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TECHNICAL ARTICLE

AMDTreat 5.0+ with PHREEQC Titration Module to Compute Caustic Chemical Quantity, Effluent Quality, and Sludge Volume

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Abstract Alkaline chemicals are commonly added to discharges from coal mines to increase pH and decrease concentrations of acidity and dissolved aluminum, iron, manganese, and associated metals. The annual cost of chemical treatment depends on the type and quantities of chemicals added and sludge produced. The AMDTreat computer program, initially developed in 2003, is widely used to compute such costs on the basis of the user-specified flow rate and water quality data for the untreated AMD. Although AMDTreat can use results of empirical titration of net-acidic or net-alkaline effluent with caustic chemicals to accurately estimate costs for treatment, such empirical data are rarely available. A titration simulation module using the geochemical program PHREEQC has been incorporated with AMDTreat 5.0+ to improve the capability of AMDTreat to estimate: (1) the quantity and cost of caustic chemicals to attain a target pH, (2) the chemical composition of the treated effluent, and (3) the volume of sludge produced by the treatment. The simulated titration results for selected caustic chemicals (NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, or NH_3) without aeration or with pre-aeration can be compared with or used in place of empirical titration data to estimate chemical quantities, treated effluent composition, sludge volume (precipitated metals plus unreacted chemical), and associated treatment costs. This paper describes the development, evaluation, and potential utilization of the PHREEQC titration module with the new AMDTreat 5.0+ computer program available at http://www.amd.osmre.gov/.

Keywords Active treatment · Chemical costs · Titration · Geochemical model · Simulation · pH · Metals

Introduction

Since its release in 2003 by the U.S. Office of Surface Mining, Reclamation, and Enforcement (OSM), the AMDTreat computer program has been widely used by mining regulatory authorities, industry, and watershed groups in the USA and other countries to estimate costs for treatment of acid mine drainage (AMD) (McKenzie 2005). AMD, as used here, includes mine water, whether acidic or alkaline, that is enriched in metals and requires treatment. AMDTreat uses site-specific information to estimate the costs to construct and operate a variety of active or passive treatment facilities specified by the user. The annual operation cost of the specified treatment depends on the

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flow rate and chemistry of the untreated AMD, the physical and chemical characteristics of the sludge produced, and the types, quantities, and efficiency of any treatment chemicals used. AMDTreat permits a user to consider the effects of these factors and numerous other environmental and engineering variables for the evaluation of AMD treatment strategies. As with prior versions of AMDTreat, the main purpose of AMDTreat 5.0+ is to facilitate standardized, present-cost estimates of the total capital costs for design and construction of an AMD treatment facility plus the long-term costs of annual operation and maintenance (McKenzie 2005). The unit cost data for construction, materials, chemicals, and sludge removal have not been changed for AMDTreat 5.0+; a user still has the option of modifying the unit values with site-specific information.

Purpose and Scope

To improve on the capabilities of AMDTreat, a standardized geochemical model was developed as an additional module to simulate chemical reactions resulting from titration (chemical dosing) of acidic or alkaline, metal-rich waters. The module considers the use of a variety of caustic chemicals and other treatment steps such as pre-aeration. This paper describes the development and potential utilization of this new geochemical titration module for the AMDTreat 5.0+ program (available at http://www.amd.osmre.gov) to estimate: (1) the quantity and cost of selected caustic chemicals (NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, or NH_3) to attain a target pH of 6–11, (2) the concentrations of dissolved metals, major ions, including sulfate, bicarbonate, iron (Fe), aluminum (Al), manganese (Mn), magnesium (Mg), calcium (Ca), sodium (Na), and total dissolved solids (TDS) in the treated effluent, and (3) the volume of sludge and associated cost for its disposal. Empirical and simulated titration data for six different test cases are presented as example applications of this program to estimate treated water quality, chemical usage, and sludge production. With the associated estimates of costs to attain water-quality goals, strategies for site-specific AMD treatment can be optimized based on environmental and economic considerations. Although use of the titration module does not require expertise in geochemistry, an understanding of chemical reactions that take place during AMD treatment and the limitations and assumptions of the modeling approach are needed to understand the results of the program output.

Treatment of AMD

AMD is commonly treated to neutralize acidity, increase pH and alkalinity, and promote removal of dissolved Al, Fe, and Mn and other contaminants of concern. Conventional treatment to decrease the concentrations of dissolved metals in AMD at active mining operations typically involves the addition of industrial strength alkaline (caustic) chemicals (Table 1) and aeration, possibly with the addition of polymers to facilitate the precipitation and settling of metal-rich (Al, Fe, Mn) hydroxide and possibly sulfate and carbonate phases (solids) (Skousen et al. 1993, 2000; U.S. Environmental Protection Agency 1983). Concentrations of trace contaminants (Zn, Cd, Cu, Pb, Cr, As, Se, and others) in the effluent may also be attenuated during such treatment by adsorption and coprecipitation reactions with Al, Fe, and Mn oxide, hydroxide, and other compounds (e.g. Cravotta 2008; Kairies et al. 2005; Webster et al. 1998). After treatment, the near-neutral to slightly alkaline effluent (pH 6–9) may be discharged to the environment or used for industrial water supply (Curtright and Giglio 2012; Veil et al. 2003). The metal-rich precipitate, or sludge, that accumulates at the treatment facility may be disposed of in landfills or old mines or processed for beneficial uses (Hedin 2002; Sibrell et al. 2009).

Generally, with the addition of a caustic chemical (NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, or NH_3), the solution pH will increase and solutes may reach saturation with respect to various solid phases. As the solids precipitate, the associated solute concentrations will decrease. For example, the precipitation of $Al(OH)_3$, $Fe(OH)_3$, and MnO_2 at circumneutral pH (6–8) can yield effluents containing less than 0.1 mg/L of concentrations of Al and oxidized forms of iron (Fe^{III}) and manganese (Mn^{III}, Mn^{IV}) at equilibrium with the respective solids (Fig. 1). However, alkaline pH (8.5–10) may be required to precipitate manganous hydroxide ($Mn(OH)_2$), ferrous hydroxide ($Fe(OH)_2$), and/or to accelerate the oxidation of FeII and precipitate $Fe(OH)_3$ (Fig. 1). Thus, because Fe^{II} and Mn^{II} are predominant contaminants in AMD from underground coal mines (Cravotta 2008; Rose and Cravotta 1998), treatment with caustic chemicals to achieve pH values greater than 8.5 is commonly practiced at active coal-mining operations. These mines commonly have large or highly variable discharge volumes and limited area for treatment, which necessitate rapid precipitation of metals and settling of solids.

Cost savings may be achieved if chemical dosing is optimized to achieve the ideal pH to remove target metals while minimizing the removal of other constituents. Specifically, dissolved sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and CO_2 tend to be abundant in AMD from coal mines (Cravotta 2008). The inadvertent precipitation of these constituents, including dissolved CO_2 as carbonate, can consume substantial quantities of treatment chemicals and increase the quantity of sludge produced. Furthermore, some caustic chemicals may not dissolve

Table 1 Caustic chemical compounds used for neutralization of coal mine drainage

Common name	Formula	Unit weight (g/mol)	Acid equivalents[a]	$CaCO_3$ factor[b]	Titration units factor[c]	Mixing efficiency factor[d]	Purity factor	Cost per unit[e]	Sludge density[f]
50 % liquid caustic[g]	NaOH	39.998	1	1,440	–	1.0	0.99	$1.59/gal	0.02–0.05
20 % liquid caustic[h]	NaOH	39.998	1	3,276	0.164	1.0	0.99	$0.70/gal	0.02–0.05
Caustic soda solid	NaOH	39.998	1	0.80	–	1.0	0.99	$0.36/lb	0.02–0.05
Hydrated lime	$Ca(OH)_2$	74.096	2	0.74	0.618	0.8	0.96	$0.10/lb	0.05–0.10
Pebble quicklime	CaO	44.011	2	0.44	0.468	0.7	0.94	$0.11/lb	0.05–0.10
Ammonia	NH_3	17.030	1	0.34	0.142	0.9	0.99	$0.50/lb	0.02–0.05
Soda ash	Na_2CO_3	105.99	2	1.06	0.884	0.6	0.99	$0.14/lb	0.02–0.05
Baking soda	$NaHCO_3$	84.009	1	1.68	–	0.9	0.99	$0.20/lb	0.02–0.05
Limestone	$CaCO_3$	100.09	2	1.00	–	0.3	0.85	$0.011/lb	0.05–0.10

[a] Equivalents (eq/mol) are the moles of acid (H^+) that can be neutralized by each mole of the chemical compound

[b] $CaCO_3$ conversion factor is the equivalent weight of a chemical needed for neutralization of a weight unit (g/g) of acidity expressed as $CaCO_3$. For example, this factor may be multiplied by the annual acid load expressed as metric tons (t)/year $CaCO_3$ to obtain a crude estimate of the annual amount of solid chemical needed as t/year. For liquid caustic, the conversion factor indicates liters of solution needed to neutralize 1 t of acid as $CaCO_3$

[c] Titration units factor is used to convert the reagent quantity in moles of solid chemical per liter of water to required AMDTreat units in pounds of reagent per gallon of water treated (all reagents except caustic soda) or gallons of 20 % caustic soda per gallon of water treated

[d] Efficiency factor is an empirical estimate of the relative effectiveness of the chemical for neutralizing acidity on the basis of its ease of mixing and dissolution. Values are default numbers in AMDTreat. The efficiency factor can be used with the $CaCO_3$ conversion factor and the purity factor to obtain an improved estimate of the quantities of various caustic chemicals needed for treatment. For example, to neutralize 100 t of acid/year as $CaCO_3$, then 96 t of industrial grade hydrated lime ($Ca(OH)_2$) would be needed ($96 = 100 \times 0.74/0.8/0.96$), of which 20 %, or 19.2 t, remains undissolved and combines with precipitate as sludge

[e] Unit costs are listed for "non-bulk" quantities; values and units are the defaults used in AMDTreat, though a tool is provided in AMDTreat to convert to and from metric units. Cost for solid and 50 % saturated solution of NaOH were computed from default cost of 20 % liquid caustic

[f] Although the default value in AMD Treat is 5 weight % solids (50 g solids/1,000 g solution), iron-rich sludge produced by reaction with caustic chemicals can have a wide range of solids concentrations. The solids concentration (proportion solids) is used to estimate sludge volume and associated sludge disposal cost on a unit volume basis. Generally, Ca-based reagents produce denser sludge than Na- or NH_3-based reagents

[g] Industrial grade "50 % liquid caustic" is 50 % of saturation and contains 555 g NaOH in 1 L (13.9 N NaOH)

[h] The actual concentration of industrial grade "20 % liquid caustic" depends on the source. To relate solid and aqueous NaOH quantities, the assumed 20 % solution concentration is 244 g/L (6.1 N), with a density of 1,244 g/L

completely, which reduces chemical treatment efficiency. The unreacted chemicals become components of the sludge.

