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

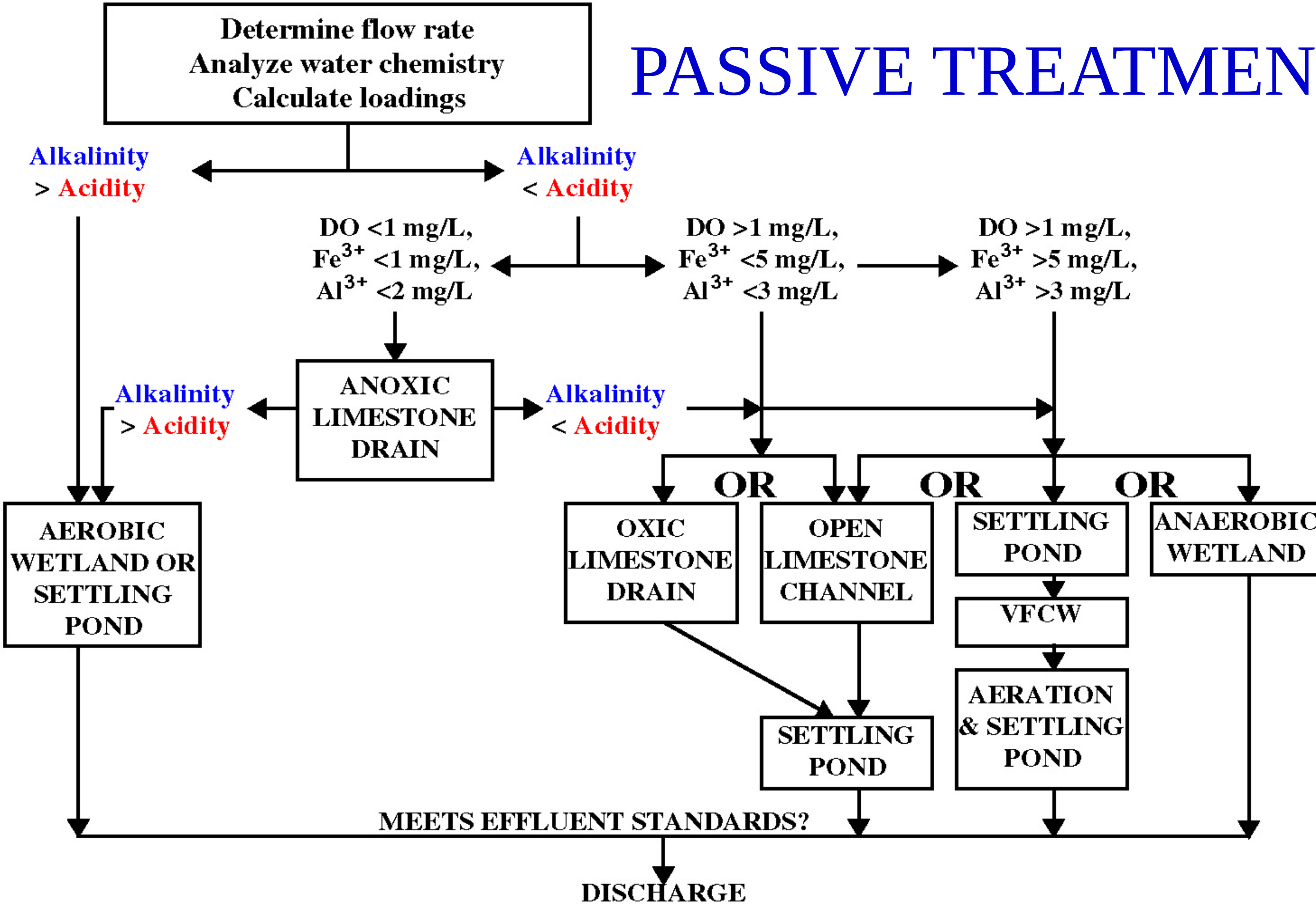
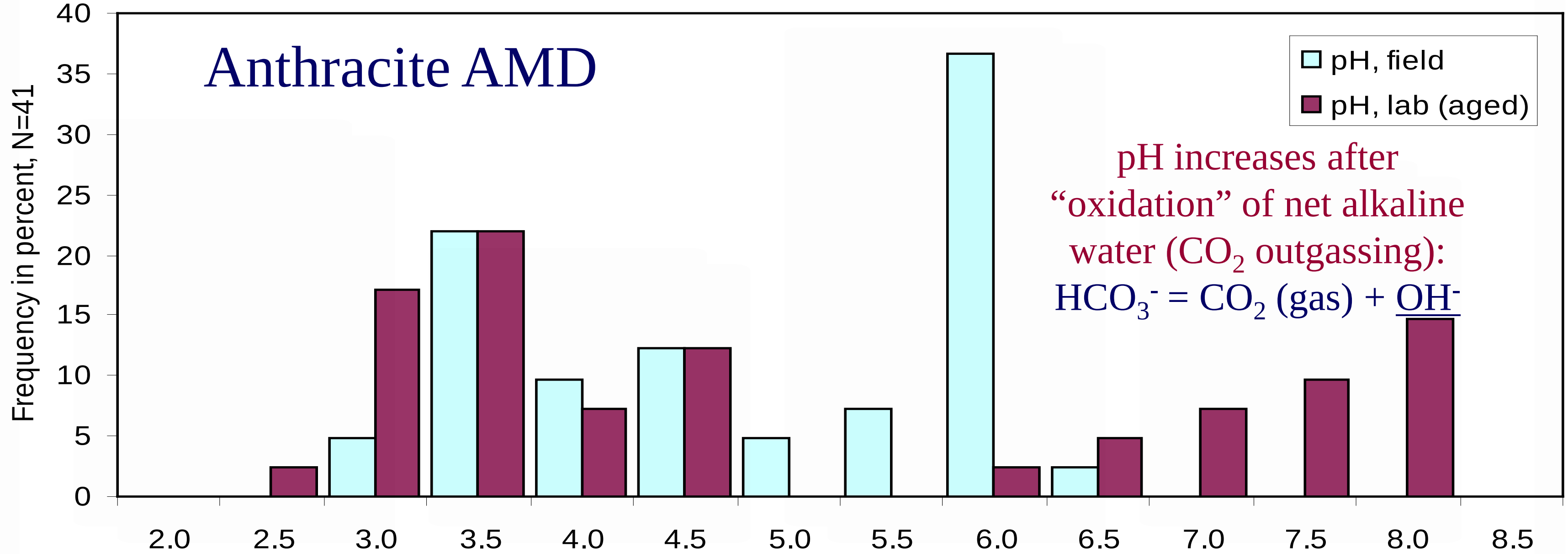


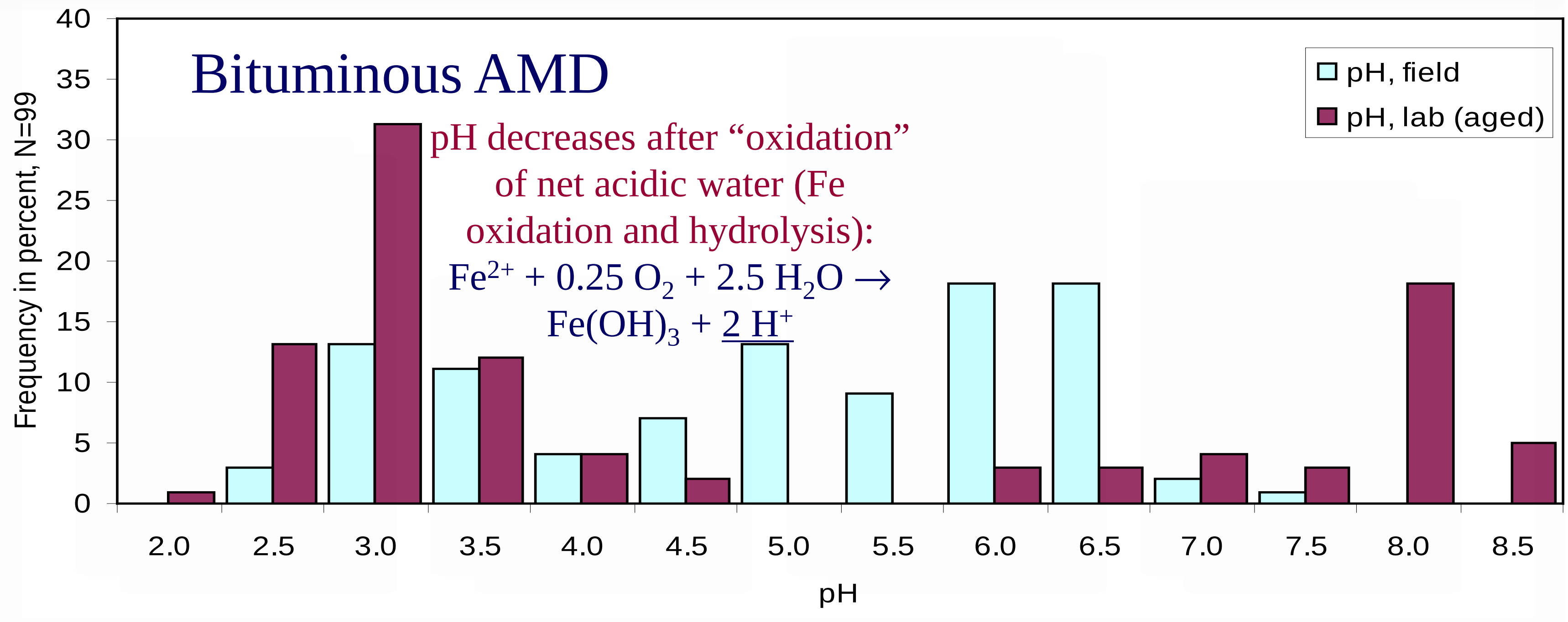
Figure 3. Flow chart for selection of passive treatment alternatives modified from Hedin and others (1994), Skousen and others (1998), and Pennsylvania Department of Environmental Protection (1999). Vertical flow compost wetland (VFCW), also known as SAPS or RAPS.

