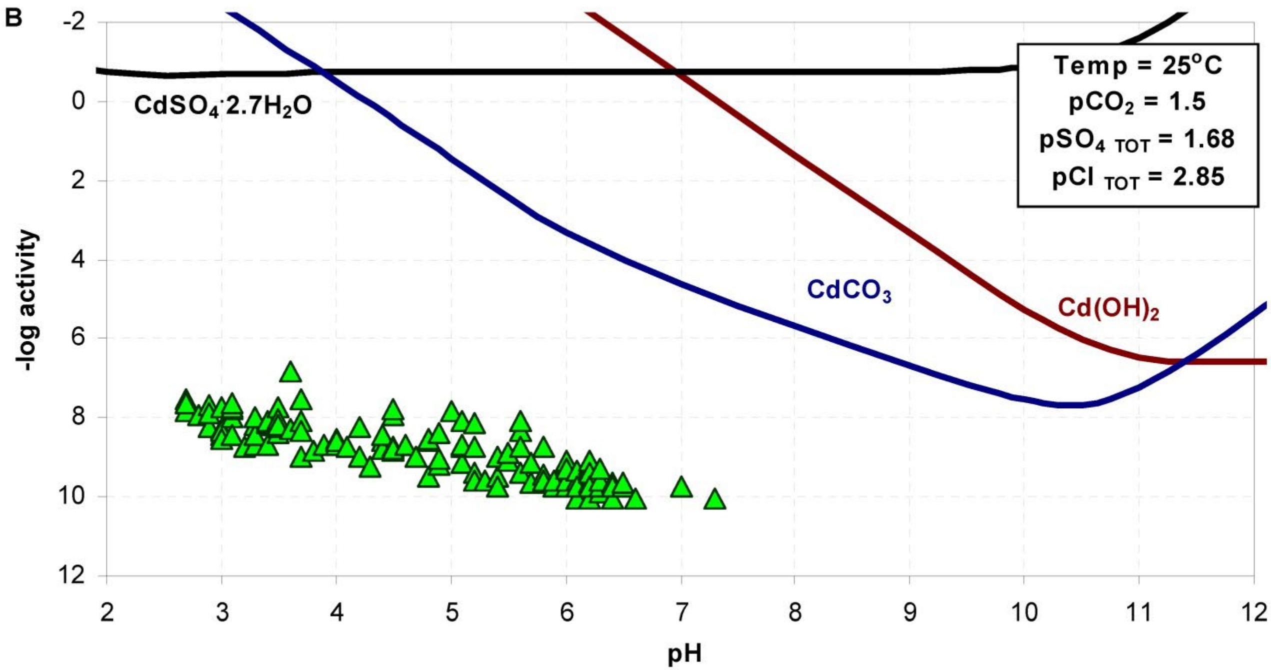


Lead and Zinc NOT Limited by Hydroxide, Carbonate, or Sulfate Solubilities

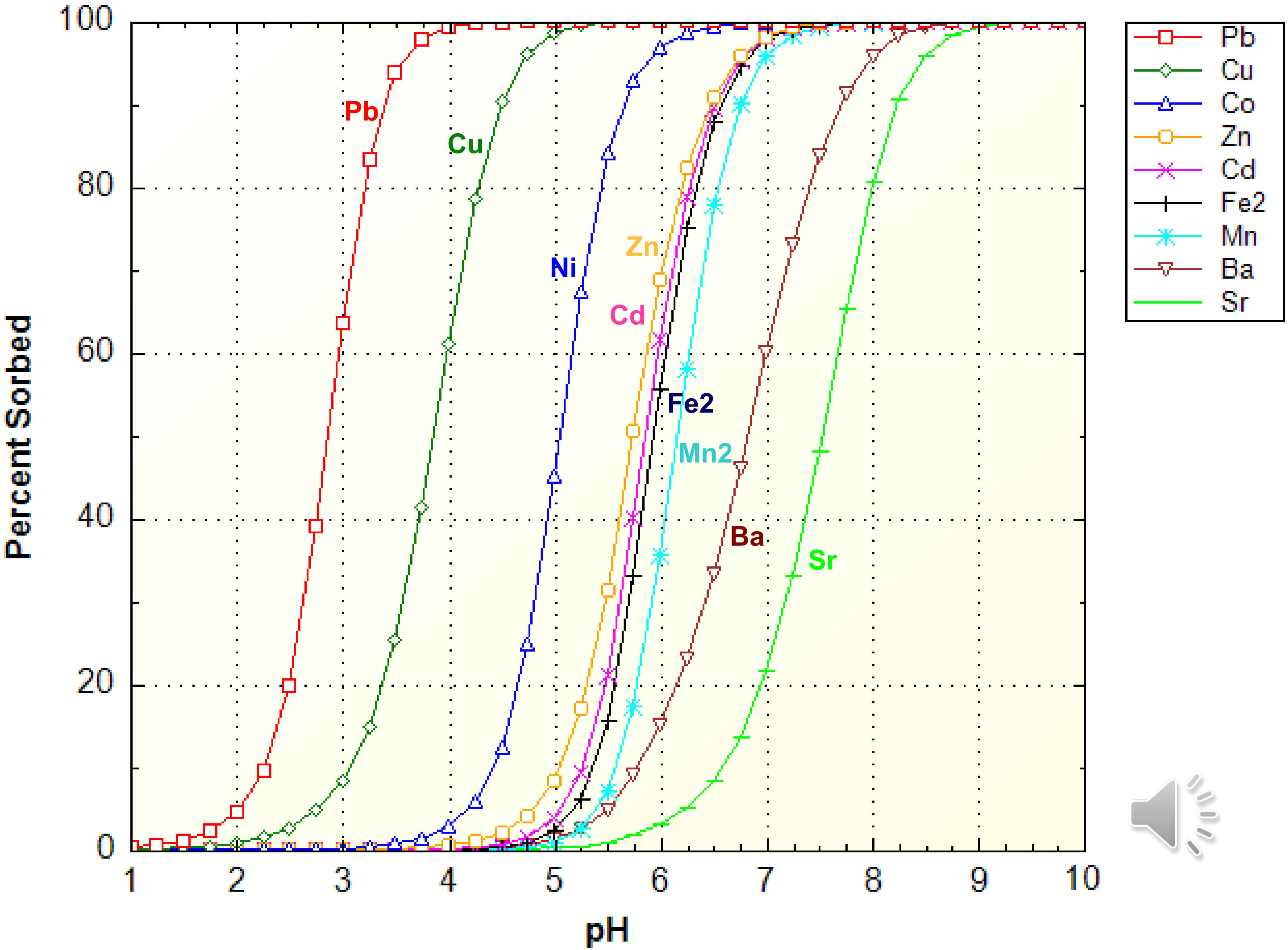


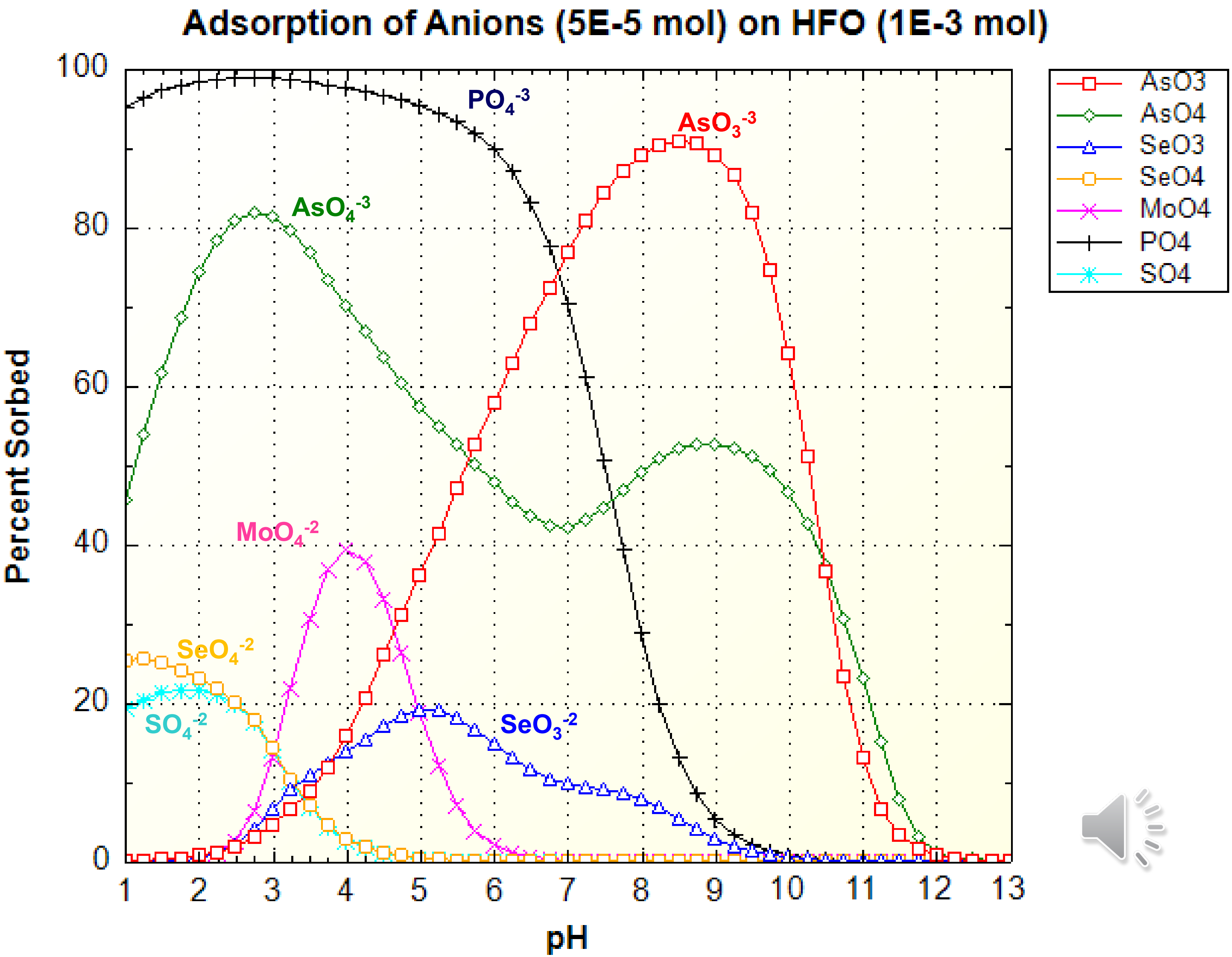
Copper and Cadmium NOT Limited by Hydroxide, Carbonate, or Sulfate Solubilities





Adsorption of Cations (1E-6 mol) on HFO (1E-3 mol)




Adsorption of Anions (5E-5 mol) on HFO (1E-3 mol)
Percent Sorbed
pH
0
20
40
60
80
100
1
2
3
4
5
6
7
8
9
10
11
12
13
PO_4^{-3}
AsO_3^{-3}
AsO_4^{-3}
MoO_4^{-2}
SeO_4^{-2}
SO_4^{-2}
SeO_3^{-2}
AsO3
AsO4
SeO3
SeO4
MoO4
PO4
SO4