Different caustic compounds can yield different reaction products. For example, the addition of lime (CaO and $Ca(OH)_2$) to SO_4-laden AMD may lead to the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), plus some of the added lime may not dissolve. Likewise, as pH is increased to values greater than 9 by the addition of lime or other caustic agents, compounds such as pyrochroite ($Mg(OH)_2$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), and Ca–Mg-carbonates may precipitate (Loop et al. 2004; Payne and Yeates 1970). Carbonate minerals, such as calcite ($CaCO_3$), generally tend to precipitate at elevated concentrations of dissolved CO_2 because the reaction of hydroxyl (OH^-) with dissolved CO_2 produces bicarbonate ($CO_2 + OH^- = HCO_3^-$). The production of HCO_3^- consumes caustic chemical and tends to maintain pH near neutral. Through the formation of carbonate species and compounds, dissolved CO_2 depresses pH and, consequently, can decrease the rates of oxidation of dissolved Fe^{II} and Mn^{II} (Geroni et al. 2012; Kirby et al. 2009). Aeration of the untreated AMD before dosing with caustic chemicals can increase pH and decrease chemical usage by facilitating the outgassing of dissolved CO_2 (Jageman et al. 1988; Means and Hilton 2004).

The amount of caustic chemicals required to neutralize acidic water after CO_2 outgassing can be estimated from the measured "hot" acidity or the computed "net" acidity, expressed as $CaCO_3$ equivalents (Kirby and Cravotta 2005; Skousen et al. 2000). This estimate of caustic equivalents (Table 1) is the default that has been used by AMDTreat and is generally appropriate for metal-laden, low-pH solutions. However, on the basis of the hot acidity or net

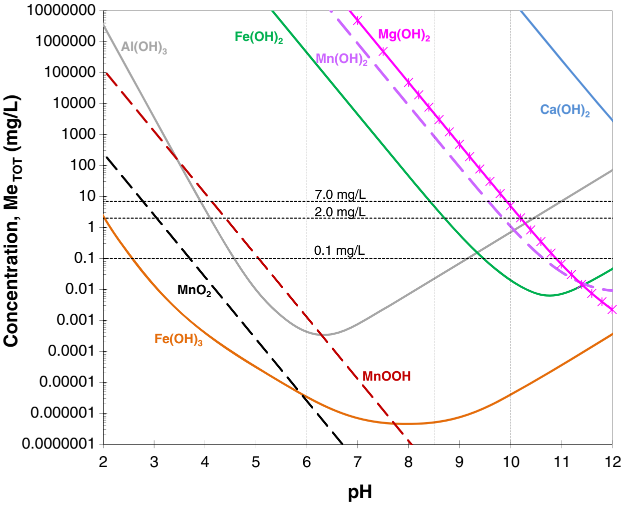

Fig. 1 Approximate solubilities of hydrous oxide (hydroxide) compounds of iron (Fe^{II} or Fe^{III}), manganese (Mn^{II}, Mn^{III}, or Mn^{IV}), aluminum, calcium, and magnesium as a function of pH at 25 °C. Computations used thermodynamic data from Ball and Nordstrom (1991) and Wolery (1992), assumed activity equals concentration, and considered only pH and formation of hydroxyl species; complexing by SO_4^{2-}, which is not considered, could increase the total concentration of dissolved Fe^{3+} and Al^{3+} species at equilibrium with the solids (Cravotta 2008)

acidity, AMDTreat *incorrectly* indicates that no caustic chemicals and associated infrastructure will be needed to treat net-alkaline, metal-laden AMD or AMD containing substantial quantities of dissolved CO_2, Mg, Ca, or SO_4. In practice, net-alkaline AMD is commonly treated with caustic chemicals to increase the pH to alkaline values and rapidly decrease the concentrations of dissolved Mn^{II} and Fe^{II}. Additional reactions with dissolved CO_2, Mg, Ca, or SO_4, which are not considered in the measured hot acidity or computed net acidity, can account for a large fraction of the chemical consumption and associated treatment costs for such practices involving a high treatment pH (Kirby and Cravotta 2005; Means and Hilton 2004). Furthermore, because of differences in the solubilities of Fe^{III} and Fe^{II} compounds and $Mn^{III–IV}$ and Mn^{II} compounds as a function of pH (Fig. 1), the actual chemical requirement for treating a net-acidic (or a net-alkaline) AMD may differ for oxidized and unoxidized solutions. Lastly, the basic AMDTreat program incorrectly assumes, by default, that all of the dissolved Fe, Mn, and Al will precipitate from the treated effluent, forming sludge. This assumption does not consider equilibrium solubilities with respect to commonly formed metal hydroxides, and does not provide information on important water-quality characteristics of the treated effluent, such as final pH, alkalinity, or concentrations of residual metals, major ions, and total dissolved solids.

Precise estimates of the quantity of a caustic chemical needed to attain a target pH plus the corresponding treated effluent composition and sludge volume can be determined with empirical titration (dosing) of the mine effluent (Means and Hilton 2004). Although AMDTreat can use such empirical titration data to accurately compute caustic chemical requirements and associated annual chemical costs for full-scale treatment of net-acidic or net-alkaline mine drainage, such data are rarely available. As an alternative to empirical titration, geochemical models may be used to evaluate the potential for oxidation, aqueous speciation, and precipitation reactions that determine the effluent composition produced by the addition of various quantities of caustic chemical(s).

Methods of Data Collection and Computer Programming

Empirical Titration and Chemical Analysis of AMD

Empirical titrations of acidic, metal-laden effluent samples from six bituminous coal mines in western Pennsylvania were conducted in 2003 and 2011 to document the effects of chemical treatment to different pH values on the concentrations of dissolved metals and major ions. Titrations were conducted in the field using a Hach Digital Titrator® with a cartridge that had been filled with high-strength caustic soda (6.1 N NaOH = "20 %" NaOH) obtained from the treatment storage tank on site. Reagent grade 1.6 N NaOH was used for empirical titration at the Nittanny mine. For Cal Pike, Ike, Millerstein, and Morris, the same NaOH solution was used for both the actual treatment and empirical titrations. However, for Manor and Nittanny, the empirical titration used NaOH while the actual treatment used quick lime (CaO). Initially, the raw water was titrated to a pH of ≈11. Subsequent titrations were conducted by quickly adding the volume of NaOH indicated to achieve various intermediate pH endpoints. At the endpoint of each titration to different pH values, the effluent sample was filtered (0.45 µm pore size) and preserved with HNO_3. Concentrations of dissolved major and trace elements (S, Si, Ca, Mg, Na, K, Fe, Mn, Al, Zn, Ni, Co, Cu) in the titrated subsamples and in the untreated and treated effluent at each facility were analyzed by inductively coupled plasma optical emission spectrometry (ICP–OES), with detection limits for Al, Fe, and Mn of 0.2, 0.02, and 0.02 mg/L, respectively. Additionally, the untreated and treated effluent at each facility were analyzed for major anions (SO_4^{2-}, Cl^-) by ion chromatography, plus alkalinity to a fixed endpoint pH of 4.5 and "hot peroxide" acidity (hot acidity) to a fixed endpoint pH of 8.3 (American Public Health Association 1998a, b). Although the quantity of chemical titrant, composition of effluent, and volume of precipitate were measured for the empirical titrations, the mineral and chemical compositions of the precipitated solids were not determined because these characteristics generally do not affect sludge disposal costs. Furthermore, although the empirical titrations demonstrated attenuation of numerous trace metals during NaOH addition, trace-metal removal was not considered in the AMDTreat program because the incidental removal of trace constituents along with Al, Fe, Mn, and associated major ions generally do not affect caustic chemical consumption or sludge production.

Programming of PHREEQC Titration Module for AMDTreat 5.0+

The new AMDTreat 5.0+ computer program was modified from AMDTreat 4.1c, written in the Visual FoxPro language (McKenzie 2005), by adding a titration simulation option using a version of the geochemical program PHREEQC (Charlton and Parkhurst 2011; Parkhurst and Appelo 1999, 2013) with the WATEQ4F thermodynamic data base (Ball and Nordstrom 1991). The general PHREEQC coding to “fix pH” by the addition of a computed quantity of a specified caustic chemical was adapted from example 7 of Parkhurst and Appelo (1999). The titration model was initially calibrated to yield results that approximately matched observed pH data and concentrations of Al, Fe, Mn, Mg, and SO_4 during the empirical titration of the Cal Pike AMD with NaOH (Cravotta et al. 2010a). After incorporating PHREEQC into a beta version of AMDTreat 5.0+, the titration model was refined to simulate the empirical titration results for the five other mine effluents, described later.

