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

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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_2 and O_2.
- ✓ 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

Al^{3+}

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

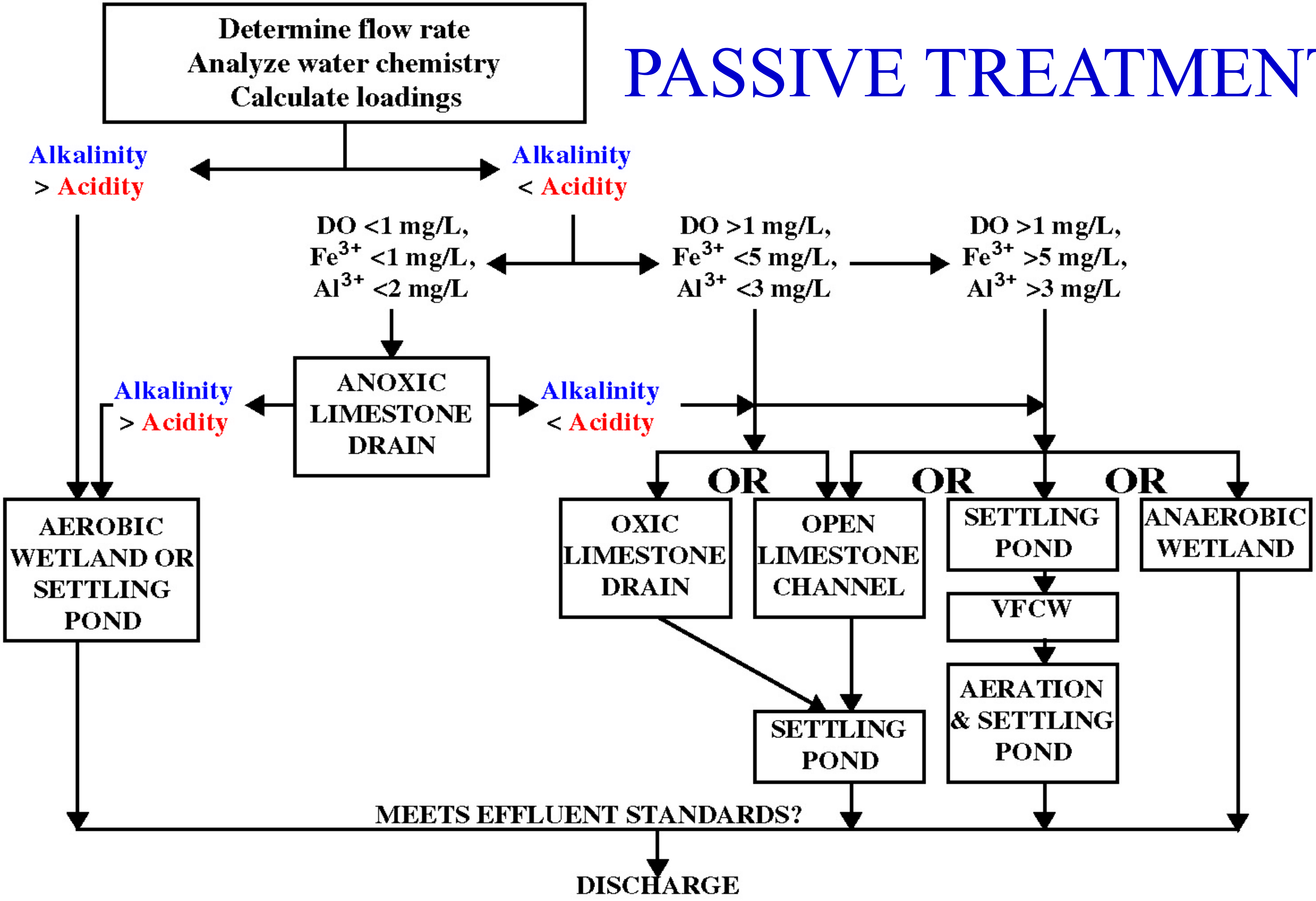
Mn^{2+}

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

ACTIVE TREATMENT

28 % – aeration; no chemicals (Ponds)
21 % – caustic soda ($NaOH$) used
40 % – lime (CaO; $Ca(OH)_2$) used
6 % – flocculent or oxidant used
4 % – limestone ($CaCO_3$) used

PASSIVE TREATMENT



Determine flow rate
Analyze water chemistry
Calculate loadings

Alkalinity > Acidity

Alkalinity < Acidity

DO <1 mg/L, Fe^{3+} <1 mg/L, Al^{3+} <2 mg/L

DO >1 mg/L, Fe^{3+} <5 mg/L, Al^{3+} <3 mg/L

DO >1 mg/L, Fe^{3+} >5 mg/L, Al^{3+} >3 mg/L

ANOXIC LIMESTONE DRAIN

Alkalinity > Acidity

Alkalinity < Acidity

AEROBIC WETLAND OR SETTLING POND

OXIC LIMESTONE DRAIN

OR

OPEN LIMESTONE CHANNEL

OR

SETTLING POND

VFCW

AERATION & SETTLING POND

OR

ANAEROBIC WETLAND

SETTLING POND

MEETS EFFLUENT STANDARDS?

DISCHARGE

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.

PASSIVE TREATMENT

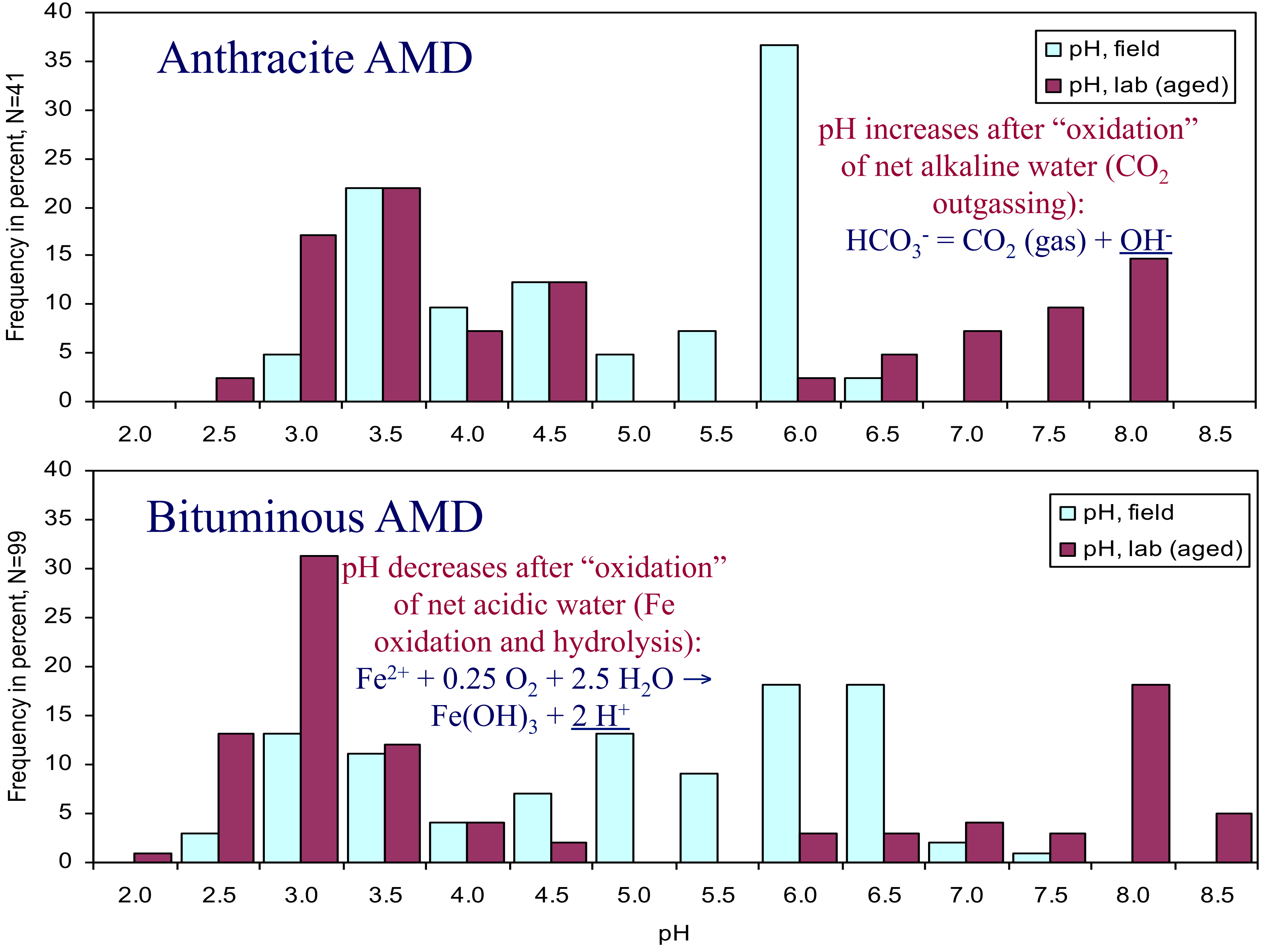
Limestone Dissolution,
O_2 Ingassing,
CO_2 Outgassing,
Fe(II) Oxidation, & Fe(III) Accumulation


Vertical Flow Limestone Beds
Bell Colliery


Pine Forest ALD & Wetlands


Silver Creek Wetlands

BIMODAL pH FREQUENCY DISTRIBUTION



pH increases after “oxidation” of net alkaline water (CO_2 outgassing):

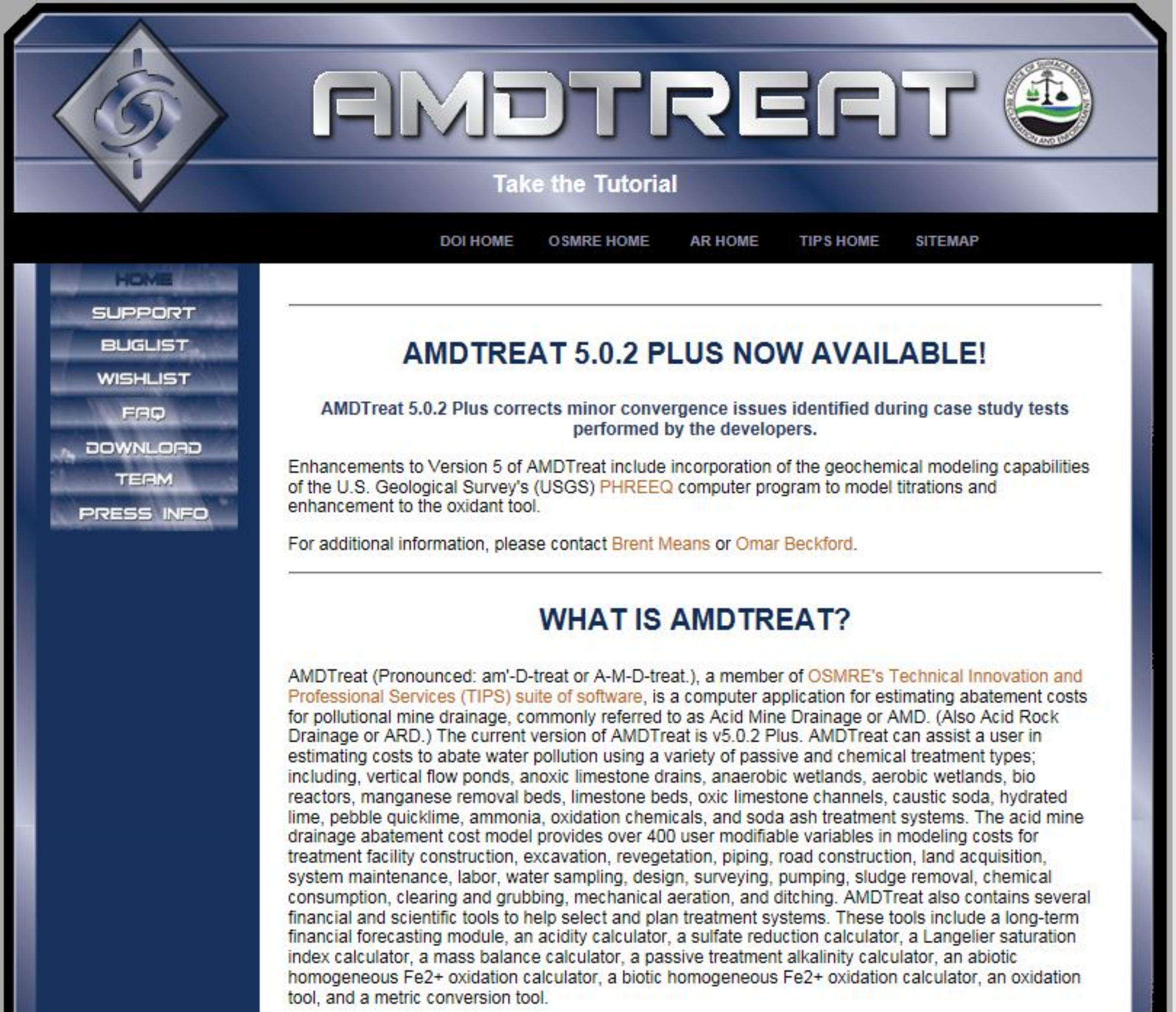
$HCO_3^- = CO_2\ (gas) + \underline{OH^-}$

pH decreases after “oxidation” of net acidic water (Fe oxidation and hydrolysis):

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

“PHREEQ-N-AMDTREAT”

http://amd.osmre.gov/



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 Fe2+ oxidation calculator, a biotic homogeneous Fe2+ oxidation calculator, an oxidation tool, and a metric conversion tool.

