

# USER-FRIENDLY GEOCHEMICAL MODELING TO EVALUATE PASSIVE AND ACTIVE TREATMENT FOR COAL-MINE DISCHARGES

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## Extended Abstract:

User-friendly aqueous geochemical tools were developed to simulate changes in water quality resulting from passive and active treatment of coal-mine drainage. The interactive geochemical tools utilize PHREEQC equilibrium (aqueous and surface speciation) and kinetics models (Parkhurst and Appelo, 2013) for gas exchange; iron and manganese oxidation and precipitation; limestone dissolution; and organic carbon oxidation combined with reduction of nitrate, sulfate, and ferric iron. Reactions with synthetic caustic chemicals (CaO, Ca(OH)<sub>2</sub>, NaOH, Na<sub>2</sub>CO<sub>3</sub>) or oxidizing agents (H<sub>2</sub>O<sub>2</sub>) also may be simulated separately or combined with sequential kinetic steps. A user interface facilitates input of initial water chemistry data and adjustment of kinetic variables. Graphical and tabular output indicates the changes in pH, metals and other solute concentrations, total dissolved solids, and specific conductance of treated effluent plus the cumulative quantity of precipitated solids as a function of detention time or the amount of caustic agent added. By adjusting kinetic variables or chemical dosing, the effects of independent or sequential treatment steps that have different detention time (volume/flow rate), aeration rate, quantities of reactive solids, and temperature can be simulated for a specified influent quality. Thus, various passive and/or active treatment strategies can be identified to achieve the desired effluent quality. Then, AMDTreat (e.g. Cravotta et al., 2015) can be used to evaluate the potential cost-effectiveness of treatments considering available land area, equipment, and funding for construction and operation.

The kinetics tool for atmospheric exchange is coupled with those for iron and manganese oxidation. A first-order rate law describes CO<sub>2</sub> outgassing and O<sub>2</sub> ingassing, which affect the pH and rates of iron and manganese oxidation (e.g. Cravotta, 2015). Different aeration technologies may be considered for which gas-exchange rate constants are assigned. The iron and manganese oxidation kinetics tools utilize pH-dependent rate models that consider the concentrations of dissolved O<sub>2</sub> (DO) and Fe<sup>II</sup> or Mn<sup>II</sup> plus catalysis by surfaces (heterogeneous oxidation) and microbes (biotic oxidation) (Stumm and Lee, 1961; Tamura et al., 1976; Davies and Morgan, 1989; Vries et al., 2017). Microbial catalysis rates are adjusted for pH, DO,

temperature, and the concentration of iron oxidizing bacteria (FeOB). The acidophilic FeOB rate increases as pH decreases from 5 to 2.8 and exceeds the abiotic Fe<sup>II</sup> oxidation rate at low pH (e.g. Kirby et al., 1999), whereas the neutrophilic FeOB rate generally does not exceed the abiotic rate, except at optimum conditions of near-neutral pH (6.5-7.5) and low DO (1.9-2.2 mg/L), where the FeOB rate can be 20 times the abiotic heterogeneous rate (Eggerichs et al., 2014). The Arrhenius equation is used to adjust the Fe<sup>II</sup> and Mn<sup>II</sup> oxidation rate constants from the reference temperature of 20 °C to other temperatures (Appelo and Postma, 2005).

The heterogeneous oxidation rate models incorporate pH-dependent adsorption of Fe<sup>II</sup> and Mn<sup>II</sup> by hydrous ferric oxide (HFO) (Dzombak and Morel, 1990) and Mn<sup>II</sup> by hydrous manganese oxide (HMO) (Tonkin et al., 2004). Increasing the available mass (surface area) of HFO or HMO, for example the recirculation of HFO solids within a reaction tank or the accumulation of HMO on limestone particles in a manganese removal bed, increases potential for attenuation of dissolved metal concentrations at a given pH.

The limestone kinetics tool simulates dissolution (and precipitation) of calcite in passive systems, including anoxic or oxic limestone beds, manganese removal beds, vertical flow pond (VFP), and compost mixes. The rate expression considers solution chemistry, mainly pH and partial pressure of CO<sub>2</sub>, plus the surface area and purity of limestone particles (Plummer et al., 1978; Appelo et al., 1998). Limestone particle surface area and volume are estimated assuming an ellipsoid shape for various aggregate sizes (e.g. Cravotta et al., 2008; Pennsylvania Department of Environmental Protection, 2000).