Although a wide variety of amorphous to crystalline phases may precipitate and accumulate in AMD environments and treatment facilities (e.g. Bigham et al. 1996; Bigham and Nordstrom 2000; Kairies et al. 2005; Loop et al. 2004; Zhu et al. 2012), only a subset of compounds has been programmed in AMDTreat 5.0+ to limit solute concentrations under equilibrium conditions (Table 2). Of various solids initially considered as potential solubility controls, a subset was identified that yielded concentrations of Al, Fe, Mn, Mg, and SO_4 that were similar to the measured concentrations (calibration) for the empirical titrations. Solids that reached equilibrium ($SI = 0$) near the pH at which solute concentrations began to decrease and that yielded concentrations approximately the same as measured values were “allowed” to precipitate in the titration simulations (Table 2, bold font). Such phases chosen as likely controls of Fe^{III}, Al, and $Mn^{III–IV}$ (amorphous $Fe(OH)_3$, basaluminite, boehmite, birnessite) during titrations are more soluble than excluded phases (goethite, gibbsite, and pyrolusite) and generally are understood to be precursors to the more crystalline solids. Additional hydroxide and carbonate minerals also were identified as possible controls of Fe^{II}, Mn^{II}, Mg, and Ca. Generally, solubility control of divalent cations by carbonates could be important for effluents with elevated concentrations of dissolved CO_2 or those treated with chemical compounds containing carbonate ($CaCO_3$, Na_2CO_3, or $NaHCO_3$). However, because of potential slow kinetics of carbonate mineral precipitation (e.g. Langmuir 1997), the carbonate phases were specified to precipitate only after becoming highly supersaturated ($SI > 2.5$). Consequently, as discussed later, the precipitation of carbonates from the solutions evaluated in this paper was avoided except where simulated treatment with Na_2CO_3 was considered.

For each of the caustic chemicals listed in Table 1, two end-member simulations with the PHREEQC titrations in AMDTreat 5.0+ were developed as options: (1) no gas exchange with the atmosphere or (2) limited gas exchange with the atmosphere. The former simulates the immediate addition of caustic chemical to fresh effluent that may contain little or no dissolved O_2 and a high concentration of dissolved CO_2, whereas the latter simulates pre-aeration of the effluent by forcing dissolved O_2 and CO_2 concentrations to equilibrium with the atmosphere before permitting oxidation reactions, mineral precipitation reactions, or the addition of caustic chemicals. After the effluent is saturated with O_2, oxidation of Fe^{II} and Mn^{II} is assumed to be spontaneous (not kinetically controlled); no gas exchange is permitted during chemical titration steps thereafter. Oxidation reactions involving O_2 and Fe^{II} or Mn^{II} typically are not instantaneous, but are kinetically limited (e.g. Stumm and Morgan 1996), so simulation of initial gas exchange and equilibration with the atmosphere may more accurately describe pre-aeration to outgas CO_2, combined with the addition of a strong oxidizing agent, as explained later.

Water-Quality Input Screen for AMDTreat 5.0+

To incorporate the titration simulations, the Water-Quality Input, Chemical Cost, and Sludge Removal screens of the AMDTreat user interface were modified to add new data input and output fields (see the images of these screens as supplemental figures in the on-line version of this paper, which can be downloaded for free by all subscribers). The water-quality input screen of AMDTreat 5.0+ requires a user to enter measured or estimated values for flow rate, and concentrations of Fe, Al, Mn, pH, alkalinity, acidity, sulfate, and DO plus optional data explained below. The input concentrations of Fe, Al, and Mn are assumed to be “dissolved,” which generally requires sample filtration ($\leq$0.45 µm pore size) before preservation and analysis. In order to activate the PHREEQC titration options in AMDTreat 5.0+, a user also must input values for the

Table 2 Mineral dissolution reactions and associated equilibrium constants (K) for PHREEQ model added to AMDTreat 5.0+; $Al(OH)_3$, $Fe(OH)_3$, and $Mn(OH)_2$ are amorphous

Solid phase name	Equilibrium reaction	Log K	Source[a]	AMDTreat[b]	SI Limit[c]
$Al(OH)_3$	$Al(OH)_3 + 3\ H^+ = Al^{3+} + 3\ H_2O$	10.80	1	Aloh3a	n.a.
Boehmite	$AlOOH + 3\ H^+ = Al^{3+} + 2\ H_2O$	9.44	1	Boehmite	0.0
Basaluminite	$Al_4(OH)_{10}SO_4 + 10\ H^+ = 4\ Al^{3+} + SO_4{}^{2-} + 10\ H_2O$	24.00	1	Basalumini	0.0
Portlandite	$Ca(OH)_2 + 2\ H^+ = Ca^{2+} + 2\ H_2O$	22.80	1	Portlandit	0.0
Calcite	$CaCO_3 + H^+ = Ca^{2+} + HCO_3{}^-$	1.85	1	Calcite	2.5
Dolomite	$CaMg(CO_3)_2 + 2\ H^+ = Ca^{2+} + Mg^{2+} + 2\ HCO_3{}^-$	3.57	1	Dolomite	n.a.
Gypsum	$CaSO_4{\cdot}2H_2O = Ca^{2+} + SO_4{}^{2-} + 2\ H_2O$	−4.58	1	Gypsum	0.0
Ettringite	$Ca_6Al_{2.02}(SO_4)_{2.79}(OH)_{12.48}{\cdot}26H_2O + 12.48\ H^+ = 6\ Ca^{2+} + 2.02\ Al^{3+} + 2.79\ SO_4{}^{2-} + 38.48\ H_2O$	61.82	4	Ettringite	0.0
Brucite	$Mg(OH)_2 + 2\ H^+ = Mg^{2+} + 2\ H_2O$	16.84	1	Brucite	0.0
Siderite	$FeCO_3 + H^+ = Fe^{2+} + HCO_3{}^-$	−0.12	1	Siderite	2.5
$Fe(OH)_2$	$Fe(OH)_2 + 2\ H^+ = Fe^{2+} + 2\ H_2O$	12.76	3	Feoh2a	0.0
$Fe(OH)_3$	$Fe(OH)_3 + 3\ H^+ = Fe^{3+} + 3\ H_2O$	4.89	1	Feoh3a	0.0
Schwertmannite	$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75} + 20.5\ H^+ = 8\ Fe^{3+} + 1.75\ SO_4{}^{2-} + 12.5\ H_2O$	18.00	5	Schwert175	n.a.
Jarosite	$KFe_3(SO_4)_2(OH)_6 + 6\ H^+ = K^+ + 3\ Fe^{3+} + 2\ SO_4{}^{2-} + 6\ H_2O$	12.51	5	Karosite	n.a.
Rhodochrosite	$MnCO_3 + H^+ = HCO_3{}^- + Mn^{2+}$	−0.06	1	Rhodochros	2.5
$Mn(OH)_2$	$Mn(OH)_2 + 2\ H^+ = Mn^{2+} + 2\ H_2O$	15.31	2	Mnoh2a	n.a.
Pyrochroite	$Mn(OH)_2 + 2\ H^+ = Mn^{2+} + 2\ H_2O$	15.20	1	Pyrochroit	0.0
Pyrolusite	$MnO_2 = 0.5\ Mn^{2+} + 0.5\ MnO_4{}^{2-}$	−17.82	1	Pyrolusite	n.a.
Birnessite	$Mn_8O_{14}{\cdot}5H_2O + 4\ H^+ = 3\ MnO_4{}^{2-} + 5\ Mn^{2+} + 7\ H_2O$	−85.55	2	Birnessite	0.0
Todorokite	$Mn_7O_{12}{\cdot}3H_2O + 16\ H^+ = MnO_4{}^{2-} + 6\ Mn^{3+} + 11\ H_2O$	−45.82	2	Todorokite	n.a.

[a] Sources of data for equilibrium constants (log K values) are "wateq" (1: Wateq4f; Ball and Nordstrom 1991), "llnl" (2: EQ3/6; Wolery 1992), and "sit" (3: thermochime; Duro et al. 2012) data bases provided with PHREEQC (Parkhurst and Appelo 2013). Supplemental data were added for ettringite (4: Myneni et al. 1998) and schwertmannite and jarosite (5: Bigham et al. 1996). Solid phase names in bold font were identified as phases that may control the concentrations of solutes during empirical titration of the Cal Pike effluent. Other phases listed such as amorphous $Al(OH)_3$ and schwertmannite could be important in different cases. To improve model fits with empirical data, log K values for boehmite and basaluminite were increased to values indicated to represent poorly crystalline, soluble Al phases

[b] AMDTreat heading is the abbreviation used in the heading of the AMDTreat PHREEQ titration matrix viewed at the Chemical Cost screen

[c] Mineral saturation index (SI) values are reported in the AMDTreat PHREEQ titration matrix for informational purposes. The SI limit is the specified SI value at which the solid is modeled to precipitate. Selected oxide, hydroxide, and sulfate minerals shown in bold font are assumed to precipitate upon reaching equilibrium (SI = 0); however, the carbonate minerals (calcite, siderite, rhodochrosite) are assumed to become highly supersaturated (SI = 2.5) before precipitating; where "n.a." is indicated, the solid is not modeled to precipitate

effluent temperature and concentrations of dissolved Ca, Mg, Na, and chloride (Fig. S1). The temperature and dissolved major-ion data are necessary for aqueous speciation calculations that use temperature-adjusted equibrium constants to estimate potential for solid phases to precipitate and remove dissolved constituents from the effluent. If input data for Ca, Mg, and Na, are not provided, AMDTreat 5.0+ has the functionality of AMDTreat 4.1c, without the PHREEQC titration options described below.

A user can input the values for acidity (hot acidity or net acidity), total inorganic carbon (TIC), and Fe^{II}, or select AMDTreat 5.0+ to estimate values for one or more of these parameters from other input data. As with prior versions of AMDTreat, net acidity (as mg/L of $CaCO_3$) is computed considering a negative contribution from alkalinity (American Public Health Association 1998b) and positive contributions from H^+ (pH) and concentrations of dissolved Fe^{III}, Fe^{II}, Mn, and Al in milligrams per liter (C^{III}_{Fe}, C^{II}_{Fe}, C_{Mn}, C_{Al}, respectively):

$$\text{Net acidity} = 50 \cdot \left(10^{(3-\text{pH})} + 3 \cdot C^{III}_{Fe}/55.85 + 2 \cdot C^{II}_{Fe}/55.85 + 2 \cdot C_{Mn}/54.94 + 3 \cdot C_{Al}/26.98\right) - \text{alkalinity} \tag{1}$$

Kirby and Cravotta (2005) showed that net acidity computed with Eq. (1) is comparable in value to the standard hot peroxide acidity method (American Public Health Association 1998b). They also showed that if the AMD is net acidic (net acidity >0; hot-peroxide acidity >0), the ultimate pH of oxidized samples will be less than 5.0 and additional alkalinity would be needed to maintain pH greater than or equal to 6.0. If the AMD is net alkaline (net acidity <0; hot-peroxide acidity <0), the ultimate pH of the oxidized AMD will be greater than or equal to 6.0. Means and Hilton (2004) and Kirby and Cravotta (2005) also showed that the cold acidity or treatment acidity (prior to complete oxidation and atmospheric equilibration) can be larger than the hot acidity because of contributions by dissolved CO_2 that are excluded from the hot acidity or calculated net acidity.