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.

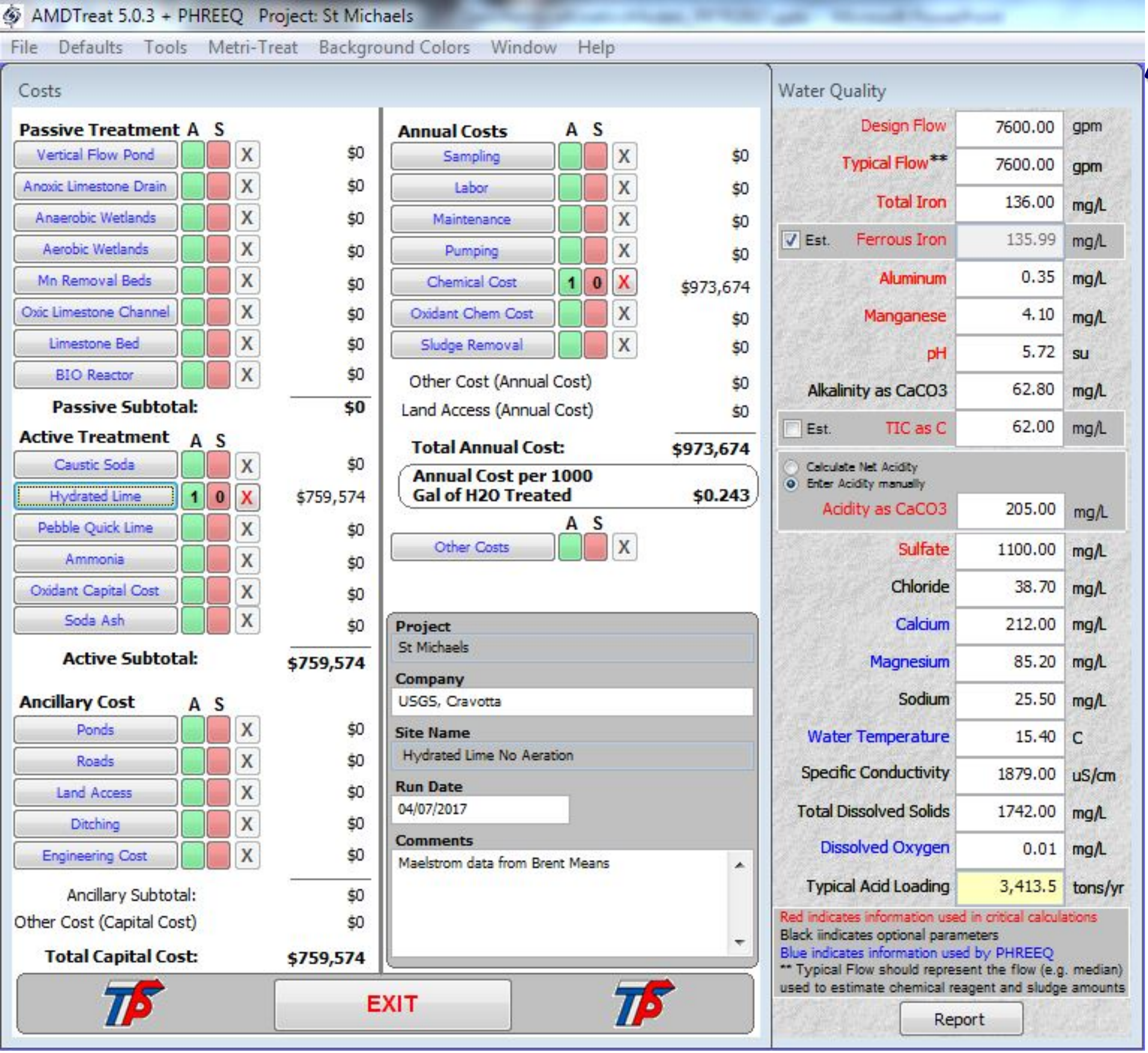
AMDTREAT 5.0+

- With the “PHREEQC chemical titration tool,” AMDTreat 5.0+ has capability to estimate:
  - ✓ Quantity and cost of caustic chemicals to attain a target pH (without and with pre-aeration);
  - ✓ Chemistry of treated effluent after reactions; and
  - ✓ Volume of sludge produced as the sum of precipitated metal hydroxides plus unreacted chemicals.

AMDTREAT 5.0+

- PHREEQ-N-AMDTreat “chemical titration tool” accurately relates caustic addition, pH, and metals solubility … but
  - ✓ assumes instantaneous, complete reactions without consideration of kinetics of gas exchange rates; and
  - ✓ ignores effects of changing pH on iron oxidation rate.

AMDTreat 5.0+ Caustic Addition—St. Michaels Discharge



Costs

Passive Treatment	A	S		
Vertical Flow Pond	🟩	🟥	X	$0
Anoxic Limestone Drain	🟩	🟥	X	$0
Anaerobic Wetlands	🟩	🟥	X	$0
Aerobic Wetlands	🟩	🟥	X	$0
Mn Removal Beds	🟩	🟥	X	$0
Oxic Limestone Channel	🟩	🟥	X	$0
Limestone Bed	🟩	🟥	X	$0
BIO Reactor	🟩	🟥	X	$0
Passive Subtotal:				**$0**

Active Treatment	A	S		
Caustic Soda	🟩	🟥	X	$0
Hydrated Lime	1	0	X	$759,574
Pebble Quick Lime	🟩	🟥	X	$0
Ammonia	🟩	🟥	X	$0
Oxidant Capital Cost	🟩	🟥	X	$0
Soda Ash	🟩	🟥	X	$0
Active Subtotal:				**$759,574**

Ancillary Cost	A	S		
Ponds	🟩	🟥	X	$0
Roads	🟩	🟥	X	$0
Land Access	🟩	🟥	X	$0
Ditching	🟩	🟥	X	$0
Engineering Cost	🟩	🟥	X	$0
Ancillary Subtotal:				$0
Other Cost (Capital Cost)				$0
Total Capital Cost:				**$759,574**

Annual Costs	A	S		
Sampling	🟩	🟥	X	$0
Labor	🟩	🟥	X	$0
Maintenance	🟩	🟥	X	$0
Pumping	🟩	🟥	X	$0
Chemical Cost	1	0	X	$973,674
Oxidant Chem Cost	🟩	🟥	X	$0
Sludge Removal	🟩	🟥	X	$0
Other Cost (Annual Cost)				$0
Land Access (Annual Cost)				$0
Total Annual Cost:				**$973,674**
Annual Cost per 1000 Gal of H20 Treated				**$0.243**

	A	S		
Other Costs	🟩	🟥	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
☑ 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
☐ Est. TIC as C	62.00	mg/L

○ Calculate Net Acidity
● 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 iindicates 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

