GEOCHEMICAL KINETICS MODULES FOR “AMDTreat 5.0+”

Charles A. Cravotta III
U.S. Geological Survey

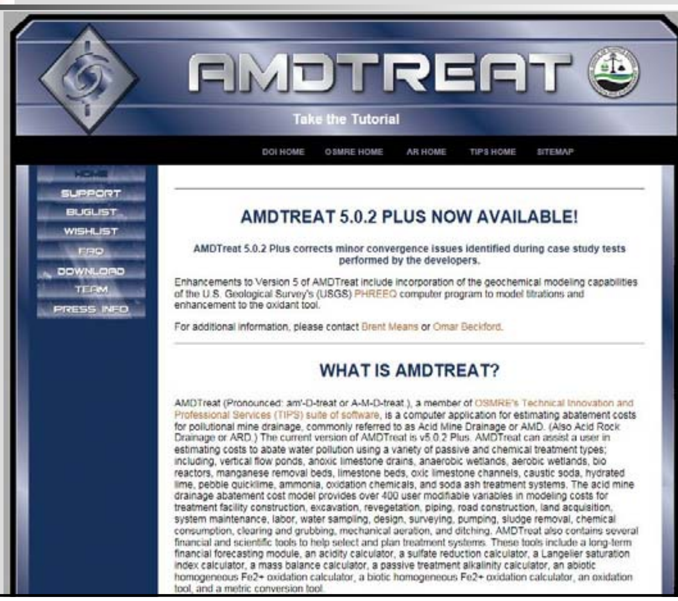
In collaboration with
Brent P. Means
U.S. Office of Surface Mining Reclamation and Enforcement

USGS
science for a changing world

“PHREEQ-N-AMDTREAT”

http://amd.osmre.gov/default.htm

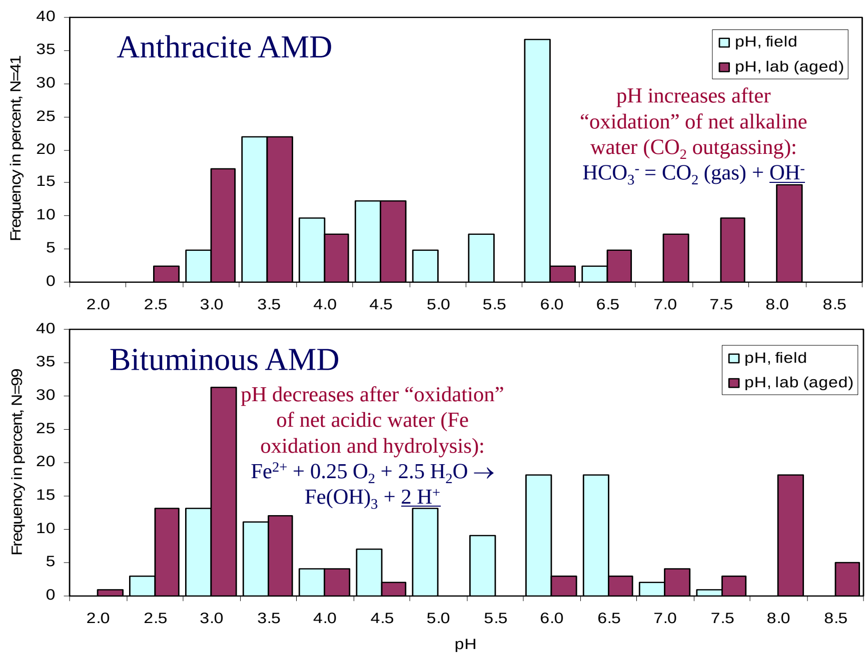
AMDTreat



Objective

- Incorporate PHREEQC "kinetics tools" to AMDTreat 5.0+
  - ✓ FeII oxidation tool that utilizes established rate equations for gas exchange and pH-dependent iron oxidation and that can be associated with commonly used aeration devices; and
  - ✓ Limestone dissolution tool that utilizes established rate equation for calcite dissolution and that can be adjusted for surface area of commonly used aggregate particle sizes.