PASSIVE TREATMENT

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

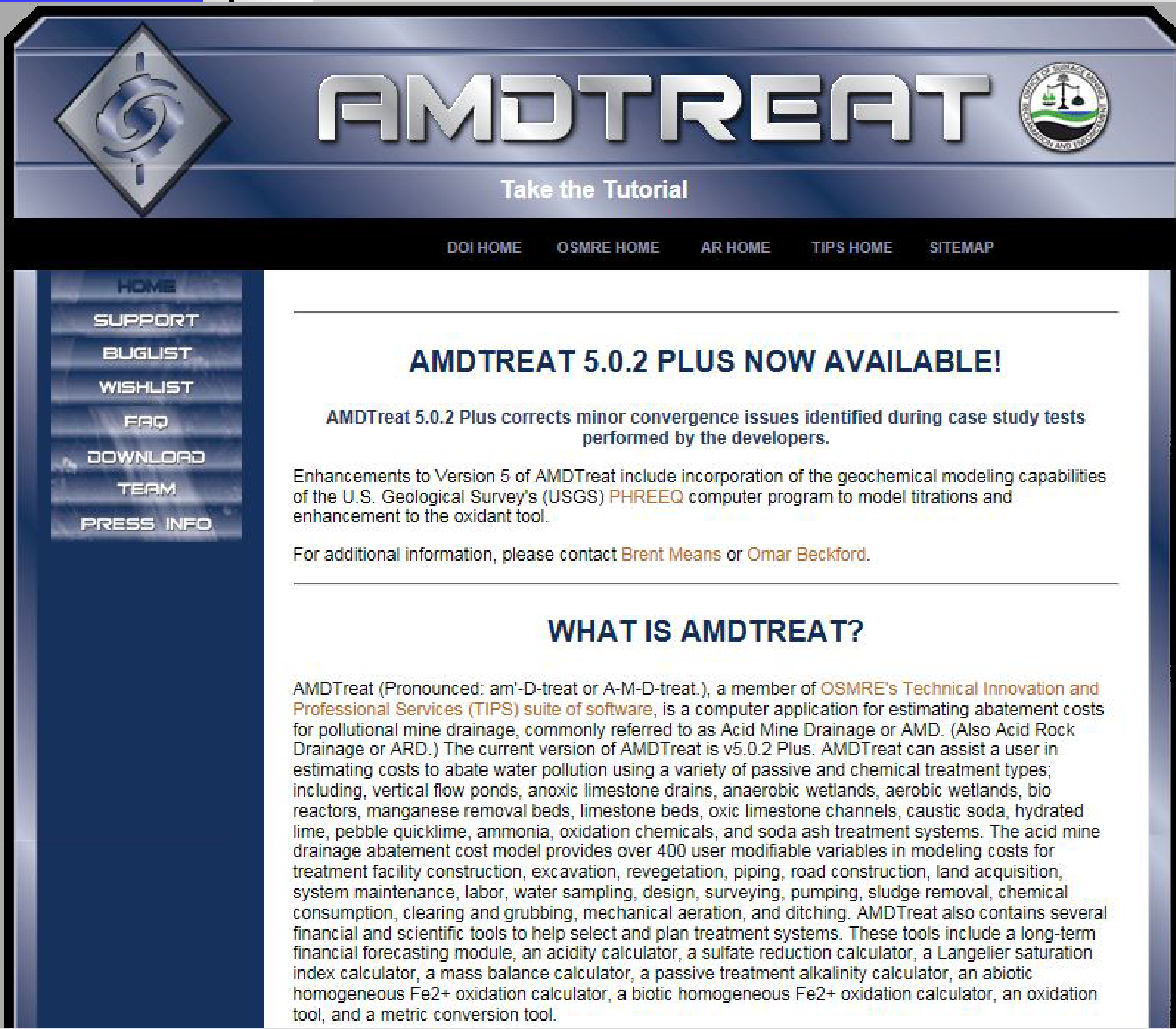
BIMODAL pH FREQUENCY DISTRIBUTION





"PHREEQ-N-AMDTREAT"

http://amd.osmre.gov/



AMDTREAT

Take the Tutorial

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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.

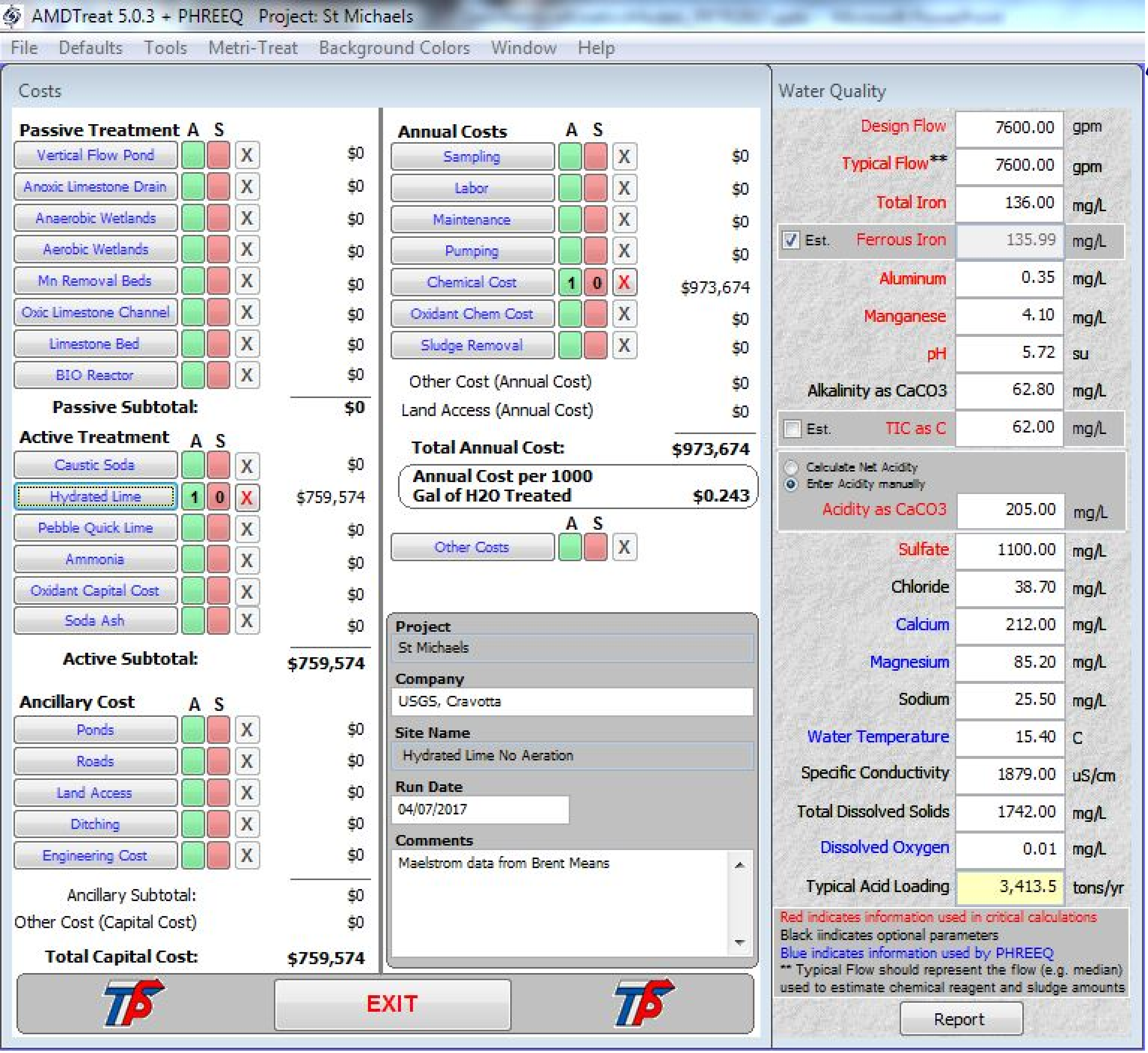
WHAT IS AMDTREAT?