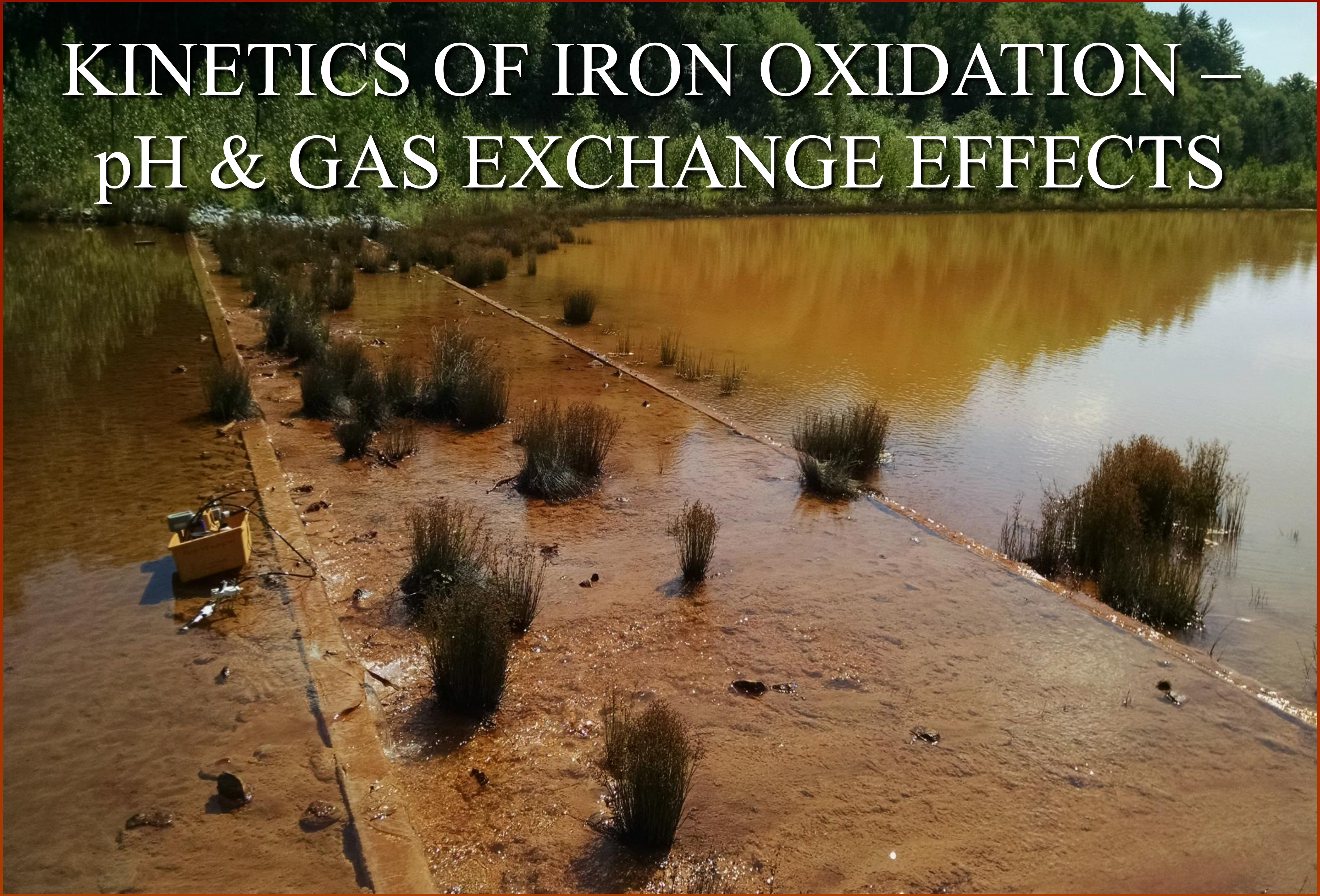
AMDTreat 5.0+.lnk

Escape Presentation

“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



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

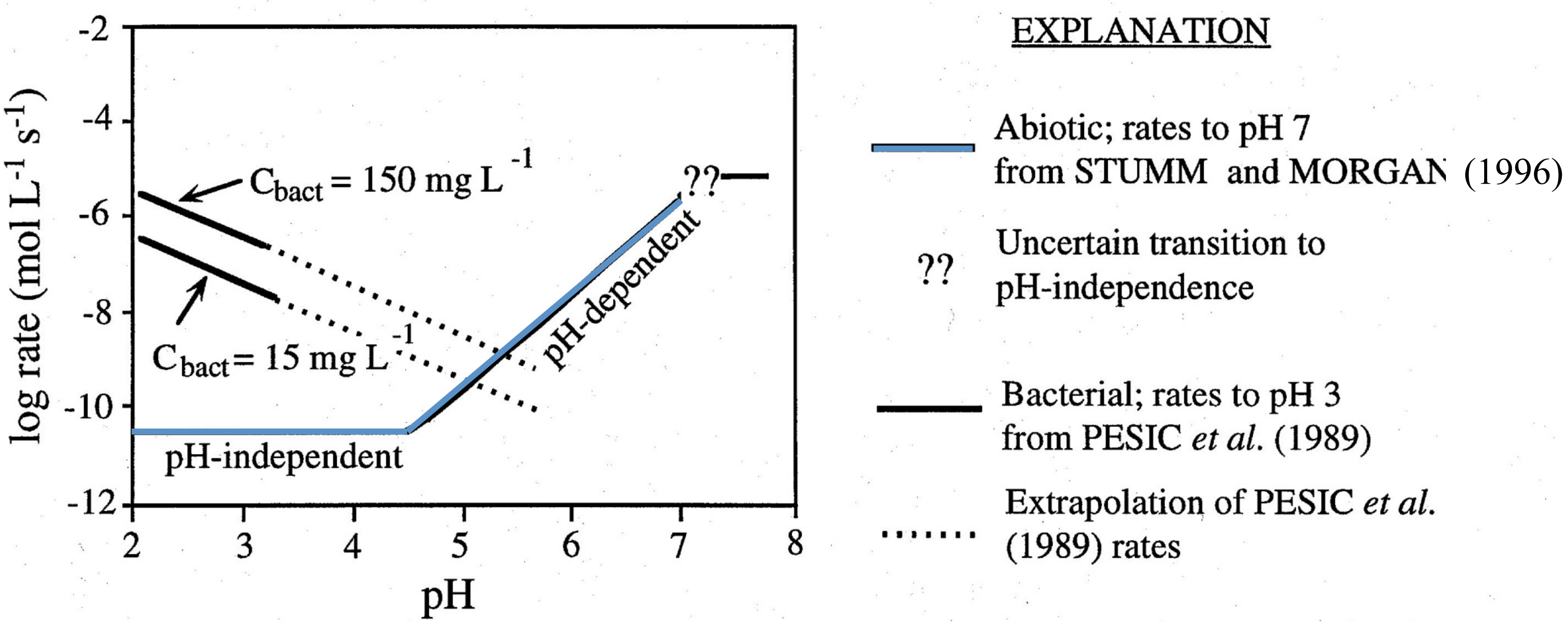


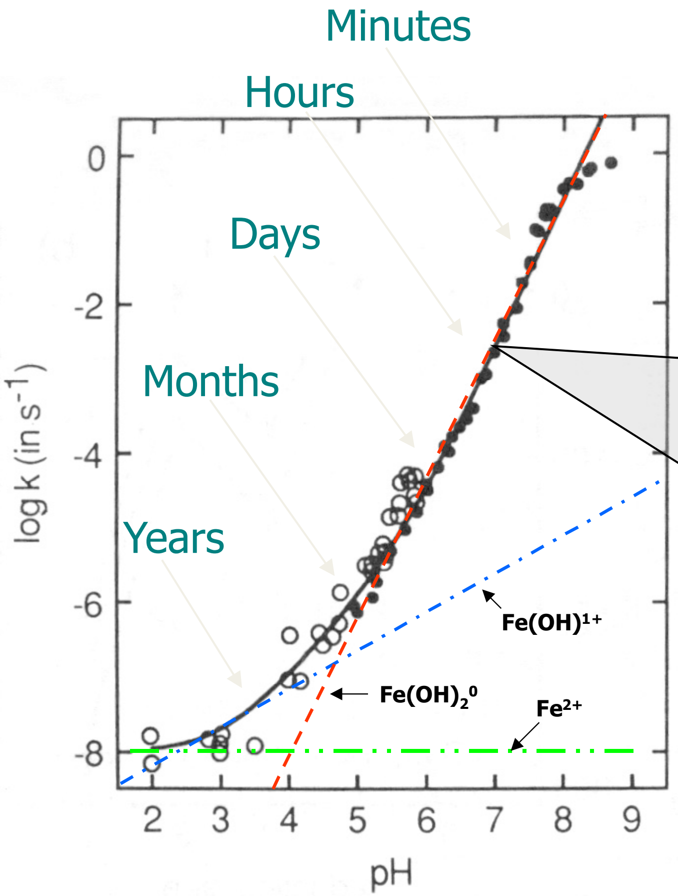
Fig. 3. Rate of Fe(II) oxidation versus pH based on abiotic and biological rate laws (Kirby et al., 1999)

** 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 FeII 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 Cbact = MPNbact ·(2.8E-10).

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



*Extrapolation of homogeneous rate law:

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

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

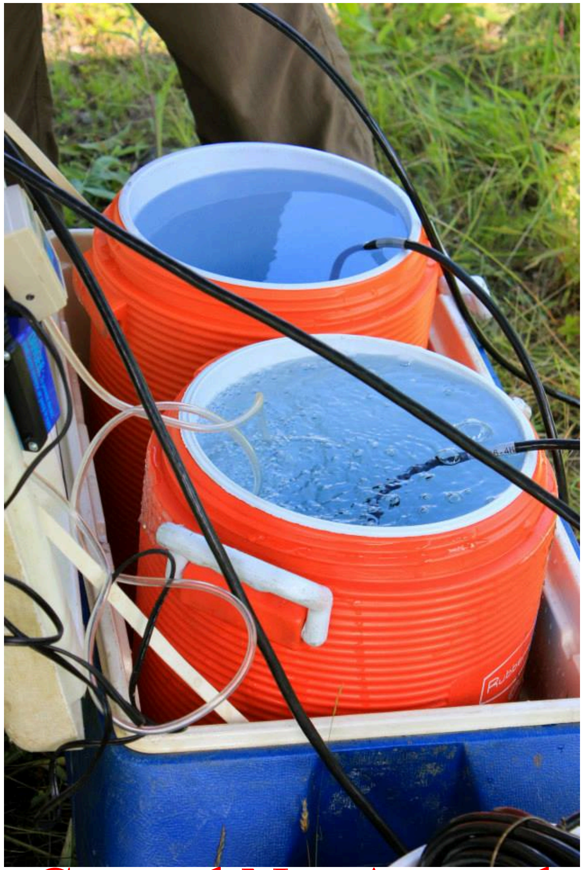
Between pH 5 and 8 the Fe(II) oxidation rate increases by 100x for each pH unit increase.*

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.

$$\log k_{T1} = \log k_{T2} + Ea / (2.303 * R) \cdot (1/T_2 - 1/T_1)$$

At $[O_2] = 0.26$ mM ($pO_2 = 0.21$ atm) and 25°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

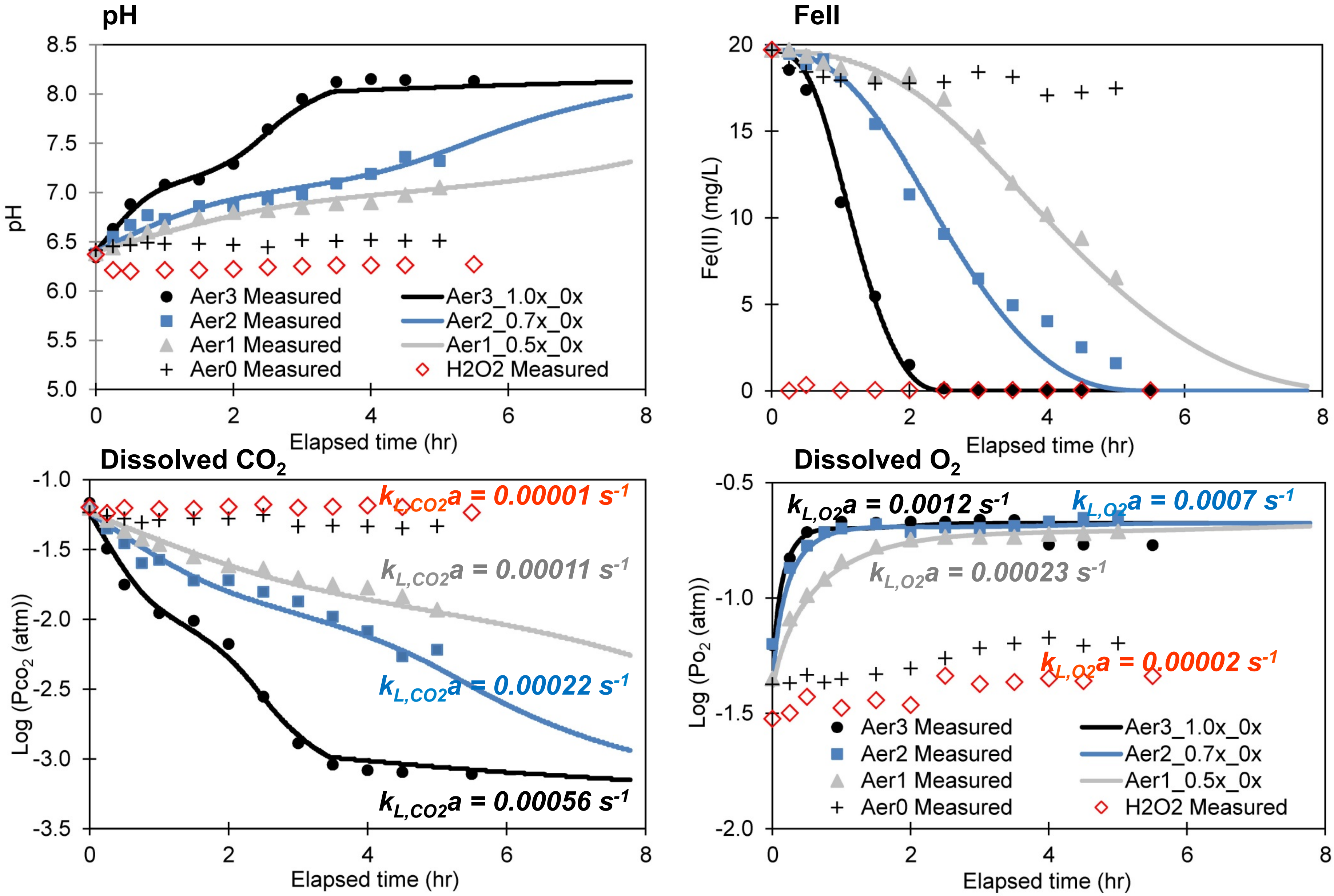
Batch Aeration Tests at Oak Hill Boreholes (summer 2013)