TREATMENT OF AMD

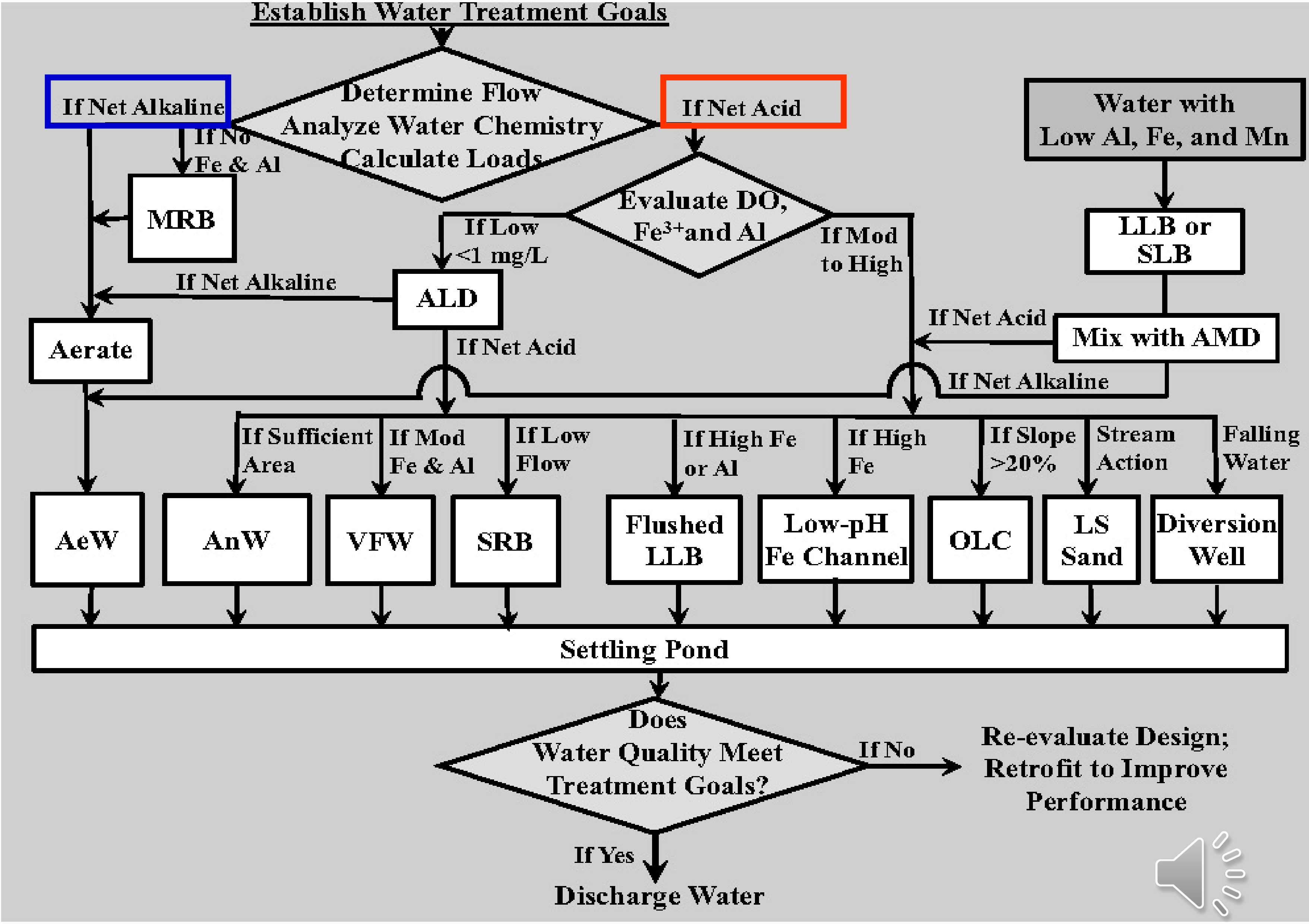
Al^{3+}

Fe^{2+} / Fe^{3+}

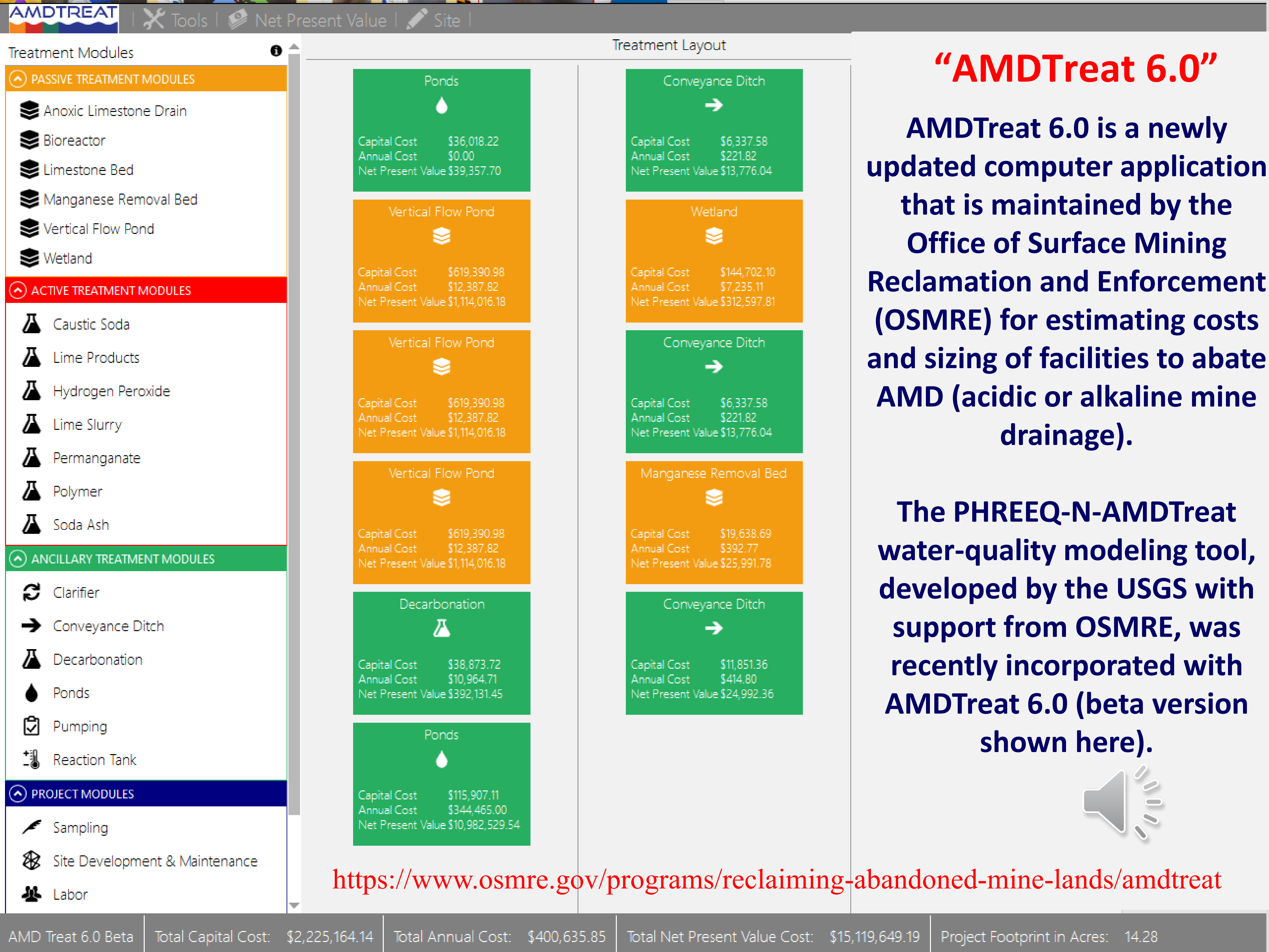
Mn^{2+}

Passive ⟵⟶ **Active**

Passive	Active
Increase pH with natural substrates & microbial activity	Increase pH with caustic chemicals &/or aeration
Reactions slow	Reactions fast, efficient
Large area footprint	Moderate area footprint
Low maintenance	High maintenance



Skousen, J.G., Zipper, C.E., Rose, A.W., Ziemkiewicz, P.F., Nairn, R., McDonald, L.M., and Kleinmann, R.L., 2017. Review of passive systems for acid mine drainage treatment. Mine Water Environ. 36, 133-153.