Reactions within a compost layer of a VFP or a biochemical reactor are simulated by the dissolution of limestone fines combined with the oxidation of organic carbon by DO, nitrate, and sulfate. A user specifies the volumetric fractions of organic material and limestone and the size of limestone particles. Aqueous sulfide produced from the reduction of sulfate by organic carbon will precipitate as FeS or adsorb to HFO. To simulate the reduction of Fe<sup>III</sup> in the compost layer, a kinetics expression couples the rates of oxidation of the adsorbed sulfide and the reductive dissolution of HFO (e.g. dos Santos Alfonso and Stumm, 1992; Peiffer et al., 1992; Poulton, 2003).

The presentation demonstrates the model to evaluate changes in water quality that may result from commonly used treatment steps for acidic or alkaline influent and describes associated implications for treatment system design and optimization. Figures 1 and 2 give examples of user input and model output, and Table 1 shows possible sizing calculations.

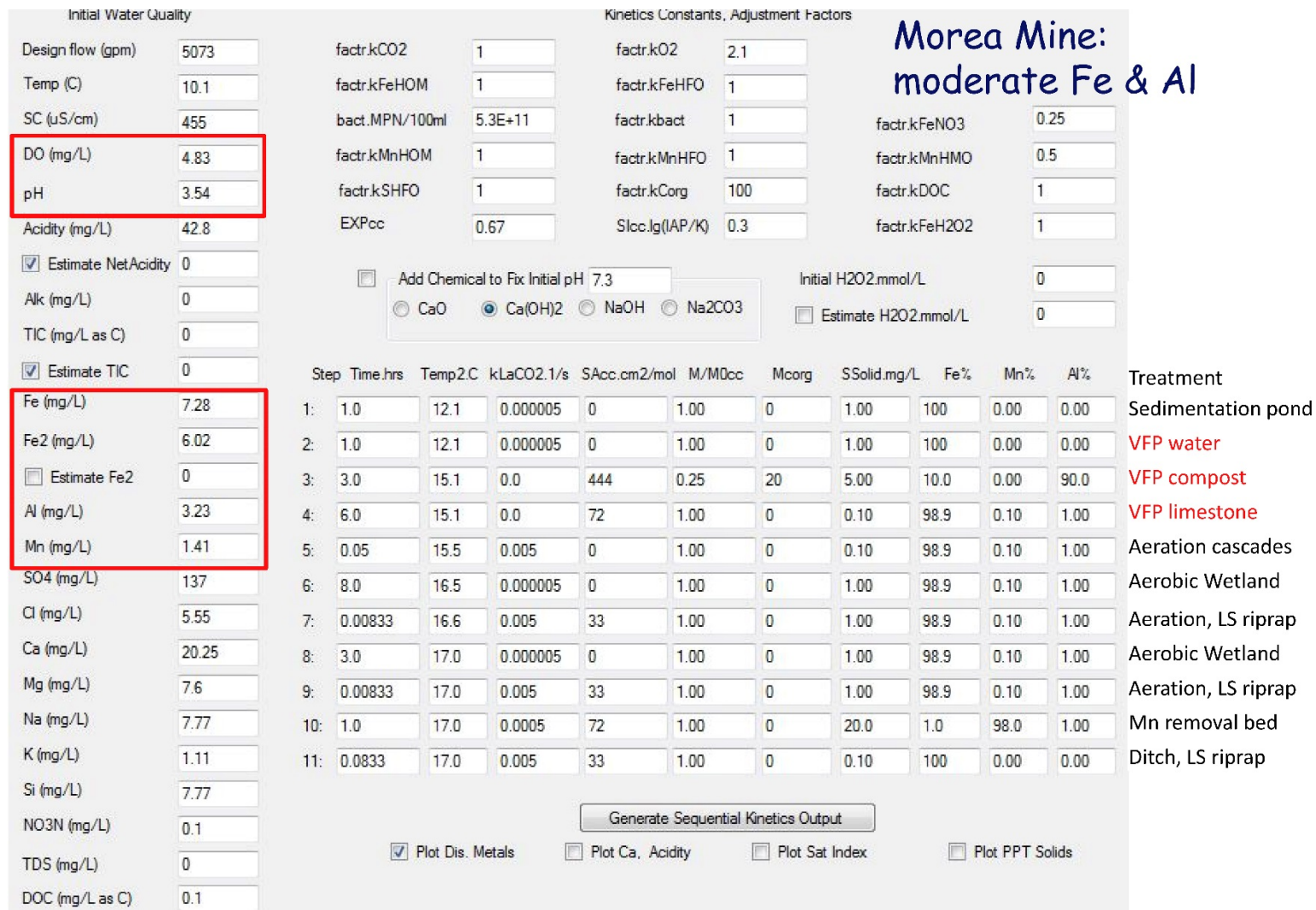


Figure 1: User interface (UI) for simulation of sequential passive treatment of net-acidic coal mine discharge through (1) sedimentation pond; (2-4) vertical flow pond (VFP); (6) aerobic pond; (8) aerobic wetlands; and (10) manganese removal bed with intermediate aeration steps (5, 7, 9, 11). Water-quality results of treatment are shown in Figure 2. Detention times are used to estimate approximate size of treatment system in Table 1.