BIMODAL pH FREQUENCY DISTRIBUTION



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

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

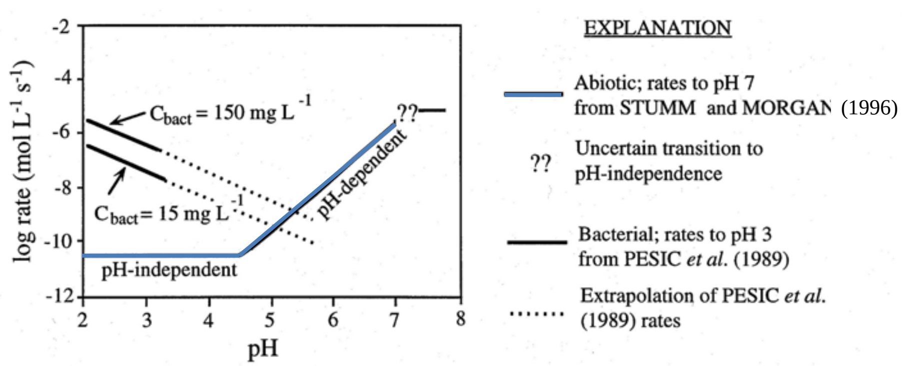


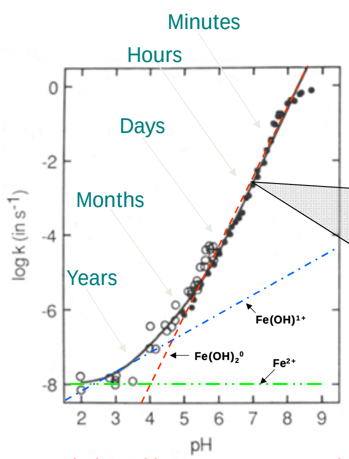
Fig. 3. Rate of Fe(II) oxidation versus pH based on abiotic and biological rate laws (Kirby et al., 1999)

** 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.

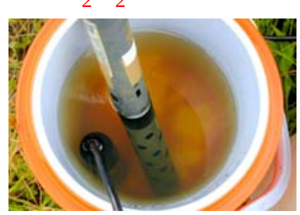
Effects of O_2 Ingassing and CO_2 Outgassing on pH and Fe(II) Oxidation Rates

Batch Aeration Tests at Oak Hill Boreholes (summer 2013)