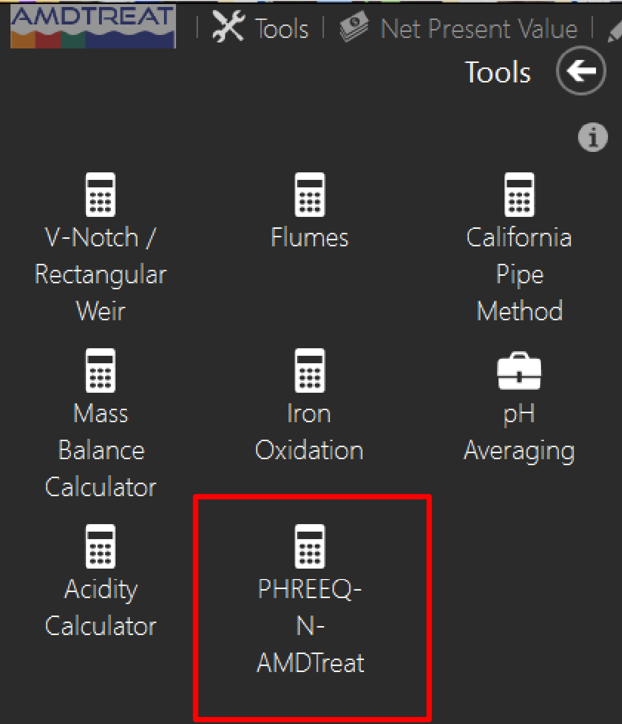
"AMDTreat 6.0"

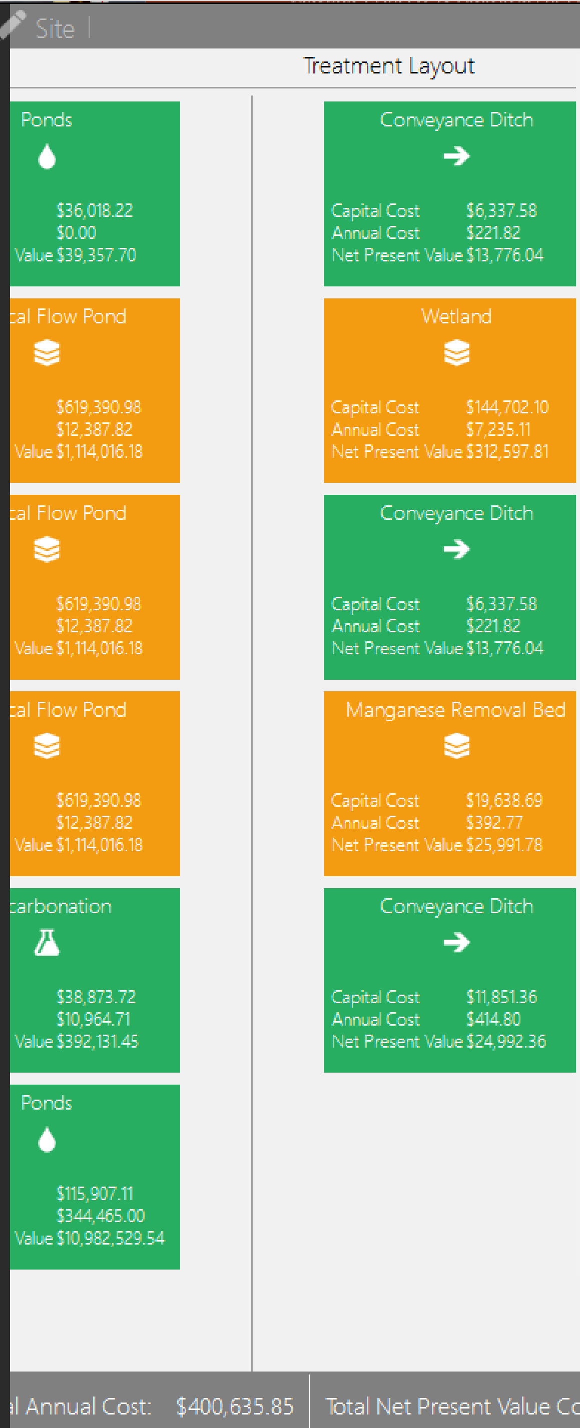
AMDTreat 6.0 is a newly updated computer application that is maintained by the Office of Surface Mining Reclamation and Enforcement (OSMRE) for estimating costs and sizing of facilities to abate AMD (acidic or alkaline mine drainage).

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

"PHREEQ-N-AMDTreat"



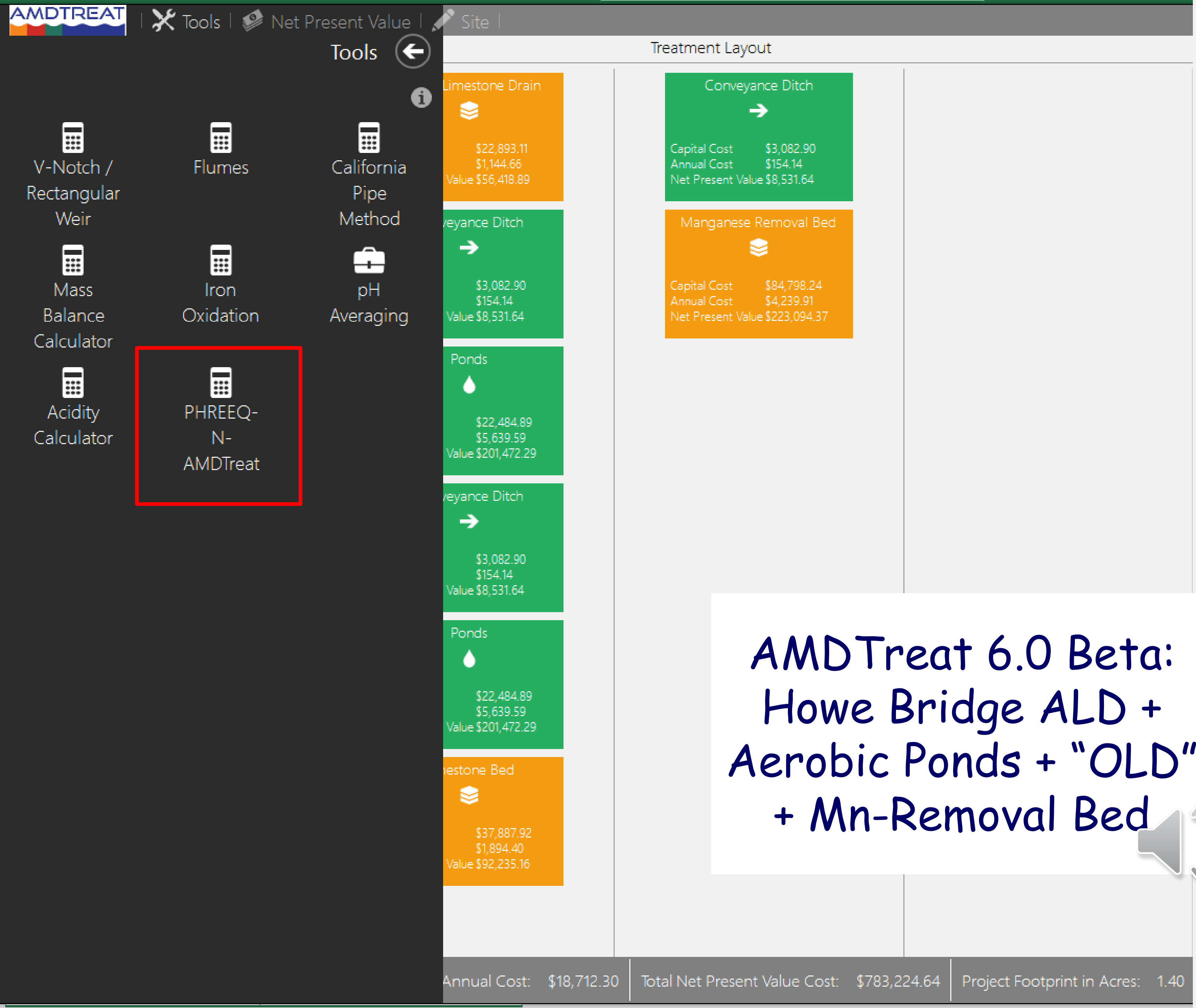


Cravotta, C.A. III, 2020. Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage (software download): U.S. Geological Survey Software Release. https://doi.org/10.5066/P9QEE3D5

