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

## Passive

<table>
<thead>
<tr>
<th>Al^{3+}</th>
<th>Fe^{2+} / Fe^{3+}</th>
<th>Mn^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase pH/oxidation with natural substrates &amp; microbial activity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactions slow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large area footprint</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low maintenance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Active

| 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 (NaOH) used
40 % – lime (CaO; Ca(OH)$_2$) used
6 % – flocculent or oxidant used
4 % – limestone (CaCO$_3$) used
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,
O₂ Ingassing,
CO₂ Outgassing,
Fe(II) Oxidation, & Fe(III) Accumulation

Vertical Flow Limestone Beds
Bell Colliery

Pine Forest ALD & Wetlands

Silver Creek Wetlands
**Anthracite Mine Discharges**

- **Frequency in percent, N=41**

- **Anthracite AMD**
  - pH increases after “oxidation” of net alkaline water (CO₂ outgassing): \[ \text{HCO}_3^- = \text{CO}_2 \text{(gas)} + \text{OH}^- \]

**Bituminous Mine Discharges**

- **Frequency in percent, N=99**

- **Bituminous AMD**
  - pH decreases after “oxidation” of net acidic water (Fe oxidation and hydrolysis): \[ \text{Fe}^{2+} + 0.25 \text{O}_2 + 2.5 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2 \text{H}^+ \]
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.
### Water Quality

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design Flow</td>
<td>7600.00 gpm</td>
</tr>
<tr>
<td>Typical Flow**</td>
<td>7600.00 gpm</td>
</tr>
<tr>
<td>Total Iron</td>
<td>136.00 mg/L</td>
</tr>
<tr>
<td>Est. Ferrous Iron</td>
<td>135.99 mg/L</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.35 mg/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>4.10 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>5.72 su</td>
</tr>
<tr>
<td>Alkalinity as CaCO3</td>
<td>62.80 mg/L</td>
</tr>
<tr>
<td>TIC as C</td>
<td>62.00 mg/L</td>
</tr>
</tbody>
</table>

### Acidity as CaCO3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>1100.00 mg/L</td>
</tr>
<tr>
<td>Chloride</td>
<td>38.70 mg/L</td>
</tr>
<tr>
<td>Calcium</td>
<td>212.00 mg/L</td>
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<tr>
<td>Magnesium</td>
<td>85.20 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>25.50 mg/L</td>
</tr>
<tr>
<td>Water Temperature</td>
<td>15.40 °C</td>
</tr>
<tr>
<td>Specific Conductivity</td>
<td>1879.00 μS/cm</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>1742.00 mg/L</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>0.01 mg/L</td>
</tr>
<tr>
<td>Typical Acid Loading</td>
<td>3,413.5 tons/yr</td>
</tr>
</tbody>
</table>

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### AMDTreat 5.0+

**Caustic Addition—St. Michaels Discharge**

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

**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).

\[ C_{bact} = 150 \text{ mg/L} = 5.3 \times 10^{11} \text{ MPNbact} \times (2.8 \times 10^{-10}) \]
Abiotic Homogeneous Fe(II) Oxidation Rate (model emphasizes pH)

*Extrapolation of homogeneous rate law:
\[-d[\text{Fe(II)}]/dt = k_1 \cdot [\text{Fe(II)}] \cdot [\text{O}_2] \cdot [\text{H}^+]^{-2}\]

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

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.

\[
\log k_T = \log k_{T2} + \frac{E_a}{(2.303 \times R)} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]

At \([\text{O}_2] = 0.26 \text{ mM (pO}_2 = 0.21 \text{ 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)
PHREEQC Coupled Kinetic Model of CO\(_2\) Outgassing & Homogeneous Fe(II) Oxidation—Oak Hill Boreholes

- \(k_{L,CO_2a} = 0.00001\) s\(^{-1}\)
- \(k_{L,O_2a} = 0.0012\) s\(^{-1}\)
- \(k_{L,O_2a} = 0.0007\) s\(^{-1}\)
- \(k_{L,CO_2a} = 0.00011\) s\(^{-1}\)
- \(k_{L,O_2a} = 0.00023\) s\(^{-1}\)
- \(k_{L,CO_2a} = 0.00022\) s\(^{-1}\)
- \(k_{L,O_2a} = 0.00002\) s\(^{-1}\)
- \(k_{L,CO_2a} = 0.00056\) s\(^{-1}\)
**CO₂ Outgassing is Proportional to O₂ 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

![Graph showing exponential relationship between k_{L,C,a} and Log(PCO₂) vs. elapsed time (hr)]

![Graph showing linear relationship between kLa [O₂] vs. kLa [CO₂]]
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

Kinetic variables can be adjusted, including CO$_2$ outgassing and O$_2$ ingassing rates plus abiotic and microbial Fe(II) oxidation rates. Constants are temperature corrected.