Control Not Aerated

Aerated

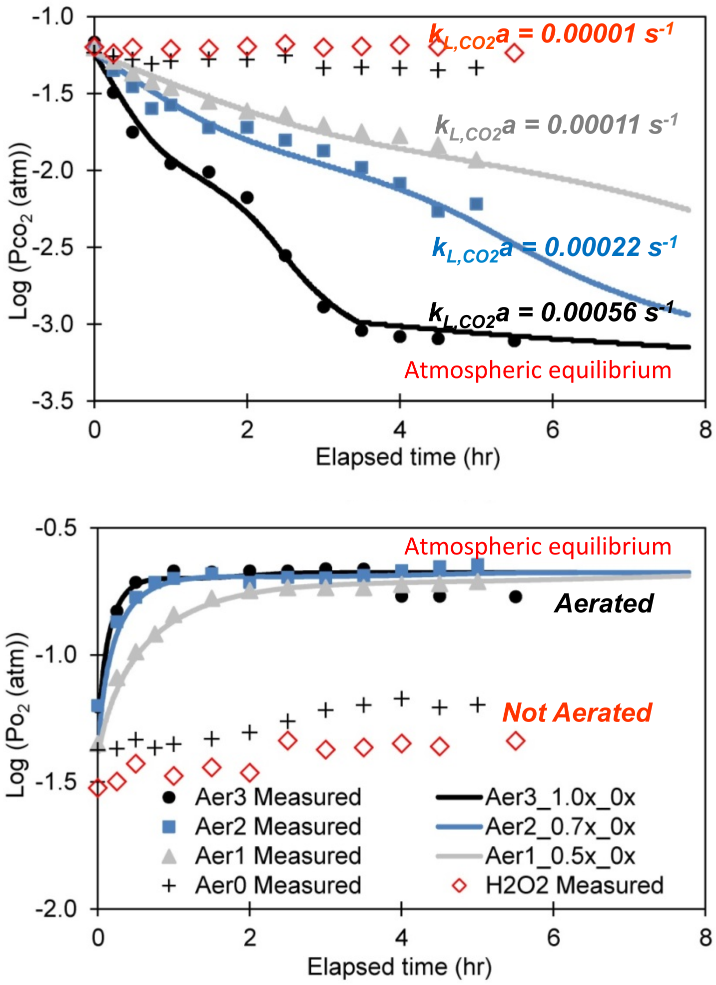
H_2O_2 Addition

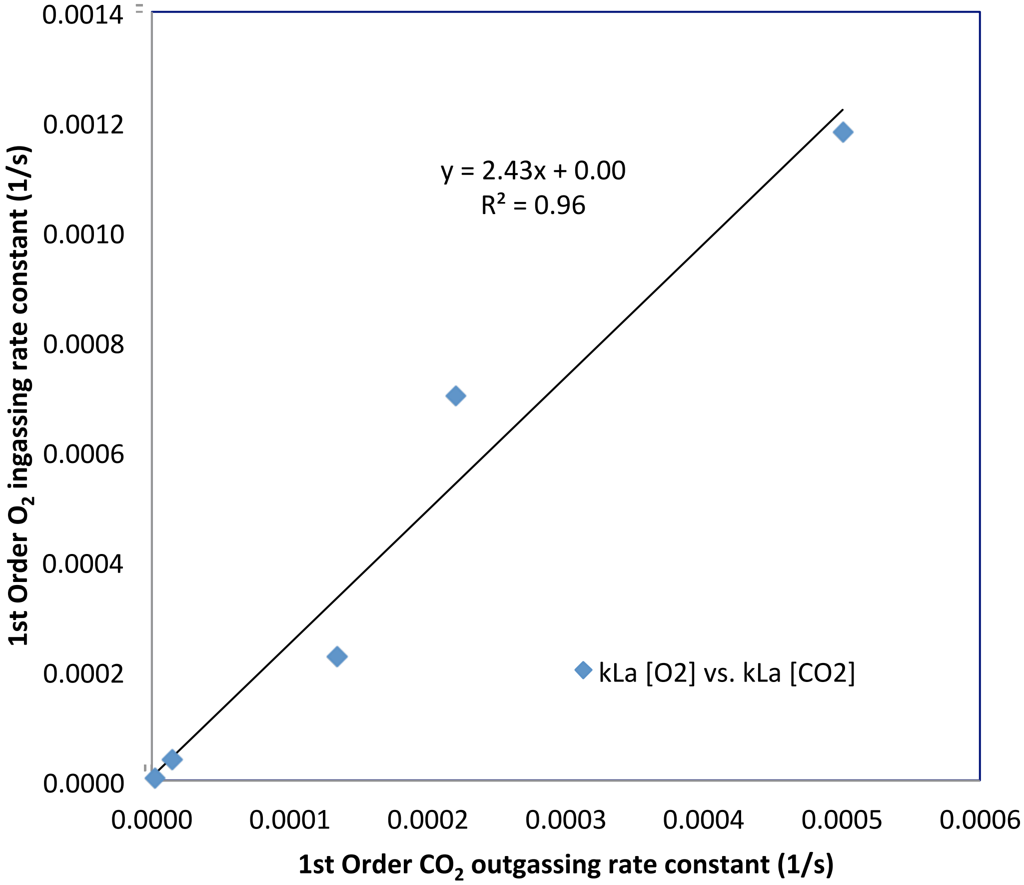
PHREEQC Coupled Kinetic Model of CO_2 Outgassing & Homogeneous Fe(II) Oxidation—Oak Hill Boreholes



CO_2 Outgassing is Proportional to O_2 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):

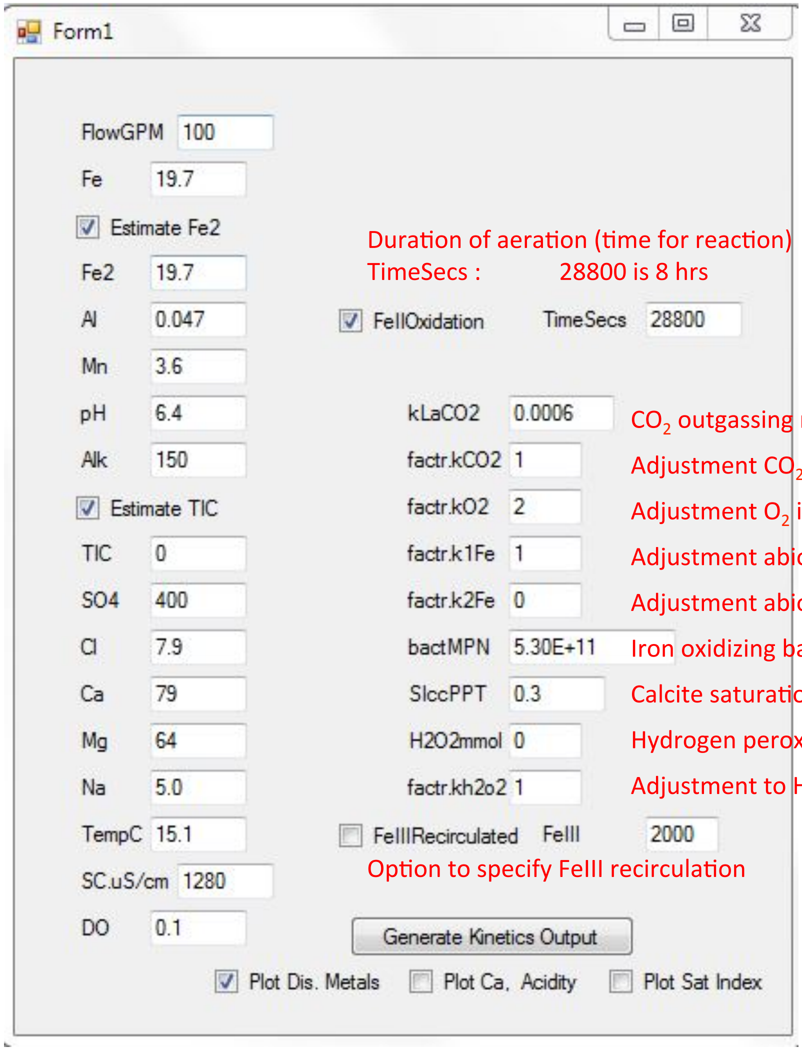
$$-d[Fe(II)]/dt = k_2 \, (Fe(III)) \cdot [Fe(II)] \cdot [O_2] \cdot \{H^+\}^{-1}$$

The **microbial oxidation rate law** describes the catalytic biological oxidation of Fe(II) by acidophilic microbes, which become relevant at pH < 5 (Pesic 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_2 Outgassing & Fe(II) Oxidation



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_2 outgassing rate in sec^{-1}
factr.kCO2	1	Adjustment CO_2 outgassing rate
factr.kO2	2	Adjustment O_2 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

☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index

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

Kinetic variables can be adjusted, including CO_2 outgassing and O_2 ingassing rates plus abiotic and microbial FeII oxidation rates. Constants are temperature corrected.

FeII.exe

Aer3: $k_{L,CO2}a = 0.00056\ s^{-1}$
Aer2: $k_{L,CO2}a = 0.00022\ s^{-1}$
Aer1: $k_{L,CO2}a = 0.00011\ s^{-1}$
Aer0: $k_{L,CO2}a = 0.00001\ s^{-1}$

User may estimate Fe2 from Fe and pH plus TIC from alkalinity and pH. And specify H_2O_2 or recirculation of FeIII. Output includes pH, solutes, net acidity, TDS, SC, and precipitated solids.

Estimated CO_2 Outgassing & O_2 Ingassing Rate Constants for Various Treatment Technologies

Table S.4 *Values of rate constants for CO_2 outgassing and O_2 ingassing used for kinetic models*

Site	Temper-ature	CO_2 Outgas			O_2 Ingas		
		$k_{L,CO2}a$			$k_{L,O2}a$		
	(°C)	(s^{-1})	log(s^{-1})	log(min^{-1})	(s^{-1})	log(s^{-1})	log(min^{-1})
Treatment Systems							
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
Oak Hill Aeration Expts.							
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^{0}C per Rathbun (1998, Eq. 56) using the expression:

kL,a_20 = kL,a_TC /(1.0241^(TC-20)).

kL,a_TC = kL,a_20 * (1.0241^(TC-20)).

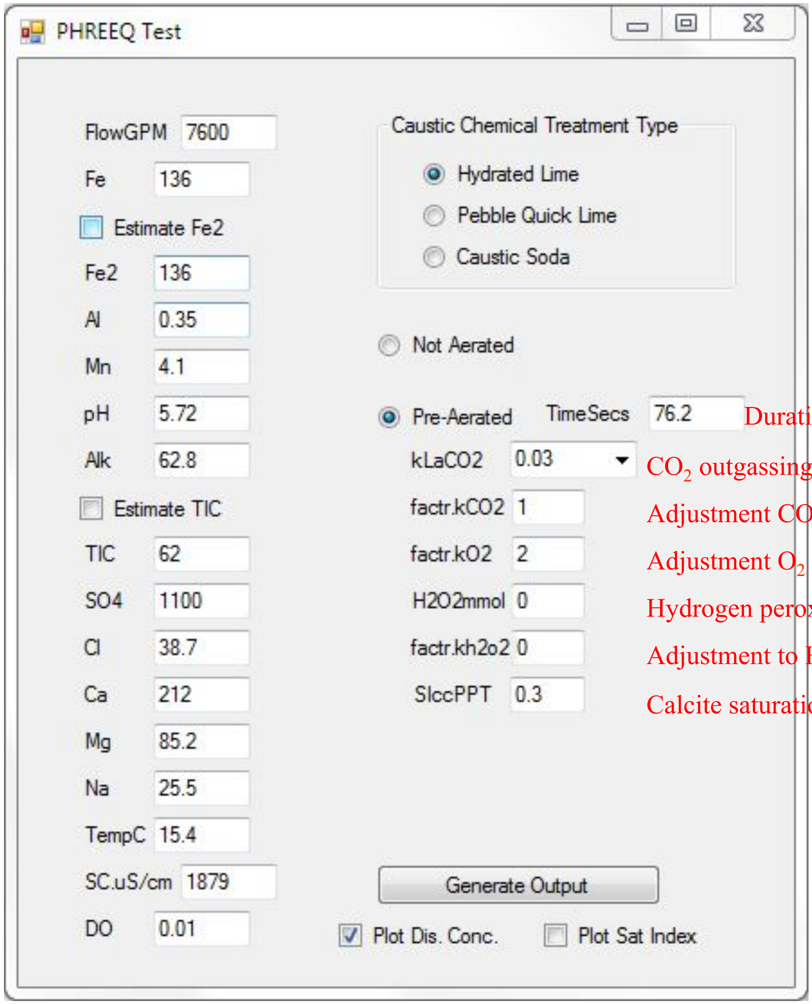
kL,a_20 = (LN((C_1-C_S)/(C_2-C_S))/t) / (1.0241$^{(TEMPC - 20)}$), where C is CO_2 or O_2.

Dissolved O_2, temperature, and pH were measured using submersible electrodes.

Dissolved CO_2 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_2 Outgassing & Fe(II) Oxidation



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	Duration of pre-aeration in sec
kLaCO2	0.03 ▾	CO_2 outgassing rate constant in sec^{-1}
factr.kCO2	1	Adjustment CO_2 outgassing rate (x kLaCO2)
factr.kO2	2	Adjustment O_2 ingassing rate (x kLaCO2)
H2O2mmol	0	Hydrogen peroxide added*
factr.kh2o2	0	Adjustment to H_2O_2 rate
SIccPPT	0.3	Calcite saturation limit

☑ 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.

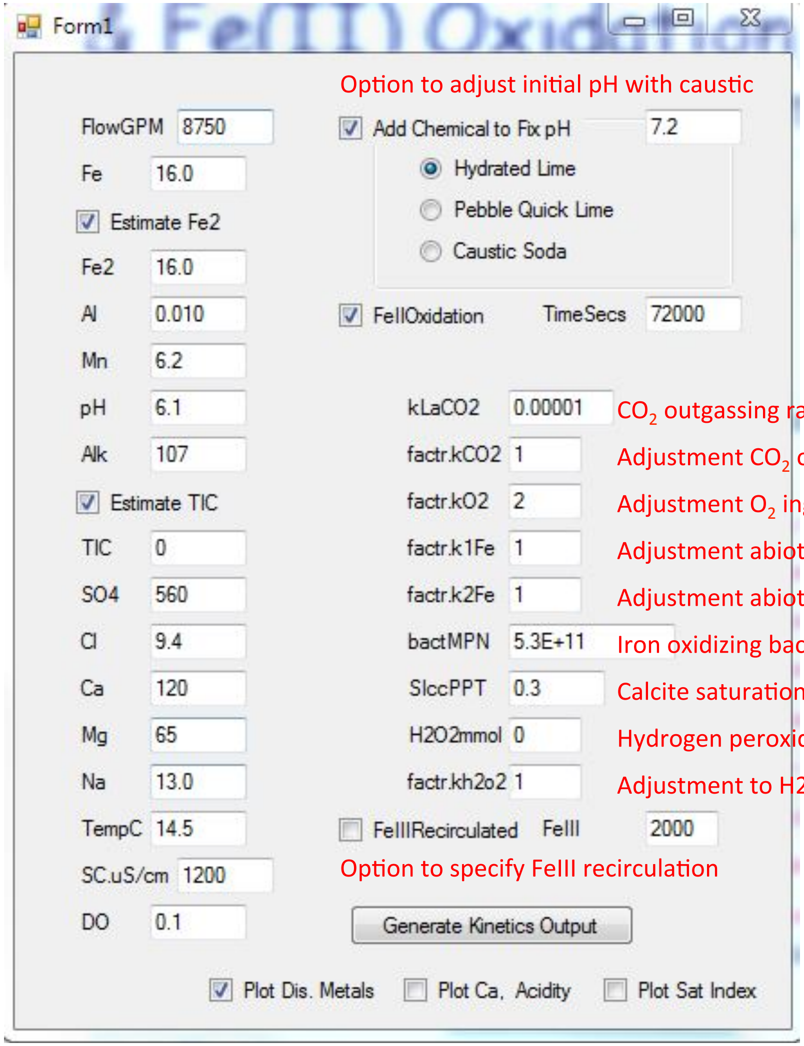
PHREEQTitration_StMichaels.exe

Dropdown kLa

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_2 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_2 outgassing rate