Cravotta, C.A. III, 2021. Interactive PHREEQ-N-AMDTreat water-quality modeling tools to evaluate performance and design of treatment systems for acid mine drainage: Applied Geochemistry, 126, 10845. https://doi.org/10.1016/j.apgeochem.2020.104845

- **TreatTrainMix2 tool simulates effects on water quality by sequential treatment steps; useful for costs/benefits analysis.**
- ✓ **CO_2 outgassing and O_2 ingassing;**
- ✓ **Iron and manganese oxidation;**
- ✓ **Limestone dissolution;**
- ✓ **Oxidation of organic carbon coupled with reduction of Fe^{III}, sulfate, and nitrate.**
- ✓ **Active treatment with H_2O_2 and/or caustic chemicals.**
- ✓ **Mass and composition of solids precipitated, including hydrous metal oxide sorbent (HMeO = HFO + HMO + HAO).**
- ***An expanded stand-alone model includes rare-earth elements attenuation by adsorption and precipitation.***

AMDTreat 6.0 Beta: Howe Bridge ALD + Aerobic Ponds + "OLD" + Mn-Removal Bed



“ALD” + Aerobic Ponds + “OLD” + Mn-Removal Bed

AMDTreat 6.0 Beta PHREEQ-N-AMDTreat tool:

Howe Bridge, high Fe & Mn

PHREEQ-N-AMDTreat | Model Input | Errors

Treatment Modules To Be Modeled

Treatment Module	Step	Treatment Layer/ Technology	Treatment pH (s.u.)	Retention Time (hrs)	Temperature (°C)	Decarbonation Rate: $kLaCO_2$ (sec^{-1})	Limestone Surface Area (cm^2/mol)	Fraction of Limestone Available To React	Solid Organic Carbon	Sorbent Mass (Fe+Mn+Al) (mg/L)	Fe %	Mn %	Al %
ALD	1	Limestone Layer	6.88	21.700(	9.80	0.0000001	AASHTO #3 (72)	1.00	0.00	19.80	84.0(	16.0(	0.00
Conveyance Ditch	2	Water Layer	6.88	0.0500	12.00	0.0100000	AASHTO #1 (45)	1.00	0.00	0.00	100.(	0.00	0.00
Ponds	3	Water Layer	6.88	20.000(	12.00	0.0000100	0	1.00	0.00	10.00	100.(	0.00	0.00
Conveyance Ditch	4	Water Layer	6.88	0.0500	12.00	0.0100000	AASHTO #1 (45)	1.00	0.00	0.00	100.(	0.00	0.00
Limestone Bed	5	Water Layer	6.88	0.0000	12.00	0.0000100	0	1.00	0.00	0.00	100.(	0.00	0.00
	6	Limestone Layer	6.88	40.000(	12.00	0.0000001	AASHTO #1 (45)	1.00	0.00	20.00	84.0(	16.0(	0.00
Conveyance Ditch	7	Water Layer	6.88	0.0500	12.00	0.0050000	AASHTO #1 (45)	1.00	0.00	0.00	100.(	0.00	0.00
Ponds	8	Water Layer	6.88	8.0000	12.00	0.0000100	0	1.00	0.00	0.00	100.(	0.00	0.00
Conveyance Ditch	9	Water Layer	6.88	0.0500	12.00	0.0100000	AASHTO #1 (45)	1.00	0.00	0.00	100.(	0.00	0.00
Mn Removal Bed	10	Limestone Layer	6.88	5.0000	12.00	0.0000001	\ASHTO #5 (144	1.00	0.00	50.00	0.00	100.(	0.00
Mn Removal Bed	11	Limestone Layer	6.88	5.0000	12.00	0.0000001	\ASHTO #5 (144	1.00	0.00	50.00	0.00	100.(	0.00