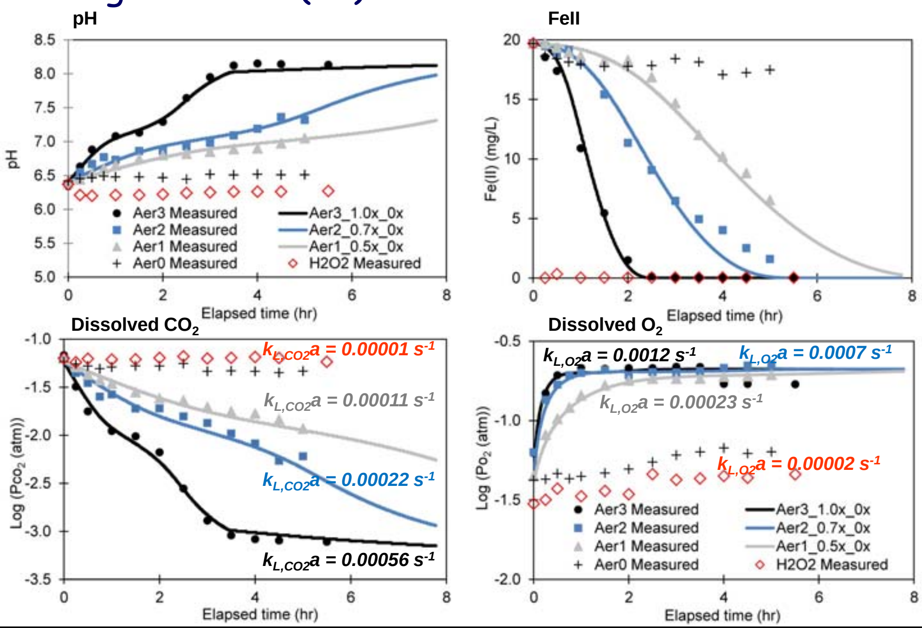
Control Not Aerated

Aerated

H_2O_2 Addition

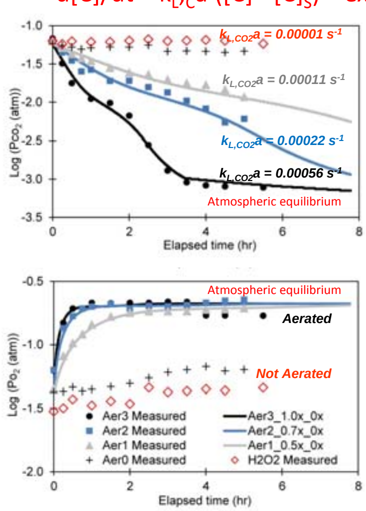


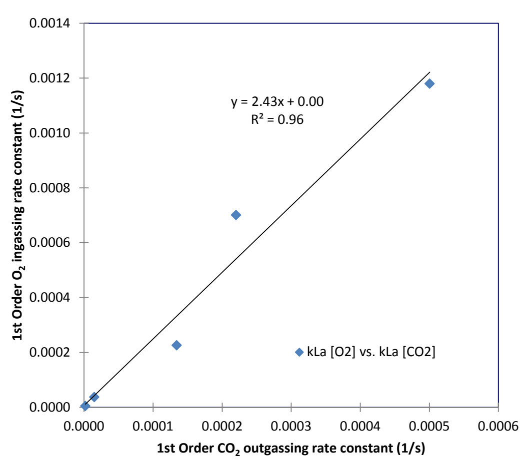
PHREEQC Coupled Kinetic Model of CO_2 Outgassing & Homogeneous Fe(II) Oxidation—Oak Hill Boreholes



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





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	-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	-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	-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	-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.

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 Fe(III) oxyhydroxide surfaces at pH > 5, where (Fe(III)) is the Fe(III) oxyhydroxide concentration expressed as Fe in mg/L (Dempsey et al., 2001; Dietz and Dempsey, 2002):

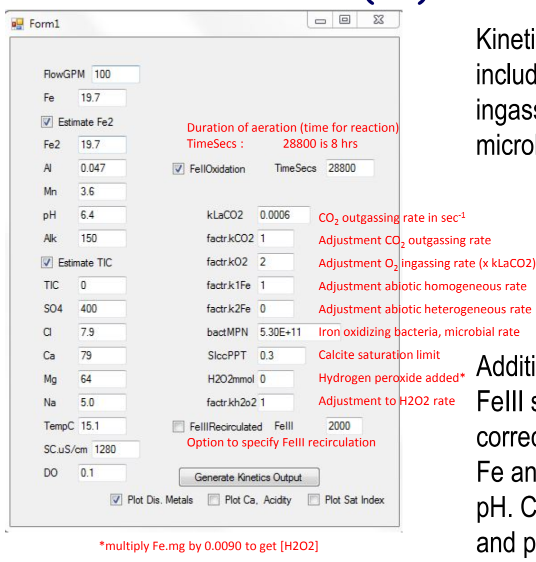
$$-d[Fe(II)]/dt = k_2\ (Fe(III)) \cdot [Fe(II)] \cdot [O_2] \cdot \{H^+\}^{-1}$$

The **microbial oxidation rate law** describes the catalytic biological oxidation of Fe(II) by acidophilic microbes 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



