A GEOCHEMICAL MODULE FOR "AMDTreat" TO COMPUTE CAUSTIC QUANTITY, EFFLUENT QUALITY, AND SLUDGE VOLUME[1]

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Abstract. Treatment with caustic chemicals typically is used to increase pH and decrease concentrations of dissolved aluminum, iron, and/or manganese in large-volume, metal-laden discharges from active coal mines. Generally, aluminum and iron can be removed effectively at near-neutral pH (6 to 8), whereas active manganese removal requires treatment to alkaline pH (~10). The treatment cost depends on the specific chemical used (NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, or NH_3) and increases with the quantities of chemical added and sludge produced. The pH and metals concentrations do not change linearly with the amount of chemical added. Consequently, the amount of caustic chemical needed to achieve a target pH and the corresponding effluent composition and sludge volume can not be accurately determined without empirical titration data or the application of geochemical models to simulate the titration of the discharge water with caustic chemical(s).

The AMDTreat computer program (http://amd.osmre.gov/) is widely used to compute costs for treatment of coal-mine drainage. Although AMDTreat can use results of empirical titration with industrial grade caustic chemicals to compute chemical costs for treatment of net-acidic or net-alkaline mine drainage, such data are rarely available. To improve the capability of AMDTreat to estimate (1) the quantity and cost of caustic chemicals to attain a target pH, (2) the concentrations of dissolved metals in treated effluent, and (3) the volume of sludge produced by the treatment, a titration simulation is being developed using the geochemical program PHREEQC (wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) that will be coupled as a module to AMDTreat. The simulated titration results can be compared with or used in place of empirical titration data to estimate chemical quantities and costs. This paper describes the development, evaluation, and potential utilization of the PHREEQC titration module for AMDTreat.

Additional Key Words: active treatment, chemical costs, titration, pH, metals.

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Introduction

To avoid the future degradation of water resources, thousands of metal-laden discharges from current coal-mining operations in the Appalachian region of eastern U.S.A. are anticipated to require sustained, active treatment. Recent mining regulations and court rulings require private trust funds or bonds be established to pay for the long-term treatment of such discharges through the 21st century (Pennsylvania Department of Environmental Protection, 2007). To ensure that funding is adequate and treatment strategies are effective, improved methods to estimate the costs of various treatment options are needed, particularly for large-volume discharges with elevated concentrations of dissolved Fe and/or Mn.

Industrial strength caustic chemicals (NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, and NH_3) commonly are used to neutralize acidity, increase pH and alkalinity, and promote the active precipitation of dissolved Fe, Mn, Al, and other metals from discharges at active coal-mining operations (U.S. Environmental Protection Agency, 1983; Skousen et al., 1993, 2000). Various solid phases may precipitate during neutralization of the effluent depending on the oxidation state of the dissolved metals, pH and other characteristics of the solution (Cravotta, 2008), and the chemical(s), if any, being used for treatment. For example, reactions involving NaOH, commonly referred to as caustic soda (Table 1), illustrate simple neutralization and more complex hydrolysis, oxidation, and precipitation processes:

$$NaOH + H^+ = H_2O + Na^+ \qquad (1)$$

$$NaOH + CO_2 = HCO_3^- + Na^+ \qquad (2)$$

$$3\ NaOH + Fe^{3+} = Fe(OH)_3 + 3\ Na^+ \qquad (3)$$

$$2\ NaOH + Fe^{2+} = Fe(OH)_2 + 2\ Na^+ \qquad (4)$$

$$2\ NaOH + Fe^{2+} + 0.25\ O_2 + 0.5\ H_2O = Fe(OH)_3 + 2\ Na^+ \qquad (5)$$

$$2\ NaOH + Fe^{2+} + CO_2 = FeCO_3 + 2\ Na^+ + H_2O \qquad (6)$$

Neutralization reactions can be written for other metals and caustic agents (Table 1) considering that the charge on the metal ion (+2, +3, +4) is equivalent to the number of moles of acid (H^+) generated by its complete hydrolysis and precipitation, and each mole of H^+ can be neutralized by the number of molar equivalents of the base cation (for example, Na^+, 0.5 Ca^{2+}, 0.5 Mg^{2+}).