Some AMD has low pH and no measurable alkalinity, but may still have elevated concentrations of dissolved CO_2 that is included in treatment acidity. Therefore, AMDTreat 5.0+ uses the TIC concentration instead of alkalinity as input to PHREEQC for carbonate speciation calculations. If a user chooses, AMDTreat 5.0+ estimates the initial TIC from input values for alkalinity, pH, and temperature, assuming equilibrium among dissolved carbonate species in accordance with the following:

$$\mathrm{TIC\ (mg/L\,as\,C)} = (\mathrm{alkalinity}/50000)/\mathrm{K_1} \cdot [\mathrm{H^+}] \cdot \left(1 + \mathrm{K_1}/[\mathrm{H+}] + \mathrm{K_1} \cdot \mathrm{K_2}/[\mathrm{H^+}]^2\right) \tag{2}$$

where $[H^+] = 10^{-pH}$, and K_1 and K_2 are the temperature-adjusted dissociation constants for carbonate species (Ball and Nordstrom 1991). If alkalinity is 0 and/or pH is less than or equal to 3.9, TIC is assumed to be 0.0001 mol/L, which corresponds to an equilibrium partial pressure of CO_2 (P_{CO_2}) of $10^{-2.5}$ atm. (10 times greater than the normal atmosphere P_{CO_2} of $10^{-3.5}$ atm.). AMD samples from 140 coal mines in Pennsylvania had P_{CO_2} values from $10^{-2.5}$ to $10^{-0.5}$ atm. and were mostly undersaturated with carbonate minerals (Cravotta 2008).

Because the solubilities of Fe^{II} and Fe^{III} hydroxides differ by orders of magnitude (Fig. 1), the proportion of dissolved Fe that is Fe^{II} or Fe^{III} can be a major factor affecting Fe precipitation and the residual dissolved Fe concentration as pH is increased by the addition of a caustic chemical. The initial distribution of Fe^{II} and Fe^{III} species is estimated by PHREEQC using the input values for total dissolved iron (undefined redox state) and Fe^{II}. Thereafter, the PHREEQC titration simulations assume that any Fe^{II} is instantaneously oxidized to consume available DO (without and with pre-aeration, as explained below). However, because data on the initial concentration of Fe^{II} may not be available or because measurable DO and Fe^{II} may indicate redox disequilibrium, a user has the options to assume an initial low value for DO ($0.01 \leq$ DO mg/L $< 1/7$ total Fe) or to use AMDTreat 5.0+ to estimate initial Fe^{II} concentrations using the input values for total dissolved Fe and pH:

$$\mathrm{pH} > 2.6 \quad \mathrm{Fe^{III}} = \mathrm{Fe} \cdot 10^{(-1.40844 \cdot \mathrm{pH} + 3.675995)} \tag{3a}$$

$$\mathrm{pH} \leq 2.6 \quad \mathrm{Fe^{III}} = \mathrm{Fe} \cdot 0.9999) \tag{3b}$$

$$\mathrm{Fe^{II}} = \mathrm{Fe} - \mathrm{Fe^{III}} \tag{3c}$$

These computations yield a greater proportion of Fe^{III} to Fe^{II} at progressively lower pH, until pH < 2.6, where 99.99 % of the total dissolved Fe is assumed to be Fe^{III}. The computations are based on an approximation of the empirical relation between the ratio of Fe^{III}/total Fe as a function of pH of AMD from coal mines in Pennsylvania (Cravotta 2008). The increase in the ratio of Fe^{III}/total Fe with decreased pH is consistent with commonly observed Eh–pH relations of AMD and associated Fe mineral stabilities (Cravotta 2008, Fig. 2).

Chemical Cost Screen of AMDTreat 5.0+

The Chemical Cost screen of AMDTreat 5.0+ displays the new "PHREEQ" (as labeled) titration options (Fig. S2). When the chemical cost screen is first activated, a user can choose treatment by one of the five available caustic chemicals: A. hydrated lime ($Ca(OH)_2$); B. pebble quick lime (CaO); C. caustic soda (NaOH); D. anhydrous ammonia (NH_3); or E. soda ash ($NaCO_3$). If none of the titration choices is selected, the caustic quantity and cost will be computed on the basis of the entered flow and net acidity or hot acidity concentration, which is the method used by all previous versions of AMDTreat. The option labeled "Titration?" permits input of the empirical titration result. The option labeled "PHREEQ" simulates titration with the caustic chemical without interaction with the atmosphere, whereas the option labeled "PHREEQ with aeration" simulates pre-aeration and the subsequent addition of the caustic chemical. For the pre-aeration simulation, the effluent DO is instantaneously saturated, or equilibrated, to a partial pressure of O_2 equivalent to 21 vol% ($P_{O_2} = 10^{-0.678}$ atm.) prior to any oxidation reactions. However, because previous studies have indicated that aerated mine water can have persistent elevated concentrations of dissolved CO_2 compared to normal air (Cravotta 2007; Geroni et al. 2012; Kirby et al. 2009), the user has the option to choose among a range of values for atmospheric CO_2 ($P_{CO_2} = 10^{-1.5}$–$10^{-3.5}$ atm.) at "equilibrium" with the pre-aerated water. On the chemical cost screen, these values are listed as the negative of the log P_{CO_2}, or pCO_2, corresponding to 1.5–3.5, respectively, where the latter value is approximately the pCO_2 of normal air and the former is a factor of 100 greater than normal air.

For the PHREEQ titrations, the pH is programmed to increase from the initial rounded pH value in 0.5 unit increments to a maximum pH of 11.0. The corresponding amount of chemical needed to attain each incremental pH value, and the resulting solute concentrations, P_{CO_2}, and mineral saturation indices are computed. As the pH increases, selected mineral phases indicated in Table 2 (and

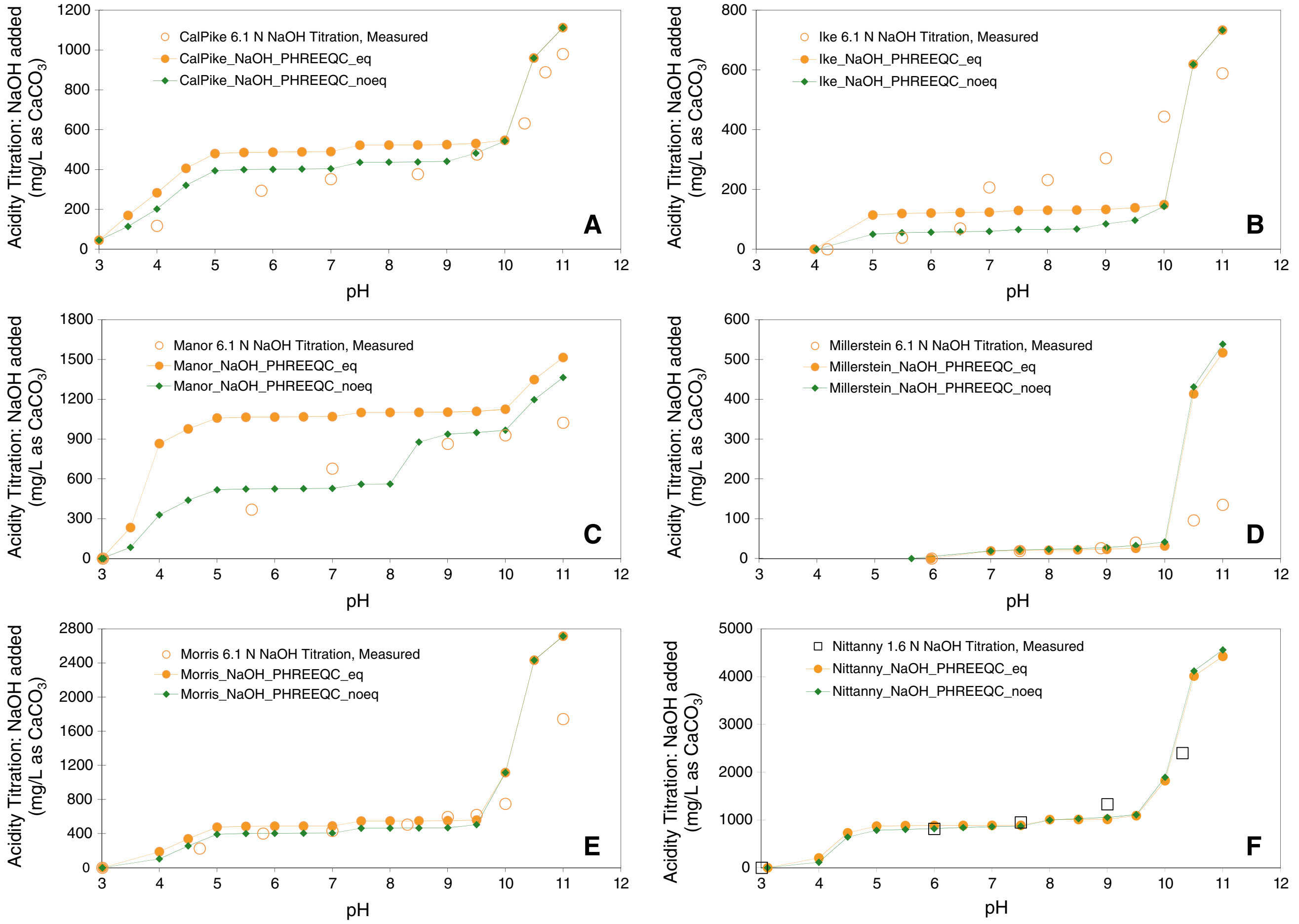

Fig. 2 Concentration of NaOH added and corresponding pH during empirical (measured) and simulated titration of effluent from six mines in Pennsylvania. Simulations use effluent composition data in Table 3 with AMDTreat 5.0+ for conditions with no gas exchange with atmosphere (PHREEQ_noeq) and with initial gas exchange with atmosphere (PHREEQ_eq)

described in more detail in "Results and Discussion" section) are programmed to precipitate on reaching saturation to maintain equilibrium (saturation index of 0). Because of apparent kinetic barriers to the precipitation of carbonate minerals during empirical titration, the carbonate minerals ($CaCO_3$, $CaMg(CO_3)_2$, $FeCO_3$, $MnCO_3$) were programmed to precipitate only after reaching a high degree of supersaturation (a saturation index of 2.5). The precipitation of solids decreases the concentrations of associated solutes in the effluent to the maximum at equilibrium with the specified solids at the treatment pH. The results of the selected PHREEQ titration simulation for a chosen chemical and aeration option are summarized in a matrix of values for pH and corresponding quantity of caustic titrant (in the traditional AMDTreat units, pounds chemical/gallon effluent or gallon chemical/gallon effluent), remaining solute concentration, TDS concentration (sum of solutes), estimated mass of precipitate, and saturation indices for various compounds (Fig. S3). The treatment water-quality matrix can be viewed on screen before selecting the final target pH for subsequent cost analysis or can be exported to a spreadsheet for evaluation outside of AMDTreat.