factr.kCO2 1 Adjustment CO_2 outgassing rate

factr.kO2 2 Adjustment O_2 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

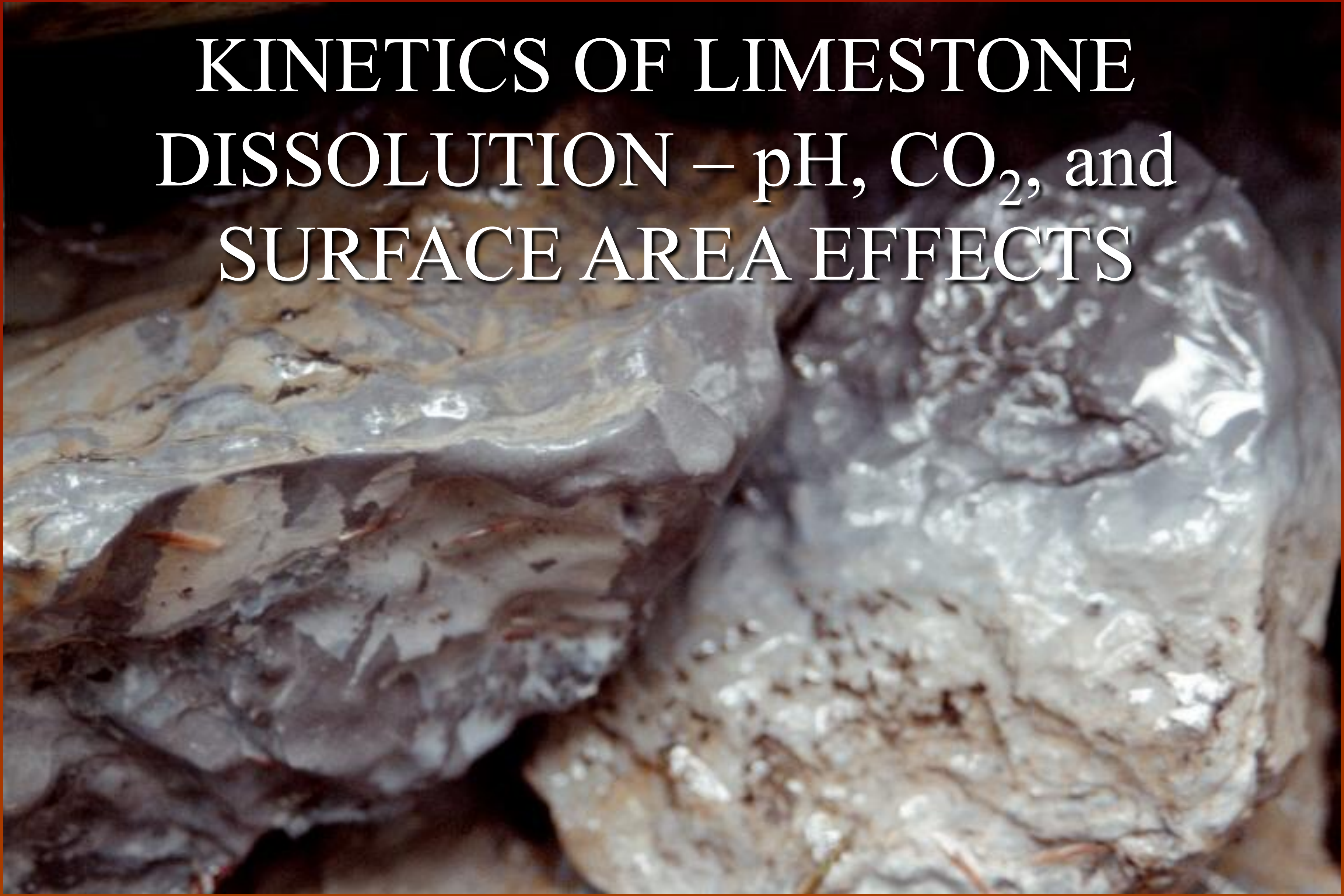
☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index

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

Variable CO_2 outgassing and O_2 ingassing rates apply. Can choose to adjust initial pH with caustic. The required quantity of caustic is reported in units used by AMDTreat.

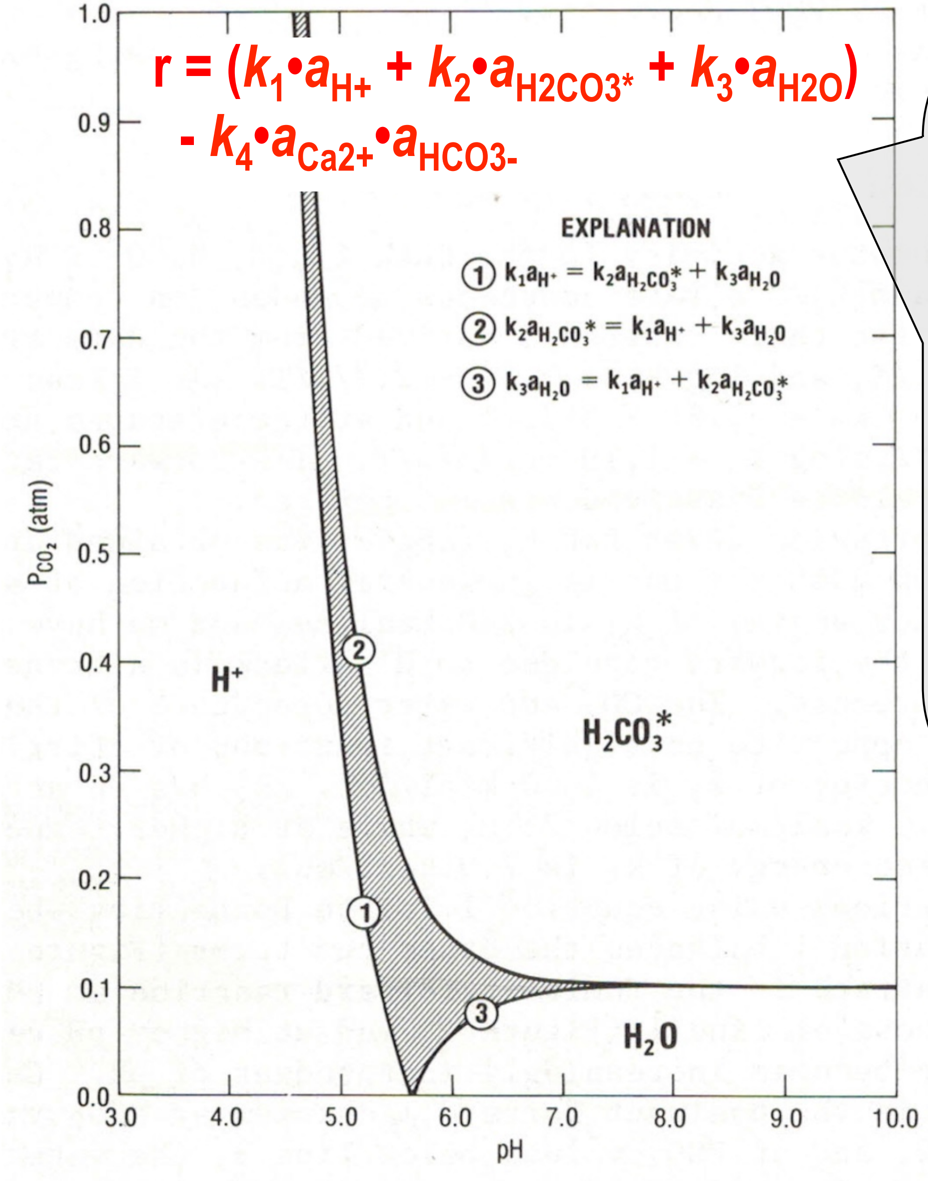
Caustic+FeII.exe

Kinetic variables, including CO_2 outgassing and O_2 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_2, and SURFACE AREA EFFECTS

Limestone Dissolution Rate Model for AMDTreat ("PWP" model emphasizes pH and CO_2)



$$r = (k_1 \bullet a_{H+} + k_2 \bullet a_{H2CO3*} + k_3 \bullet a_{H2O}) - k_4 \bullet a_{Ca2+} \bullet a_{HCO3-}$$

According to Plummer, Wigley, and Parkhurst (1978), the rate of $CaCO_3$ dissolution is a function of three forward (dissolution) reactions:

$CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^-$

k_1 $CaCO_3 + H_2CO_3^* \longrightarrow Ca^{2+} + 2\ HCO_3^-$

k_2 $CaCO_3 + H_2O \longrightarrow Ca^{2+} + HCO_3^- + OH^-$

k_3 and the backward (precipitation) reaction: $Ca^{2+} + HCO_3^- \longrightarrow CaCO_3 + H^+$

k_4

Although H^+, $H_2CO_3^*$, and H_2O 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 (generalized expression corrects for surface area)

Appelo and Postma (2005) give a generalized rate expression for calcite dissolution that considers physical characteristics of the system as well as solution chemistry:

$$R = k \bullet (A / V) \bullet (1 - \Omega)^{n}$$

where A is calcite surface area, V is volume of solution, Ω is saturation state (IAP/K = 10^{SIcc}), and *k* and n are empirical coefficients that are obtained by fitting observed rates.

For the "PWP" model applied to 1 liter solution, the overall rate becomes:

$$\boxed{R = (k_1 \bullet a_{H+} + k_2 \bullet a_{H2CO3^*} + k_3 \bullet a_{H2O}) \bullet (A) \bullet (1 - 10^{(n \bullet SIcc)})}$$

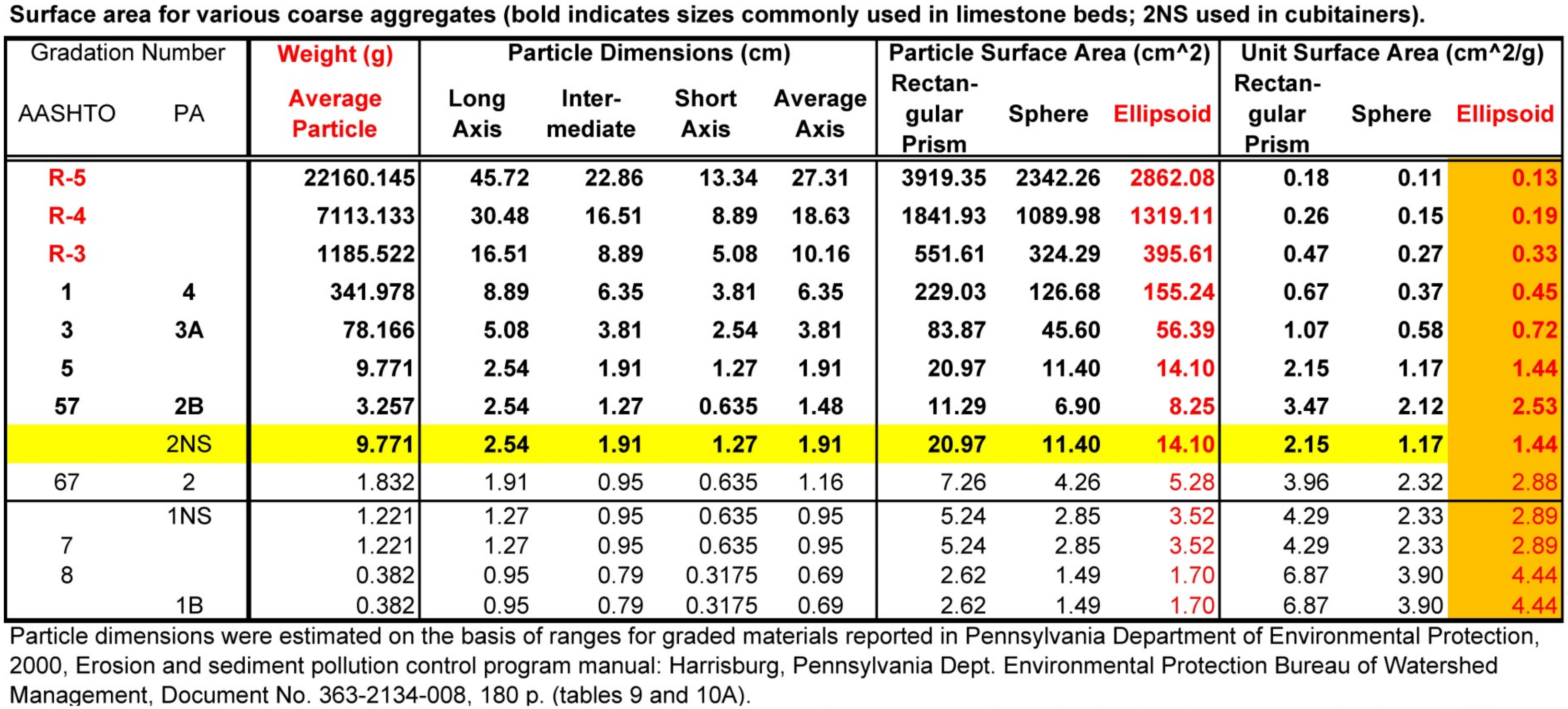
Plummer and others (1978) reported the forward rate constants as a function of temperature (T, in K), in millimoles calcite per centimeter squared per second (mmol/cm^2/s):

$$\log k_1 = 0.198 - 444 / T$$

$$\log k_2 = 2.84 - 2177 / T$$

$$\log k_3 = -5.86 - 317 / T \text{ for } T \leq 298; \ \log k_3 = -1.10 - 1737 / T \text{ for } T > 298$$