Total Retention Time (hrs) **99.9**

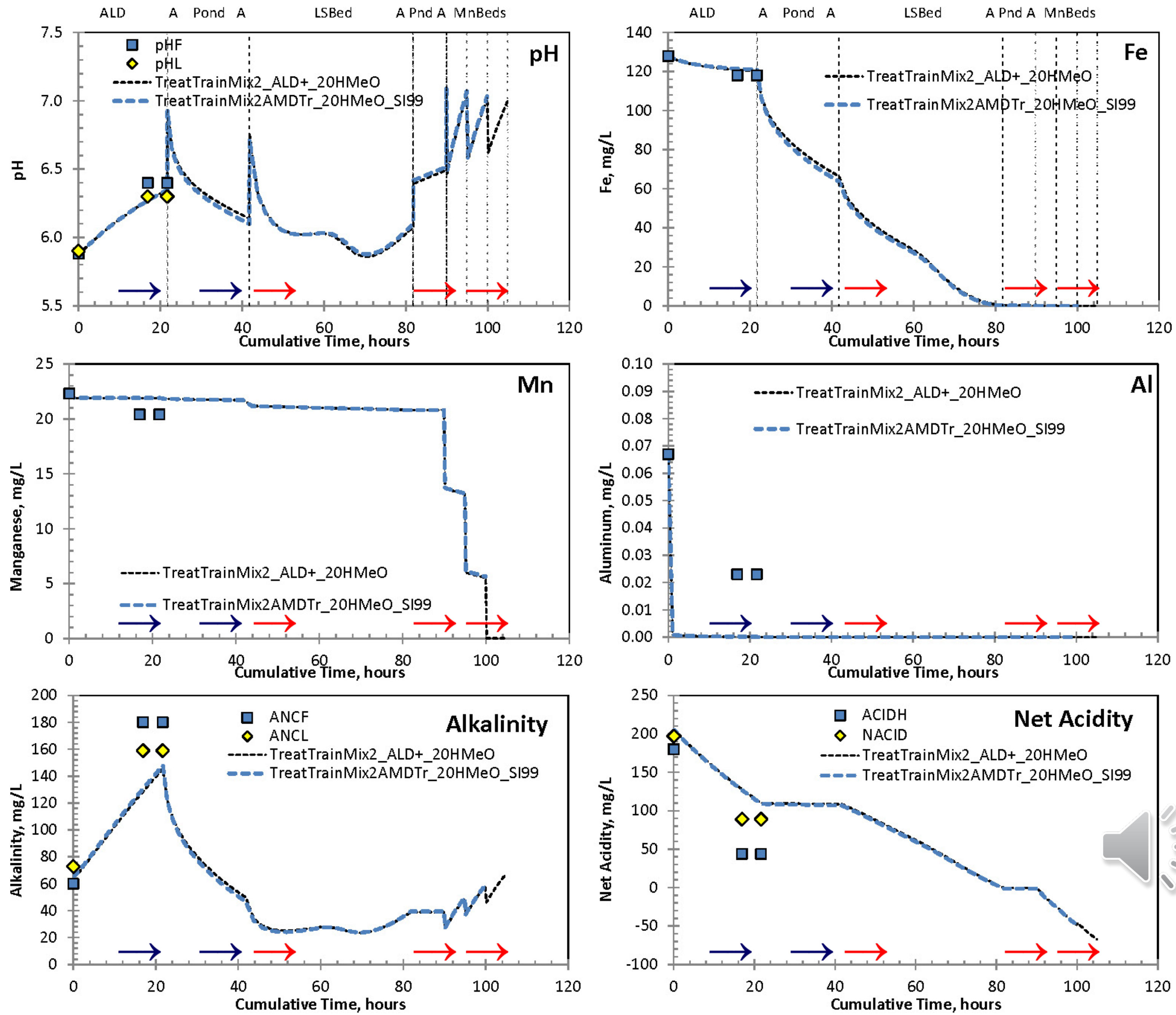
Model Output

☑ Print PHREEQC Output Report

Select Workspace | C:\Users\cravotta\Documents\AMDTreat_geochem_data\AMDTreatBeta\HoweBric

AMDTreat 6.0 Beta “PHREEQ-N-AMDTreat” tool (1) anoxic limestone drain; (3) aerobic pond; *plus (5) oxic limestone bed; (7) aerobic pond; and (9-11) manganese removal beds* with intermediate aeration steps (2, 4, 6, 8). *Steps 5-11 added…*

Howe Bridge ALD + Aerobic Ponds + OLD + Mn-Removal Bed



AMDTREAT | Tools | Net Present Value | Site

Treatment Modules

- PASSIVE TREATMENT MODULES
- ACTIVE TREATMENT MODULES
- ANCILLARY TREATMENT MODULES
- PROJECT MODULES
- PLACEHOLDER MODULE
  - Placeholder

Treatment Layout

Anoxic Limestone Drain
Capital Cost $22,893.11
Annual Cost $1,144.66
Net Present Value $56,418.89

Conveyance Ditch
Capital Cost $3,082.90
Annual Cost $154.14
Net Present Value $8,531.64

Ponds
Capital Cost $22,484.89
Annual Cost $5,639.59
Net Present Value $201,472.29

Conveyance Ditch
Capital Cost $3,082.90
Annual Cost $154.14
Net Present Value $8,531.64

Ponds
Capital Cost $22,484.89
Annual Cost $5,639.59
Net Present Value $201,472.29

Limestone Bed
Capital Cost $37,887.92
Annual Cost $1,894.40
Net Present Value $92,235.16

Conveyance Ditch
Capital Cost $3,082.90
Annual Cost $154.14
Net Present Value $8,531.64

Manganese Removal Bed
Capital Cost $84,798.24
Annual Cost $4,239.91
Net Present Value $223,094.37

AMDTreat 6.0 Beta: Howe Bridge ALD + Aerobic Ponds + "OLD" + Mn-Removal Bed

Total capital cost: $193,632
Net present value cost: $783,225
Project footprint: 1.40 acres

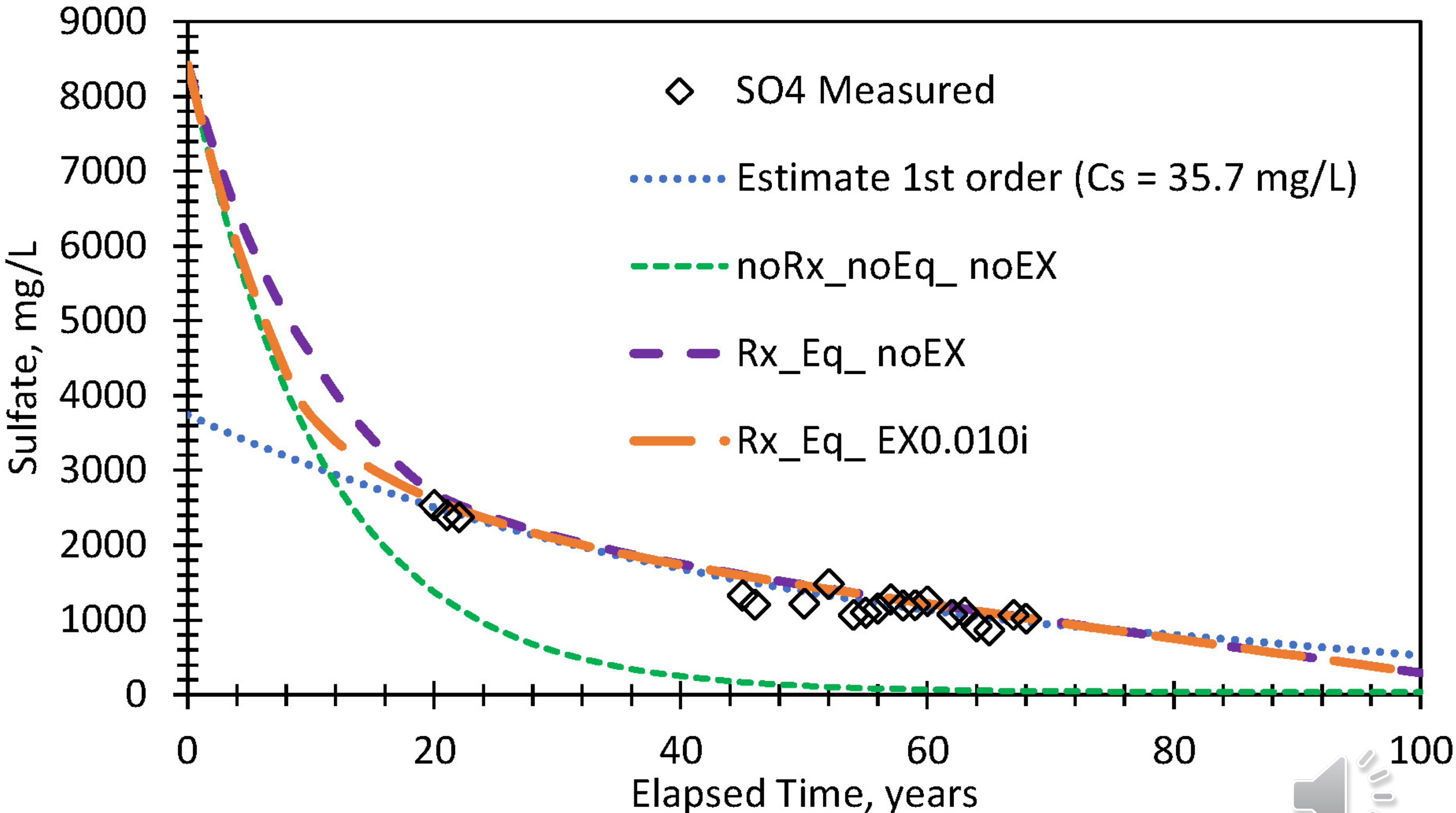
AMD Treat 6.0 Beta | Total Capital Cost: $193,631.94 | Total Annual Cost: $18,712.30 | Total Net Present Value Cost: $783,224.64 | Project Footprint in Acres: 1.40