After review of the water-quality matrix, a user must accept a target pH in order for AMDTreat 5.0+ to compute relevant costs. Once accepted, the annual quantity and cost of the selected caustic chemical are displayed on the lower right corner of the chemical cost screen (Fig. S2). Although these are not used in capital cost computations, the user can copy and paste the titration amount indicated for the selected chemical and target pH as the "Titration?" input in the Capital Cost screen (Fig. S4) to document the anticipated annual chemical usage. Because the quantity of precipitated solids is used to estimate the sludge volume and costs, this estimate is automatically transferred to the Sludge Removal screen.

Sludge Removal Screen of AMDTreat 5.0+

Previous versions of AMDTreat assumed that all the initial Fe, Al, and Mn precipitated as hydroxides from the treated water and were the sole components of the sludge. By inference, the treated effluent would not contain any dissolved Fe, Al, or Mn, and the sludge would not contain unreacted caustic chemicals. If a PHREEQ titration option is not chosen, the previous assumption that all Fe, Al, and Mn are precipitated as $Fe(OH)_3$, $Al(OH)_3$, and $Mn(OH)_2$ is used as the default. However, the new AMDTreat 5.0+ estimates the sludge mass as the sum of: (1) unreacted caustic chemical based on the mixing efficiency factor, which varies greatly for different caustic agents (Table 1) plus (2) estimated precipitated solids computed by default or with the PHREEQ titration options.

The PHREEQ titrations estimate the mass of precipitated solids based on the simulated decrease in Fe, Al, Mn, Mg, and SO_4 concentrations at the selected pH. Various hydroxide, sulfate, hydroxysulfate, and carbonate minerals may precipitate removing solutes from the treated water. To compute the sludge mass produced by treatment, Fe, Al, Mn, and Mg are assumed to precipitate as $Fe(OH)_3$, $Al(OH)_3$, $Mn(OH)_2$, and $Mg(OH)_2$, respectively, and SO_4 as gypsum ($CaSO_4{\cdot}2H_2O$), which in addition to the unreacted solid chemicals, can make up a large fraction of the sludge (e.g. Means and Hilton 2004).

If either of the PHREEQ titration options for any of the caustic chemicals is selected *and* a target pH is accepted, the total concentration of precipitated solids is automatically transferred to the Sludge Removal screen (Fig. S5). The solids concentration data are then used for computing the sludge volume. The sludge volume and associated sludge removal costs are estimated by adding the mass of precipitated solids to the mass of unreacted chemical and adjusting for the specified sludge density (percent solids) displayed on the Sludge Removal screen. Users of AMDTreat may use default values or specify different values for chemical purity and mixing efficiency, sludge density, and unit costs to obtain a range of sludge cost estimates.

Results and Discussion: Empirical and Simulated Treatment of AMD

Comparison of Empirical and Simulated Effluent Compositions by Treatment with Caustic Soda

Empirical titration data for six mine discharge samples with a range of compositions (Table 3) were compared with results of treatment simulations by AMDTreat 5.0+ (Figs. 2, 3, 4). The comparison demonstrates the utility of AMDTreat 5.0+ "PHREEQ titration" options to simulate the pH and associated solute concentrations in treated effluent. The Cal Pike data for measured and simulated titrations were used for calibration of the PHREEQ titration model incorporated with AMDTreat 5.0+ and thus were emphasized in interim reports by Cravotta et al. (2010a, b). The untreated Cal Pike effluent had a pH of 2.8, acidity of 500 mg/L as $CaCO_3$, and elevated concentrations of dissolved constituents (Fe = 44.1 mg/L; Al = 34.1 mg/L; Mn = 48.1 mg/L; Mg = 122.2 mg/L; Ca = 105.2 mg/L; SO_4 = 1505 mg/L). In this paper, additional empirical titration data for the Ike, Manor, Millerstein, and Morris mine discharges (Means and Hilton 2004), plus the Nittanny mine discharge sampled in 2011, are used as validation data sets to demonstrate the effects of variable pH (2.8–6.0), acidity (16–982 mg/L as $CaCO_3$), and concentrations of Fe (0.75–326 mg/L), Al (0.25–128 mg/L), Mn (5.2–129 mg/L), Mg (57–652 mg/L), Ca (101–422 mg/L), and CO_2 (1.2–19.2 mg/L as TIC) on the simulated titration results. For all six cases, results of empirical titration with NaOH are compared with simulated results by AMDTreat 5.0+ for treatment with NaOH (Figs. 2, 3, 4). Later, the simulated results for titration of the Nittanny effluents with CaO are compared with results of actual treatment with CaO based on field samples of the treated effluent.

Titration of each of the six effluents with NaOH was simulated for scenarios assuming no gas exchange with the atmosphere (_noeq) and initial gas exchange and equilibration with the atmosphere (_eq) (Figs. 2, 3, 4). These simulations demonstrate the potential effects of pre-aeration and the addition of caustic chemicals on pH and remaining solute concentrations in effluent. Because the empirical titrations were "cold acidity" tests where atmospheric interactions were intentionally minimized, the caustic quantities and chemical compositions recorded for empirical tests were generally consistent with the simulations without aeration or gas exchange (Figs. 2, 3a, c, e, 4a, c, e). The caustic quantities indicated by the paired simulations (_noeq vs. _eq) diverged as the pH increased to intermediate values and then converged at high pH values (Fig. 2). The divergence resulted because the divalent metals (unoxidized Fe^{II} and Mn^{II}) behaved conservatively in the simulations without gas exchange (did not interact with caustic) until high pH, where they precipitated. In contrast, oxidized Fe^{III} and $Mn^{III\text{-}IV}$ reacted with caustic and precipitated at lower pH values, as indicated by greater acidity (titrant added) at low pH for the simulations with initial atmospheric equilibrium (pre-aerated) compared to those without gas exchange.

For each titration scenario, consumption of NaOH was non-linear with respect to pH because of buffering at pH 3–5 and pH 9–11 (Fig. 2). Characteristic pH buffering at pH 3–5 has been interpreted to result from the formation of aqueous Fe^{III} and Al hydroxyl complexes and the consequent precipitation of ferric and aluminum hydroxide compounds (Kirby and Cravotta 2005; Ott 1988). Likewise, buffering at pH 9–11 can be interpreted to result from hydrolysis reactions involving Fe^{II}, Mn^{II}, and Mg and the

Table 3 Chemical compositions of untreated effluent from six mines in Pennsylvania where empirical titrations with NaOH were conducted

Water quality input	Mine discharge name					
	Cal pike	Ike	Manor	Millerstein	Morris	Nittany
Design flow (gpm)	1,000	1,000	1,000	1,000	1,000	1,000
Typical flow (gpm)	160	270	470	184	269	50
Total iron (mg/L Fe)	44.1	24	326	4.12	0.75	40.7
Ferrous iron (mg/L FeII)	6.0	24	326 (6)	4.12	0.75	29.6
Aluminum (mg/L Al)	34.1	5.95	33	0.25	61	128
Manganese (mg/L Mn)	48	24	4.7	5.2	57	129
pH	2.8	4.2	3.0	6.0	3.0	3.0
Alkalinity (mg/L as $CaCO_3$)	0	2	0	6	0	0
Total inorganic carbon (mg/L TIC)	1.2	1.2	1.2	14.2	1.2	19.2
Hot acidity (mg/L as $CaCO_3$)	500	123	880	16	510	982
Sulfate (mg/L SO_4)	1,502	1,341	1,726	1,380	4,223	5,000
Chloride (mg/L Cl)	6.0	2.0	20.0	4.0	1.7	1.9
Calcium (mg/L Ca)	105	150	190	101	186	422
Magnesium (mg/L Mg)	112	134	57	113	460	652
Sodium (mg/L Na)	8	7.5	3.81	46	18	17.8
Temperature (°C)	16	16	16	16	16	16
Dissolved oxygen (mg/L DO)	0.8	1.8	2.2	0.6	0.11	4.1

Data presented in this table for filtered (0.45 μm pore size) samples were used as "test cases" for water-quality input to AMDTreat 5.0+ for comparison of PHREEQ titration simulations with empirical field titrations using NaOH

precipitation of $Fe(OH)_2$, pyrochroite ($Mn(OH)_2$), and brucite ($Mg(OH)_2$).

The simulated and measured changes in Fe concentrations during titrations (Figs. 3, 4) were complicated because of poorly defined (mixed) and/or unstable oxidation state of Fe. Generally, the simulations without atmospheric equilibration indicated Fe concentration values that were similar to measured values for Cal Pike, Manor, Millerstein, Morris, and Nittany (Figs. 3a, e, 4a, c, e). For Millerstein (Fig. 4a, b) and Morris (Fig. 4c, d), simulations with initial atmospheric equilibration indicated similar pH and Fe concentration trends as those without atmospheric equilibration, presumably because Fe^{III} was the predominant oxidation state in the influent or the initial DO was sufficient for oxidation of Fe^{II} to Fe^{III} before NaOH addition. However, measured pH and Fe values for Ike were intermediate between those indicated by the two end-member simulations (Fig. 3c, d), possibly because Fe^{II} began to oxidize to Fe^{III} during the empirical titrations. The simulations for Cal Pike, Manor, and Nittany without atmospheric equilibration (Figs. 3a, e, 4e) indicate that after precipitation of Fe^{III} that was initially present or formed in the sample, concentrations of remaining Fe^{II} were relatively constant until pH increased to about 8.5 after which the precipitation of $Fe^{II}(OH)_2$ limited the Fe concentrations to values less than 1 mg/L, until reaching a minimum Fe concentration at a pH of approximately 10.5. In contrast, the simulations with initial atmospheric equilibration (Figs. 3b, d, f, 4b, d, f) indicate that concentrations of Fe, which had oxidized to Fe^{III}, decreased to less than 1 mg/L at pH 5 until reaching the solubility minimum for $Fe^{III}(OH)_3$ at approximately pH 8.5; however, at pH values greater than 8.5, the Fe concentrations increased with pH because of the formation of $Fe^{III}(OH)_4^-$.