Table 1. Chemical compounds used for neutralization of coal-mine drainage

Common Name	Chemical Name	Formula	Unit Weight (g/mol)	Acid equiv-alents[a] (eq/mol)	$CaCO_3$ factor[b] (g/g $CaCO_3$)	Efficiency factor[c]	Purity of industrial grade chemical	Cost per unit[d]	Sludge density (proportion solids)[e]
50% Liquid Caustic[f]	Sodium hydroxide	NaOH	39.998	1	1440	1.0	0.99	\$1.59/gal	0.02-0.05
20% Liquid Caustic[g]	Sodium hydroxide	NaOH	39.998	1	3276	1.0	0.99	\$0.70/gal	0.02-0.05
Caustic Soda (solid)	Sodium hydroxide	NaOH	39.998	1	0.80	1.0	0.99	\$0.36/lb	0.02-0.05
Soda Ash	Sodium carbonate	Na_2CO_3	105.991	2	1.06	0.6	0.99	\$0.14/lb	0.02-0.05
Baking Soda	Sodium bicarbonate	$NaHCO_3$	84.009	1	1.68	0.9	0.99	\$0.20/lb	0.02-0.05
Limestone	Calcium carbonate	$CaCO_3$	100.091	2	1.00	0.3	0.85	\$0.011/lb	0.05-0.10
Hydrated Lime	Calcium hydroxide	$Ca(OH)_2$	74.096	2	0.74	0.8	0.96	\$0.10/lb	0.05-0.10
Pebble Quicklime	Calcium oxide	CaO	44.011	2	0.44	0.7	0.94	\$0.11/lb	0.05-0.10
Ammonia	Anhydrous ammonia	NH_3	17.030	1	0.34	0.9	0.99	\$0.50/lb	0.02-0.05

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[a] An equivalents is 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 1 weight unit of acidity expressed as $CaCO_3$. For example, this factor may be multiplied by the annual acid load expressed as metric tons/yr $CaCO_3$ to obtain a crude estimate of the annual amount of solid chemical needed as metric tons/yr. For liquid caustic, the conversion factor indicates liters of solution needed to neutralize 1 metric ton of acid as $CaCO_3$; divide value by 3.785 to obtain result in gallons.

[c] 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 (U.S. Office of Surface Mining Reclamation and Enforcement, 2006). 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 metric tons of acid/yr as $CaCO_3$, then 96 metric tons of industrial grade hydrated lime ($Ca(OH)_2$) would be needed ($96 = 100 \cdot 0.74 / 0.8 / 0.96$).

[d] Unit costs are listed for "non-bulk" quantities; values and units are the defaults in AMDTreat (U.S. Office of Surface Mining Reclamation and Enforcement, 2006). Cost for solid and 50% saturated solution of NaOH were computed from default cost of 20% liquid caustic.

[e] Although the default value in AMDTreat is 5 weight % solids (50 g solids/1000 g solution), iron-rich sludge produced by reaction with caustic chemicals can have a wide range of solids concentrations. The solids concentration value is used to estimate sludge volume and associated sludge disposal cost on a unit volume basis. Generally, calcium-based reagents produce denser sludge than sodium- or ammonia-based reagents.

[f] Industrial grade "50% liquid caustic" is 50 *percent of saturation* and contains 555 g NaOH in 1 liter (13.88 N NaOH).

[g] The actual concentration of industrial grade "20% liquid caustic" depends on the source. For generalized calculations to relate solid and aqueous NaOH quantities, the assumed 20% solution concentration is 244 g/L (6.1 N) with density of 1244 g/L. A solution concentration of 20 *weight percent* would contain 250 g NaOH in 1 liter (6.25 N NaOH) and have a density of 1250 g/L. A solution concentration of 20 *percent of saturation* (NaOH solubility is 1110 g/L at 20 °C) would contain 222 g NaOH in 1 liter (5.55 N NaOH) and have a density of 1222 g/L.

