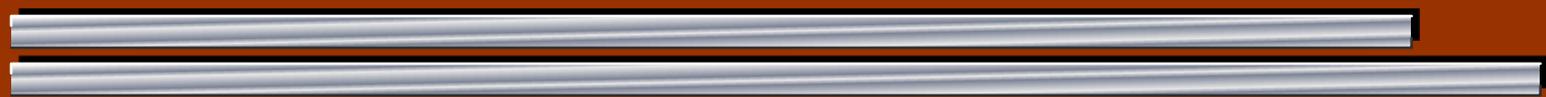




# Geochemical Modeling to Evaluate Remediation Options for Iron-Laden Mine Discharges

Charles “Chuck” Cravotta III  
U.S. Geological Survey  
Pennsylvania Water Science Center  
[cravotta@usgs.gov](mailto:cravotta@usgs.gov)



# Summary

Aqueous geochemical tools using PHREEQC have been developed by USGS for OSMRE's "AMDTreat" cost-analysis software:

- ✓ Iron-oxidation kinetics model considers pH-dependent abiotic and biological rate laws plus effects of aeration rate on the pH and concentrations of CO<sub>2</sub> and O<sub>2</sub>.
- ✓ Limestone kinetics model considers solution chemistry plus the effects of surface area of limestone fragments.
- ✓ Potential water quality from various treatments can be considered for feasibility and benefits/costs analysis.

# TREATMENT OF COAL MINE DRAINAGE



Passive

Active



Increase pH/oxidation  
with natural substrates &  
microbial activity

Reactions slow

Large area footprint

Low maintenance

Increase pH/oxidation  
with aeration &/or  
industrial chemicals

Reactions fast, efficient

Moderate area footprint

High maintenance

# ACTIVE TREATMENT

- 28 % – aeration; no chemicals (Ponds)
- 21 % – caustic soda ( $\text{NaOH}$ ) used
- 40 % – lime ( $\text{CaO}$ ;  $\text{Ca}(\text{OH})_2$ ) used
- 6 % – flocculent or oxidant used
- 4 % – limestone ( $\text{CaCO}_3$ ) used



# PASSIVE TREATMENT

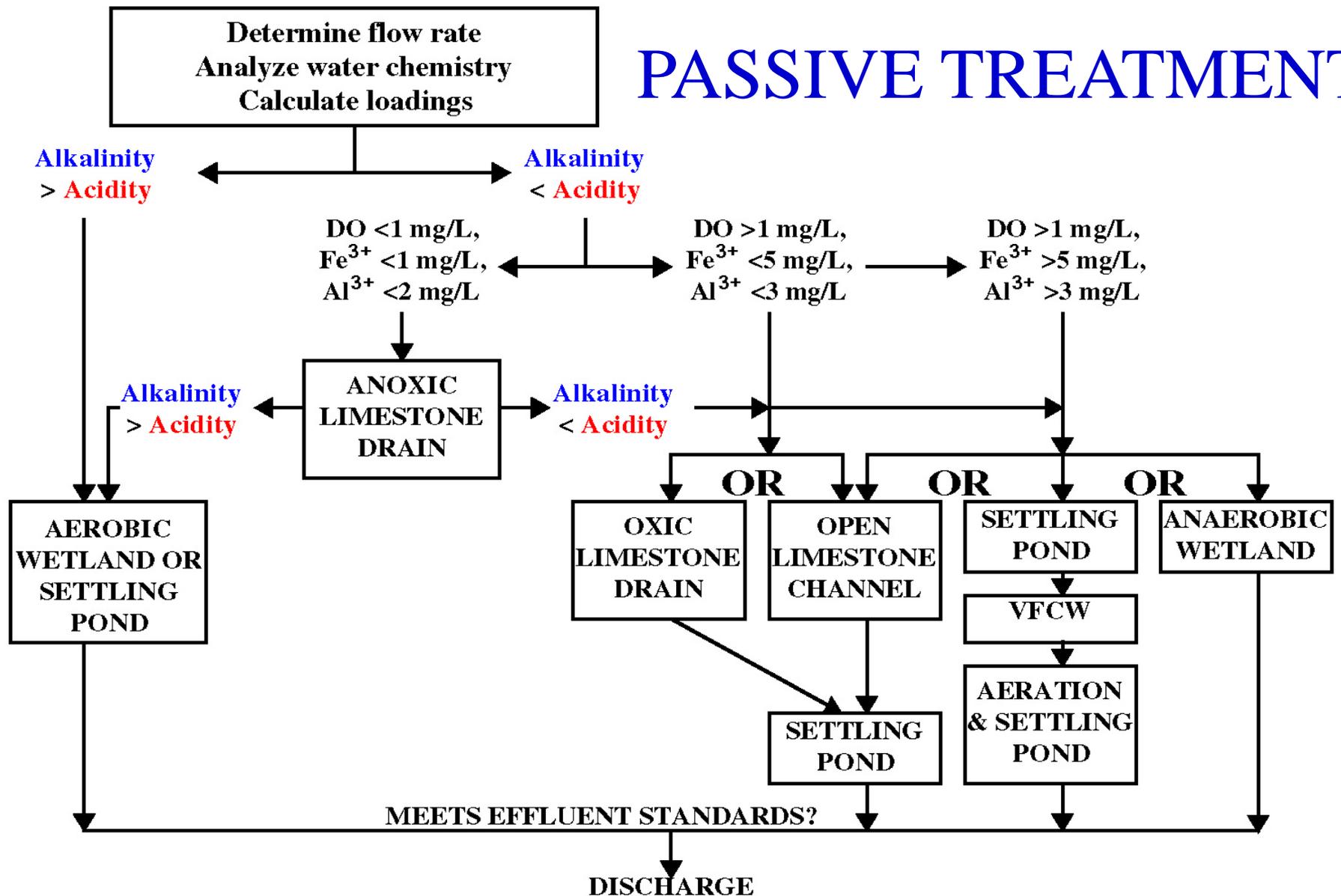


Figure 3. Flow chart for selection of passive treatment alternatives modified from Hedin and others (1994), Skousen and others (1998), and Pennsylvania Department of Environmental Protection (1999). Vertical flow compost wetland (VFCW), also known as SAPS or RAPS.

Vertical Flow Limestone Beds  
Bell Colliery



# PASSIVE TREATMENT

Limestone Dissolution,  
O<sub>2</sub> Ingassing,  
CO<sub>2</sub> Outgassing,  
Fe(II) Oxidation, & Fe(III)  
Accumulation