As pH increased to approximately 6.5, the measured and simulated concentrations of Al decreased to less than 0.5 mg/L (Figs. 3, 4) because of the precipitation of Al-hydroxide compounds, which have solubility minima at approximately pH 6.5 (Fig. 1). At pH 6–8, both the simulated and measured Al concentrations are less than 0.5 mg/L (Figs. 3, 4); however, the simulated concentrations are less than measured Al values. These differences could indicate that the measured Al concentrations: (1) include contributions by colloidal material that passed the 0.45 μm filters and/or (2) may be limited by the precipitation of amorphous $Al(OH)_3$ or some other compound that has a higher solubility than the Al-hydroxide phase (boehmite) specified to precipitate in the simulations. As the pH increased to alkaline values, the simulated and measured concentrations of Al increased because of the formation of $Al(OH)_4^-$ complexes. Nevertheless, at pH values greater than 9, measured Al concentrations were less than the concentrations indicated by simulations, indicating some other phases could be limiting Al at high pH. At pH greater than 10, simulated concentrations of Al and Ca decreased (Figs. 3, 4) because of the precipitation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$). Although SO_4^{2-} concentrations were relatively constant during titrations with NaOH, the precipitation of ettringite, schwertmannite ($Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$), and/or basaluminite

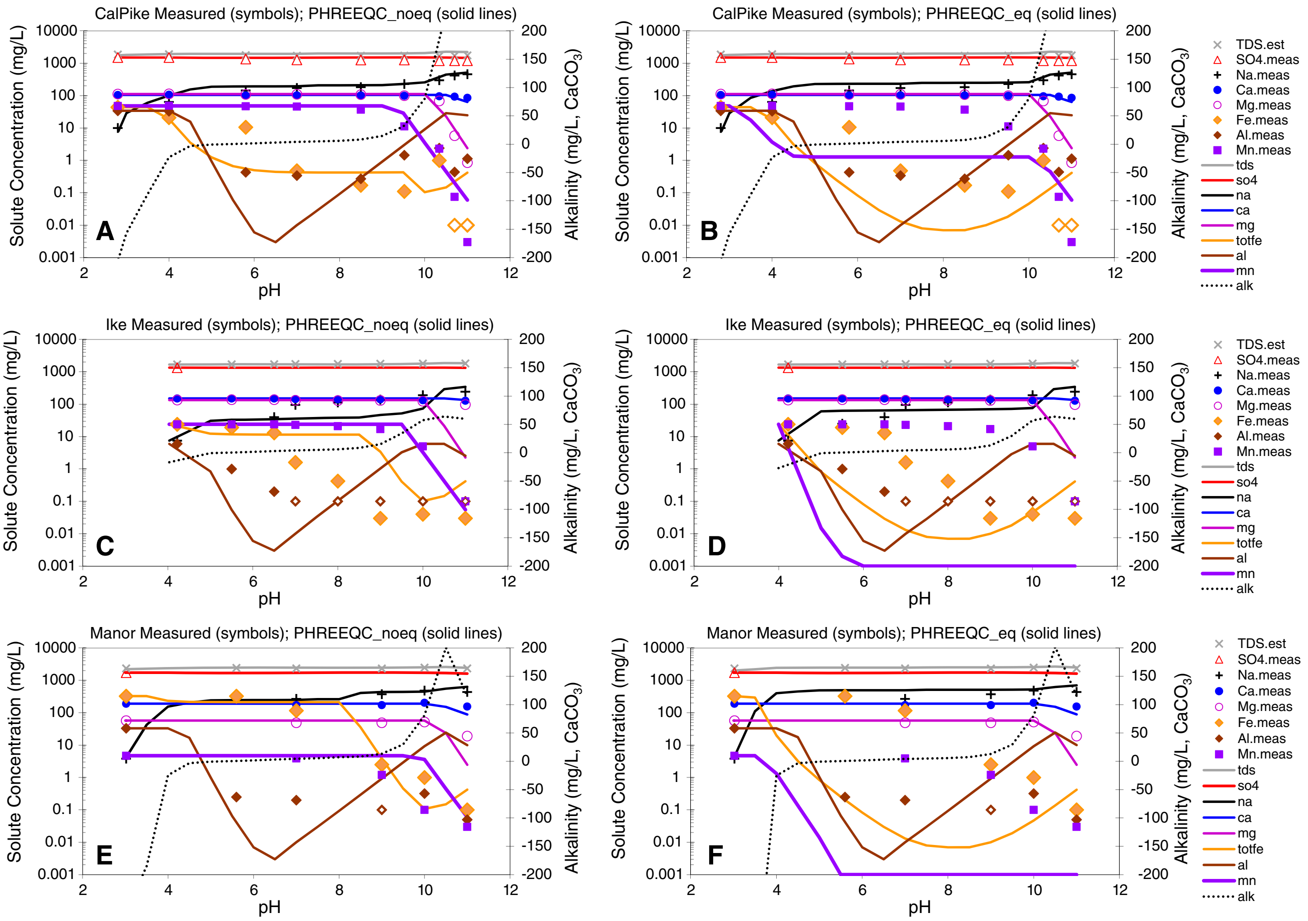

Fig. 3 Measured (*point symbols*) and simulated (*lines*) chemical concentrations as a function of pH during titration with NaOH; measured Fe and Al values below detection limits are shown at half the limit as *open symbols*. Simulations use starting effluent composition data in Table 3 and assume conditions with no gas exchange with atmosphere (PHREEQ_noeq; *left side*) or with initial gas exchange with atmosphere (PHREEQ_eq; *right side*)

($Al_4(OH)_{10}SO_4$) could account for minor decreases in the measured SO_4^{2-} concentrations (Figs. 3, 4, and supplemental Fig. S6). With the addition of CaO or $Ca(OH)_2$, gypsum precipitation also could become a primary sink for SO_4^{2-}.

The observed changes in pH and Mn concentrations were consistent with simulations without atmospheric equilibration, which indicates Mn^{II} is the predominant oxidation state for Mn in the AMD samples. At pH values greater than 10, the Mn^{II} concentrations decreased because of precipitation of pyrochroite, $Mn(OH)_2$, while those of Mg also decreased because of precipitation of brucite, $Mg(OH)_2$ (Figs. 3a, c, e, 4a, c, e). In contrast, the simulations with initial atmospheric equilibration (Figs. 3b, d, f, 4b, d, f) consistently indicated lower Mn concentrations than measured at a given pH. The implication is that if Mn could be oxidized before adding caustic chemicals, its concentrations could be decreased at near-neutral pH values, thus avoiding the precipitation of Mg, which adds to chemical consumption and sludge volume. Nevertheless, the extensive oxidation of Mn at low pH values simulated by the pre-aeration step is not realistic because of the slow kinetics of abiotic oxidation (Stumm and Morgan 1996). Thus, comparing the results for the two titration simulations could be interpreted to indicate potential benefits from the addition of strong chemical oxidants, such as ozone (Sato and Robbins 2000) or permanganate (Skousen et al. 1993). If a user wants to consider these additional chemical costs, AMDTreat 5.0+ has another module for Oxidant Chemical Cost that can be selected for that purpose (below Chemical Cost on Water Quality Input Screen, Fig. S1).

Cost Analysis for Simulated Treatment of Cal Pike Effluent Using Different Caustic Chemicals

Titration of the Cal Pike effluent with each of the chemicals available within the Chemical Cost Screen of AMDTreat 5.0+ (NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, or NH_3) was simulated to demonstrate possible differences in the