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)	Particle Dimensions (cm)				Particle Surface Area (cm^2)			Unit Surface Area (cm^2/g)		
AASHTO	PA	Average Particle	Long Axis	Inter-mediate	Short Axis	Average Axis	Rectan-gular Prism	Sphere	Ellipsoid	Rectan-gular Prism	Sphere	Ellipsoid
R-5		**22160.145**	**45.72**	**22.86**	**13.34**	**27.31**	**3919.35**	**2342.26**	**2862.08**	**0.18**	**0.11**	**0.13**
R-4		**7113.133**	**30.48**	**16.51**	**8.89**	**18.63**	**1841.93**	**1089.98**	**1319.11**	**0.26**	**0.15**	**0.19**
R-3		**1185.522**	**16.51**	**8.89**	**5.08**	**10.16**	**551.61**	**324.29**	**395.61**	**0.47**	**0.27**	**0.33**
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^2/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^2/g by 100 g/mol to get surface area (A) units of cm^2/mol used in AMDTreat rate model.*

Surface area computed for various geometric forms:

Sphere: 4pi*(Average of Axes/2)^2

Rectangular Prism: 2*(Long Axis*Short Axis)+2*(Long Axis*Intermediate Axis)+2*(Short Axis*Intermediate Axis)

Ellipsoid: (pi*D^2)/S, where D=2*(vol/(4/3pi))^(1/3) S=1.15-0.25E E=Long Axis/D

Volume computed for same geometric forms:

Sphere: 4/3*pi*(Average Axis/2)^3

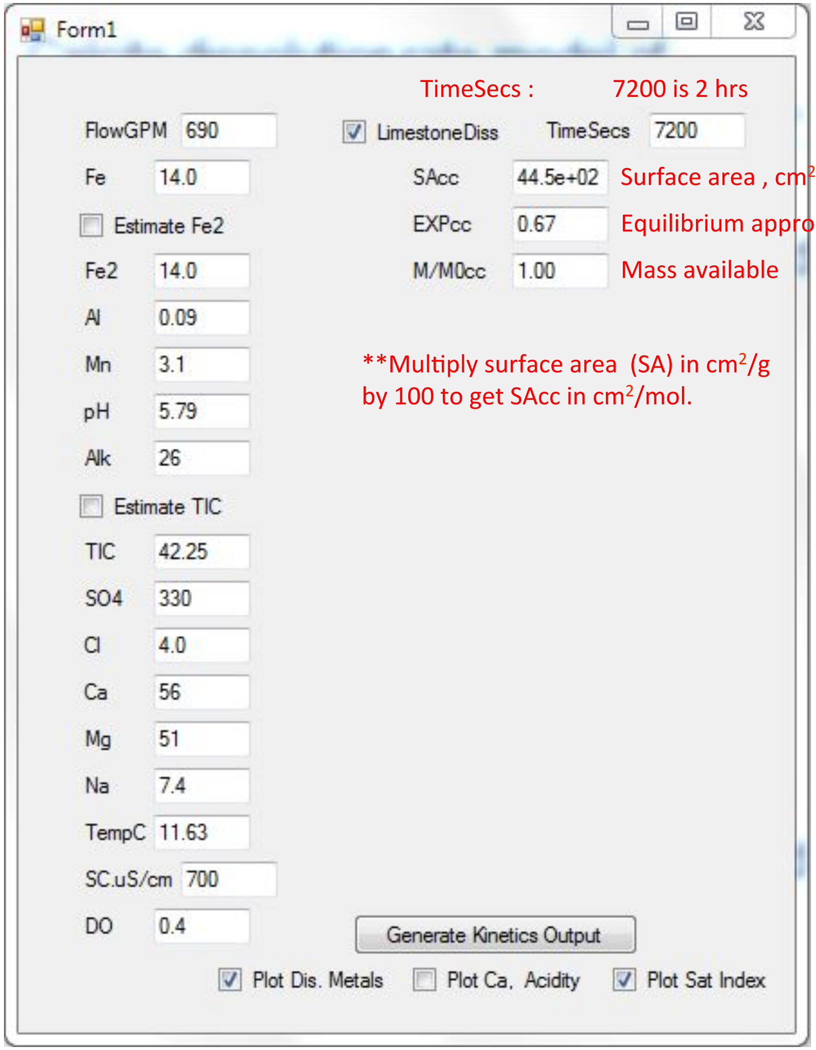
Rectangular Prism: (Long Axis*Short Axis*Intermediate Axis)

Ellipsoid: 4/3*pi* (Long Axis/2*Short Axis/2*Intermediate Axis/2)

For ellipsoid sphere, this reduces to 0.5236*Long Axis*Short Axis*Intermediate Axis

Santomartino and Webb (2007, AG, 22:2344–2361) estimated volume of ellipsoid as 0.6*volume of rectangular prism of same dimensions.

New Module For AMDTreat – PHREEQC Kinetic Model of Limestone Dissolution



Form1

TimeSecs : 7200 is 2 hrs

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 7200

SAcc 44.5e+02 Surface area , cm^2/mol **

EXPcc 0.67 Equilibrium approach

M/M0cc 1.00 Mass available

**Multiply surface area (SA) in cm^2/g by 100 to get SAcc in cm^2/mol.

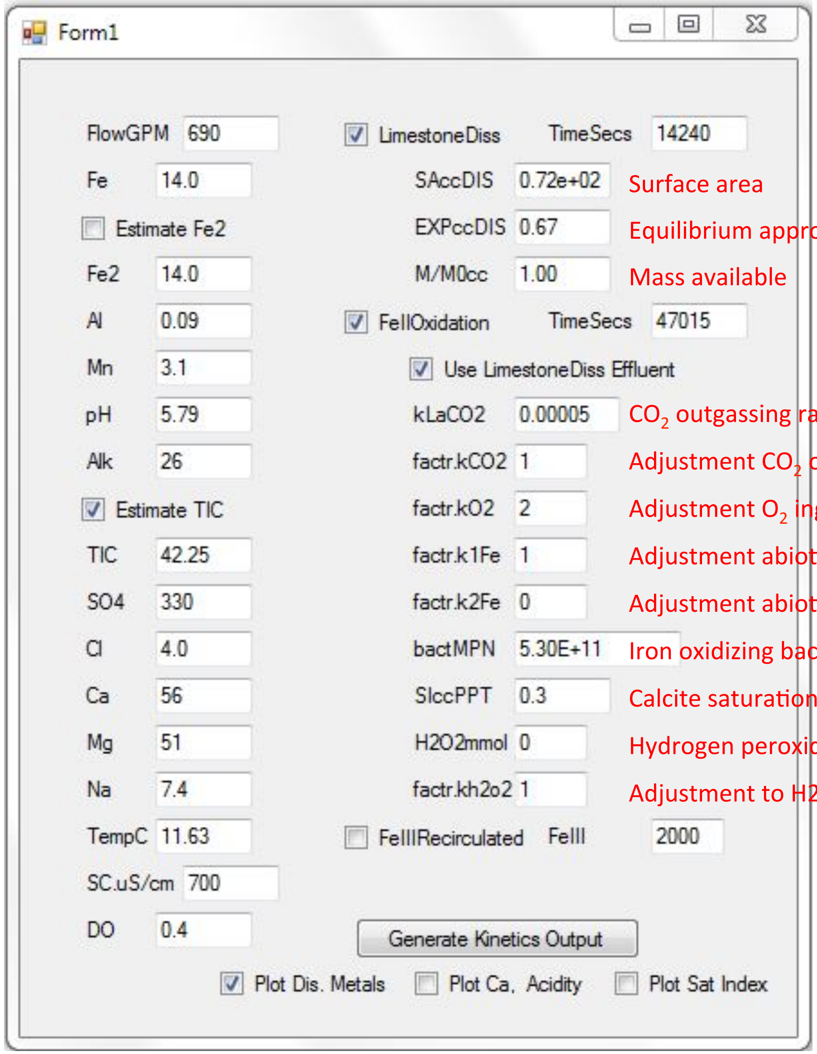
☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☑ Plot Sat Index

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^2/g, respectively.

Limestone.PWP.exe

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

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



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_2 outgassing rate

factr.kCO2 1 Adjustment CO_2 outgassing rate

factr.kO2 2 Adjustment O_2 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

SIccPPT 0.3 Calcite saturation limit

H2O2mmol 0 Hydrogen peroxide added

factr.kh2o2 1 Adjustment to H2O2 rate

☐ FeIIIRecirculated FeIII 2000

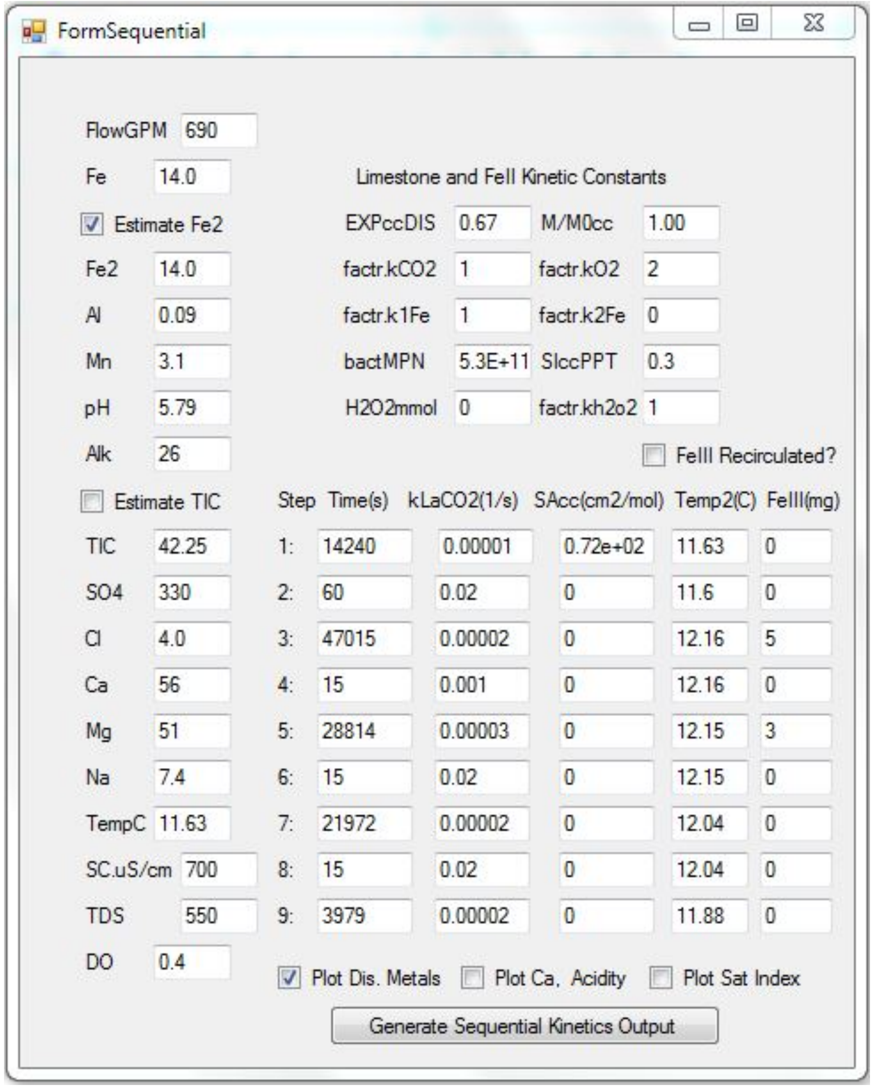
☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index

Rate models for calcite dissolution, CO_2 outgassing and O_2 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



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

TDS 550

DO 0.4

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

SIccPPT 0.3

H2O2mmol 0

factr.kh2o2 1

☐ FeIII Recirculated?