Adjustment CO$_2$ outgassing rate
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$_2$O$_2$ or recirculation of Fe(II). Output includes pH, solutes, net acidity, TDS, SC, and precipitated solids.

*multiply Fe.mg by 0.0090 to get [H2O2]
Estimated $\text{CO}_2$ Outgassing & $\text{O}_2$ Ingassing Rate Constants for Various Treatment Technologies

**Table S.4** Values of rate constants for $\text{CO}_2$ outgassing and $\text{O}_2$ ingassing used for kinetic models

<table>
<thead>
<tr>
<th>Site</th>
<th>Temperature (°C)</th>
<th>$\text{CO}<em>2$ Outgas $k</em>{L,\text{CO}_2}a$ (log(s$^{-1}$))</th>
<th>$\text{O}<em>2$ Ingas $k</em>{L,\text{O}_2}a$ (log(s$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maelstrom (Sykesville, Trent, St.Michaels)</td>
<td>20</td>
<td>0.03 Fast -1.52</td>
<td>0.26 0.06 -1.22 0.56</td>
</tr>
<tr>
<td>Surface Aerator (Renton, Rushton)</td>
<td>20</td>
<td>0.001 -3.00 -1.22 0.002 -2.70 -0.92</td>
<td></td>
</tr>
<tr>
<td>Mechanical Aerator (Lancashire)</td>
<td>20</td>
<td>0.0006 -3.22 -1.44 0.0012 -2.92 -1.14</td>
<td></td>
</tr>
<tr>
<td>Aeration Cascade/Level Spreader (Silver Cr)</td>
<td>20</td>
<td>0.01 -2.00 -0.22 0.02 -1.70 0.08</td>
<td></td>
</tr>
<tr>
<td>Rip-rap Spillway/Ditch (Silver Cr, Pine Forest,)</td>
<td>20</td>
<td>0.005 -2.30 -0.52 0.01 -2.00 0.22</td>
<td></td>
</tr>
<tr>
<td>Pond (Silver Cr, Pine Forest, Lion Mining, Flight93)</td>
<td>20</td>
<td>0.00001 Slow -5.00 -3.22 0.00002 -4.70 -2.92</td>
<td></td>
</tr>
<tr>
<td>Wetland (Silver Cr, Pine Forest, Lion Mining)</td>
<td>20</td>
<td>0.00001 -5.00 -3.22 0.00002 -4.70 -2.92</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oak Hill Aeration Expts.</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aer3</td>
<td>20</td>
<td>0.0005625 Fast -3.25</td>
<td>-1.47 0.001125 -2.95 -1.17</td>
</tr>
<tr>
<td>Aer2</td>
<td>20</td>
<td>0.0002475 -3.61</td>
<td>-1.83 0.000495 -3.31 -1.53</td>
</tr>
<tr>
<td>Aer1</td>
<td>20</td>
<td>0.0001508 -3.82</td>
<td>-2.04 0.000302 -3.52 -1.74</td>
</tr>
<tr>
<td>Aer0</td>
<td>20</td>
<td>0.0000169 Slow -4.77</td>
<td>-2.99 3.38E-05 -4.47 -2.69</td>
</tr>
</tbody>
</table>

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

\[
k_{L,a_{20}} = k_{L,a_{TC}} / (1.0241^{(TC-20)}).
\]

\[
k_{L,a_{TC}} = k_{L,a_{20}} \times 1.0241^{(TC-20)}.
\]

\[
k_{L,a_{20}} = \left(\frac{\ln((C_1-C_S)/(C_2-C_S))/t}{1.0241^{(\text{TEMPC} - 20)}}\right),\] where C is $\text{CO}_2$ or $\text{O}_2$. Dissolved $\text{O}_2$, temperature, and pH were measured using submersible electrodes. Dissolved $\text{CO}_2$ 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

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

Duration of pre-aeration in sec

CO$_2$ outgassing rate constant in sec$^{-1}$

Adjustment CO$_2$ outgassing rate (x kLaCO$_2$)