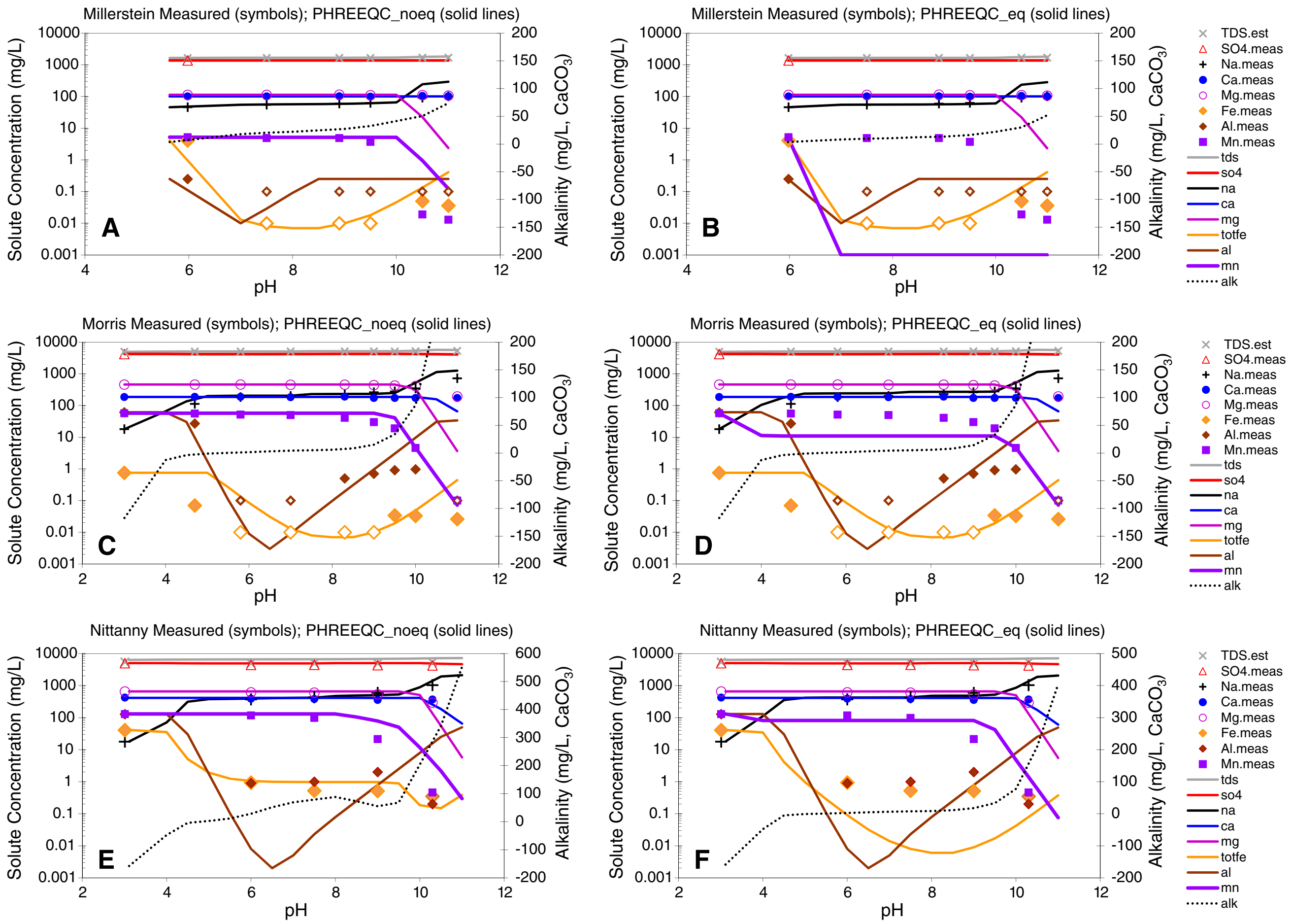

Fig. 4 Measured (*point symbols*) and simulated (*lines*) chemical concentrations as a function of pH during titration with NaOH; measured Fe and Al values below detection limit are shown at half the limit as *open symbols*. Simulations use starting effluent composition data in Table 3 and assume conditions with no gas exchange with atmosphere (PHREEQ_noeq; *left side*) or with initial gas exchange with atmosphere (PHREEQ_eq; *right side*)

estimated quantities and costs for the various caustic agents. Simulated solute concentrations as a function of pH for scenarios without and with pre-aeration were similar among NaOH, ammonia (NH_3), hydrated lime ($Ca(OH)_2$), and quick lime (CaO) (supplemental Tables S1 and S2). Because the metals and associated major solutes generally precipitated at the equilibrium pH values indicated for hydroxide phases (Fig. 1), pH was the critical factor controlling solute concentrations. Thus, regardless of the caustic agent, the concentrations of Fe^{III} and Al decreased to minimum values at pH 6–8 and then increased with pH in accordance with solubility control by hydroxides. Decreases in Fe^{II} concentrations were consistently indicated at pH values greater than 8.5 and decreases in Mn^{II} were indicated at pH values greater than 9.5 (Figs. 1, 3, 4; Tables S1 and S2). Additionally, with an increase in Ca concentration from dissolution of CaO or $Ca(OH)_2$ (Tables S1 and S2), the partial removal of Al (as ettringite) at pH values greater than 10 and SO_4 (as gypsum) were indicated where saturation with these phases was achieved (e.g. Fig. 3a, b). Of note, simulated treatment with soda ash (Na_2CO_3) (Tables S1 and S2) and other carbonate phases not included with AMDTreat 5.0+ ($NaHCO_3$, $CaCO_3$) produced simulated pH and concentration trends that differed from the other caustic chemicals. Dissolution of soda ash and other carbonate additives created conditions at high pH that favored the precipitation of $FeCO_3$, $MnCO_3$, and $CaCO_3$ with consequent decreases in the concentrations of associated divalent cations at pH values less than those for precipitation of the corresponding hydroxides.

The titration simulations indicated that treatment using NaOH, $Ca(OH)_2$, CaO, or NH_3 for similar aeration scenarios produced treated effluents with similar concentrations of metals as a function of pH over the pH range of 6–10. Nevertheless, because of differences in the mixing efficiencies and unit costs for chemicals, the estimated quantities and costs of different chemicals to attain a target pH ranged widely.

To evaluate the needed quantities and costs of different chemicals for treatment, a target pH of 10.0 or 8.5 may be considered for reference, where a pH of 10 is the common target for precipitation of $Mn(OH)_2$ and a pH of 8.5 results in direct precipitation of $Fe(OH)_2$ plus additional precipitation of $Fe(OH)_3$, owing to enhanced kinetics of oxidation of Fe^{II} at high pH (e.g. Stumm and Morgan 1996). Because a pH value of 8.0 or 8.5 is approximately the endpoint for hot acidity titrations, it is a useful reference point to relate the chemical equivalents on the basis of measured hot acidity or computed net acidity and the corresponding quantities of caustic chemicals computed by simulated titrations.

To neutralize the net acidity of 500 mg/L as $CaCO_3$ for the Cal Pike effluent, an equivalent amount of 0.50 g/L as $CaCO_3$ was assumed for all chemicals. By multiplying the equivalent value by the $CaCO_3$ conversion factor for each chemical in Table 1, the corresponding quantity of the pure chemical was computed (supplemental Tables S3 and S4). This is the default computation method for chemical requirement used by AMDTreat. Then, the quantity of industrial grade chemical, corrected for treatment efficiency and purity, was estimated for treatment of 3785 L (1000 gallons). Likewise, chemical requirements indicated by the simulated titrations to different pH endpoints were used to compute estimated treatment costs as a function of pH for treatment of 3785 L (1000 gallons). For these examples, default values for unit costs of chemicals, chemical purity, chemical efficiency, and sludge disposal (Table 1) were used to compute the annual treatment costs.

The equivalent quantities of NaOH, $Ca(OH)_2$, or CaO that were estimated based on the net acidity (500 mg/L as $CaCO_3$; 0.50 g/L chemical as $CaCO_3$) were similar to estimates based on titration simulations to a target pH 8.0 or 8.5 with pre-aeration (Table S4), but were less than the estimated chemical requirement to reach a pH of 8.5 without aeration. Generally, in the absence of aeration (without oxidation) or addition of carbonate, Mn^{II} removal would not be expected until pH 10 (Fig. 3, Table S1). However, to achieve a target pH of 10 for the removal of Mn^{II} without aeration, the Cal Pike titration simulations indicated approximately 10–15 % greater quantities of the caustic chemicals would be needed than estimated using net acidity equivalents.

To achieve a target pH of 10 or greater, approximately the same quantity of a given caustic chemical would be needed to reach that pH, with or without pre-aeration (Tables S1 and S2). At such high pH values, Mn^{II} removal can be assured, along with the possible removal of Mg, Ca, and SO_4, depending on effluent composition and chemical used. Nevertheless, treatment to such high pH values may not be necessary to meet effluent goals if the dissolved Mn^{II} and Fe^{II} can be rapidly oxidized before the addition of caustic chemicals, and runs the risk of Al redissolution.

The pre-aeration simulation indicated that removal of Fe as $Fe(OH)_3$ and Mn as MnO_2 may be possible at near-neutral pH (Fig. 3b; Table S2). Although these oxidized phases are thermodynamically stable in the presence of O_2, oxidation of Fe^{II} and Mn^{II} may not be achieved solely by aeration because of slow oxidation kinetics at pH less than 8 (Stumm and Morgan 1996). To rapidly oxidize Fe^{II} at neutral and lower pH, pre-treatment with an oxidizing agent such as hydrogen peroxide (Cole et al. 1977; Leavitt 2010) could be considered, whereas to rapidly oxidize Fe^{II} and Mn^{II}, ozone or potassium permanganate could be considered (Sato and Robbins 2000; Skousen et al. 1993). By promoting oxidation (indicated by pre-aeration simulation) before the addition of caustic chemicals (Table S2), the estimated caustic chemical quantities for treatment to a pH of 8.0–8.5 may be substantially less than those estimated to achieve Mn^{II} removal at higher pH without aeration (Table S1). Treatment of an oxidized solution at pH 8.0–8.5 avoids Mg precipitation and thus uses a smaller quantity of caustic chemicals and produces less sludge than treatment of an unoxidized solution to pH 10. Because of the simulated precipitation of Mg as $Mg(OH)_2$, the estimated sludge volume for the Cal Pike effluent nearly doubled from pH 9.5–10.5 (Tables S1 and S2). Thus, the inadvertent precipitation of Mg not only consumes caustic chemicals but also adds to the sludge volume, which increases costs for the operation and maintenance of treatment systems.

In contrast with the simulated treatment of the Cal Pike effluent with NaOH, $Ca(OH)_2$, CaO, or NH_3, the simulated titration with Na_2CO_3 without aeration indicated the potential for removal of Mn^{II}, Ca, and Mg as $MnCO_3$, $CaCO_3$, and $CaMg(CO_3)_2$. The potential for precipitation of such carbonates was greatest at alkaline pH values (>8.5) and was sensitive to the specified degree of supersaturation ($SI \geq 2.5$) before "allowing" precipitation. As a consequence of the precipitation of $CaCO_3$, $CaMg(CO_3)_2$, and other carbonates in the titration model, the estimated sludge volumes produced by treating the Cal Pike AMD to a pH of 8.0 with soda ash were 10 % greater than the sludge volumes estimated for other chemical treatments (Table S1). If $MnCO_3$ were to precipitate at lower levels of supersaturation ($0 < SI < 0.5$), substantial removal of Mn^{II} feasibly could be achieved at a pH less than 9. Thus, soda ash and other carbonate based agents may have limited usefulness for treatment of AMD with high concentrations of Mn^{II} and low concentrations of Ca and Mg.