Pine Forest ALD & Wetlands

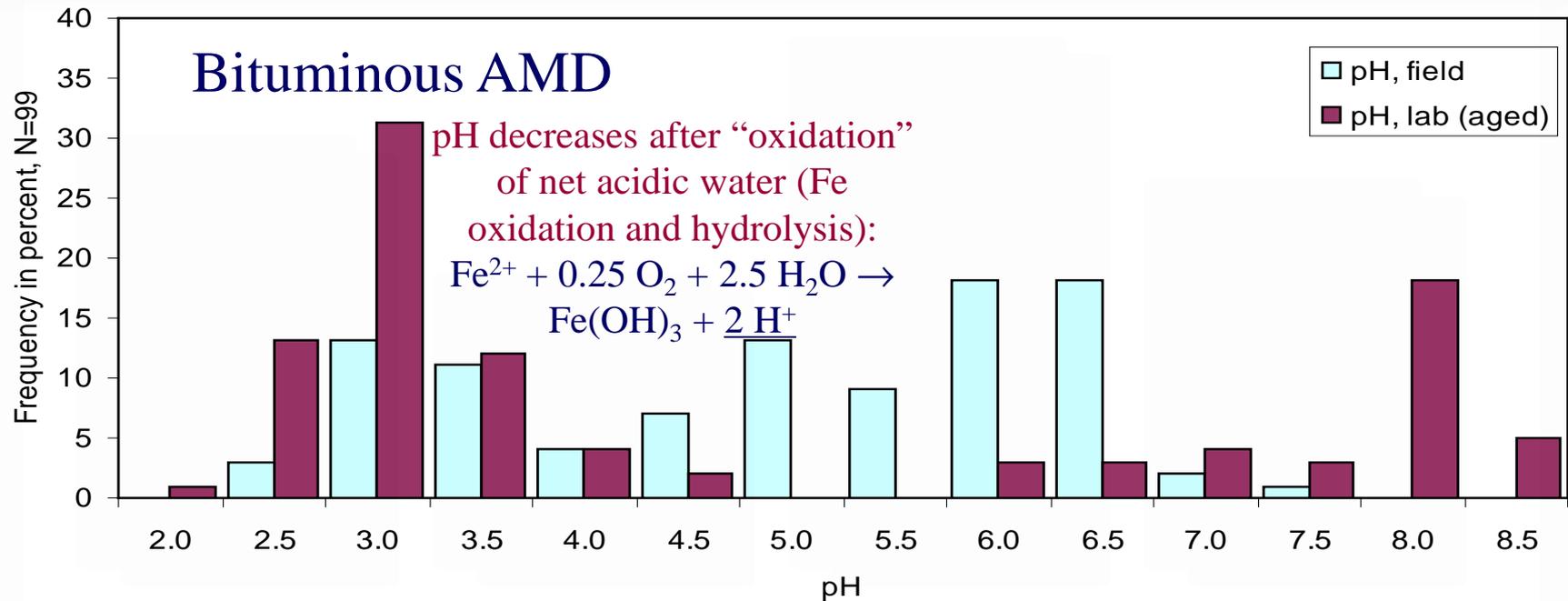
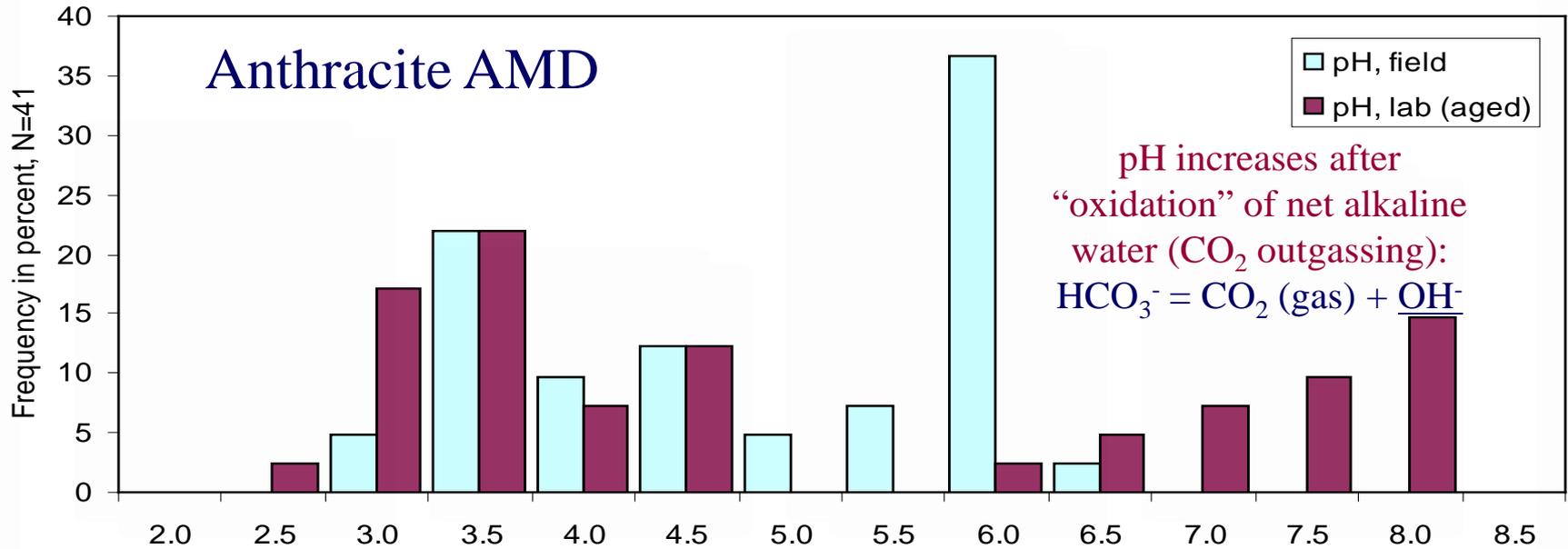


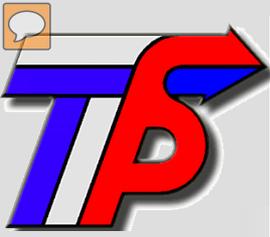
Silver Creek Wetlands





# BIMODAL pH FREQUENCY DISTRIBUTION





# “PHREEQ-N-AMDTREAT”

<http://amd.osmre.gov/>

AMDTreat is a computer application for estimating abatement costs for AMD (acidic or alkaline mine drainage).

AMDTreat is maintained by OSMRE.

The current version of AMDTreat 5.0+ is being recoded from FoxPro to C++ to facilitate its use on computer systems running Windows 10. The PHREEQC geochemical models described below will be incorporated to run with the recoded program.



## AMDTREAT



Take the Tutorial

[DOI HOME](#) [OSMRE HOME](#) [AR HOME](#) [TIPS HOME](#) [SITEMAP](#)

[HOME](#)  
[SUPPORT](#)  
[BUGLIST](#)  
[WISHLIST](#)  
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[TEAM](#)  
[PRESS INFO](#)

### AMDTREAT 5.0.2 PLUS NOW AVAILABLE!

AMDTreat 5.0.2 Plus corrects minor convergence issues identified during case study tests performed by the developers.

Enhancements to Version 5 of AMDTreat include incorporation of the geochemical modeling capabilities of the U.S. Geological Survey's (USGS) PHREEQ computer program to model titrations and enhancement to the oxidant tool.

For additional information, please contact [Brent Means](#) or [Omar Beckford](#).

### WHAT IS AMDTREAT?

AMDTreat (Pronounced: am'-D-treat or A-M-D-treat.), a member of OSMRE's **Technical Innovation and Professional Services (TIPS) suite of software**, is a computer application for estimating abatement costs for pollutional mine drainage, commonly referred to as Acid Mine Drainage or AMD. (Also Acid Rock Drainage or ARD.) The current version of AMDTreat is v5.0.2 Plus. AMDTreat can assist a user in estimating costs to abate water pollution using a variety of passive and chemical treatment types; including, vertical flow ponds, anoxic limestone drains, anaerobic wetlands, aerobic wetlands, bio reactors, manganese removal beds, limestone beds, oxic limestone channels, caustic soda, hydrated lime, pebble quicklime, ammonia, oxidation chemicals, and soda ash treatment systems. The acid mine drainage abatement cost model provides over 400 user modifiable variables in modeling costs for treatment facility construction, excavation, revegetation, piping, road construction, land acquisition, system maintenance, labor, water sampling, design, surveying, pumping, sludge removal, chemical consumption, clearing and grubbing, mechanical aeration, and ditching. AMDTreat also contains several financial and scientific tools to help select and plan treatment systems. These tools include a long-term financial forecasting module, an acidity calculator, a sulfate reduction calculator, a Langelier saturation index calculator, a mass balance calculator, a passive treatment alkalinity calculator, an abiotic homogeneous Fe<sup>2+</sup> oxidation calculator, a biotic homogeneous Fe<sup>2+</sup> oxidation calculator, an oxidation tool, and a metric conversion tool.

# AMDTreat 5.0+ Caustic Addition— St. Michaels Discharge



AMDTreat 5.0+.lnk

Escape Presentation

Costs			
<b>Passive Treatment A S</b>			
Vertical Flow Pond	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Anoxic Limestone Drain	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Anaerobic Wetlands	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Aerobic Wetlands	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Mn Removal Beds	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Oxic Limestone Channel	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Limestone Bed	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
BIO Reactor	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
<b>Passive Subtotal:</b>			<b>\$0</b>
<b>Active Treatment A S</b>			
Caustic Soda	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Hydrated Lime	<input checked="" type="checkbox"/>	<input type="checkbox"/>	X \$759,574
Pebble Quick Lime	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Ammonia	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Oxidant Capital Cost	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Soda Ash	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
<b>Active Subtotal:</b>			<b>\$759,574</b>
<b>Ancillary Cost A S</b>			
Ponds	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Roads	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Land Access	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Ditching	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Engineering Cost	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Ancillary Subtotal:			\$0
Other Cost (Capital Cost)			\$0
<b>Total Capital Cost:</b>			<b>\$759,574</b>

Annual Costs A S			
Sampling	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Labor	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Maintenance	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Pumping	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Chemical Cost	<input checked="" type="checkbox"/>	<input type="checkbox"/>	X \$973,674
Oxidant Chem Cost	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Sludge Removal	<input type="checkbox"/>	<input type="checkbox"/>	X \$0
Other Cost (Annual Cost)			\$0
Land Access (Annual Cost)			\$0
<b>Total Annual Cost:</b>			<b>\$973,674</b>
<b>Annual Cost per 1000 Gal of H2O Treated \$0.243</b>			
<b>Other Costs A S</b>			
Other Costs	<input type="checkbox"/>	<input type="checkbox"/>	X

Project
St Michaels
Company
USGS, Cravotta
Site Name
Hydrated Lime No Aeration
Run Date
04/07/2017
Comments
Maelstrom data from Brent Means

Water Quality		
Design Flow	7600.00	gpm
Typical Flow**	7600.00	gpm
Total Iron	136.00	mg/L
<input checked="" type="checkbox"/> Est. Ferrous Iron	135.99	mg/L
Aluminum	0.35	mg/L
Manganese	4.10	mg/L
pH	5.72	su
Alkalinity as CaCO3	62.80	mg/L
<input type="checkbox"/> Est. TIC as C	62.00	mg/L
<input type="radio"/> Calculate Net Acidity		
<input checked="" type="radio"/> Enter Acidity manually		
Acidity as CaCO3	205.00	mg/L
Sulfate	1100.00	mg/L
Chloride	38.70	mg/L
Calcium	212.00	mg/L
Magnesium	85.20	mg/L
Sodium	25.50	mg/L
Water Temperature	15.40	C
Specific Conductivity	1879.00	uS/cm
Total Dissolved Solids	1742.00	mg/L
Dissolved Oxygen	0.01	mg/L
Typical Acid Loading	3,413.5	tons/yr

Red indicates information used in critical calculations  
 Black indicates optional parameters  
 Blue indicates information used by PHREEQ  
 \*\* Typical Flow should represent the flow (e.g. median) used to estimate chemical reagent and sludge amounts

Report

# “New” PHREEQC Kinetics Models for AMDTreat 5.0+

- ✓ FeII oxidation model that utilizes established rate equations for gas exchange and pH-dependent iron oxidation and that can be associated with commonly used aeration devices/steps (including decarbonation);
- ✓ Limestone dissolution model that utilizes established rate equation for calcite dissolution and that can be adjusted for surface area of commonly used aggregate particle sizes.