The maximum concentration of a metal at equilibrium with a solid compound at a specific pH can be estimated given thermodynamic data on the solubility of the compound and the stability of associated aqueous complexes (Langmuir, 1997; Nordstrom, 2004). For example, at near-neutral pH (6 to 8), solubilities are less than 0.1 mg/L for dissolved Al^{3+} and oxidized forms of Fe^{3+} and Mn^{3+}, Mn^{4+}, Mn^{6+} at equilibrium with $Al(OH)_3$, $Fe(OH)_3$, and MnO_2, respectively (Fig. 1); however, solubilities are greater than 10 mg/L for reduced forms of Fe^{2+} and Mn^{2+} with respect to $Fe(OH)_2$ and $Mn(OH)_2$. Increased pH (9 to 10) is needed to precipitate $Fe(OH)_2$ and $Mn(OH)_2$ and/or oxidation is needed to promote the precipitation of less soluble $Fe(OH)_3$ and MnO_2 compounds.

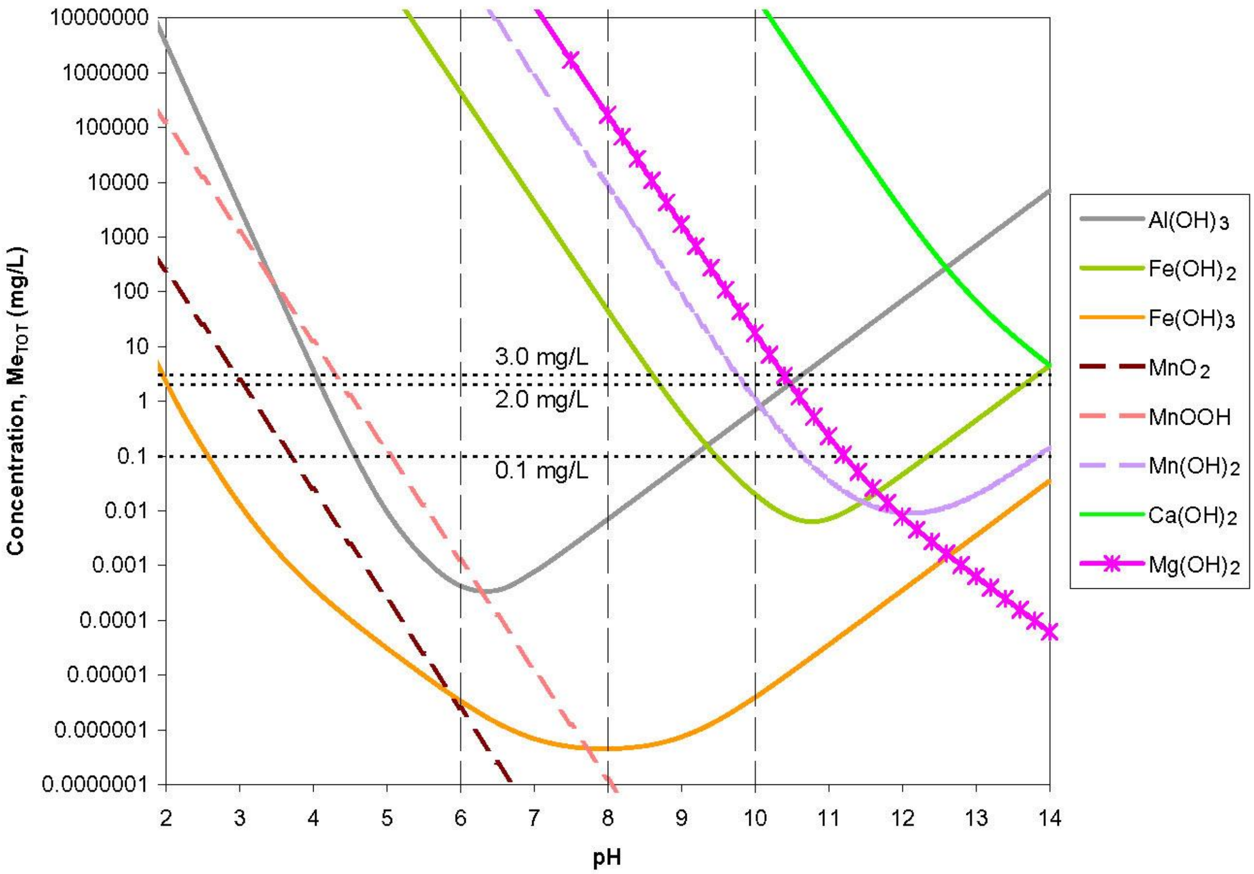

Figure 1. Approximate solubilities of hydrous oxide (hydroxide) compounds of iron (Fe^{2+} or Fe^{3+}), manganese (Mn^{2+}, Mn^{3+}, or Mn^{4+}), Al, CA, and Mg as a function of pH at 25 °C. Computations used thermodynamic data from Ball and Nordstrom (1991) and Wolery (1992), assumed activity equals 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).

The incremental addition of caustic chemicals to a metal-laden solution generally will increase pH; however, the amount of caustic needed to attain a target pH and the corresponding effluent composition and sludge volume can not be determined without empirical titration (dosing) data or the application of geochemical models to simulate titration with the caustic chemical(s). In addition to the precipitation of Fe, Mn, and Al, compounds of Mg ($Mg(OH)_2$) and, to a lesser extent, Ca ($CaCO_3$; $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) may precipitate as the solution pH increases to alkaline values (Payne and Yeates, 1970; Loop et al., 2004). The precipitation of such phases can consume substantial quantities of treatment chemicals and increase the quantity of sludge produced (Means and Hilton, 2004). Furthermore, the pH will not change linearly with each unit of chemical added because hydrolysis reactions with dissolved metals and CO_2 (Eqns. 2-6) tend to buffer pH (Ott, 1986, 1988; Cravotta and Kirby, 2004). Although reaction of caustic