The annual costs of chemicals plus the cost of sludge disposal are routinely expressed in terms of cost per unit volume of effluent treated (Tables S3 and S4). Because these costs vary as a function of the pH of treatment, specific pH and effluent concentration goals may be considered when comparing the costs of treatment with different chemicals. For example, regardless of the caustic chemical used, the effluent compositions were predicted to be similar for the treatment of the Cal Pike AMD to pH 10 to 10.5 without aeration and to pH 8.0 with pre-aeration (Tables S1 and S2). Lime, as $Ca(OH)_2$ or CaO, was the least costly agent for treatment to pH 10 to 10.5 without aeration or treatment to pH 8.0 with pre-aeration (Tables S3 and S4). For treatment to a pH less than 9.0, ammonia was indicated to be less expensive than caustic soda and soda ash; however, caustic soda was less costly than ammonia and soda ash for increasing pH to values greater than 9 (Tables S3 and S4).

Comparison of Simulated and Actual Treatment of Nittanny AMD with Lime

In this section, the titration simulation ability of AMDTreat 5.0+ is used to evaluate the actual CaO treatment of the Nittanny Mine AMD, which was the most mineralized of the six samples in this study. On the date the empirical titration with NaOH was conducted, the untreated discharge had a pH of 3, nearly 1,000 mg/L of acidity, and elevated concentrations of SO_4 (5,000 mg/L), Fe (40.7 mg/L; 29.6 mg/L as Fe^{II}), Mn (129 mg/L), Al (128 mg/L), Mg (652 mg/L), and Ca (422 mg/L); similar chemistry was observed on a previous sampling date (Table 3). The untreated water flowed from mine spoil into an open pit from which it was pumped to the treatment system. The treatment added CaO slurry to the raw water; the effluent was then discharged to a series of two shallow settling ponds of approximately 0.2 ha each. Gypsum crystals coated with iron oxide formed a hard crust on the bottom of the second pond near the outflow where the treated effluent was sampled. On both sampling occasions, the treated effluent had pH of 7 but still had elevated Mn (5.5–9.9 mg/L) and was marginally alkaline to moderately acidic (hot acidity −1.5 to 42 mg/L; net acidity of 4–20 mg/L) with decreased concentrations of SO_4 (2,700–3,100 mg/L), Fe ($\leq$1.0 mg/L), Al ($\leq$0.08 mg/L), and Mg (150–240 mg/L), and increased concentrations of Ca (930–1,070 mg/L). Although the observed pH of the treated effluent was near neutral for both sample sets, the pH was unstable during the first sampling event when the acidity and Mn were greatest. Within hours of sampling, the pH decreased to 3.5, presumably because of oxidation and hydrolysis of Mn^{II} in the absence of dissolved Fe.

The AMDTreat titration simulation with CaO to pH 7 did not produce the observed changes on chemical concentrations, particularly for Mn, Mg, Ca, and SO_4 (Fig. 5a). To decrease concentrations to those in the observed data, titration with CaO to a pH of 10 to 10.5 would be needed (Fig. 5b). As shown in Fig. 5b, if the initial treatment with CaO produced a pH of 10.2, then Mn and Mg feasibly could decrease to observed concentrations by the formation of $Mn(OH)_2$ and $Mg(OH)_2$. Likewise the added Ca would increase saturation with respect to gypsum, promoting the observed removal of SO_4.

Although the field data were not collected at the inflow to the treatment ponds immediately after initial dosing with CaO, the pH at this location could have been near 10.2 and then decreased within the ponds and thereafter as a consequence of oxidation of dissolved Mn^{II}. Although reaction kinetics are not included with the equilibrium simulations offered with AMDTreat 5.0+, reaction rates could be a critical factor affecting treatment performance and the ability to predict effluent compositions. The assumption of equilibrium conditions for geochemical systems has validity when reactions are rapid or where time is sufficient for reactions to be completed, such as slow-moving groundwater (Blowes and Ptacek 1994; Cravotta 2008). However, the equilibrium assumption may not be valid for short residence times within treatment systems because of kinetic factors affecting the exchange of gases and the oxidation of Mn^{II} and Fe^{II} (Hem and Lind 1983; Kirby et al. 2009). The empirical titration results with NaOH were in good agreement with the AMDTreat simulations of treatment with NaOH without aeration for the Nittanny Mine effluent (Fig. 4E), indicating rapid equilibration under these conditions. Nevertheless, gypsum supersaturation was indicated by simulations of treatment with NaOH or CaO. In fact, gypsum eventually precipitated from the filtered effluent samples during sample storage, forming fine crystals and causing slow decreases in Ca and SO_4 concentrations. Thus, the new AMDTreat 5.0+ treatment simulations may offer insights on treatment performance, sampling design, and optimal treatment strategies; however, the simulations should not be considered the final answer.

Conclusions

New titration options using the geochemical program, PHREEQC, were added to the chemical cost module in AMDTreat 5.0+. These titration options permit a user to select different chemical agents (NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, or NH_3) and different equilibrium conditions for dissolved gases (no exchange or limited exchange with the atmosphere by pre-aeration to a specified CO_2 gas pressure). The simulations indicate the incremental amounts of a selected caustic chemical needed to increase pH to values from 6 to 11, the corresponding solute concentrations (Al, Fe, Mn, Mg, Ca, Na, SO_4) remaining in the treated effluent, and the resultant sludge volume. The simulations assume that neutralization, gas exchange, and associated oxidation and precipitation reactions are instantaneous and that

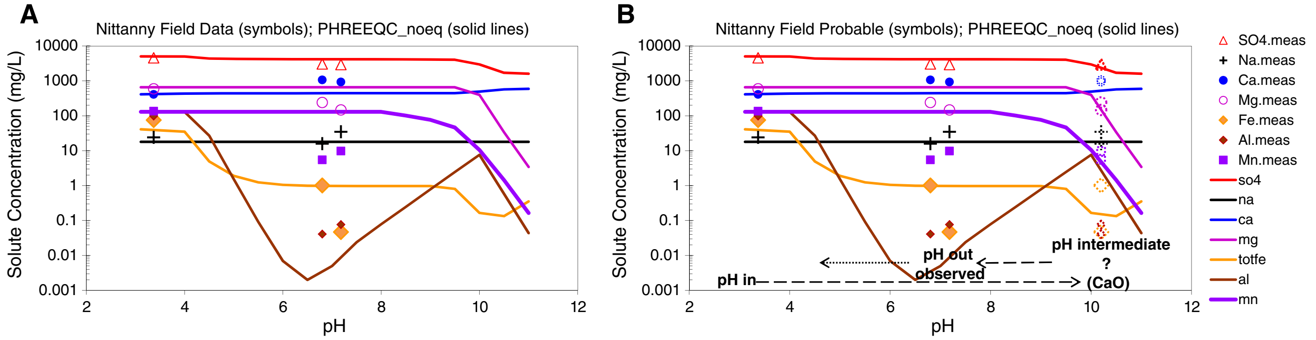

Fig. 5 Measured (*point symbols*) and simulated (*lines*) titration of "Nittanny" effluent with CaO compared to field results of CaO treatment ponds. Symbols at pH values near 3 and 7 indicate observed data values at inflow and outflow of treatment system, respectively; symbols (*dashed outlines*) at pH 10.2 indicate possible data values at the presumed pH immediately after addition of CaO, before the pH decreased due to Mn^{II} oxidation within the treatment ponds

equilibrium conditions are achieved among solid phases and aqueous species.

Empirical NaOH titration data for AMD from six coal mines were used to calibrate and evaluate the validity of the titration model results. For these empirical titrations, the oxidation of Fe and Mn was limited in extent by the initial dissolved O_2 concentration and was simulated by titrations without gas exchange. Most of the caustic consumption was indicated to result from the precipitation of initial Al as $Al(OH)_3$ and Fe^{III} as $Fe(OH)_3$ at pH values less than 6, Fe^{II} as $Fe(OH)_2$ at pH values greater than 8.5, and Mn^{II} as pyrochroite ($Mn(OH)_2$) with Mg as brucite ($Mg(OH)_2$) at pH values greater than 9.5. Although the simulations without and with gas exchange produced different trends for Fe and Mn because of differences in solubilities of reduced versus oxidized solids (Fe^{II} vs. Fe^{III} or Mn^{II} vs. $Mn^{III\text{-}IV}$), they produced similar trends for Al, SO_4, Mg, and Ca. The simulated treatment after pre-aeration demonstrated the potential for removal of dissolved Fe and Mn at relatively low pH, possibly achieved by use of chemical oxidants, thus avoiding treatment to alkaline pH and the consequent precipitation of $Mg(OH)_2$, which consumes caustic chemical and adds to the sludge volume.

The PHREEQC titration results can be used with or in place of empirical titration data to evaluate alternative treatment strategies, but should not be used as the sole basis for treatment system design. The simulations do not identify the actual mineral phases precipitating nor describe kinetics of chemical reactions, mixing, particle formation and settling, and other dynamic processes within an active treatment system. Furthermore, no attempt has been made to simulate geochemical processes such as adsorption and coprecipitation that have been documented to control trace element concentrations in AMD systems.

The new capability of AMDTreat 5.0+ to model major chemical reactions that occur when mine drainage is treated is important for accurately estimating the two largest components of treatment costs—chemical requirements and sludge production. Users can use the titration modeling capabilities of AMDTreat 5.0+ to examine the potential relations among treatment chemical, effluent quality, sludge quantity, and treatment costs. Specific capabilities of the PHREEQ module in AMDTreat 5.0+ include:

- Ability to evaluate potential for nuisance mineral precipitation;
- Ability to evaluate the effect of dissolved CO_2 on treatment costs;
- Ability to evaluate the effect of pre-treatment oxidization (degassing of CO_2 and ingassing of O_2) on treatment strategy, costs, and effluent quality; and
- Ability to evaluate the effect of various treatment chemicals and treatment pH on TDS and sludge volume.

AMDTreat 5.0+ retains the flexibility of previous versions by permitting use of default values or user adjusted values for chemical purity, chemical mixing efficiency, and sludge density plus unit cost values for all aspects of treatment (materials, equipment, chemicals, construction, and labor). With the new titration simulations, AMDTreat 5.0+ can be used to evaluate costs and effects of treatment strategies with different chemicals to achieve a desired effluent composition. Minimizing treatment costs while ensuring effluent quality goals are met could help industry, government agencies, and others involved in watershed improvement projects. AMDTreat has an extensive website where software can be downloaded free of charge and additional information can be obtained. The web address is http://www.amd.osmre.gov/.

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