# KINETICS OF IRON OXIDATION – pH & GAS EXCHANGE EFFECTS



# Iron Oxidation Kinetics are pH Dependent (abiotic and microbial processes can be involved)

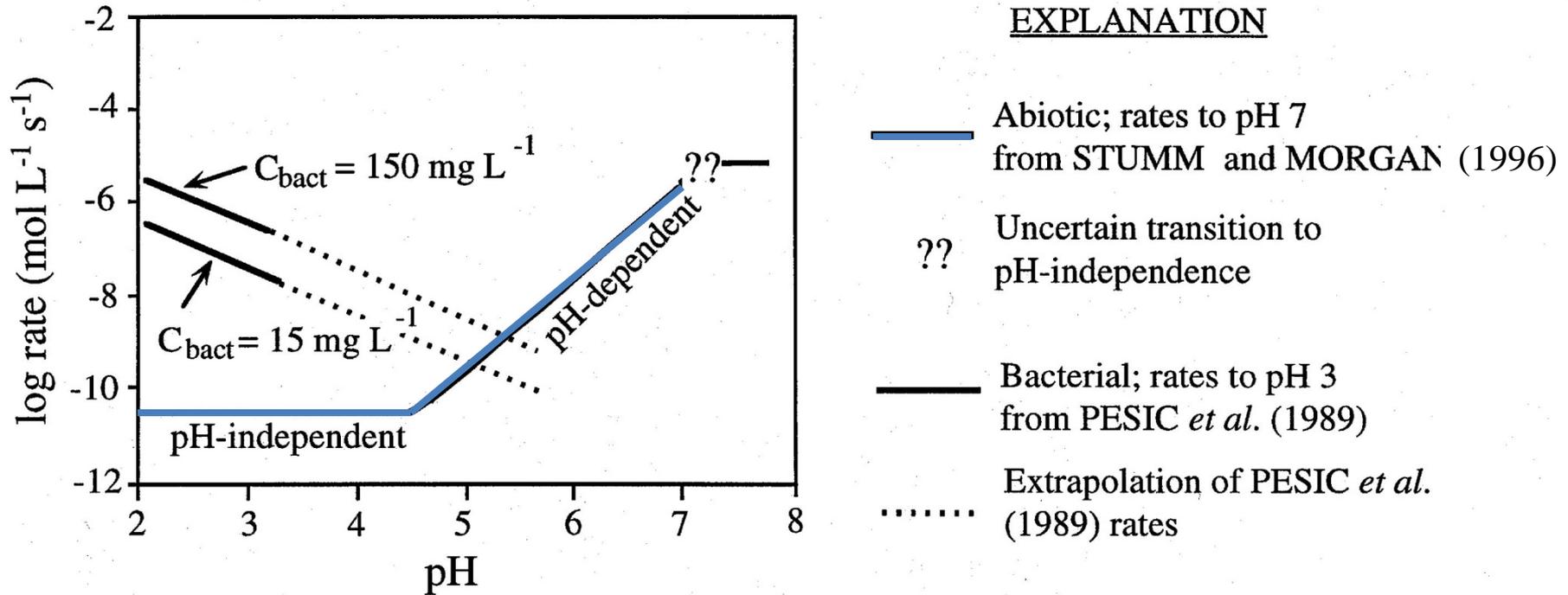


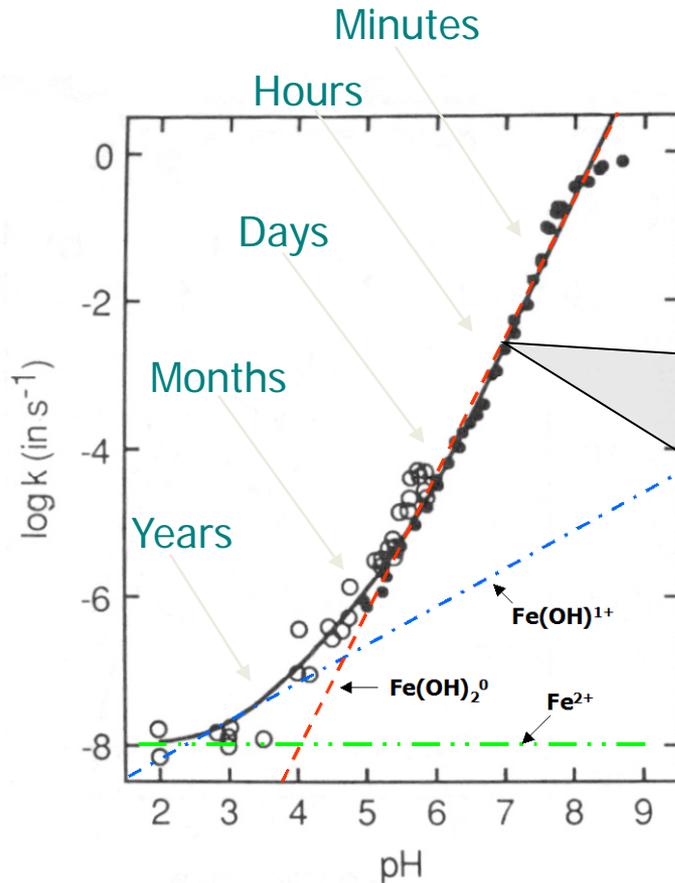
Fig. 3. Rate of Fe(II) oxidation versus pH based on abiotic and biological rate laws (Kirby *et al.*, 1999)

\*\*  $C_{bact}$  is concentration of iron-oxidizing bacteria, in mg/L, expressed as dry weight of bacteria ( $2.8E-13$  g/cell or  $2.8E-10$  mg/cell ).

The AMDTreat Fell oxidation kinetic model uses most probable number of iron-oxidizing bacteria per liter (MPNbact).

$C_{bact} = 150$  mg/L is equivalent to  $MPNbact = 5.3E11$ , where  $C_{bact} = MPNbact \cdot (2.8E-10)$ .

# Abiotic Homogeneous Fe(II) Oxidation Rate (model emphasizes pH)



\*Extrapolation of homogeneous rate law:



$$k_1 = 3 \times 10^{-12} \text{ mol/L/min}$$

Between pH 5 and 8 the Fe(II) oxidation rate increases by 100x for each pH unit increase.\*

At a given pH, the rate increases by 10x for a 15 °C increase. Using the activation energy of 23 kcal/mol with the Arrhenius equation, the rate can be adjusted for temperature.

$$\log k_{T_1} = \log k_{T_2} + Ea / (2.303 \cdot R) \cdot (1/T_2 - 1/T_1)$$

At  $[\text{O}_2] = 0.26 \text{ mM}$  ( $p\text{O}_2 = 0.21 \text{ atm}$ ) and  $25^\circ\text{C}$ . Open circles (o) from Singer & Stumm (1970), and solid circles (•) from Millero et al. (1987).

Dashed lines are estimated rates for the various dissolved Fe(II) species.