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+ Caustic Addition—St. Michaels Discharge

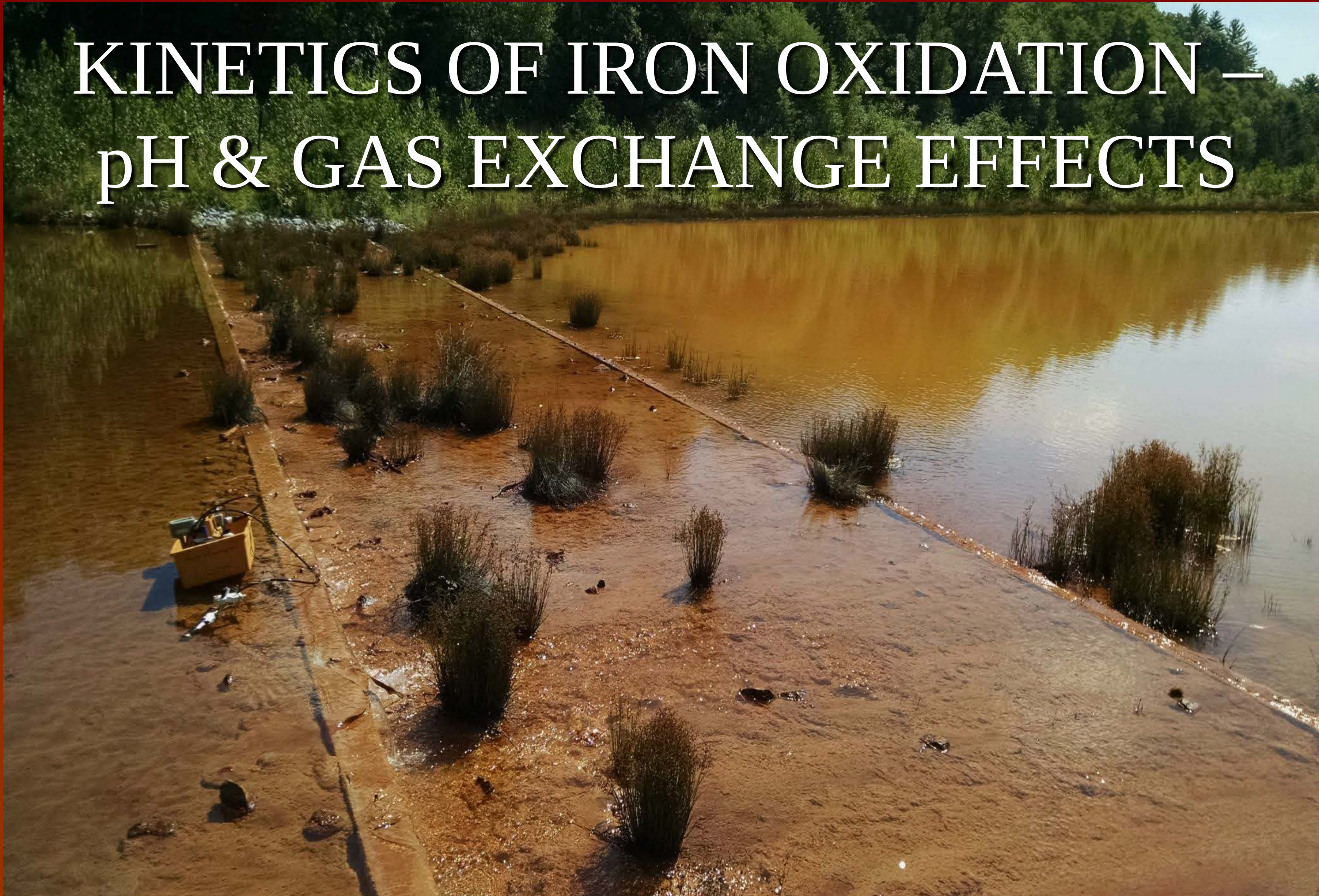
AMDTreat 5.0+.lnk

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)