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

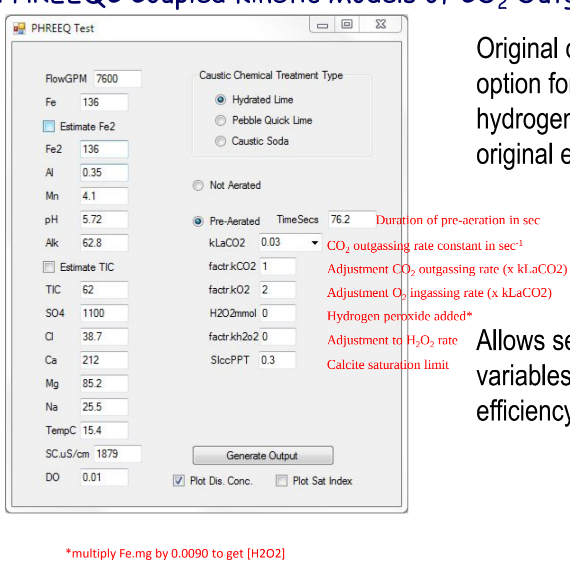
FeII.exe

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}

Addition of H_2O_2 and recirculation of FeIII simulated. Constants temperature corrected. Options to estimate Fe2 from Fe and pH plus TIC from alkalinity and pH. Computes net acidity, TDS, SC, and precipitated solids.

Revised AMDTreat Chemical Cost Module — Caustic Titration with Pre-Aeration (Decarbonation)

PHREEQC Coupled Kinetic Models of CO_2 Outgassing & Fe(II) Oxidation

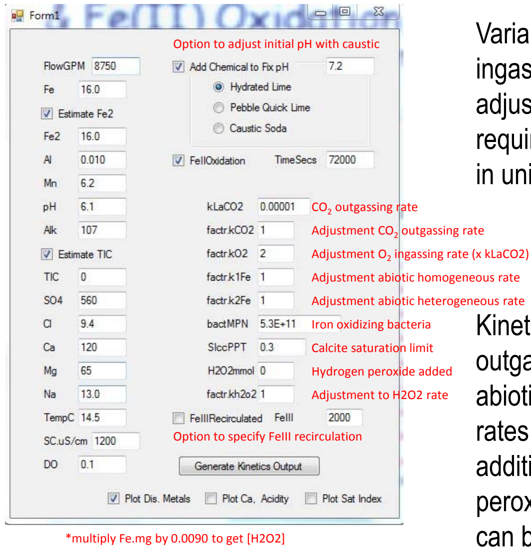


Original option for no aeration, plus new option for **kinetic pre-aeration** (w/wo hydrogen peroxide) that replaces original equilibrium aeration.

PHREEQTitration_StMichaels.exe

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

New Module For AMDTreat — PHREEQC Coupled Kinetic Models of CO_2 Outgassing & Fe(II) Oxidation, with Caustic Pre-Treatment

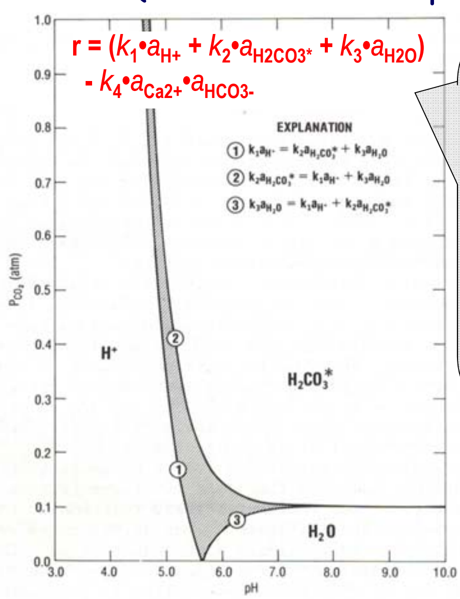


Variable CO_2 outgassing and O_2 ingassing rates apply. Can choose to adjust initial pH with caustic. The required quantity of caustic is reported in units used by AMDTreat.

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.

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 (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:

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

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):

$\log k_1 = 0.198 - 444 / T$

$\log k_2 = 2.84 - 2177 / T$

$\log k_3 = -5.86 - 317 / T$ for $T \le 298$; $\log k_3 = -1.10 - 1737 / T$ 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