# Effects of $O_2$ Ingassing and $CO_2$ Outgassing on pH and Fe(II) Oxidation Rates

## Batch Aeration Tests at Oak Hill Boreholes (summer 2013)



Control Not Aerated



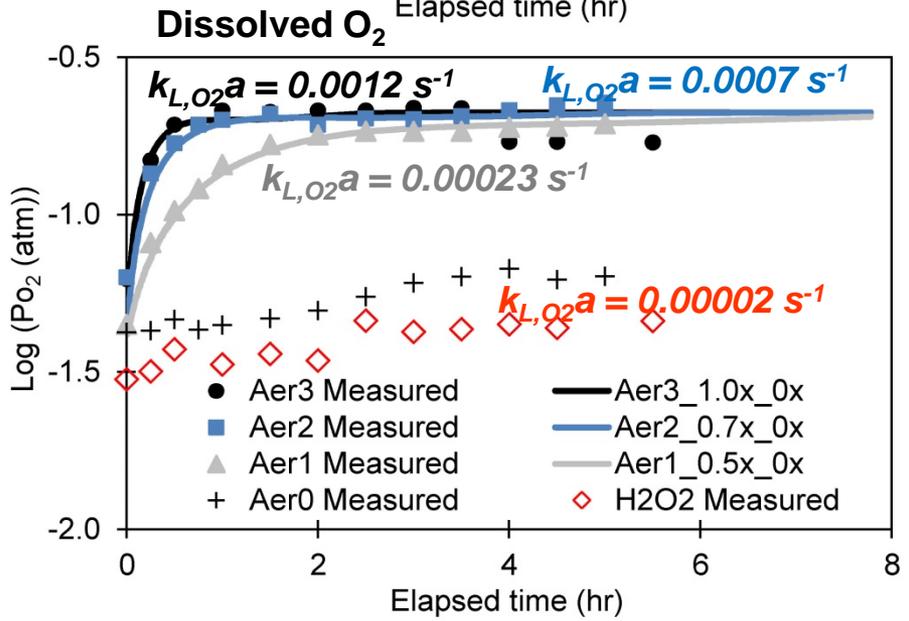
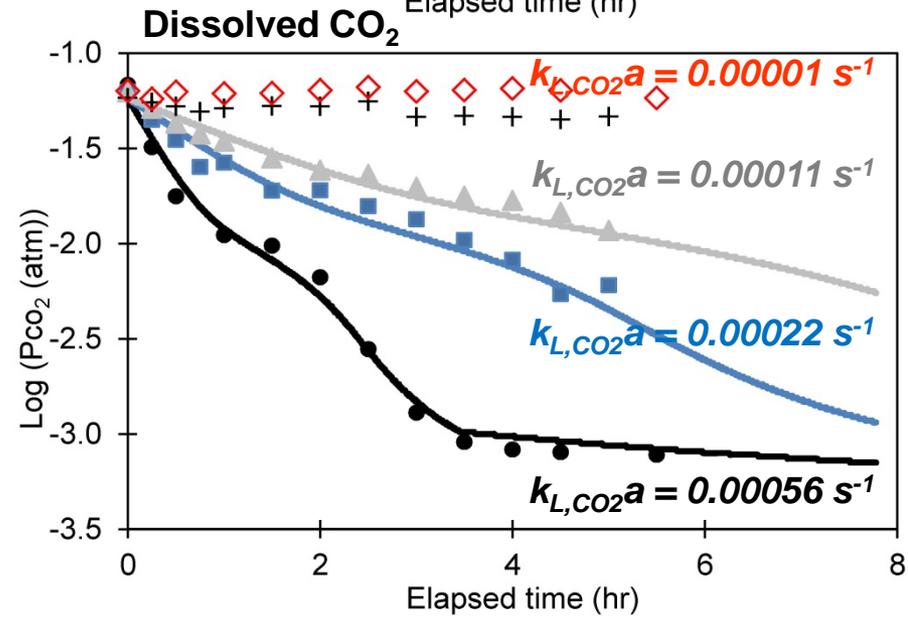
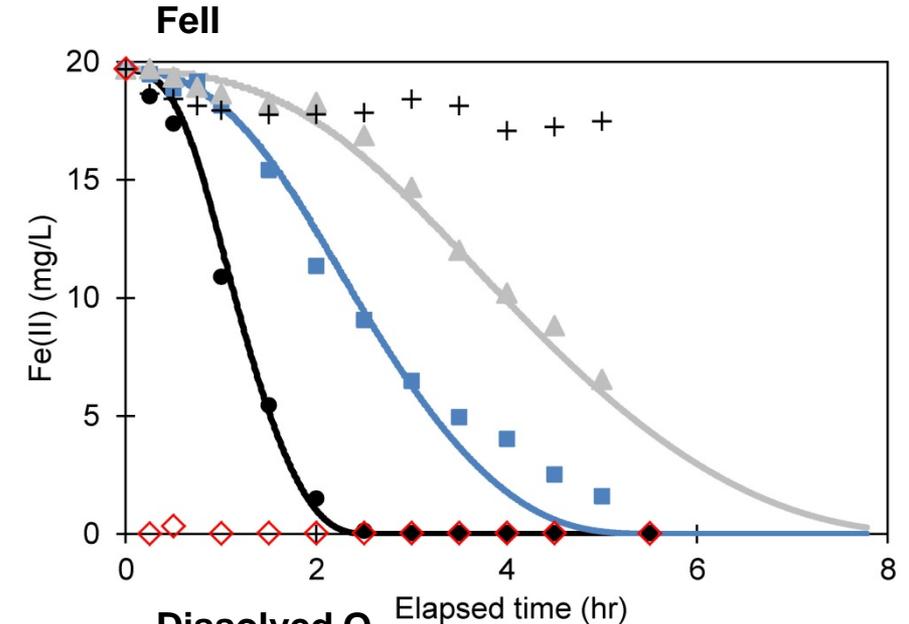
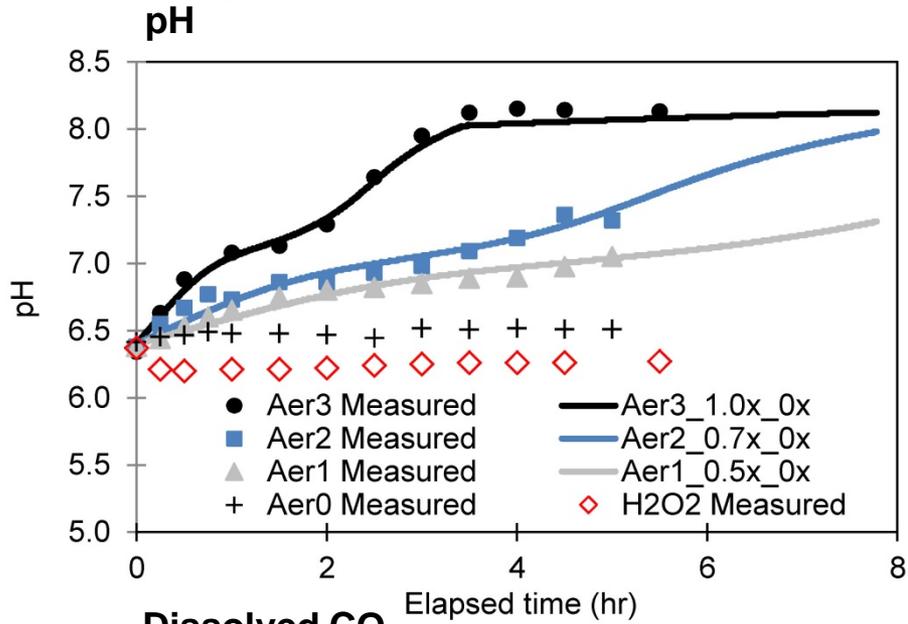
Aerated