Decadal-Scale AMD Chemical Evolution

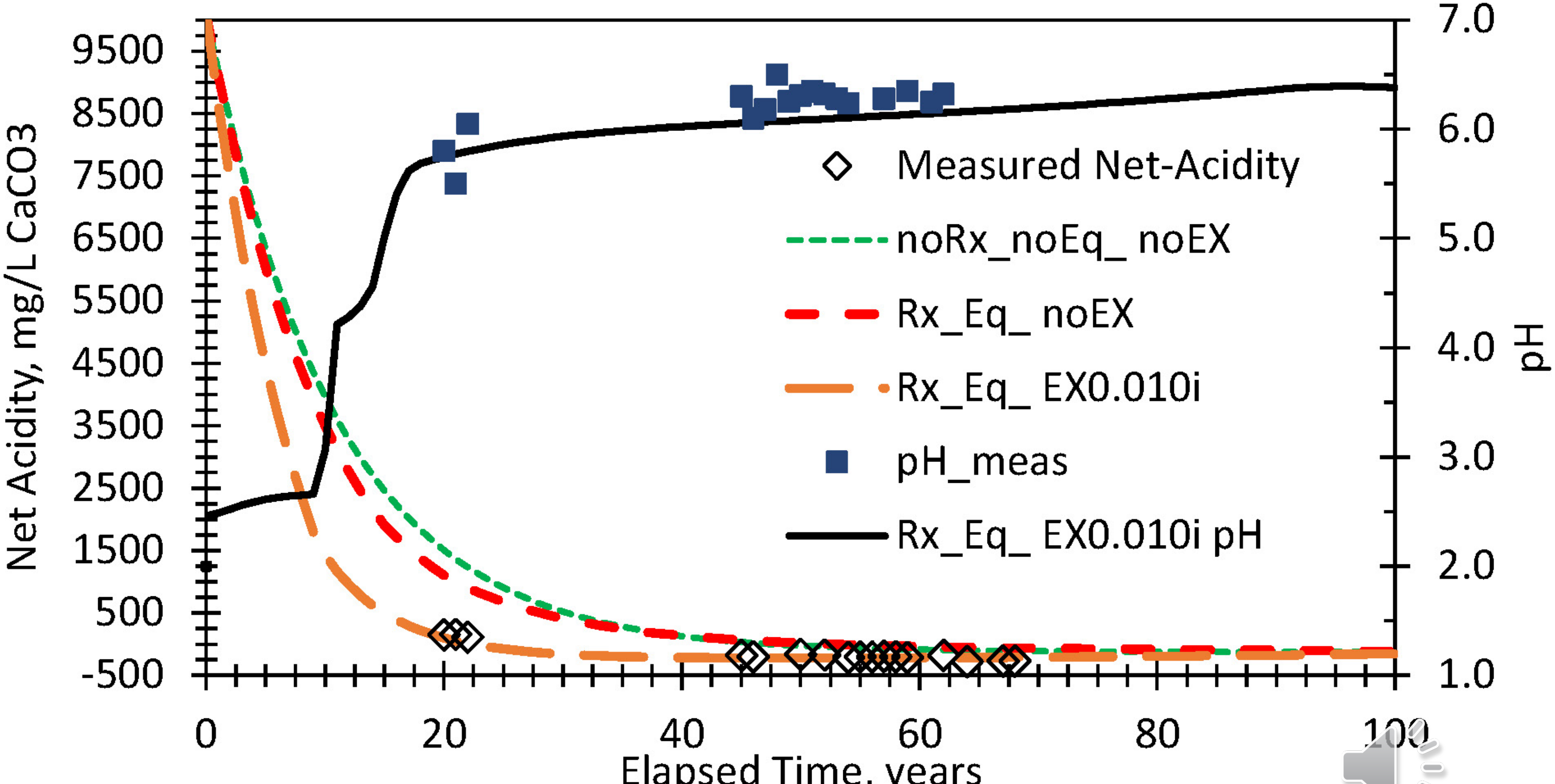
- All treatment systems have a finite lifetime and require maintenance and replacement … eventually treatment may not be needed.
- "Naturally" improving effluent quality could warrant future use of lower-cost treatment technologies.
- First-flush geochemical models and exponential decay models may be helpful to predict future conditions and appropriate, adaptive treatments.