with dissolved CO_2 produces bicarbonate (HCO_3^-) alkalinity (Eqn. 2), the production of HCO_3^- tends to maintain pH near neutral. Aeration of the effluent before dosing with caustic chemicals can decrease chemical usage by decreasing the dissolved CO_2 concentration, increasing pH, and increasing oxidation rates and oxidation states of dissolved iron and manganese (Jageman et al., 1988; Kirby et al., 2009).

The AMDTreat computer program is widely used to estimate costs for active and passive treatment of mine drainage (McKenzie, 2005; U.S. Office of Surface Mining Reclamation and Enforcement, 2006). The treatment cost depends on the chemical used (Table 1) and increases with the quantities of chemical added and sludge produced. Although AMDTreat can use titration data to compute chemical requirements and associated chemical costs for net-acidic or net-alkaline mine drainage, such data are rarely available. Typically, the amount of chemical to neutralize the effluent is assumed to equal the measured “hot” acidity or the computed “net” acidity (Skousen et al., 2000; Cravotta and Kirby, 2004). This estimate of caustic equivalents (Table 1), which is the default used by AMDTreat, provides a “ball park” value of the chemical quantity needed for treatment of net-acidic effluent. However, for the same net acidity, the chemical requirement may differ for oxidized and unoxidized solutions. Furthermore, for net-alkaline effluent that may require active treatment to pH 10 to remove Fe^{2+} or Mn, AMDTreat wrongly assumes that no caustic chemicals and associated infrastructure would be needed and, thus, underestimates treatment cost. Furthermore, AMDTreat does not provide information on the potential quality of the effluent produced by the specified treatment.

This paper describes the development and potential utilization of a geochemical titration module for AMDTreat to estimate (1) the quantity and cost of selected caustic chemicals to attain a target pH, (2) the concentrations of dissolved metals in treated effluent, and (3) the volume of sludge produced by the treatment. Empirical and simulated titration data are presented as preliminary examples of this new method to refine cost estimates for chemical usage and sludge disposal.