$H_2O_2$  Addition



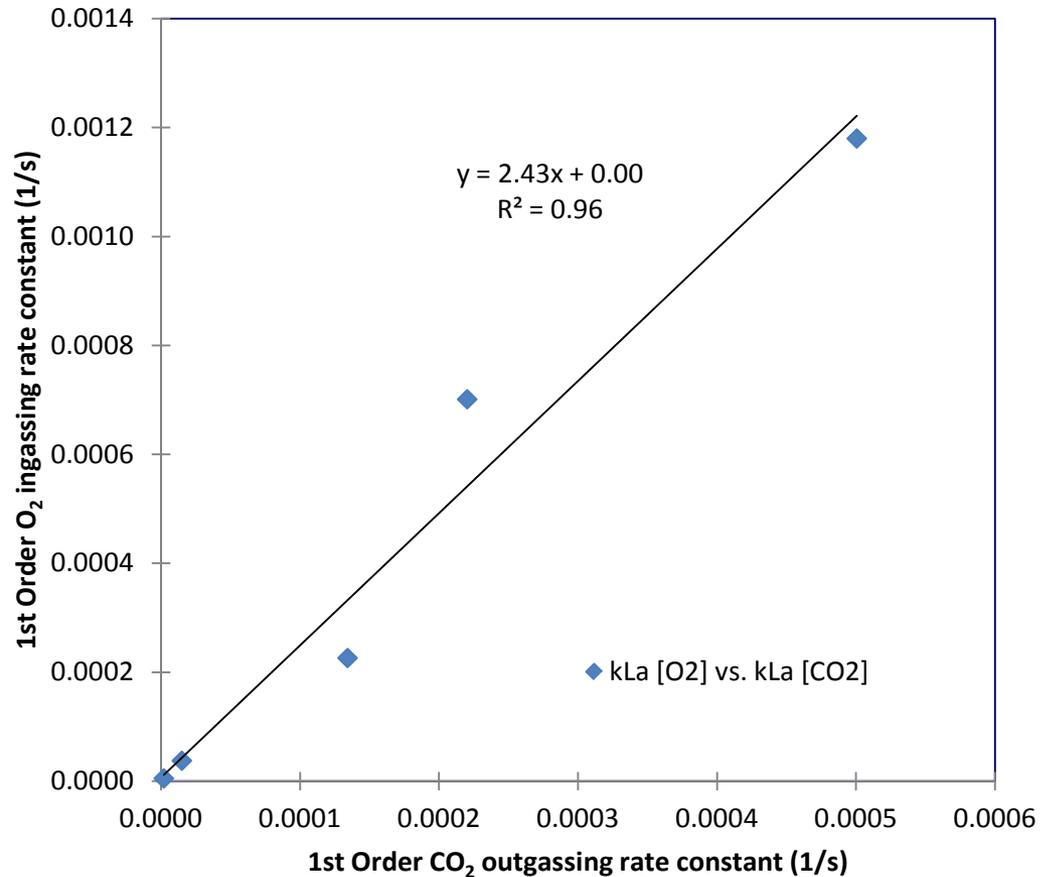
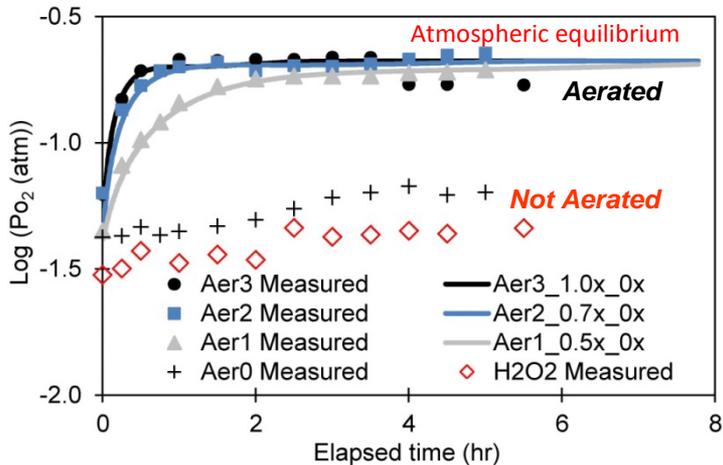
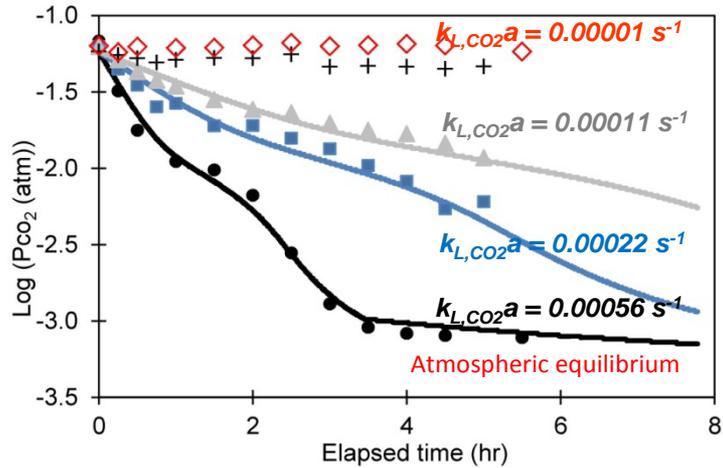
# PHREEQC Coupled Kinetic Model of CO<sub>2</sub> Outgassing & Homogeneous Fe(II) Oxidation—Oak Hill Boreholes





# CO<sub>2</sub> Outgassing is Proportional to O<sub>2</sub> Ingassing (model specifies first-order rates for out/in gassing)

$-d[C]/dt = k_{L,C}a \cdot ([C] - [C]_s)$  exponential, asymptotic approach to steady state



# New Iron Oxidation Rate Model for "AMDTreat" (combines abiotic and microbial oxidation kinetics)

The **homogeneous oxidation rate law** (Stumm and Lee, 1961; Stumm and Morgan, 1996), expressed in terms of  $[O_2]$  and  $\{H^+\}$  ( $=10^{-pH}$ ), describes the abiotic oxidation of dissolved Fe(II):

$$-d[Fe(II)]/dt = k_1 \cdot [Fe(II)] \cdot [O_2] \cdot \{H^+\}^{-2}$$

The **heterogeneous oxidation rate law** describes the catalytic abiotic oxidation of sorbed Fe(II) on precipitated Fe(III) oxyhydroxide surfaces, where (Fe(III)) is the Fe(III) oxyhydroxide concentration expressed as Fe in mg/L (Dempsey et al., 2001; Dietz and Dempsey, 2002):

$$-d[Fe(II)]/dt = k_2 (Fe(III)) \cdot [Fe(II)] \cdot [O_2] \cdot \{H^+\}^{-1}$$

The **microbial oxidation rate law** describes the catalytic biological oxidation of Fe(II) by acidophilic microbes, which become relevant at  $pH < 5$  (Pestic et al., 1989; Kirby et al., 1999):

$$-d[Fe(II)]/dt = k_{bio} \cdot C_{bact} \cdot [Fe(II)] \cdot [O_2] \cdot \{H^+\}$$

where  $k_{bio}$  is the rate constant in  $L^3/mg/mol^2/s$ ,  $C_{bact}$  is the concentration of iron-oxidizing bacteria in mg/L (dry weight), [ ] indicates aqueous concentration in mol/L.

# New Iron Oxidation Rate Model for "AMDTreat"— PHREEQC Coupled Kinetic Models of CO<sub>2</sub> Outgassing & Fe(II) Oxidation

Form1

FlowGPM 100

Fe 19.7

Estimate Fe2

Fe2 19.7

Al 0.047

Mn 3.6

pH 6.4

Alk 150

Estimate TIC

TIC 0

SO4 400

Cl 7.9

Ca 79

Mg 64

Na 5.0

TempC 15.1

SC.uS/cm 1280

DO 0.1

Duration of aeration (time for reaction)  
TimeSecs : 28800 is 8 hrs

FeIIOxidation TimeSecs 28800

kLaCO2 0.0006 CO<sub>2</sub> outgassing rate in sec<sup>-1</sup>

factr.kCO2 1 Adjustment CO<sub>2</sub> outgassing rate

factr.kO2 2 Adjustment O<sub>2</sub> ingassing rate (x kLaCO2)

factr.k1Fe 1 Adjustment abiotic homogeneous rate

factr.k2Fe 0 Adjustment abiotic heterogeneous rate

bactMPN 5.30E+11 Iron oxidizing bacteria, microbial rate

SlccPPT 0.3 Calcite saturation limit

H2O2mmol 0 Hydrogen peroxide added\*

factr.kh2o2 1 Adjustment to H2O2 rate

FeIIIRecirculated FeIII 2000  
Option to specify FeIII recirculation

Generate Kinetics Output

Plot Dis. Metals  Plot Ca, Acidity  Plot Sat Index

Kinetic variables can be adjusted, including CO<sub>2</sub> outgassing and O<sub>2</sub> ingassing rates plus abiotic and microbial FeII oxidation rates. Constants are temperature corrected.



FeII.exe

**Aer3:**  $k_{L,CO_2}a = 0.00056 \text{ s}^{-1}$   
**Aer2:**  $k_{L,CO_2}a = 0.00022 \text{ s}^{-1}$   
**Aer1:**  $k_{L,CO_2}a = 0.00011 \text{ s}^{-1}$   
**Aer0:**  $k_{L,CO_2}a = 0.00001 \text{ s}^{-1}$

User may estimate Fe2 from Fe and pH plus TIC from alkalinity and pH. And specify H<sub>2</sub>O<sub>2</sub> or recirculation of FeIII. Output includes pH, solutes, net acidity, TDS, SC, and precipitated solids.

\*multiply Fe.mg by 0.0090 to get [H2O2]

# Estimated CO<sub>2</sub> Outgassing & O<sub>2</sub> Ingassing Rate Constants for Various Treatment Technologies

**Table S.4** Values of rate constants for CO<sub>2</sub> outgassing and O<sub>2</sub> ingassing used for kinetic models

Site	Temperature (°C)	CO <sub>2</sub> Outgas			O <sub>2</sub> Ingas			
		k <sub>L,CO2a</sub> (s <sup>-1</sup> )	log(s <sup>-1</sup> )	log(min <sup>-1</sup> )	k <sub>L,O2a</sub> (s <sup>-1</sup> )	log(s <sup>-1</sup> )	log(min <sup>-1</sup> )	
<b>Treatment Systems</b>								
Maelstrom (Sykesville, Trent, St.Michaels)	20	0.03	Fast	-1.52	0.26	0.06	-1.22	0.56
Surface Aerator (Renton, Rushton)	20	0.001		-3.00	-1.22	0.002	-2.70	-0.92
Mechanical Aerator (Lancashire)	20	0.0006		-3.22	-1.44	0.0012	-2.92	-1.14
Aeration Cascade/Level Spreader (Silver Cr)	20	0.01		-2.00	-0.22	0.02	-1.70	0.08
Rip-rap Spillway/Ditch (Silver Cr, Pine Forest,	20	0.005		-2.30	-0.52	0.01	-2.00	-0.22
Pond (Silver Cr, Pine Forest, Lion Mining, Flight93)	20	0.00001	Slow	-5.00	-3.22	0.00002	-4.70	-2.92
Wetland (Silver Cr, Pine Forest, Lion Mining)	20	0.00001		-5.00	-3.22	0.00002	-4.70	-2.92
<b>Oak Hill Aeration Expts.</b>								
Aer3	20	0.0005625	Fast	-3.25	-1.47	0.001125	-2.95	-1.17
Aer2	20	0.0002475		-3.61	-1.83	0.000495	-3.31	-1.53
Aer1	20	0.0001508		-3.82	-2.04	0.000302	-3.52	-1.74
Aer0	20	0.0000169	Slow	-4.77	-2.99	3.38E-05	-4.47	-2.69

\*Gas mass-transfer rate corrected to 20°C per Rathbun (1998, Eq. 56) using the expression:

$$k_{L,a\_20} = k_{L,a\_TC} / (1.0241^{(TC-20)}).$$

$$k_{L,a\_TC} = k_{L,a\_20} * (1.0241^{(TC-20)}).$$

$k_{L,a\_20} = (\text{LN}((C_1 - C_s)/(C_2 - C_s))/t) / (1.0241^{(\text{TEMP}_{PC} - 20)})$ , where C is CO<sub>2</sub> or O<sub>2</sub>.