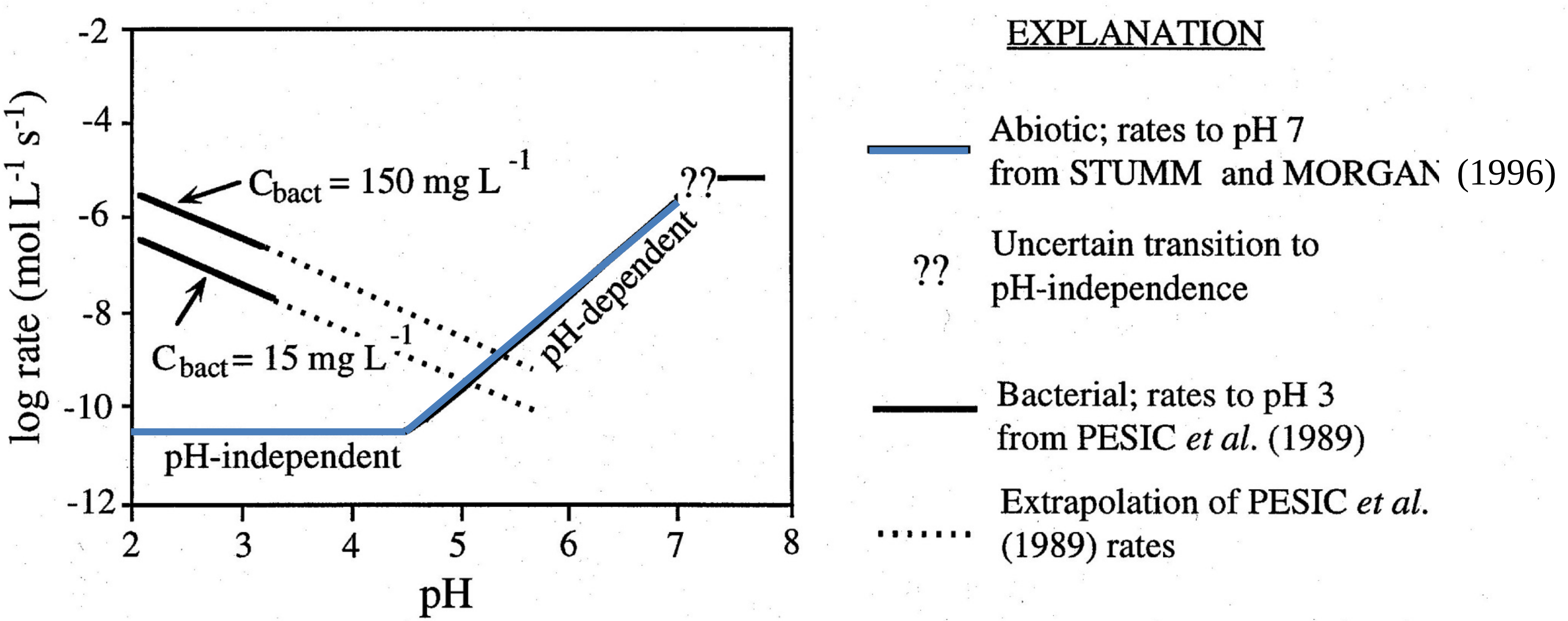


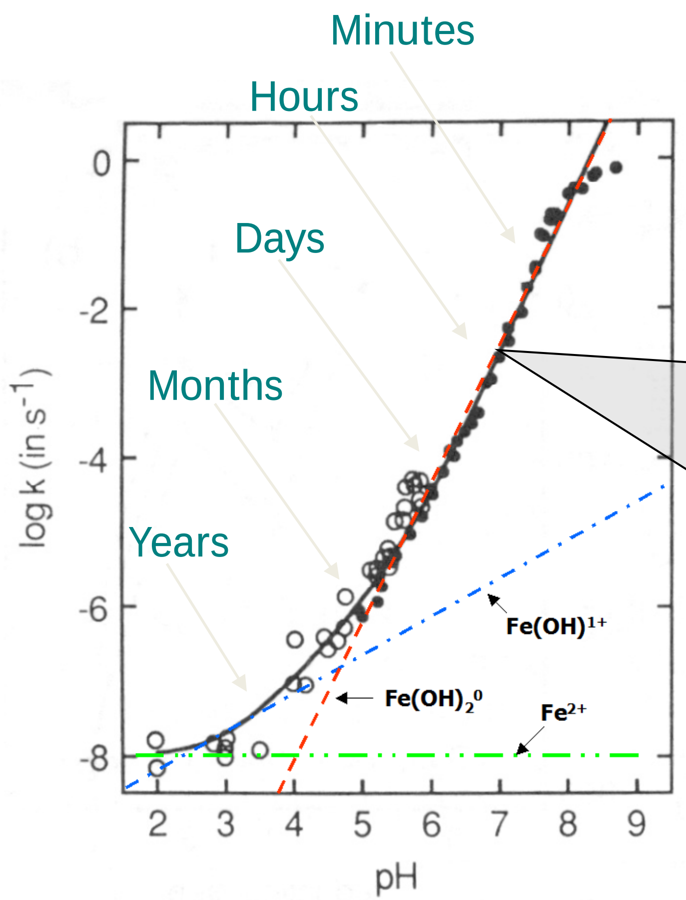
Fig. 3. Rate of Fe(II) oxidation versus pH based on abiotic and biological rate laws (Kirby et al., 1999)

** 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.

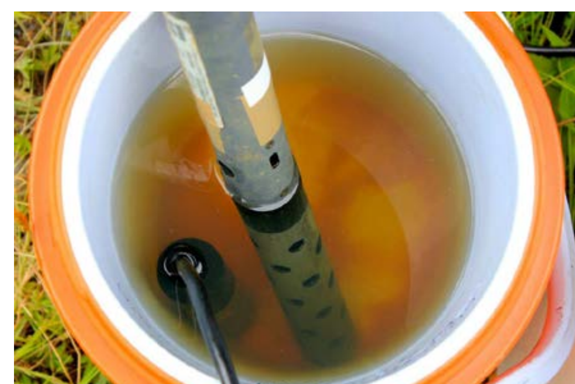
Effects of O_2 Ingassing and CO_2 Outgassing on pH and Fe(II) Oxidation Rates

Batch Aeration Tests at Oak Hill Boreholes (summer 2013)

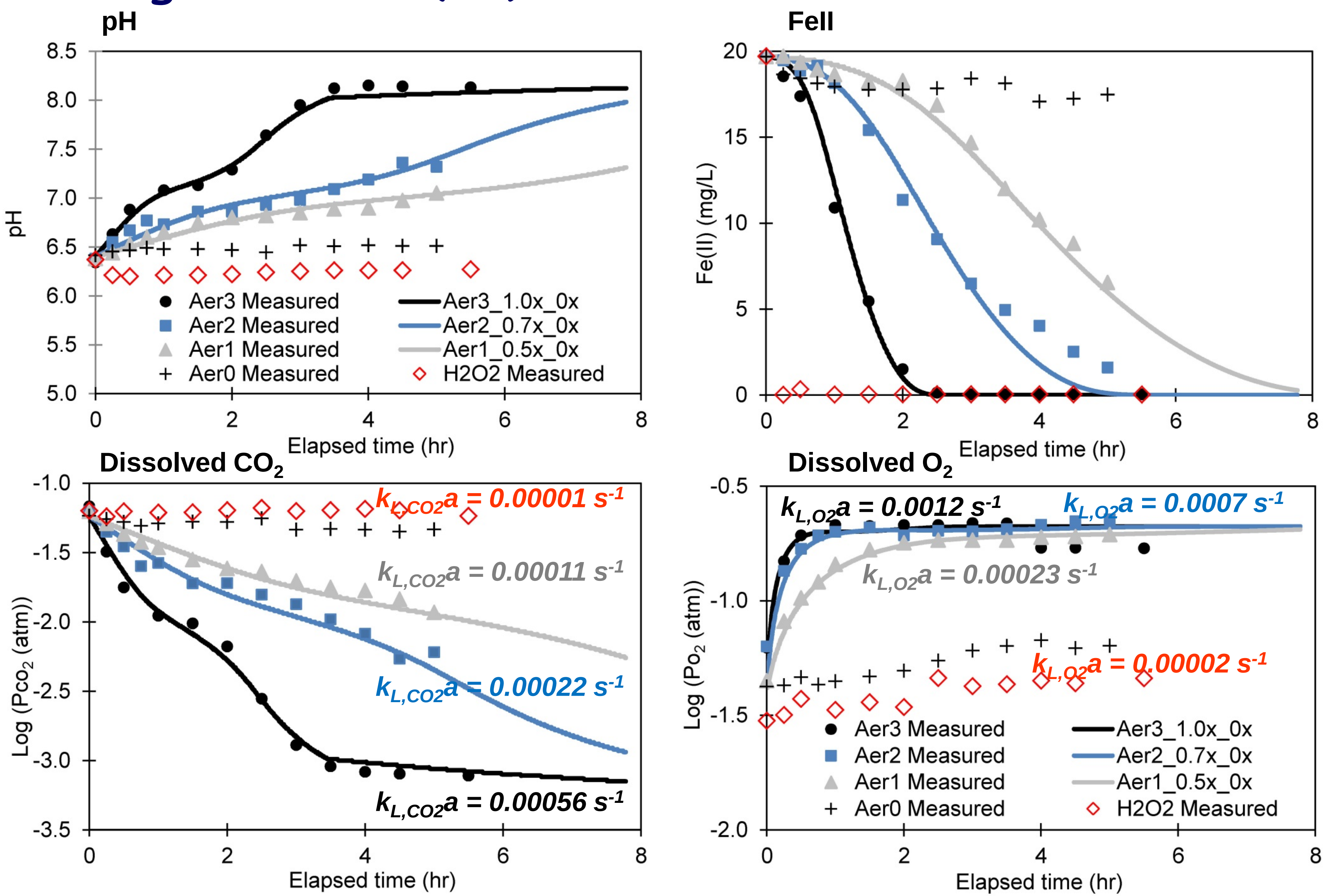
Control Not Aerated

Aerated

H_2O_2 Addition

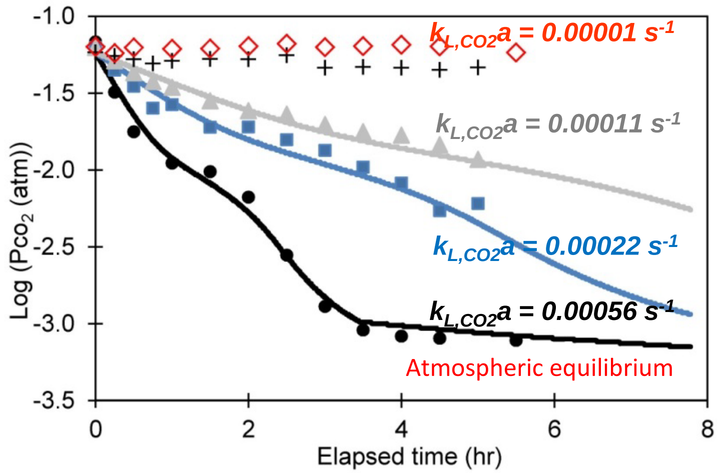


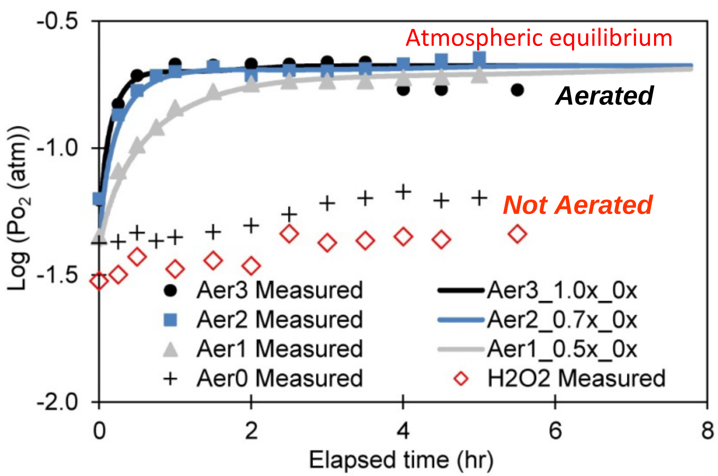
PHREEQC Coupled Kinetic Model of CO_2 Outgassing & Homogeneous Fe(II) Oxidation—Oak Hill Boreholes