Step	Time(s)	kLaCO2(1/s)	SAcc(cm2/mol)	Temp2(C)	FeIII(mg)
1:	14240	0.00001	0.72e+02	11.63	0
2:	60	0.02	0	11.6	0
3:	47015	0.00002	0	12.16	5
4:	15	0.001	0	12.16	0
5:	28814	0.00003	0	12.15	3
6:	15	0.02	0	12.15	0
7:	21972	0.00002	0	12.04	0
8:	15	0.02	0	12.04	0
9:	3979	0.00002	0	11.88	0

☑ Plot Dis. Metals ☐ Plot Ca, Acidity ☐ Plot Sat Index

Sequential steps: Variable detention times, adjustable CO_2 outgassing rates, limestone surface area, temperature, and FeIII.

Limestone+FeIIseq.exe

Next slide

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

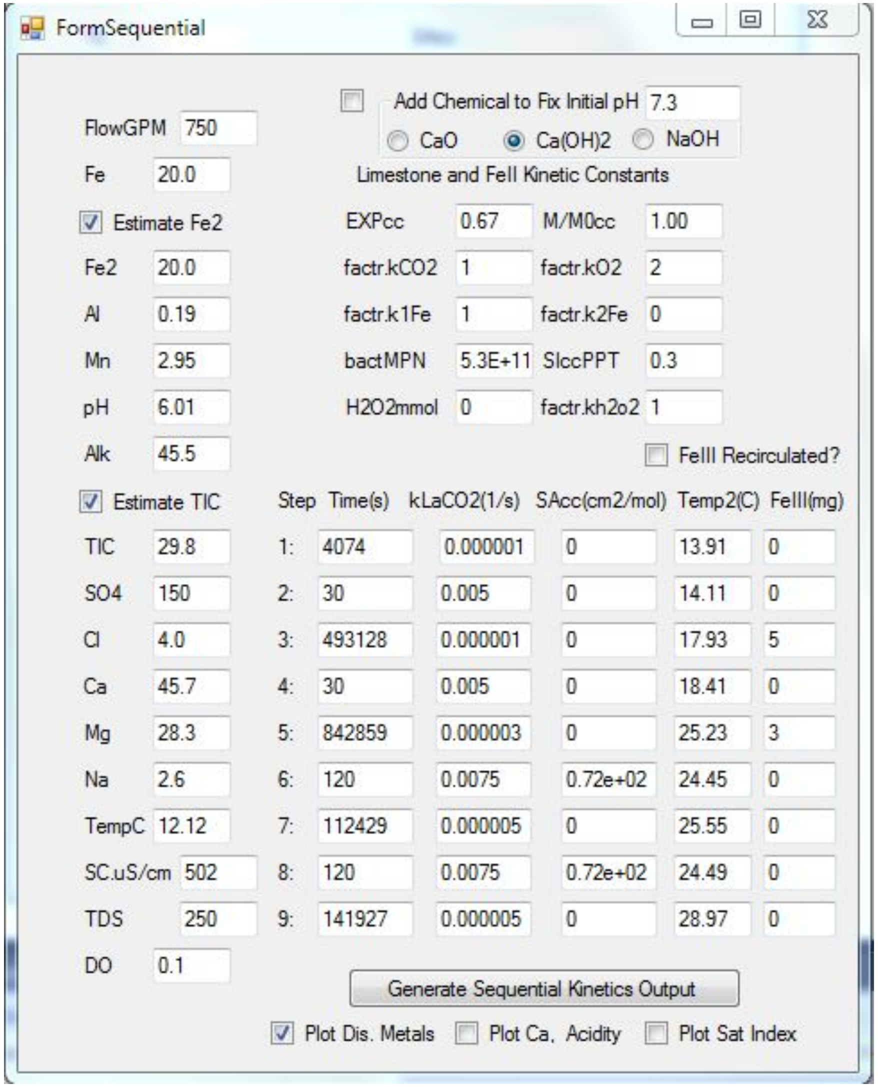
Step	Treatment
1	ALD
2	Riprap
3	Pond
4	Cascade
5	Wetland
6	Cascade
7	Wetland
8	Cascade
9	Wetland

Limestone+FeIIseq_PineFor151212.exe

LS+FeIIseq_kinetics.sel - Shortcut.lnk

PineForest_Field_151212t.xlsx - Shortcut.lnk

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



☐ Add Chemical to Fix Initial pH 7.3
○ CaO ● Ca(OH)2 ○ NaOH

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

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

☑ 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_2 outgassing rates, limestone surface area, temperature, and FeIII.

Caustic+Limestone+FeIIseq.exe

Next slide

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

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

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.

Disclaimer / Release Plans

“Although this software program has been used by the U.S. Geological Survey (USGS), no warranty, expressed or implied, is made by the USGS or the U.S. Government as to the accuracy and functioning of the program and related program material nor shall the fact of distribution constitute any such warranty, and no responsibility is assumed by the USGS in connection therewith.”

- ✓ FY2017 Development, beta testing and review.
- ✓ FY2018 Official USGS “software release” planned:
- ✓ https://water.usgs.gov/software/lists/geochemical
- ✓ FY2018 Incorporation of PHREEQC treatment simulations with AMDTreat to be released by OSMRE:
- ✓ http://amd.osmre.gov/

Questions?

- ✓ Are the current models capable of simulating manganese (MnII) oxidation kinetics?
- ✓ Can the models simulate the adsorption of cations by hydrous ferric oxides (HFO) as a kinetic process?
- ✓ Have you considered adsorption based rate models for the heterogeneous FeII and MnII oxidation kinetics?
- ✓ Does the limestone model consider changes in surface area of due to its dissolution or the accumulation of HFO coatings?
- ✓ Does the microbial FeII oxidation rate model consider oxidation by neutrophilic iron bacteria such as Gallionella or Leptothrix?
- ✓ What about the simulation of anaerobic processes in a BCR (Biochemical Reactor) and precipitation of metal sulfides?

References

Burrows JE, Cravotta CA III, Peters SC (2017) Enhanced Al and Zn removal from coal-mine drainage during rapid oxidation and precipitation of Fe oxides at near-neutral pH: Applied Geochemistry 78, 194-210.

Cravotta CA III (2003) Size and performance of anoxic limestone drains to neutralize acidic mine drainage: Journal of Environmental Quality 32, 1277-1289.

Cravotta CA III (2015) Monitoring, field experiments, and geochemical modeling of Fe(II) oxidation kinetics in a stream dominated by net-alkaline coal-mine drainage, Pennsylvania, U.S.A. Applied Geochemistry 62, 96-107.

Cravotta CA III, Means B, Arthur W, McKenzie R, Parkhurst DL (2015) AMDTreat 5.0+ with PHREEQC titration module to compute caustic chemical quantity, effluent quality, and sludge volume. Mine Water and the Environment 34, 136-152.

Davison W, Seed G (1983) The kinetics of the oxidation of ferrous iron in synthetic and natural waters. Geochimica et Cosmochimica Acta 47, 67-79.

Dempsey BA, Roscoe HC, Ames R, Hedin R, Byong-Hun J (2001) Ferrous oxidation chemistry in passive abiotic systems for the treatment of mine drainage. Geochemistry: Exploration, Environment, Analysis 1, 81-88.

Dietz JM, Dempsey BA (2002) Innovative treatment of alkaline mine drainage using recirculated iron oxides in a complete mix reactor. American Society of Mining and Reclamation 19th Annual Meeting, p. 496-516.

Geroni JN, Cravotta CA III, Sapsford DJ (2012) Evolution of the chemistry of Fe bearing waters during CO_2 degassing. Applied Geochemistry 27, 2335-2347.

Kirby CS, Elder-Brady JA (1998) Field determination of Fe^{2+} oxidation rates in acid mine drainage using a continuously-stirred tank reactor. Applied Geochemistry 13, 509-520.

Kirby CS, Thomas HM, Southam G, Donald R (1999) Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage. Applied Geochemistry 14, 511-530.

Kirby CS, Dennis A, Kahler A (2009) Aeration to degas CO_2, increase pH, and increase iron oxidation rates for efficient treatment of net alkaline mine drainage: Applied Geochemistry 24, 1175-1184.

Langmuir D (1997) Aqueous environmental geochemistry. Prentice Hall, New Jersey, USA, 600 p. (especially p. 58-62)

Parkhurst DL, Appelo CAJ (2013) Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Techniques Methods 6-A43, 497 p.

Pesic B, Oliver DJ, Wichlacz P (1989) An electrochemical method of measuring the oxidation rate of ferrous to ferric iron with oxygen in the presence of *Thiobacillus ferrooxidans*. Biotechnology and Bioengineering 33, 428-439.

Plummer LN, Wigley ML, Parkhurst DL (1978) The kinetics of calcite dissolution in CO_2-water systems at 5° to 60°C and 0.0 to 1.0 atm CO_2. American Journal of Science 278, 179-216.

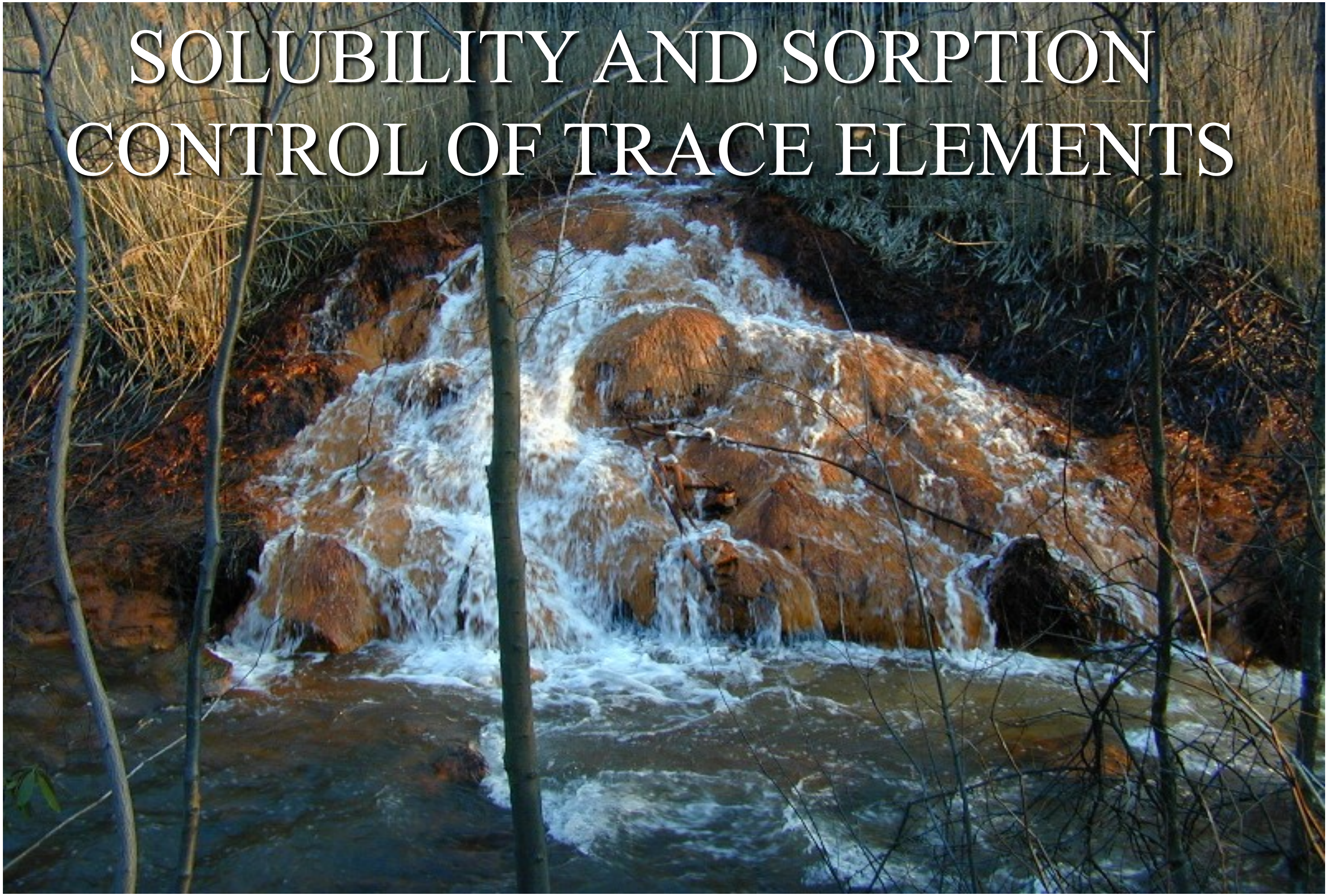
Rathbun RE (1998) Transport, behavior, and fate of volatile organic compounds in streams: USGS Professional Paper 1589, 151 p.