Methods

In October 2003, empirical titrations of acidic, metal-laden effluent from the “Cal Pike” coal-mine site in western Pennsylvania were conducted to document effects of on-site chemical treatment. A Hach Digital Titrator® was used in the field with a cartridge that had been filled with industrial strength liquid caustic (6.1 N NaOH = “20 %” NaOH) from a chemical storage tank on site. Multiple titrations were conducted on the untreated effluent to progressively greater pH endpoints, and the volume of caustic solution added during each titration was recorded. At the end of each titration, filtered (0.45-µm pore size) effluent samples were collected to document changes in solute concentrations with treatment to that pH. Concentrations of major anions (SO_4^{2-}, Cl^-) in unpreserved subsamples were analyzed by ion chromatography, and concentrations of major cations (Ca, Mg) and selected trace metals (Fe, Mn, Al) in acidified subsamples were analyzed by inductively coupled plasma optical emission spectrometry at a commercial laboratory (Crock et al., 1999). The alkalinity and “hot peroxide” acidity (hot acidity) were titrated to fixed endpoint pH of 4.5 and 8.3, respectively (American Public Health Association, 1998a, 1998b). For comparison with the hot acidity, the net acidity was computed considering positive contributions from H^+ (pH) and concentrations of dissolved Fe, Mn, and Al in milligrams per liter (C_{Fe}, C_{Mn}, C_{Al}, respectively) as:

$$\text{Net Acidity (mg/L } CaCO_3\text{)} =$$

$$50 \cdot (10^{(3-\mathrm{pH})} + 3 \cdot C_{Fe}^{3+}/55.85 + 2 \cdot C_{Fe}^{2+}/55.85 + 2 \cdot C_{Mn}/54.94 + 3 \cdot C_{Al}/26.98) - \text{Alkalinity} \tag{7}$$

The analytical data on pH and associated changes in concentrations of solutes resulting from the addition of caustic chemicals to the Cal Pike effluent were evaluated using the geochemical program PHREEQC (Parkhurst and Appelo, 1999). Titration simulations were developed using the initial chemistry of the effluent plus reported solubility data for compounds that could be used as caustic chemicals or that could precipitate and control solute concentrations under equilibrium conditions (Table 2). Two approaches were used for the titration simulations. In one approach, finite amounts of the caustic chemical were added incrementally, and the pH and associated solute concentrations were summarized. In a second approach, described hereafter, the pH was specified to increase incrementally, and the corresponding amount of chemical needed to attain that pH and the resulting solute concentrations and mineral saturation indices were computed. Temperature of 16 ºC, initial dissolved oxygen concentration of 0.5 mg/L, and redox speciation based on the H_2O/O_2 couple were specified for these computations. The preliminary models were refined to simulate the observed solute concentrations as a function of pH by allowing specific phases to precipitate upon reaching saturation.

Although developed to simulate the empirical titration of the Cal Pike effluent with NaOH, the goal was a generalized geochemical model that could be used to estimate chemical reactions resulting from titration with a variety of caustic chemicals and other treatment processes such as pre-aeration. For each of the caustic chemicals listed in Table 1, a pair of simulations was produced—no gas exchange with the atmosphere (_noeq) and limited gas exchange with the atmosphere (_eq). The former simulated the immediate addition of caustic chemical to fresh effluent, whereas the latter simulated pre-aeration of the effluent by forcing dissolved gas concentrations to equilibrium with the atmosphere ($Pco_2 = 10^{-3.40}$ atm; $Po_2 = 10^{-0.678}$ atm) before the addition of caustic chemicals; no gas exchange was permitted during titration steps thereafter.

AMDTreat 4.1c (U.S. Office of Surface Mining Reclamation and Enforcement, 2006) was used to estimate costs for the active treatment of the Cal Pike effluent with different caustic chemicals on the basis of the net-acidity and the PHREEQC titrations. To summarize the costs of chemicals for treatment to specified pH values, estimates of chemical purity, efficiency, and unit costs that are used as default values for these computations by AMDTreat (Table 1) were extracted for spreadsheet calculations. Costs also were estimated for sludge disposal. The quantity of sludge produced was estimated as the sum of unreacted caustic chemical, based on the efficiency factor, and the decrease in metals relative to initial concentrations. The metals were assumed to have precipitated as hydroxide or carbonate compounds ($Fe(OH)_3$, $Al(OH)_3$, $Mn(OH)_2$, $Mg(OH)_2$, $CaCO_3$). Assuming sludge had a total solids concentration of 5 or 10 weight percent (%) (Table 1), the volume of sludge and cost of sludge disposal for a unit cost of $0.06/gal were estimated. Users of AMDTreat may specify other values for chemical purity and efficiency, sludge density, and unit costs to obtain a range of cost estimates.