Dissolved O<sub>2</sub>, temperature, and pH were measured using submersible electrodes.

Dissolved CO<sub>2</sub> was computed from alkalinity, pH, and temperature data.

# Revised AMDTreat Chemical Cost Module – Caustic Titration with Pre-Aeration (Decarbonation) PHREEQC Coupled Kinetic Models of CO<sub>2</sub> Outgassing & Fe(II) Oxidation

The screenshot shows the PHREEQ Test software interface with the following parameters and options:

- FlowGPM: 7600
- Fe: 136
- Estimate Fe2
- Fe2: 136
- Al: 0.35
- Mn: 4.1
- pH: 5.72
- Alk: 62.8
- Estimate TIC
- TIC: 62
- SO4: 1100
- Cl: 38.7
- Ca: 212
- Mg: 85.2
- Na: 25.5
- TempC: 15.4
- SC.uS/cm: 1879
- DO: 0.01
- Caustic Chemical Treatment Type:
  - Hydrated Lime
  - Pebble Quick Lime
  - Caustic Soda
- Not Aerated
- Pre-Aerated
  - TimeSecs: 76.2
  - kLaCO2: 0.03
  - factr.kCO2: 1
  - factr.kO2: 2
  - H2O2mmol: 0
  - factr.kh2o2: 0
  - SlccPPT: 0.3
- Buttons: Generate Output
- Checkboxes:  Plot Dis. Conc.,  Plot Sat Index

Original option for no aeration, plus new option for **kinetic pre-aeration** (w/wo hydrogen peroxide) that replaces original equilibrium aeration.



Dropdown kLa

PHREEQTitration\_StMichaels.exe

Duration of pre-aeration in sec

CO<sub>2</sub> outgassing rate constant in sec<sup>-1</sup>

Adjustment CO<sub>2</sub> outgassing rate (x kLaCO2)

Adjustment O<sub>2</sub> ingassing rate (x kLaCO2)

Hydrogen peroxide added\*

Adjustment to H<sub>2</sub>O<sub>2</sub> rate

Calcite saturation limit

Allows selection and evaluation of key variables that affect chemical usage efficiency.

\*multiply Fe.mg by 0.0090 to get [H2O2]

# New Module For AMDTreat – PHREEQC Coupled Kinetic Models of CO<sub>2</sub> Outgassing & Fe(II) Oxidation, with Caustic Pre-Treatment

Form1

Option to adjust initial pH with caustic

FlowGPM 8750

Fe 16.0

Estimate Fe2

Fe2 16.0

Al 0.010

Mn 6.2

pH 6.1

Alk 107

Estimate TIC

TIC 0

SO4 560

Cl 9.4

Ca 120

Mg 65

Na 13.0

TempC 14.5

SC.uS/cm 1200

DO 0.1

Add Chemical to Fix pH 7.2

Hydrated Lime

Pebble Quick Lime

Caustic Soda

FeIIoxidation TimeSecs 72000

kLaCO2 0.00001 CO<sub>2</sub> outgassing rate

factr.kCO2 1 Adjustment CO<sub>2</sub> outgassing rate

factr.kO2 2 Adjustment O<sub>2</sub> ingassing rate (x kLaCO2)

factr.k1Fe 1 Adjustment abiotic homogeneous rate

factr.k2Fe 1 Adjustment abiotic heterogeneous rate

bactMPN 5.3E+11 Iron oxidizing bacteria

SlccPPT 0.3 Calcite saturation limit

H2O2mmol 0 Hydrogen peroxide added

factr.kh2o2 1 Adjustment to H2O2 rate

FeIIIRecirculated FeIII 2000

Option to specify FeIII recirculation

Generate Kinetics Output

Plot Dis. Metals  Plot Ca, Acidity  Plot Sat Index

\*multiply Fe.mg by 0.0090 to get [H2O2]

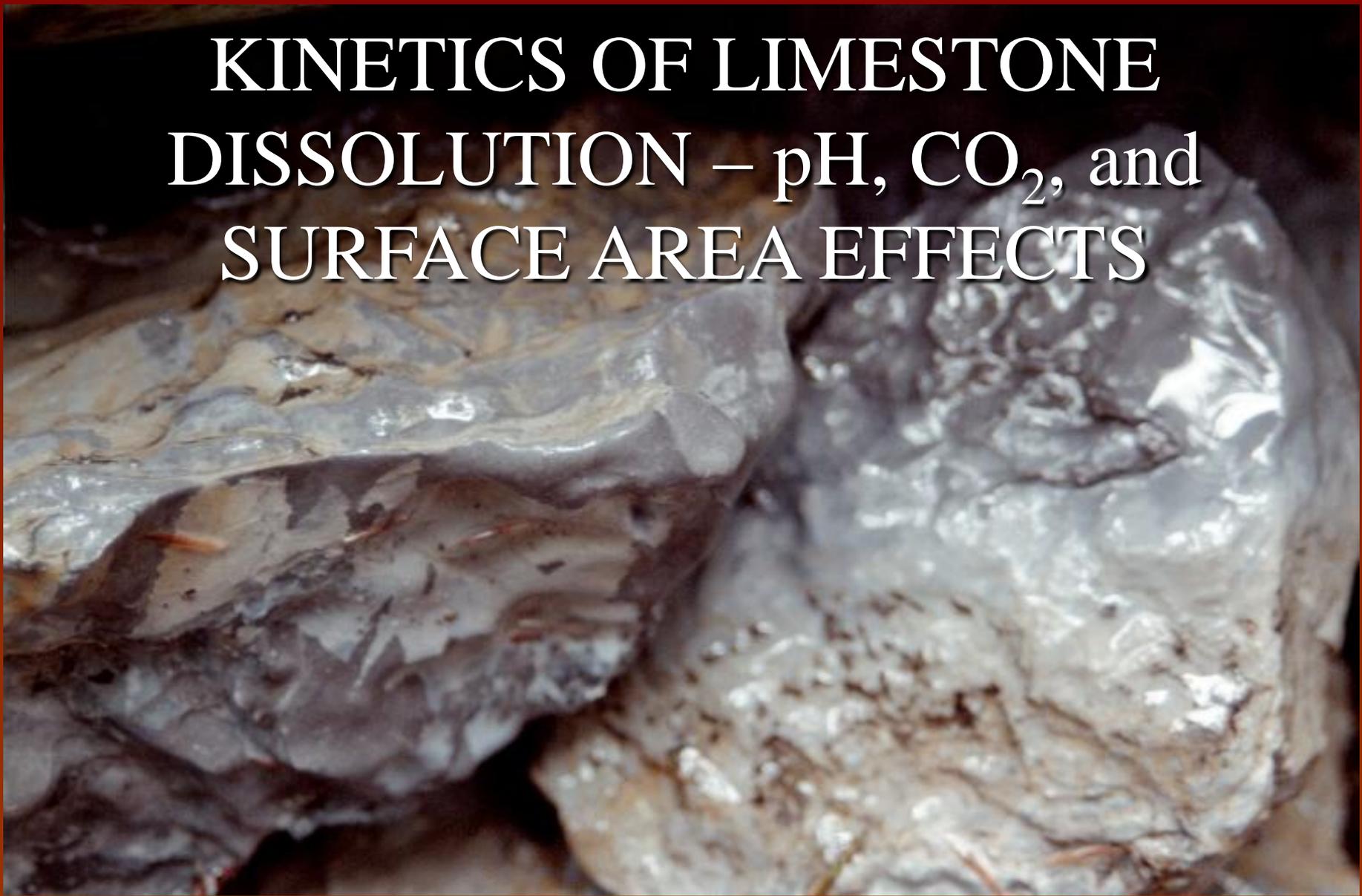
Variable CO<sub>2</sub> outgassing and O<sub>2</sub> ingassing rates apply. Can choose to adjust initial pH with caustic. The required quantity of caustic is reported in units used by AMDTreat.