Adjustment O$_2$ ingassing rate (x kLaCO$_2$)

Hydrogen peroxide added*

Adjustment to H$_2$O$_2$ rate

Calcite saturation limit

* multiply Fe.mg by 0.0090 to get [H$_2$O$_2$]
New Module For AMDTreat — PHREEQC Coupled Kinetic Models of \( \text{CO}_2 \) Outgassing & Fe(II) Oxidation, with Caustic Pre-Treatment

Variable \( \text{CO}_2 \) outgassing and \( \text{O}_2 \) ingassing rates apply. Can choose to adjust initial pH with caustic. The required quantity of caustic is reported in units used by AMDTreat.

Kinetic variables, including \( \text{CO}_2 \) outgassing and \( \text{O}_2 \) ingassing rates plus abiotic and microbial Fe(II) oxidation rates, can be adjusted by user. In addition to caustic chemicals, hydrogen peroxide and recirculation of Fe(III) solids can be simulated.

*multiply Fe.mg by 0.0090 to get [H2O2]
KINETICS OF LIMESTONE DISSOLUTION – pH, CO$_2$, and SURFACE AREA EFFECTS
Limestone Dissolution Rate Model for AMDTreat ("PWP" model emphasizes pH and CO₂)

According to Plummer, Wigley, and Parkhurst (1978), the rate of CaCO₃ dissolution is a function of three forward (dissolution) reactions:

\[ \text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \]
\[ k_1 \text{CaCO}_3 + \text{H}_2\text{CO}_3^* \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^- \]
\[ k_2 \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \]

Although H⁺, H₂CO₃*, and H₂O 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.
Appelo and Postma (2005) give a generalized rate expression for calcite dissolution that considers physical characteristics of the system as well as solution chemistry:

\[
R = k \cdot \left( \frac{A}{V} \right) \cdot (1 - \Omega)^n
\]

where \(A\) is calcite surface area, \(V\) is volume of solution, \(\Omega\) 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:

\[
R = (k_1 \cdot a_{H^+} + k_2 \cdot a_{H_2CO_3^\ast} + k_3 \cdot a_{H_2O}) \cdot (A) \cdot (1 - 10^{n \cdot SIcc})
\]

Plummer and others (1978) reported the forward rate constants as a function of temperature (\(T, \text{in} \ K\)), 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)*

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: $4\pi*(\text{Average Axis}/2)^2$
- Rectangular Prism: $2*(\text{Long Axis} \times \text{Short Axis})+2*(\text{Long Axis} \times \text{Intermediate Axis})+2*(\text{Short Axis} \times \text{Intermediate Axis})$
- Ellipsoid: $\pi*(\text{D}^2)/S$, where $D=2*(\text{vol}/(4/3\pi))^{1/3}$, $S=1.15-0.25E$, $E=\text{Long Axis}/D$

Volume computed for same geometric forms:
- Sphere: $4/3\pi*(\text{Average Axis}/2)^3$
- Rectangular Prism: $(\text{Long Axis} \times \text{Short Axis} \times \text{Intermediate Axis})$
- Ellipsoid: $4/3\pi*(\text{Long Axis}/2 \times \text{Short Axis}/2 \times \text{Intermediate Axis}/2)$

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

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

<table>
<thead>
<tr>
<th>Gradation Number</th>
<th>Weight (g)</th>
<th>Particle Dimensions (cm)</th>
<th>Particle Surface Area (cm$^2$/g)</th>
<th>Unit Surface Area (cm$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average Particle</td>
<td>Rectangular Prism</td>
<td>Sphere</td>
<td>Ellipsoid</td>
</tr>
<tr>
<td>AASHTO PA</td>
<td>Long Axis</td>
<td>Intermediate</td>
<td>Short Axis</td>
<td>Average Axis</td>
</tr>
<tr>
<td>R-5</td>
<td>22160.145</td>
<td>45.72</td>
<td>22.86</td>
<td>13.34</td>
</tr>
<tr>
<td>R-4</td>
<td>7113.133</td>
<td>30.48</td>
<td>16.51</td>
<td>8.89</td>
</tr>
<tr>
<td>R-3</td>
<td>1185.522</td>
<td>16.51</td>
<td>8.89</td>
<td>5.08</td>
</tr>
<tr>
<td>1</td>
<td>341.978</td>
<td>8.89</td>
<td>6.35</td>
<td>3.81</td>
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<td>3</td>
<td>78.166</td>
<td>5.08</td>
<td>3.81</td>
<td>2.54</td>
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<td>1.91</td>
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<td>0.635</td>
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<td>1.91</td>
<td>1.27</td>
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<td>1.91</td>
<td>0.95</td>
<td>0.635</td>
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<tr>
<td>1NS</td>
<td>1.221</td>
<td>1.27</td>
<td>0.95</td>
<td>0.635</td>
</tr>
<tr>
<td>7</td>
<td>1.221</td>
<td>1.27</td>
<td>0.95</td>
<td>0.635</td>
</tr>
<tr>
<td>8</td>
<td>0.382</td>
<td>0.95</td>
<td>0.79</td>
<td>0.3175</td>
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<tr>
<td>1B</td>
<td>0.382</td>
<td>0.95</td>
<td>0.79</td>
<td>0.3175</td>
</tr>
</tbody>
</table>