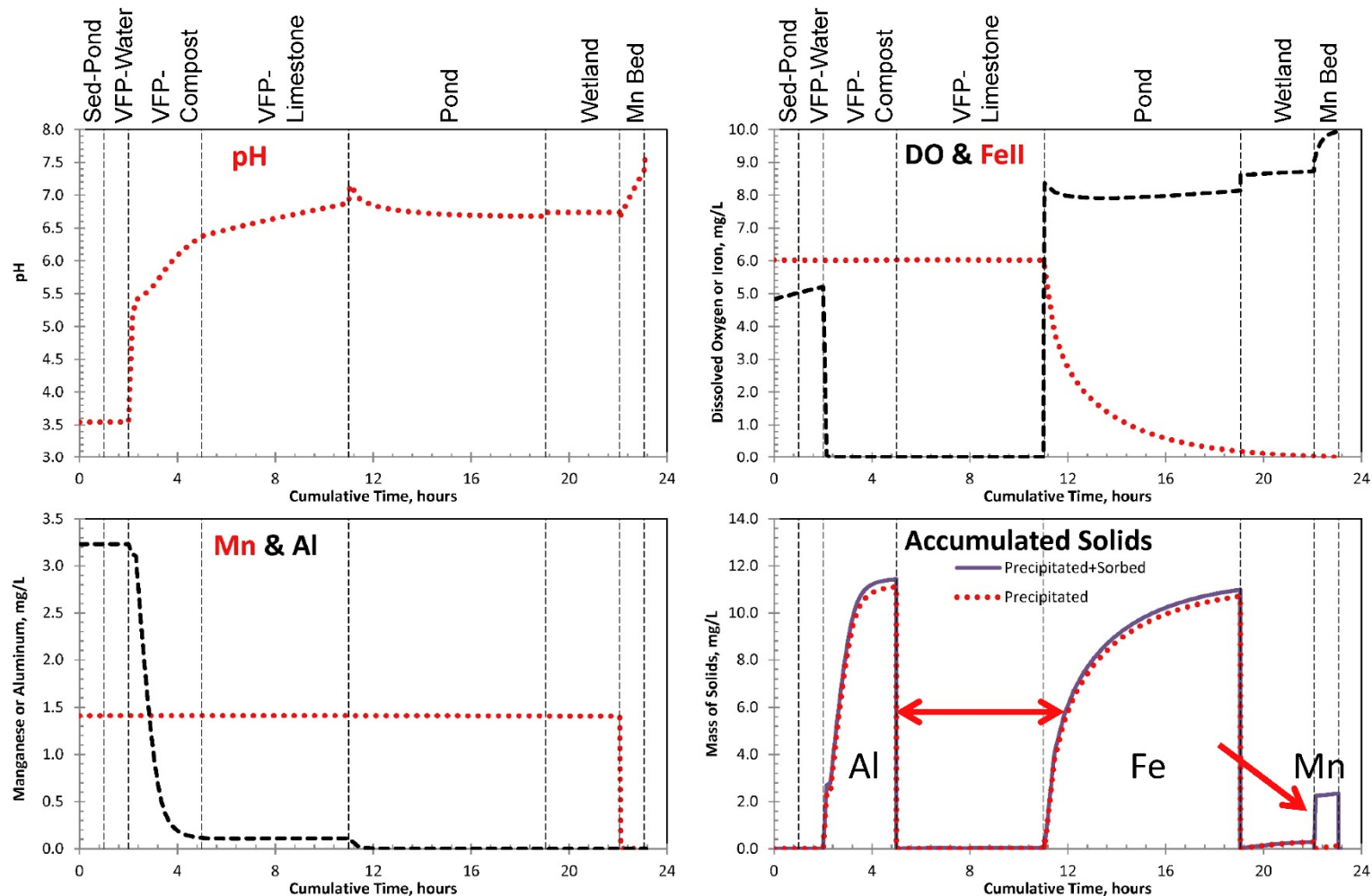


Figure 2: Results of PHREEQC kinetics model for passive treatment of coal-mine drainage as a function of the cumulative detention time for 11 numbered sequential steps (Fig. 1, Table 1): (1) 4-ft deep sediment pond; (2) 2-ft deep VFP water layer, (3) 2-ft thick VFP compost layer composed of 25% limestone fines and 75% organic matter having 45% porosity, (4) 4-ft thick VFP limestone layer having 45% porosity; (6) 4-ft deep aerobic pond; (8) 1-ft deep aerobic wetlands; and (10) 0.5-ft deep manganese removal bed, with aeration steps (5, 7, 9, 11) between major treatment steps.

Table 1. Example treatment system sizing calculations based on detention time estimates used in PHREEQC kinetics model

Step	Treatment	flow rate, ft <sup>3</sup> /s	detention time, sec	detention time, hr	depth, ft	porosity	volume, ft <sup>3</sup>	area of water surface, ft <sup>2</sup>	area of water surface, acres	lime-stone particle size, AASHTO	lime-stone particle size, cm <sup>2</sup> /mol	CaCO <sub>3</sub> fraction in bulk, M/M <sub>0cc</sub>	lime-stone mass, tons	compost organics mass, tons
1	Sedimentation pond	11.30	3600	1.00	4.00	1.00	40697	10174	0.23			1.00	0	0