Table 2. Dissolution and precipitation reactions and associated thermodynamic equilibrium constants (K) for geochemical modeling

Solid Phase Name	Equilibrium Reaction	Log K[a]		
		model	wateq	llnl
$Al(OH)_3$ (amorphous)	$Al(OH)_3 + 3 H^+ = Al^{3+} + 3 H_2O$	10.80	10.80	na
Gibbsite	$Al(OH)_3 + 3 H^+ = Al^{3+} + 3 H_2O$	8.11	8.11	7.76
Boehmite	$AlOOH + 3 H^+ = Al^{3+} + 2 H_2O$	8.58	8.58	7.56
Jurbanite	$AlOHSO_4 + H^+ = Al^{3+} + SO_4^{2-} + H_2O$	-3.23	-3.23	na
Basaluminite	$Al_4(OH)_{10}SO_4 + 10 H^+ = 4 Al^{3+} + SO_4^{2-} + 10 H_2O$	22.70	22.70	na
Lime	$CaO + 2 H^+ = Ca^{2+} + H_2O$	32.58	na	32.58
Portlandite	$Ca(OH)_2 + 2 H^+ = Ca^{2+} + 2 H_2O$	22.80	22.80	22.56
Aragonite	$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	1.99	1.99	1.99
Calcite	$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	1.85	1.85	1.85
Dolomite	$CaMg(CO_3)_2 + 2 H^+ = Ca^{2+} + Mg^{2+} + 2 HCO_3^-$	3.57	3.57	2.51
Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2 H_2O$	-4.58	-4.58	-4.48
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	na	na
Brucite	$Mg(OH)_2 + 2 H^+ = Mg^{2+} + 2 H_2O$	16.84	16.84	16.30
Siderite	$FeCO_3 + H^+ = Fe^{2+} + HCO_3^-$	-0.12	-0.12	-0.19
Fe(OH)$_2$	$Fe(OH)_2 + 2 H^+ = Fe^{2+} + 2 H_2O$	13.90	na	13.90
Fe(OH)$_3$ (amorphous)	$Fe(OH)_3 + 3 H^+ = Fe^{3+} + 3 H_2O$	4.89	4.89	5.66
Goethite	$FeOOH + 3 H^+ = Fe^{3+} + 2 H_2O$	-1.00	-1.00	0.53
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	na	na
Rhodochrosite	$MnCO_3 + H^+ = HCO_3^- + Mn^{2+}$	-0.06	-0.06	-0.19
Pyrochroite	$Mn(OH)_2 + 2 H^+ = Mn^{2+} + 2 H_2O$	15.20	15.20	15.31
Manganite	$MnOOH + 3 H^+ = Mn^{3+} + 2 H_2O$	-0.24	-0.24	-0.16
Pyrolusite	$MnO_2 = 0.5 Mn^{2+} + 0.5 MnO_4^{2-}$	-17.82	-17.82	-17.64
Birnessite	$MnO_2 = 0.5 Mn^{2+} + 0.5 MnO_4^{2-}$	-15.60	-15.60	na
Birnessite	$Mn_8O_{14} \cdot 5H_2O + 4 H^+ = 3 MnO_4^{2-} + 5 Mn^{2+} + 7 H_2O$	-85.55	na	-85.55
Todorokite	$Mn_7O_{12} \cdot 3H_2O + 16 H^+ = MnO_4^{2-} + 6 Mn^{3+} + 11 H_2O$	-45.82	na	-45.82
Sodium carbonate	$Na_2CO_3 + H^+ = 2 Na^+ + HCO_3$-	11.18	na	11.18
Nahcolite	$NaHCO_3 = Na^+ + HCO_3^-$	-0.55	-0.55	-0.11

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[a] Equilibrium constants are from “wateq” (Wateq4f; Ball and Nordstrom, 1991) and “llnl” (EQ3/6 ; Wolery, 1992) data bases, which are provided with the PHREEQC computer code (Parkhurst and Appelo, 1999). Data for ettringite (Myneni et al., 1998) and schwertmannite (Bigham et al., 1996) supplement these sources. Names in bold font were identified as phases the may control the concentrations of solutes during titration of the Cal Pike effluent. Other phases listed such as amorphous $Al(OH)_3$ and gypsum could be important in different cases.