First-Flush Model of Lowber Discharge—Progressive Decrease in Sulfate

Predictable(?) to 100+ Years

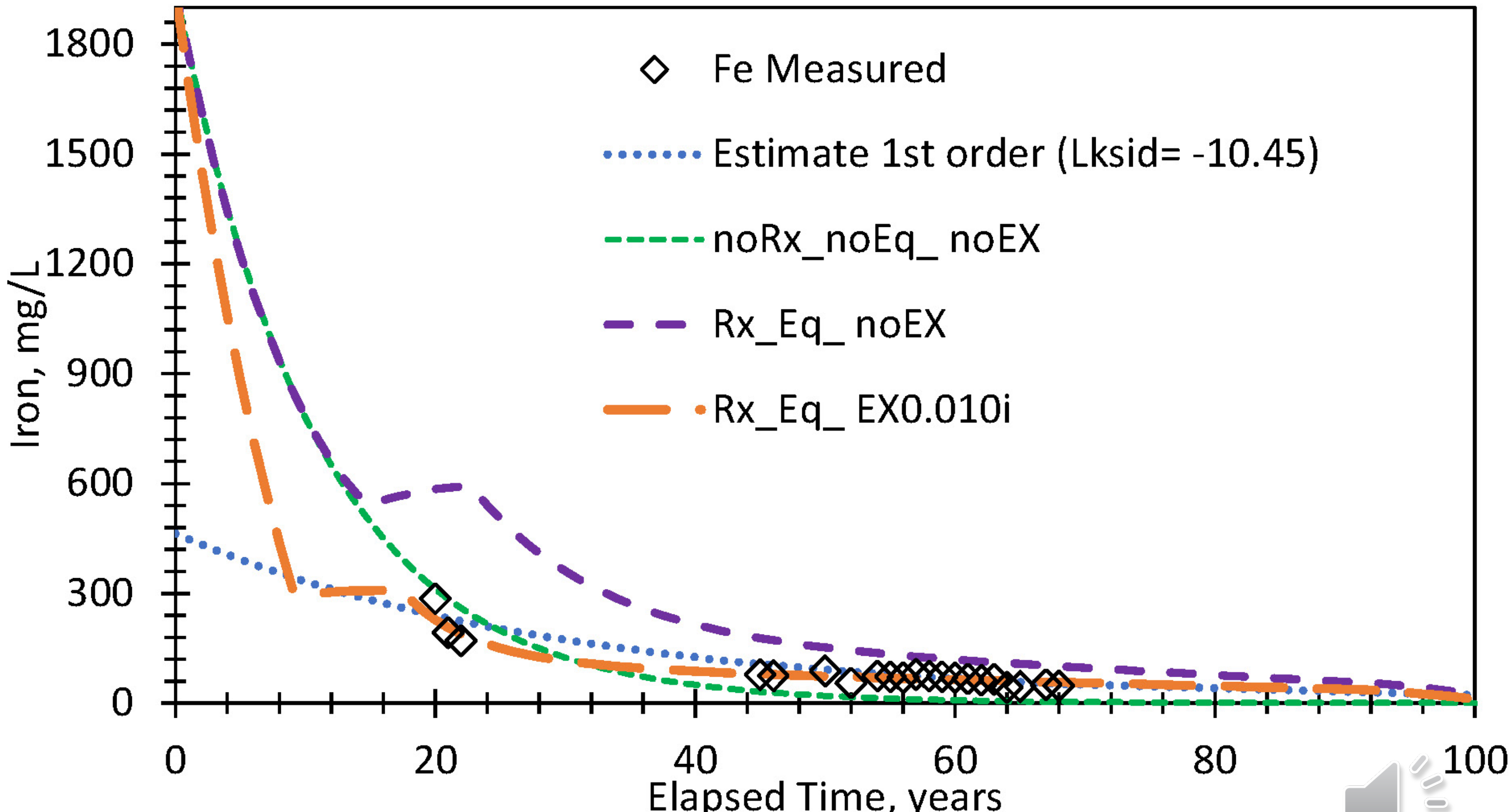


First-Flush Model of Lowber Discharge—
Rapid Transition from Net-Acidic to Net-Alkaline Character
Difficult to Predict Timing of Transition



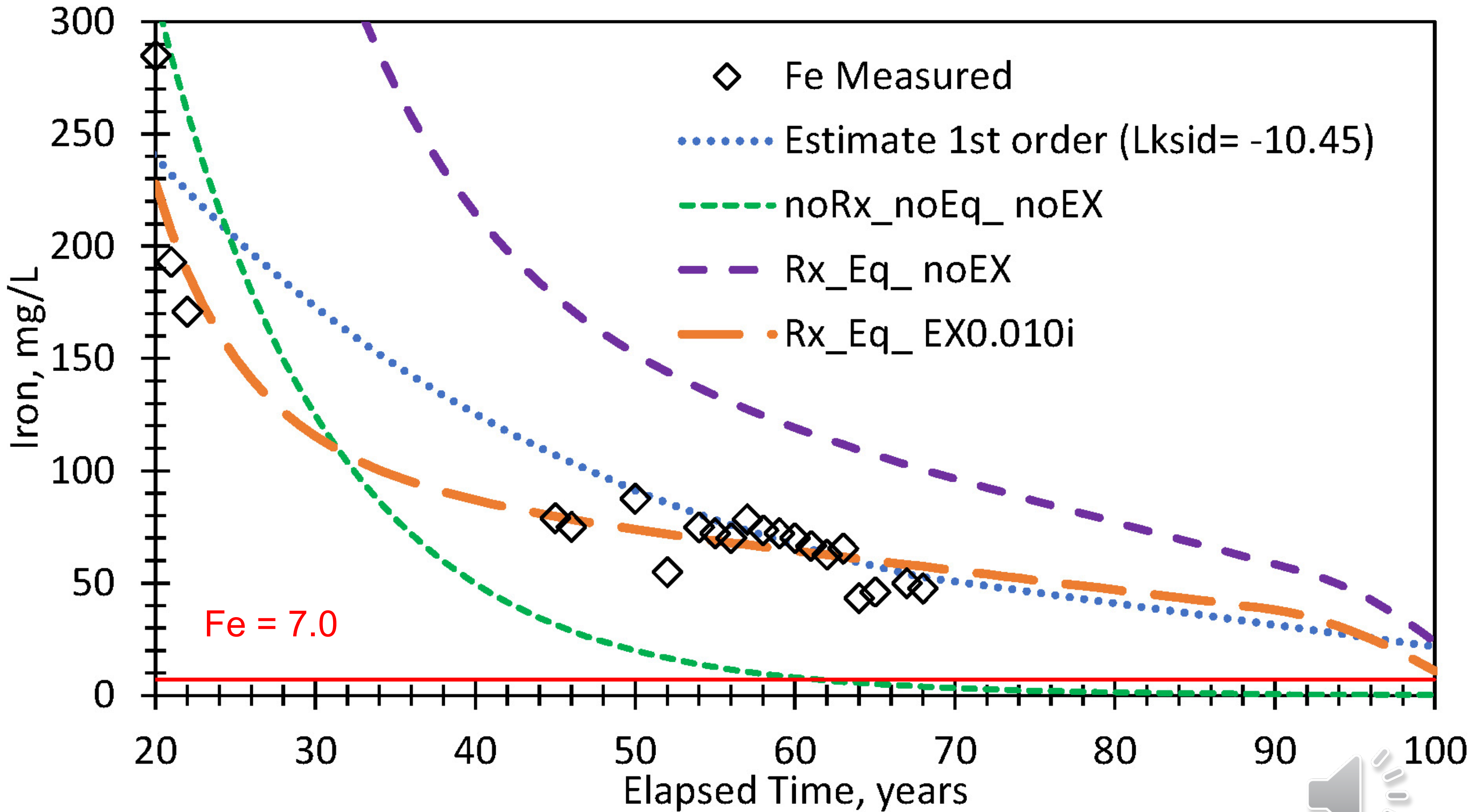
First-Flush Model of Lowber Discharge—Decrease in Dissolved Iron

Siderite(?) Equilibrium Could Maintain/Sustain Dissolved Fe



First-Flush Model of Lowber Discharge—Decrease in Dissolved Iron

Siderite(?) Equilibrium Could Maintain/Sustain Dissolved Fe



SUMMARY/CONCLUSIONS

- Water losses to mines can eliminate or reduce streamflow and affect downstream water supplies.
- Acidity, sulfate, and metals in AMD are influenced by quantifiable hydrogeochemical processes.
- Treatment of AMD to increase pH (> 6) and remove iron (< 7 mg/L) can attenuate many associated trace metals *but* may be required for decades.
- Management of AMD requires (1) understanding of contaminant sources and attenuation mechanisms and (2) adapting to changes in hydrogeochemical conditions.