2	VFP water	11.30	3600	1.00	2.00	1.00	40697					1.00	0	0
3	VFP compost	11.30	10800	3.00	2.00	0.45	271310			8	444	0.25	3086	6244
4	VFP limestone	11.30	21600	6.00	4.00	0.45	542620	106828	2.45	3	72	1.00	24686	0
5	Aeration	11.30	180	0.05	0.10	1.00	2035	20348	0.47			1.00	0	0
6	Oxidation Pond	11.30	28800	8.00	4.00	1.00	325572	81393	1.87			1.00	0	0
7	Aeration	11.30	30	0.01	0.10	0.45	753	7533	0.17	R-3	33	1.00	34	0
8	Aerobic Wetland	11.30	10800	3.00	1.00	1.00	122090	122090	2.80			1.00	0	0
9	Aeration	11.30	30	0.01	0.10	0.45	753	7533	0.17	R-3	33	1.00	34	0
10	Mn removal bed	11.30	3600	1.00	0.50	0.45	90437	180873	4.15	3	72	1.00	4114	0
11	Ditch	11.30	300	0.08	0.50	0.45	7533	15067	0.35	R-3	33	1.00	343	0
<b>1 to 11</b>	<b>Total:</b>			<b>23.15</b>	<b>18.30</b>			<b>551840</b>	<b>12.66</b>				<b>32298</b>	<b>6244</b>

*Volume is computed as the product of flow rate and detention time. Design flow rate of 5073 gal/min = 11.30 ft<sup>3</sup>/s.*

*Area is computed as the volume divided by depth; for the VFP, volumes and depths for each of the three steps are summed before computing area.*

*Masses of limestone and compost are computed as the product of their respective volume and bulk density.*

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