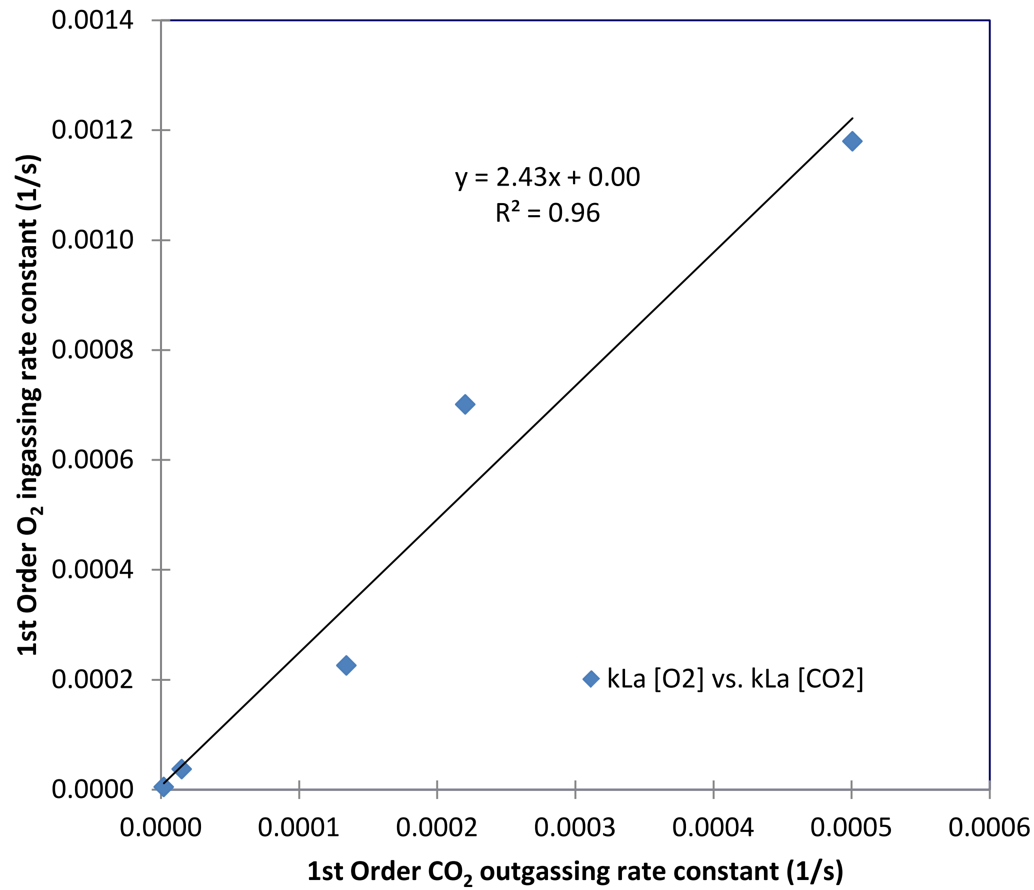


CO_2 Outgassing is Proportional to O_2 Ingassing (model specifies first-order rates for out/in gassing)

$-d[C]/dt = k_{L,C}a \cdot ([C] - [C]_S)$ 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):

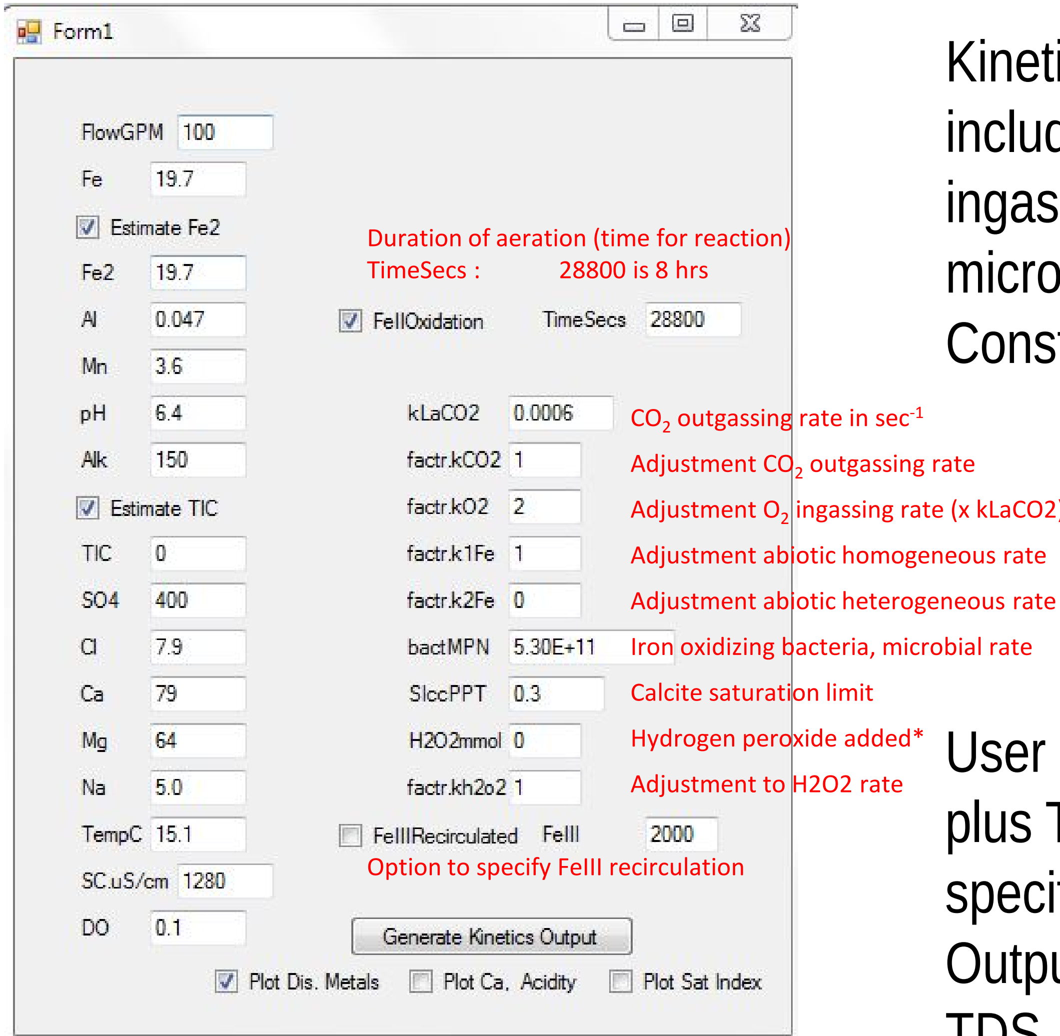
$$-d[Fe(II)]/dt = k_2\,(Fe(III)) \cdot [Fe(II)] \cdot [O_2] \cdot \{H^+\}^{-1}$$

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



*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: $k_{L,CO_2}a = 0.00056\ s^{-1}$

Aer2: $k_{L,CO_2}a = 0.00022\ s^{-1}$

Aer1: $k_{L,CO_2}a = 0.00011\ s^{-1}$

Aer0: $k_{L,CO_2}a = 0.00001\ s^{-1}$

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	Temperature	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°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)).

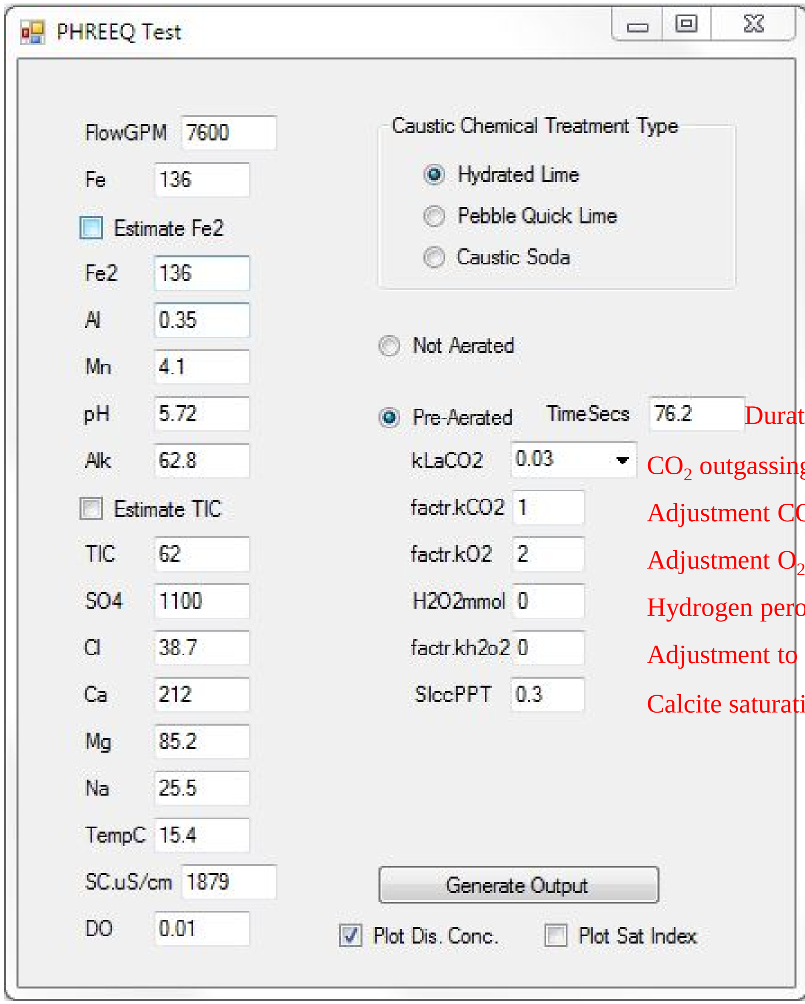
kL,a_20 = (LN((C_1-C_S)/(C_2-C_S))/t) / ($1.0241^{(TEMPC - 20)}$), where C is CO_2 or O_2.