Results and Discussion

The untreated Cal Pike effluent had pH of 2.8 and elevated concentrations of dissolved metals and other 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) compared to a majority of legacy mine discharges in Pennsylvania (Cravotta, 2008). The measured hot acidity of 498±40 mg/L as $CaCO_3$[a] and computed net acidity of 456±20 mg/L as $CaCO_3$ (Eqn. 7)[b] were comparable to “cold” acidity values of 343, 368, and 464 mg/L as $CaCO_3$ estimated by titration with liquid caustic (20 % NaOH) to pH of 7.0, 8.5, and 9.5, respectively (Fig. 2). Cravotta and Kirby (2004) explained that cold acidity generally will be greater than or equal to the hot acidity or the computed net acidity because of dissolved CO_2 acidity that is included with the cold acidity measurement. General agreement among different estimates of acidity for the Cal Pike effluent implies that dissolved CO_2 was not an important source of acidity for this effluent compared to contributions from dissolved metals and protons.

The empirical and simulated titrations of the Cal Pike effluent with NaOH produced nonlinear changes in pH and metals concentrations (Figs. 2 and 3). The titration curves revealed characteristic pH buffering (resistance to pH change) at pH of 3 to 5 and 9 to 12 (Fig. 2). Similar cold acidity titration curves and associated pH buffering have been reported for metal-laden effluents from other mines in Pennsylvania (Ott, 1986, 1988; Cravotta and Kirby, 2004). The pH buffering at pH 3 to 5 has been interpreted to result from the formation of aqueous Fe^{3+} and Al^{3+} hydroxyl complexes and the consequent precipitation of $Fe(OH)_3$ and $Al(OH)_3$ compounds. Substantial decreases in the measured and simulated concentrations of Fe and Al to values less than 0.1 mg/L as pH increased from 2.8 to 5 (Fig. 3) are consistent with anticipated solubility control by $Fe(OH)_3$ and $Al(OH)_3$ compounds (Fig. 1). Likewise, buffering at pH 9 to 11 can be interpreted to result from hydrolysis reactions involving Mn^{2+} and Mg^{2+} and the precipitation of pyrochroite ($Mn(OH)_2$) and brucite ($Mg(OH)_2$), which is consistent with decreases in concentrations of these constituents at pH values greater than 9 (Fig. 3). At pH

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[a] Precision of ±40 for hot acidity is based on duplicate results for hot acidity of the Cal Pike effluent after its treatment to pH 4.0 (404 and 444 mg/L as $CaCO_3$).

[b] Net acidity of 456 mg/L as $CaCO_3$ is the average of 436 and 476 mg/L as $CaCO_3$ that consider all iron to be ferrous or ferric, respectively; iron speciation was not measured.