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).
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 cm²/g, respectively.

Surface area and exponential corrections permit application to larger particle sizes (0.45 to 1.44 cm²/g) used in treatment systems.
New Module For AMDTreat — PHREEQC Coupled Kinetic Models of Limestone Dissolution & Fe(II) Oxidation

Rate models for calcite dissolution, CO₂ outgassing and O₂ ingassing, and Fell oxidation are combined to evaluate possible reactions in passive treatment systems.

Can simulate limestone treatment followed by gas exchange and Fell 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.

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

limestone+fellseq.exe
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+Fellseq_PineFor151212.exe
LS+Fellseq_kinetics.se - Shortcut.ink
PineForest_Field_151212t.xlsx - Shortcut.ink
Sequential steps: Pre-treatment with caustic and/or peroxide and, for each subsequent step, variable detention times, adjustable CO₂ outgassing rates, limestone surface area, temperature, and FeIII.

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

<table>
<thead>
<tr>
<th>Step</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pond</td>
</tr>
<tr>
<td>2</td>
<td>Aeration</td>
</tr>
<tr>
<td>3</td>
<td>Pond</td>
</tr>
<tr>
<td>4</td>
<td>Aeration</td>
</tr>
<tr>
<td>5</td>
<td>Pond</td>
</tr>
<tr>
<td>6</td>
<td>Riprap</td>
</tr>
<tr>
<td>7</td>
<td>Wetland</td>
</tr>
<tr>
<td>8</td>
<td>Riprap</td>
</tr>
<tr>
<td>9</td>
<td>Wetland</td>
</tr>
</tbody>
</table>
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](https://water.usgs.gov/software/lists/geochemical)

✔ FY2018 Incorporation of PHREEQC treatment simulations with AMDTreat to be released by OSMRE:

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?


Plummer LN, Wigley ML, Parkhurst DL (1978) The kinetics of calcite dissolution in CO$_2$-water systems at 5$^\circ$ to 60$^\circ$C and 0.0 to 1.0 atm CO$_2$. American Journal of Science 278, 179-216.


Solubilities of Metal Hydroxides

METALS HAVE LOW SOLUBILITY 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

Dissolved Fe is predominantly Fe$^{II}$

Solid phase
Fe$^{II}$(OH)$_2$
Fe$^{II}$(OH)$_2$

Fe$^{III}$(OH)$_3$

Fe$^{III}$(OH)$_3$

Fe$^{III}$(OH)$_3$

Fe$^{III}$(OH)$_3$

Fe$^{III}$OOH

Aqueous phase
Temp = 25°C
pSO$_4^{TOT}$ = 2.3
pK$^+$ = 4.30
pCO$_2$ = 2.0
SORPTION OF CATIONS ON “HFO”

PERCENT DISSOLVED

PERCENT ADSORBED

pH

3 4 5 6 7 8 9 10 11

3 4 5 6 7 8 9 10 11

Sr+2 Ba+2 Mn+2 Ni+2 Co2 Cu+2 Zn+2 Cd+2 CrIII Pb+2

3 4 5 6 7 8 9 10 11

100 90 80 70 60 50 40 30 20 10 0

100 90 80 70 60 50 40 30 20 10 0
SORPTION OF ANIONS ON “HFO”

PERCENT DISSOLVED versus pH

PERCENT ADSORBED versus pH

Anions:
- SO₄²⁻
- CrO₄²⁻
- PO₄³⁻
- AsO₄³⁻
- SeO₃²⁻