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



Duration of pre-aeration in sec

CO_2 outgassing rate constant in sec^{-1}

Adjustment CO_2 outgassing rate (x kLaCO2)

Adjustment O_2 ingassing rate (x kLaCO2)

Hydrogen peroxide added*

Adjustment to H_2O_2 rate

Calcite saturation limit

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

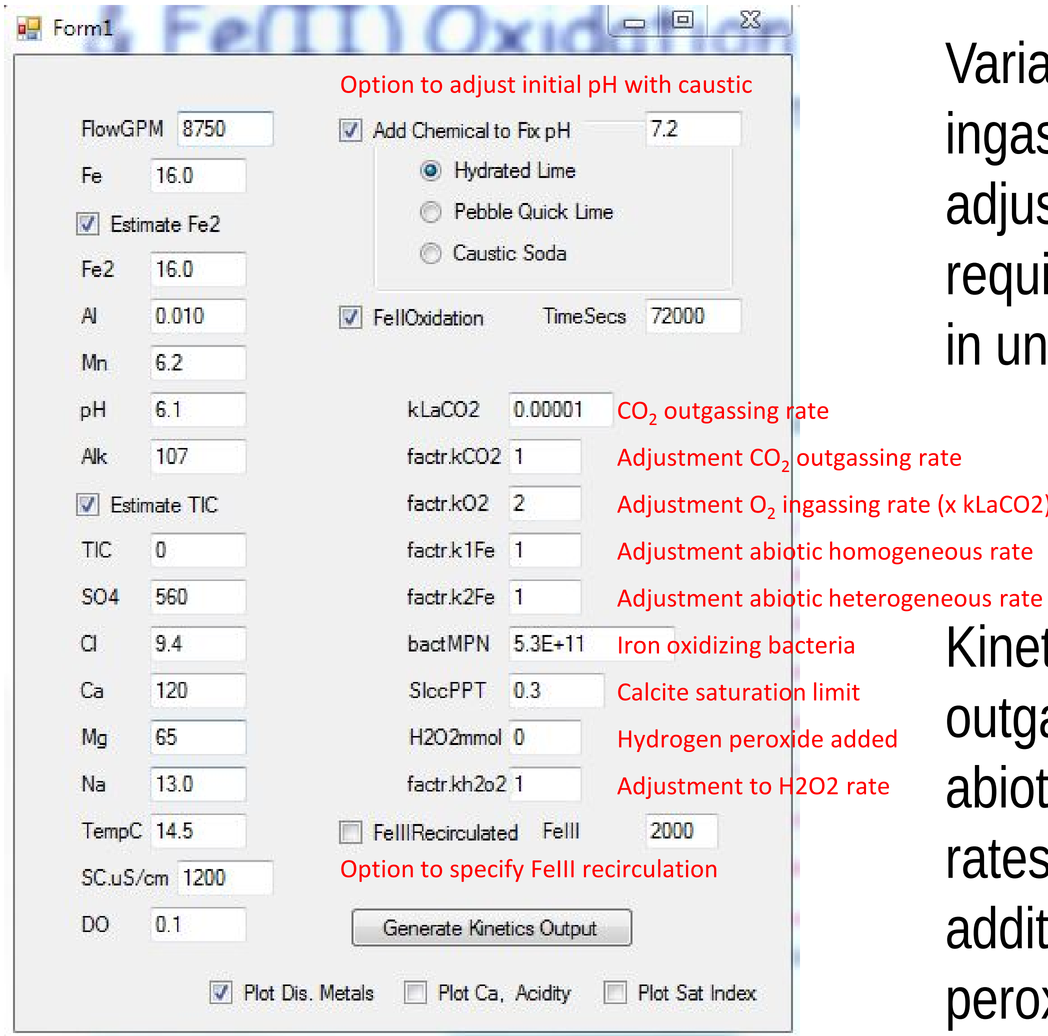
Dropdown kLa

PHREEQTitration_StMichaels.exe

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



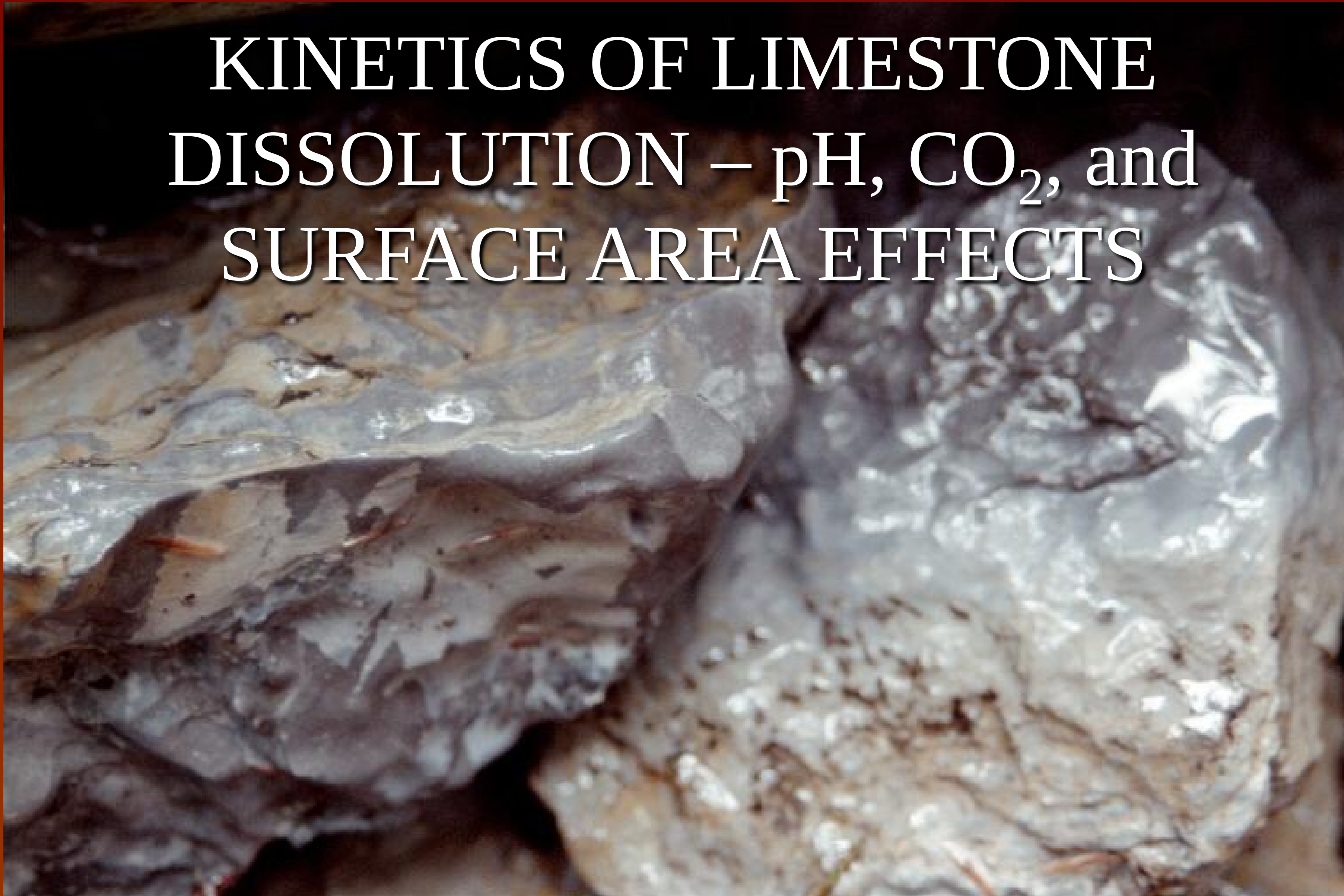
*multiply Fe.mg by 0.0090 to get [H2O2]