Caustic+FeII.exe

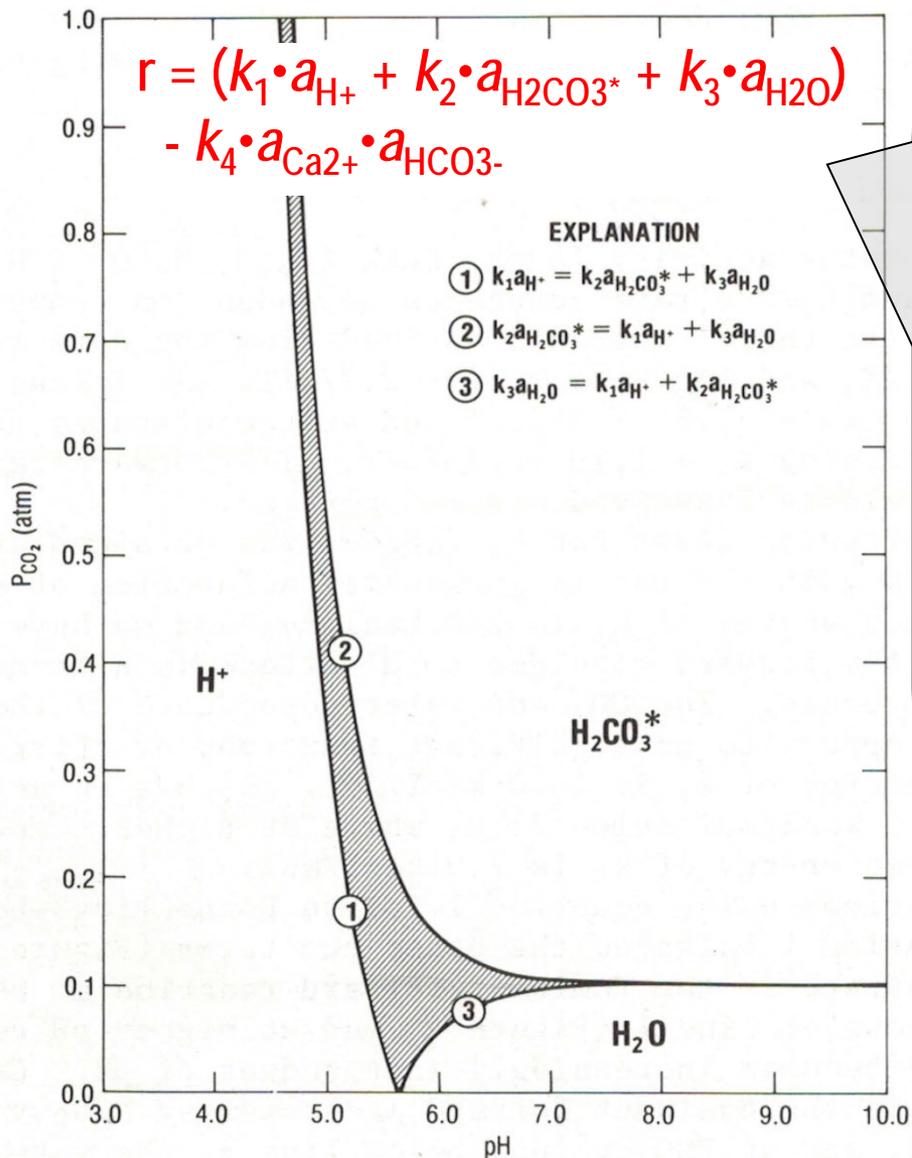
Kinetic variables, including CO<sub>2</sub> outgassing and O<sub>2</sub> ingassing rates plus abiotic and microbial FeII oxidation rates, can be adjusted by user. In addition to caustic chemicals, hydrogen peroxide and recirculation of FeIII solids can be simulated.

# KINETICS OF LIMESTONE DISSOLUTION – pH, CO<sub>2</sub>, and SURFACE AREA EFFECTS

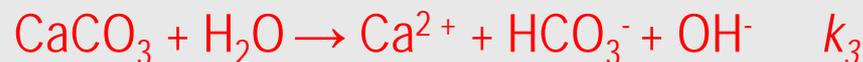


# Limestone Dissolution Rate Model for AMD Treat

("PWP" model emphasizes pH and CO<sub>2</sub>)



According to Plummer, Wigley, and Parkhurst (1978), the rate of CaCO<sub>3</sub> dissolution is a function of three forward (dissolution) reactions:



and the backward (precipitation) reaction:



Although H<sup>+</sup>, H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, and H<sub>2</sub>O reaction with calcite occur simultaneously, the forward rate is dominated by a single species in the fields shown. More than one species contributes significantly to the forward rate in the gray stippled area. Along the lines labeled 1, 2, and 3, the forward rate attributable to one species balances that of the other two.

# Limestone Dissolution Rate Model for AMDTreat (surface area correction for coarse aggregate)

Surface area for various coarse aggregates (bold indicates sizes commonly used in limestone beds; 2NS used in cubitainers).

Gradation Number		Weight (g) Average Particle	Particle Dimensions (cm)				Particle Surface Area (cm <sup>2</sup> )			Unit Surface Area (cm <sup>2</sup> /g)		
AASHTO	PA		Long Axis	Inter-mediate	Short Axis	Average Axis	Rectan-gular Prism	Sphere	Ellipsoid	Rectan-gular Prism	Sphere	Ellipsoid
<b>R-5</b>		<b>22160.145</b>	<b>45.72</b>	<b>22.86</b>	<b>13.34</b>	<b>27.31</b>	<b>3919.35</b>	<b>2342.26</b>	<b>2862.08</b>	<b>0.18</b>	<b>0.11</b>	<b>0.13</b>
<b>R-4</b>		<b>7113.133</b>	<b>30.48</b>	<b>16.51</b>	<b>8.89</b>	<b>18.63</b>	<b>1841.93</b>	<b>1089.98</b>	<b>1319.11</b>	<b>0.26</b>	<b>0.15</b>	<b>0.19</b>
<b>R-3</b>		<b>1185.522</b>	<b>16.51</b>	<b>8.89</b>	<b>5.08</b>	<b>10.16</b>	<b>551.61</b>	<b>324.29</b>	<b>395.61</b>	<b>0.47</b>	<b>0.27</b>	<b>0.33</b>
1	4	341.978	8.89	6.35	3.81	6.35	229.03	126.68	155.24	0.67	0.37	0.45
3	3A	78.166	5.08	3.81	2.54	3.81	83.87	45.60	56.39	1.07	0.58	0.72
5		9.771	2.54	1.91	1.27	1.91	20.97	11.40	14.10	2.15	1.17	1.44
57	2B	3.257	2.54	1.27	0.635	1.48	11.29	6.90	8.25	3.47	2.12	2.53
	2NS	9.771	2.54	1.91	1.27	1.91	20.97	11.40	14.10	2.15	1.17	1.44
67	2	1.832	1.91	0.95	0.635	1.16	7.26	4.26	5.28	3.96	2.32	2.88
	1NS	1.221	1.27	0.95	0.635	0.95	5.24	2.85	3.52	4.29	2.33	2.89
7		1.221	1.27	0.95	0.635	0.95	5.24	2.85	3.52	4.29	2.33	2.89
8		0.382	0.95	0.79	0.3175	0.69	2.62	1.49	1.70	6.87	3.90	4.44
	1B	0.382	0.95	0.79	0.3175	0.69	2.62	1.49	1.70	6.87	3.90	4.44

Particle dimensions were estimated on the basis of ranges for graded materials reported in Pennsylvania Department of Environmental Protection, 2000, Erosion and sediment pollution control program manual: Harrisburg, Pennsylvania Dept. Environmental Protection Bureau of Watershed Management, Document No. 363-2134-008, 180 p. (tables 9 and 10A).

**Plummer, Wigley, and Parkhurst (1978) reported unit surface area (SA) of 44.5 and 96.5 cm<sup>2</sup>/g for “coarse” and “fine” particles, respectively, used for empirical testing and development of PWP rate model. These SA values are 100 times larger than those for typical limestone aggregate. Multiply cm<sup>2</sup>/g by 100 g/mol to get surface area (A) units of cm<sup>2</sup>/mol used in AMDTreat rate model.**

Surface area computed for various geometric forms:

Sphere:  $4\pi \cdot (\text{Average of Axes}/2)^2$

Rectangular Prism:  $2 \cdot (\text{Long Axis} \cdot \text{Short Axis}) + 2 \cdot (\text{Long Axis} \cdot \text{Intermediate Axis}) + 2 \cdot (\text{Short Axis} \cdot \text{Intermediate Axis})$

Ellipsoid:  $(\pi \cdot D^2)/S$ , where  $D = 2 \cdot (\text{vol}/(4/3\pi))^{1/3}$   $S = 1.15 - 0.25E$   $E = \text{Long Axis}/D$

Volume computed for same geometric forms:

Sphere:  $4/3 \cdot \pi \cdot (\text{Average Axis}/2)^3$

Rectangular Prism:  $(\text{Long Axis} \cdot \text{Short Axis} \cdot \text{Intermediate Axis})$

Ellipsoid:  $4/3 \cdot \pi \cdot (\text{Long Axis}/2 \cdot \text{Short Axis}/2 \cdot \text{Intermediate Axis}/2)$

For ellipsoid sphere, this reduces to  $0.5236 \cdot \text{Long Axis} \cdot \text{Short Axis} \cdot \text{Intermediate Axis}$

Santomartino and Webb (2007, AG, 22:2344–2361) estimated volume of ellipsoid as  $0.6 \cdot \text{volume of rectangular prism of same dimensions}$ .