Singer PC, Stumm W (1970) Acidic mine drainage: the rate-determining step. Science 167, 121-123

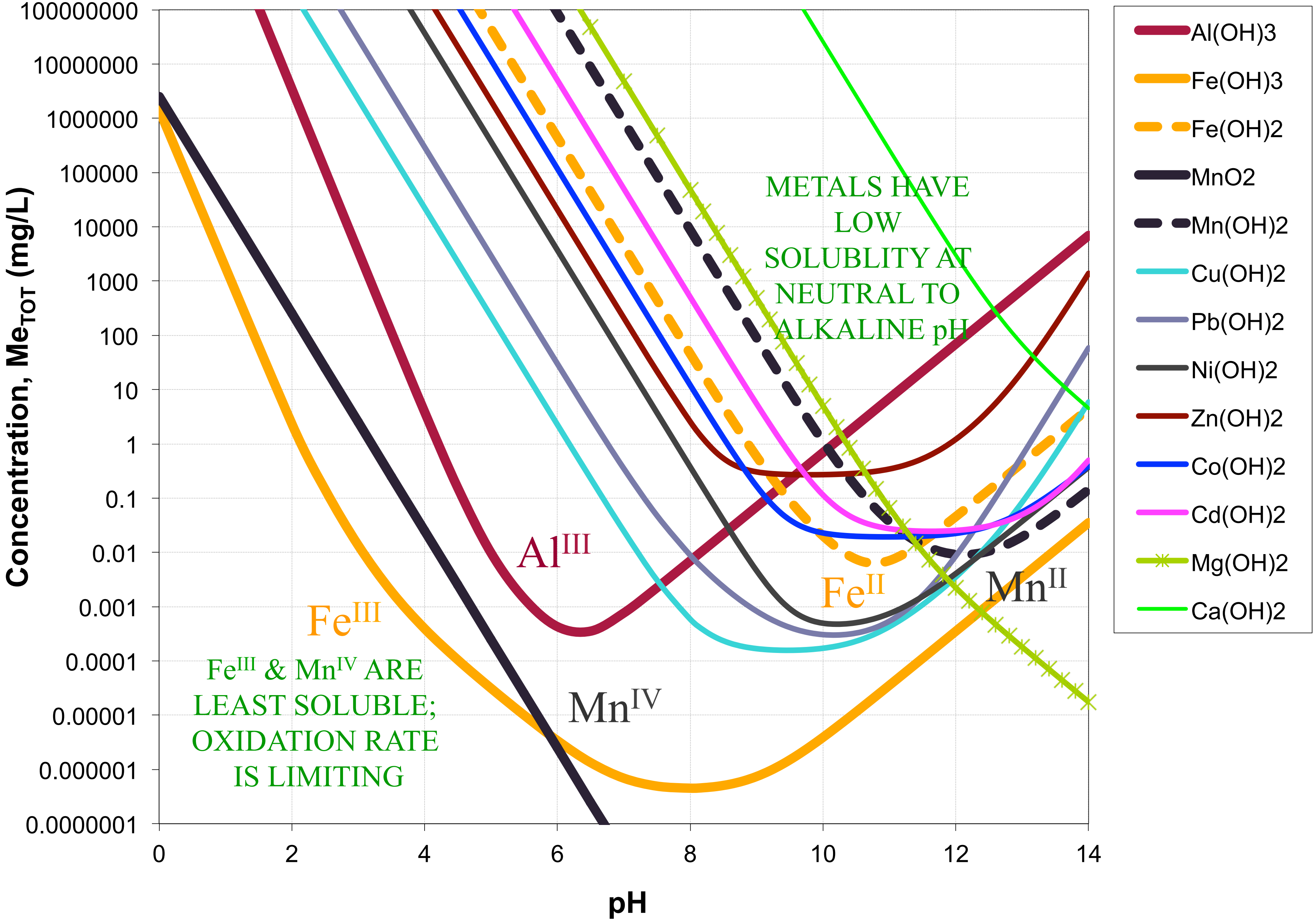
Stumm W, Lee G.F. (1961) Oxygenation of ferrous iron. Industrial and Engineering Chemistry 53, 143-146.

Stumm W, Morgan JJ (1996) Aquatic chemistry--chemical equilibria and rates in natural waters (3rd): New York, Wiley-Interscience, 1022 p. (especially p. 682-691)

SOLUBILITY AND SORPTION CONTROL OF TRACE ELEMENTS



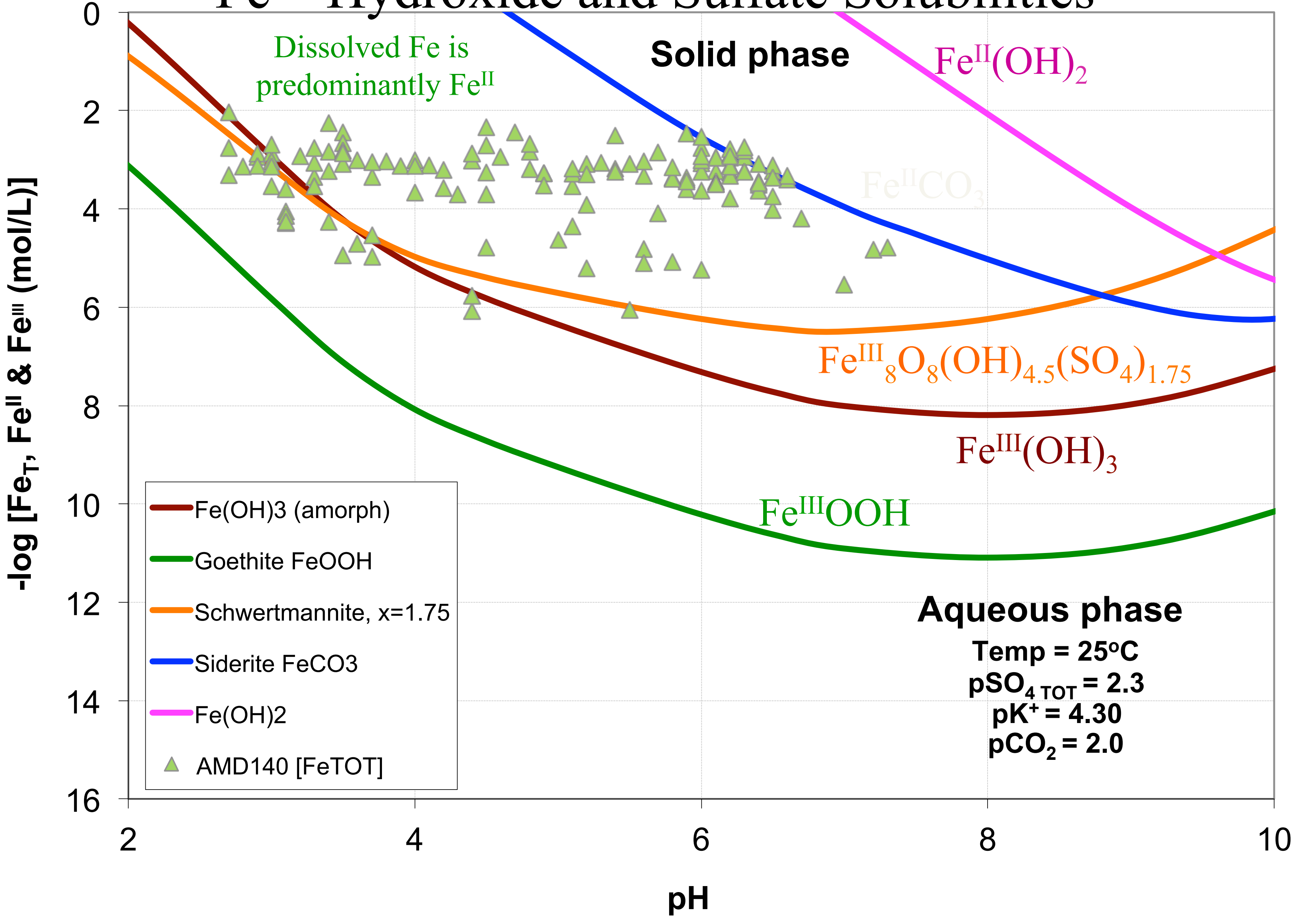
Solubilities of Metal Hydroxides



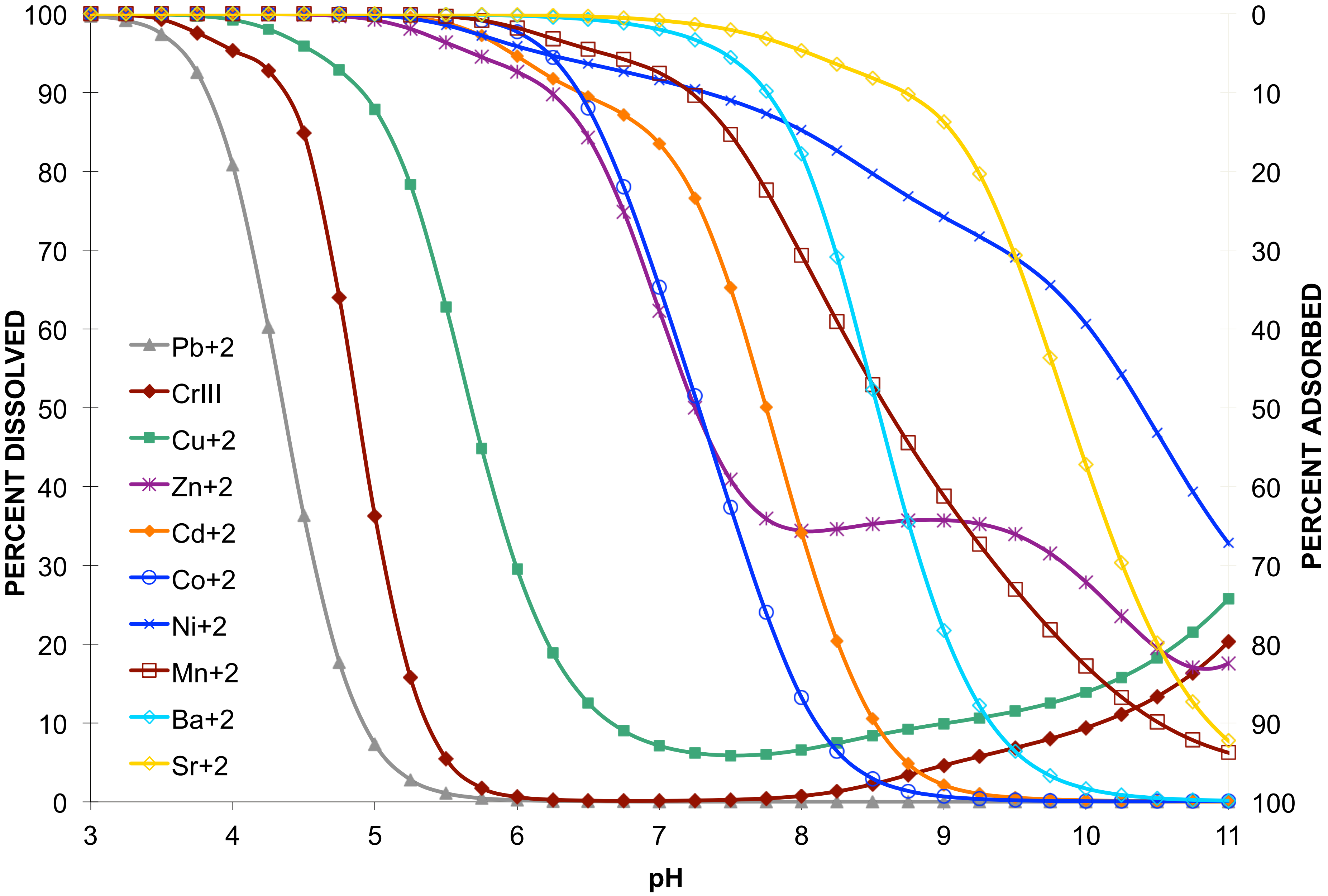
METALS HAVE LOW SOLUBLITY AT NEUTRAL TO ALKALINE pH

Fe^{III} & Mn^{IV} ARE LEAST SOLUBLE; OXIDATION RATE IS LIMITING

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



SORPTION OF CATIONS ON “HFO”



SORPTION OF ANIONS ON “HFO”