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



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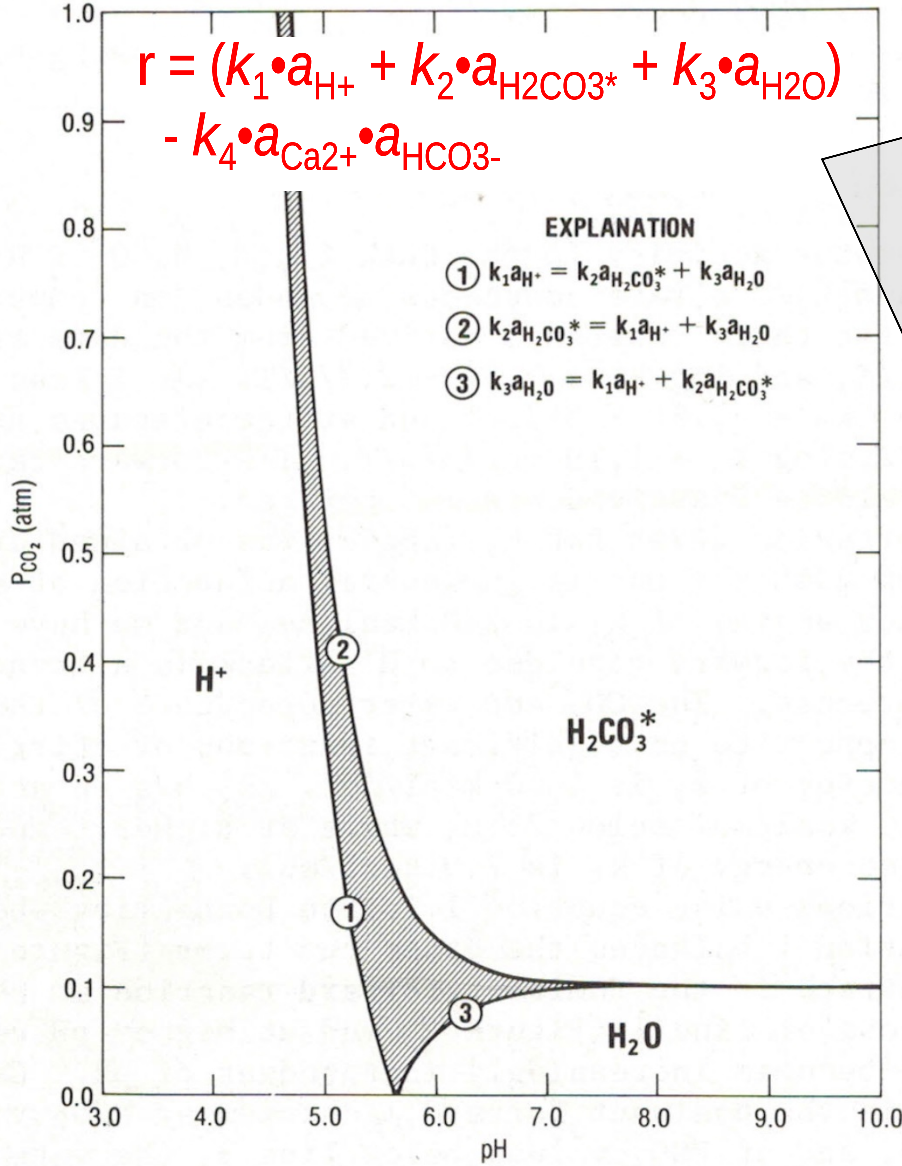
Limestone Dissolution Rate Model for AMDTreat ("PWP" model emphasizes pH and CO_2)

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



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

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$ — k_1

$CaCO_3 + H_2CO_3^* \rightarrow Ca^{2+} + 2\ HCO_3^-$ — k_2

$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-$ — k_3

and the backward (precipitation) reaction:

$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+$ — 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 (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

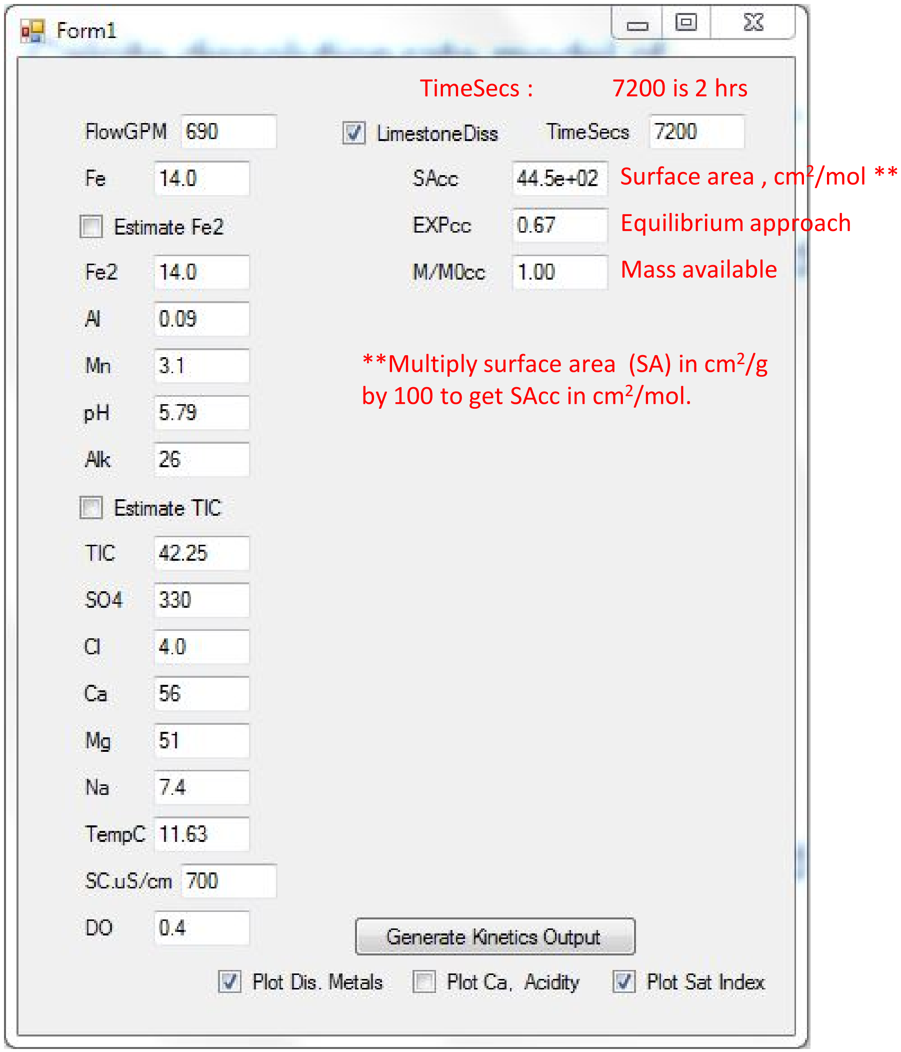
Rectangular Prism: (Long Axis*Short Axis*Intermediate Axis)