# New Module For AMDTreat – PHREEQC Kinetic Model of Limestone Dissolution

The screenshot shows a software window titled 'Form1' with various input fields and checkboxes. The 'TimeSecs' field is set to 7200, with a note '7200 is 2 hrs'. The 'LimestoneDiss' checkbox is checked. The 'SAcc' field is set to 44.5e+02, with a note 'Surface area, cm<sup>2</sup>/mol \*\*'. The 'EXPcc' field is set to 0.67, with a note 'Equilibrium approach'. The 'M/M0cc' field is set to 1.00, with a note 'Mass available'. A red note states: '\*\*Multiply surface area (SA) in cm<sup>2</sup>/g by 100 to get SAcc in cm<sup>2</sup>/mol.' The 'Generate Kinetics Output' button is visible at the bottom. The 'Plot Dis. Metals', 'Plot Ca, Acidity', and 'Plot Sat Index' checkboxes are checked.

Parameter	Value
FlowGPM	690
Fe	14.0
Estimate Fe2	<input type="checkbox"/>
Fe2	14.0
Al	0.09
Mn	3.1
pH	5.79
Alk	26
Estimate TIC	<input type="checkbox"/>
TIC	42.25
SO4	330
Cl	4.0
Ca	56
Mg	51
Na	7.4
TempC	11.63
SC.uS/cm	700
DO	0.4

Calcite dissolution rate model of Plummer, Wigley, and Parkhurst (PWP; 1978). Empirical testing and development of PWP rate model based on "coarse" and "fine" calcite particles with surface areas of 44.5 and 96.5 cm<sup>2</sup>/g, respectively.



Limestone.PWP.exe

Surface area and exponential corrections permit application to larger particle sizes (0.45 to 1.44 cm<sup>2</sup>/g) used in treatment systems.

# New Module For AMDTreat – PHREEQC Coupled Kinetic Models of Limestone Dissolution & Fe(II) Oxidation

Form1

FlowGPM 690

Fe 14.0

Estimate Fe2

Fe2 14.0

Al 0.09

Mn 3.1

pH 5.79

Alk 26

Estimate TIC

TIC 42.25

SO4 330

Cl 4.0

Ca 56

Mg 51

Na 7.4

TempC 11.63

SC.uS/cm 700

DO 0.4

LimestoneDiss TimeSecs 14240

SAccDIS 0.72e+02 Surface area

EXPccDIS 0.67 Equilibrium approach

M/M0cc 1.00 Mass available

FeIIoxidation TimeSecs 47015

Use LimestoneDiss Effluent

kLaCO2 0.00005 CO<sub>2</sub> outgassing rate

factr.kCO2 1 Adjustment CO<sub>2</sub> outgassing rate

factr.kO2 2 Adjustment O<sub>2</sub> ingassing rate (x kLaCO2)

factr.k1Fe 1 Adjustment abiotic homogeneous rate

factr.k2Fe 0 Adjustment abiotic heterogeneous rate

bactMPN 5.30E+11 Iron oxidizing bacteria

SlccPPT 0.3 Calcite saturation limit

H2O2mmol 0 Hydrogen peroxide added

factr.kh2o2 1 Adjustment to H2O2 rate

FeIIIRecirculated FeIII 2000

Generate Kinetics Output

Plot Dis. Metals  Plot Ca, Acidity  Plot Sat Index

Rate models for calcite dissolution, CO<sub>2</sub> outgassing and O<sub>2</sub> ingassing, and FeII oxidation are combined to evaluate possible reactions in passive treatment systems.



Limestone+FeII.exe

Can simulate limestone treatment followed by gas exchange and FeII oxidation in an aerobic pond or aerobic wetland, or the independent treatment steps (not in sequence).

# PHREEQC Coupled Kinetic Models Sequential Steps

## Limestone Dissolution + Fe(II) Oxidation

### Pine Forest ALD + Aerobic Wetlands

FormSequential

FlowGPM 690

Fe 14.0

Estimate Fe2

Fe2 14.0

Al 0.09

Mn 3.1

pH 5.79

Alk 26

FeIII Recirculated?

Estimate TIC

Limestone and FeII Kinetic Constants

EXPccDIS 0.67 M/M0cc 1.00

factr.kCO2 1 factr.kO2 2

factr.k1Fe 1 factr.k2Fe 0

bactMPN 5.3E+11 SlccPPT 0.3

H2O2mmol 0 factr.kh2o2 1

	Step	Time(s)	kLaCO2(1/s)	SAcc(cm2/mol)	Temp2(C)	FeIII(mg)
TIC	1:	14240	0.00001	0.72e+02	11.63	0
SO4	2:	60	0.02	0	11.6	0
Cl	3:	47015	0.00002	0	12.16	5
Ca	4:	15	0.001	0	12.16	0
Mg	5:	28814	0.00003	0	12.15	3
Na	6:	15	0.02	0	12.15	0
TempC	7:	21972	0.00002	0	12.04	0
SC.uS/cm	8:	15	0.02	0	12.04	0
TDS	9:	3979	0.00002	0	11.88	0

DO 0.4

Plot Dis. Metals  Plot Ca, Acidity  Plot Sat Index

Generate Sequential Kinetics Output

Sequential steps: Variable detention times, adjustable CO<sub>2</sub> outgassing rates, limestone surface area, temperature, and FeIII.



Next slide

Limestone+FeIIseq.exe

Can simulate passive treatment by anoxic or oxic limestone bed, open (limestone) channels or spillways, aerobic cascades, ponds, and wetlands.

# PHREEQC Coupled Kinetic Models Sequential Steps— Pine Forest ALD + Aerobic Wetlands



Step	Treatment
1	ALD
2	Riprap
3	Pond
4	Cascade
5	Wetland
6	Cascade
7	Wetland
8	Cascade
9	Wetland



Limestone+FeIIseq\_PineFor151212.exe



LS+FeIIseq\_kinetics.sel - Shortcut.Ink



PineForest\_Field\_151212t.xlsx - Shortcut.Ink

# PHREEQC Coupled Kinetic Models Sequential Steps Caustic + Limestone Dissolution + Fe(II) Oxidation Silver Creek Aerobic Wetlands

FormSequential

FlowGPM 750

Fe 20.0

Estimate Fe2

Fe2 20.0

Al 0.19

Mn 2.95

pH 6.01

Alk 45.5

Estimate TIC

TIC 29.8

SO4 150

Cl 4.0

Ca 45.7

Mg 28.3

Na 2.6

TempC 12.12

SC.uS/cm 502

TDS 250

DO 0.1

Add Chemical to Fix Initial pH 7.3

CaO  Ca(OH)2  NaOH

Limestone and FeII Kinetic Constants

EXPcc 0.67 M/M0cc 1.00

factr.kCO2 1 factr.kO2 2

factr.k1Fe 1 factr.k2Fe 0

bactMPN 5.3E+11 SlccPPT 0.3

H2O2mmol 0 factr.kh2o2 1

FeIII Recirculated?

	Step	Time(s)	kLaCO2(1/s)	SAcc(cm2/mol)	Temp2(C)	FeIII(mg)
	1:	4074	0.000001	0	13.91	0
	2:	30	0.005	0	14.11	0
	3:	493128	0.000001	0	17.93	5
	4:	30	0.005	0	18.41	0
	5:	842859	0.000003	0	25.23	3
	6:	120	0.0075	0.72e+02	24.45	0
	7:	112429	0.000005	0	25.55	0
	8:	120	0.0075	0.72e+02	24.49	0
	9:	141927	0.000005	0	28.97	0

Generate Sequential Kinetics Output

Plot Dis. Metals  Plot Ca, Acidity  Plot Sat Index

Sequential steps: Pre-treatment with caustic and/or peroxide and, for each subsequent step, variable detention times, adjustable CO<sub>2</sub> outgassing rates, limestone surface area, temperature, and FeIII.



Next slide

Caustic+Limestone+FeIIseq.exe

Can simulate active treatment, including chemical addition or aeration, *or* passive treatment, including anoxic or oxic limestone bed, open (limestone) channels or spillways, aerobic cascades, ponds, and wetlands.

# PHREEQC Coupled Kinetic Models Sequential Steps— Silver Creek Aerobic Wetlands



Caustic+LS+FeIIseq\_SilCr160808.exe



Caustic+LS+FeIIseq\_kinetics.sel - Shortcut.lnk



SilverCrk\_Field\_160808t.xlsx - Shortcut.lnk

# Conclusions

- ✓ Geochemical kinetics tools using PHREEQC have been developed to evaluate mine effluent treatment options.
- ✓ Graphical and tabular output indicates the pH and solute concentrations in effluent.
- ✓ By adjusting kinetic 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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