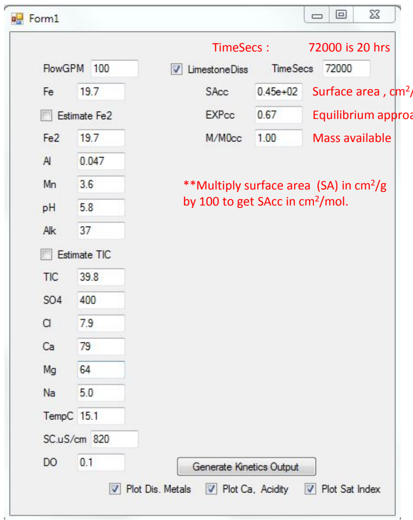
Particle dimensions were estimated on the basis of ranges for graded materials reported in Pennsylvania Department of Environmental Protection, 2000, Erosion and sediment pollution control program manual: Harrisburg, Pennsylvania Dept. Environmental Protection Bureau of Watershed Management, Document 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

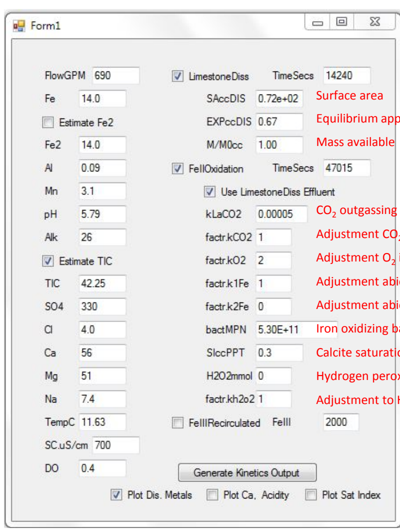


Calcite dissolution rate model of Plummer, Wigley, and Parkhurst (PWP; 1978). Empirical testing and development of PWP rate model based on "coarse" and "fine" calcite particles with surface areas of 44.5 and 96.5 cm^2/g, respectively.

Limestone.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

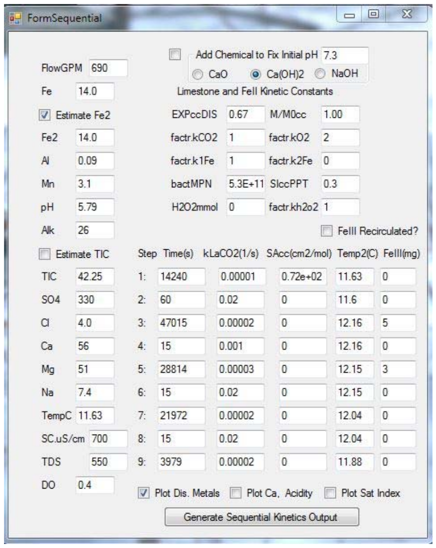


Rate models for calcite dissolution, CO_2 outgassing and O_2 ingassing, and FeII oxidation are combined to evaluate possible reactions in passive treatment systems.

Limestone+FeII_PineForest.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 Caustic $\pm$ Limestone Dissolution $\pm$ Fe(II) Oxidation Pine Forest ALD + 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+LS+FeIIseq_PineFor151212.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.

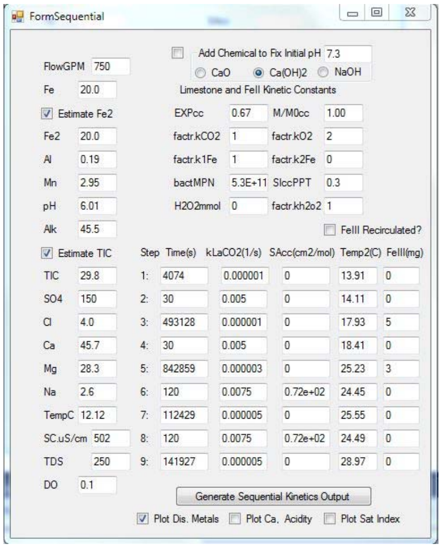
PHREEQC Coupled Kinetic Models Sequential Steps— Pine Forest ALD + Aerobic Wetlands

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

Caustic+LS+FeIIseq_PineFor151212.exe

PineForest_Field_151212t.xlsx - Shortcut.lnk

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



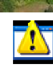
Sequential steps: Pre-treatment with caustic and/or peroxide and, for each subsequent step, variable detention times, adjustable CO_2 outgassing rates, limestone surface area, temperature, and FeIII.

Caustic+LS+FeIIseq_SilCr160808.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



SilverCrk_Field_160808t.xlsx - Shortcut.lnk

References

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^o to 60^oC 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)