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

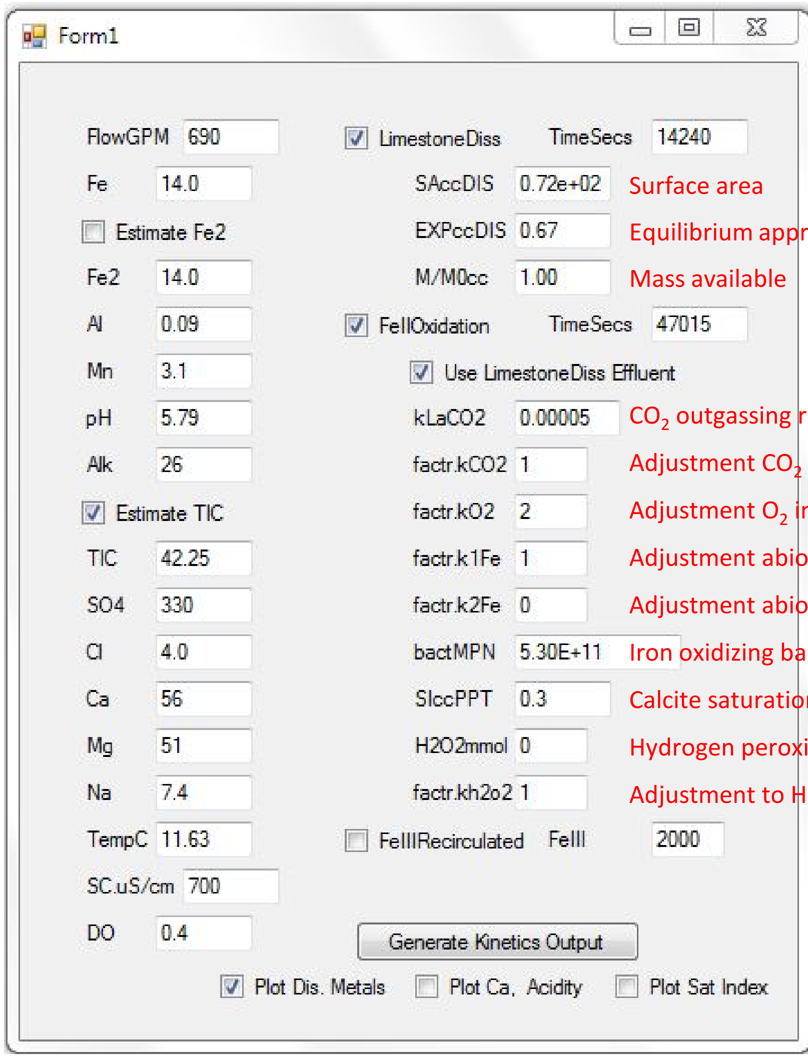


Calcite dissolution rate model of Plummer, Wigley, and Parkhurst (PWP; 1978). Empirical testing and development of PWP rate model based on “coarse” and “fine” calcite particles with surface areas of 44.5 and 96.5 cm^2/g, respectively.

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



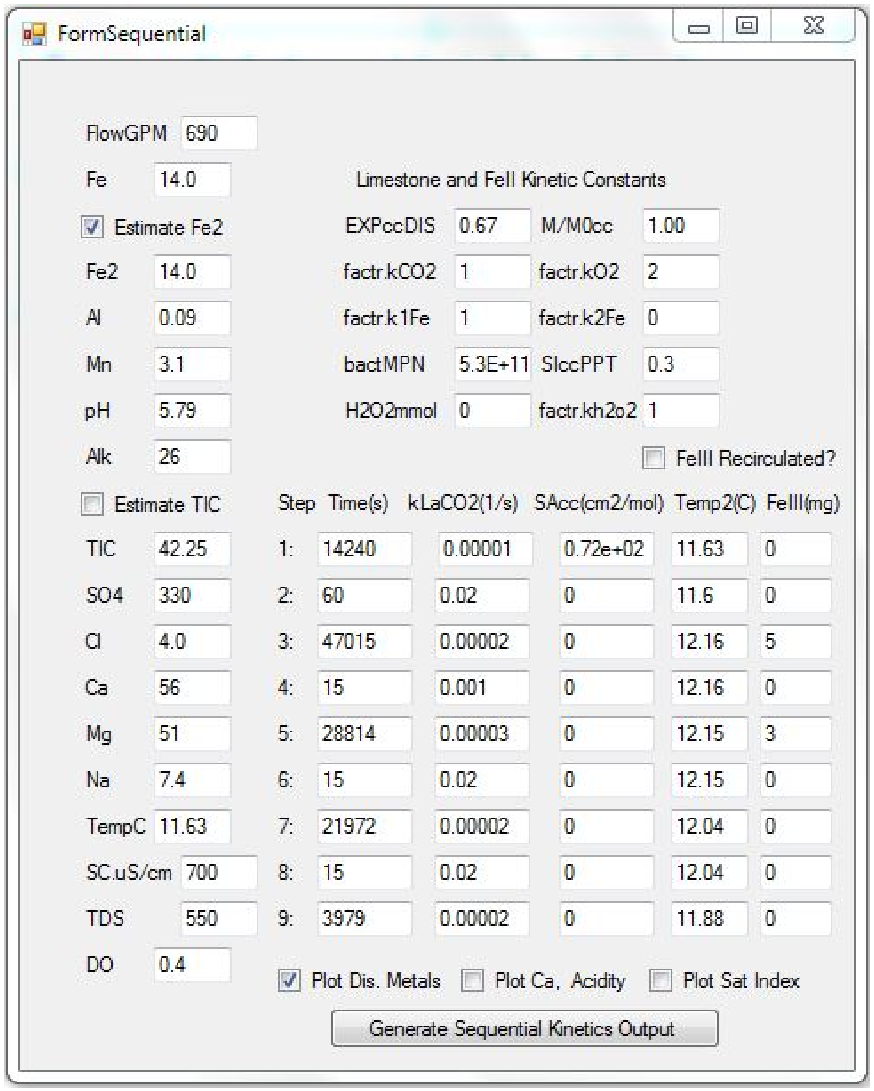
Surface area
Equilibrium approach
Mass available
CO_2 outgassing rate
Adjustment CO_2 outgassing rate
Adjustment O_2 ingassing rate (x kLaCO2)
Adjustment abiotic homogeneous rate
Adjustment abiotic heterogeneous rate
Iron oxidizing bacteria
Calcite saturation limit
Hydrogen peroxide added
Adjustment to H2O2 rate

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



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

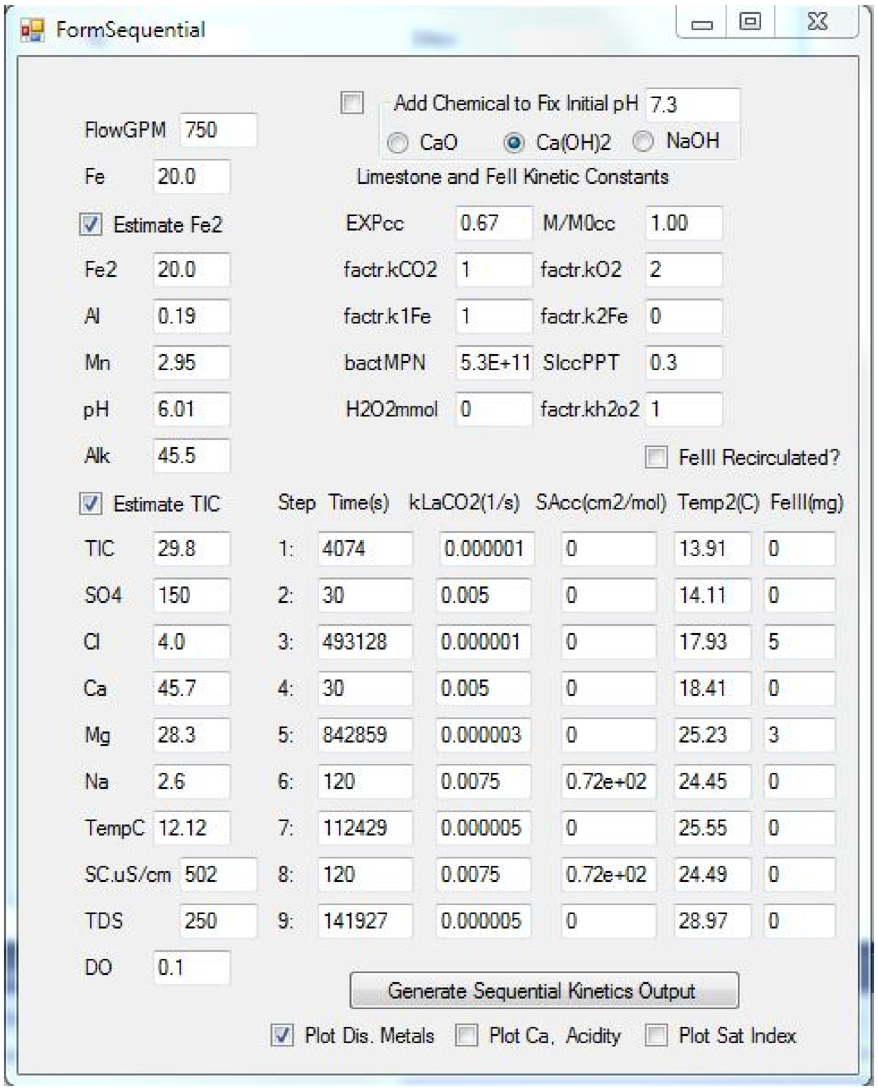
Step	Treatment
1	ALD
2	Riprap
3	Pond
4	Cascade
5	Wetland
6	Cascade
7	Wetland
8	Cascade
9	Wetland

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



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.

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