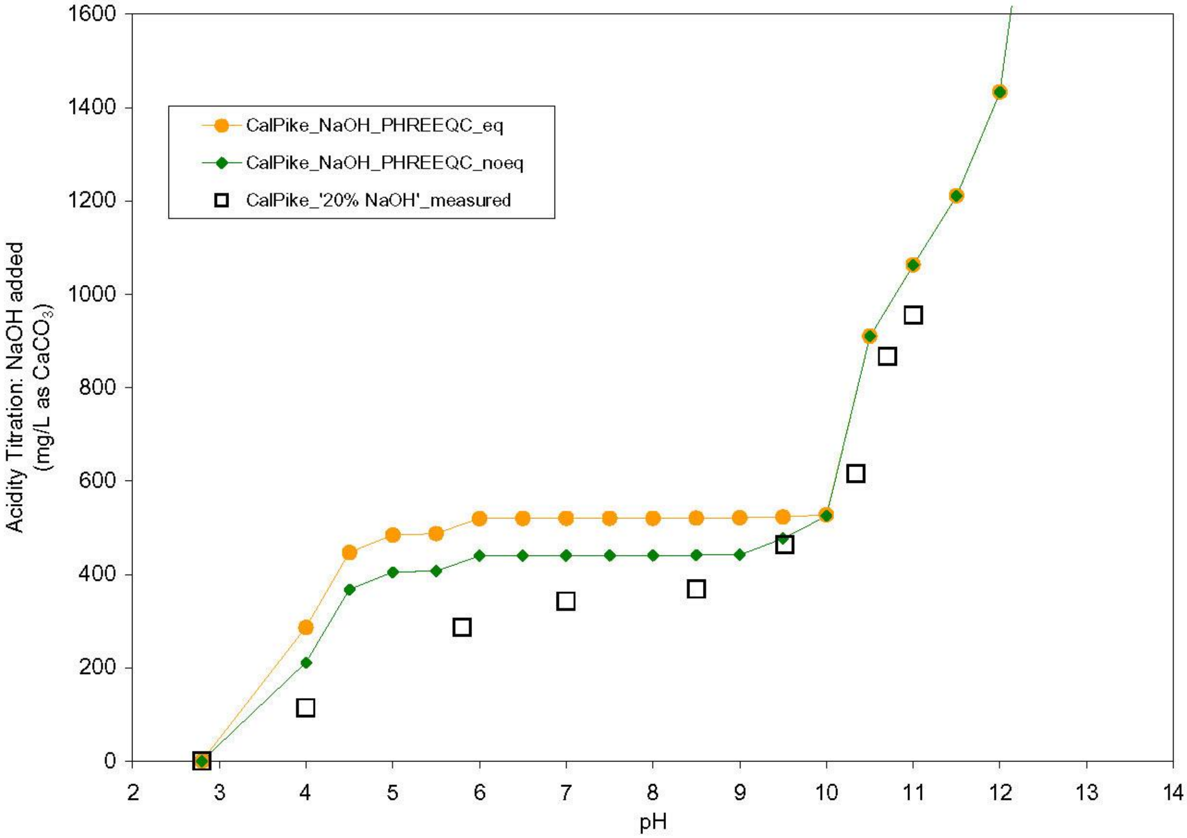

Figure 2. Data for titration of "Cal Pike" effluent with NaOH at 16 °C: Measured (open symbols) and simulated (filled symbols) values for amount of NaOH added, as $CaCO_3$ equivalent concentration, and corresponding pH. Measured titration used industrial grade 20 % liquid caustic solution. Simulated titrations illustrate no gas exchange (_noeq) and pre-aeration (_eq), where initial O_2 and CO_2 were equilibrated to atmospheric concentrations before adding NaOH.

greater than 10, concentrations of Ca^{2+} also decreased (Fig. 3), which is consistent with solubility control by ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$). The precipitation of ettringite, gypsum ($CaSO_4·2H_2O$), schwertmannite ($Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$), and/or basaluminite ($Al_4(OH)_{10}SO_4$) also could account for decreases in the measured SO_4^{2-}concentration during the titration (Fig. 3).

Although a wide variety of hydroxide, hydroxysulfate, carbonate, and/or silicate compounds possibly could precipitate and limit solute concentrations in mine effluents, a finite set of phases was desired for the simulated titration of the Cal Pike effluent. Thus, of various solids initially considered (Table 2), a subset was tentatively identified for use in the titration simulations that yielded concentrations of solutes that were similar to the measured concentrations (calibration). These phases were selected considering trends in measured concentrations of solutes and computed mineral saturation indices (SI) as a function of pH (Figs. 3 and 4). 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). Phases chosen as likely controls of Fe^{3+}, Al^{3+}, Mn^{3+}, and Mn^{4+} (amorphous $Fe(OH)_3$, basaluminite, boehmite, birnessite) during titrations generally were more soluble than excluded phases (goethite, gibbsite, pyrolusite). Additional hydroxide and carbonate minerals also were identified as possible controls of Fe^{2+}, Mn^{2+}, Mg^{2+}, and Ca^{2+}. Generally, solubility control of divalent cations by carbonates was anticipated to be important with the addition of chemical compounds containing carbonate ($CaCO_3$, Na_2CO_3, $NaHCO_3$) or for effluents with elevated concentrations of dissolved CO_2.

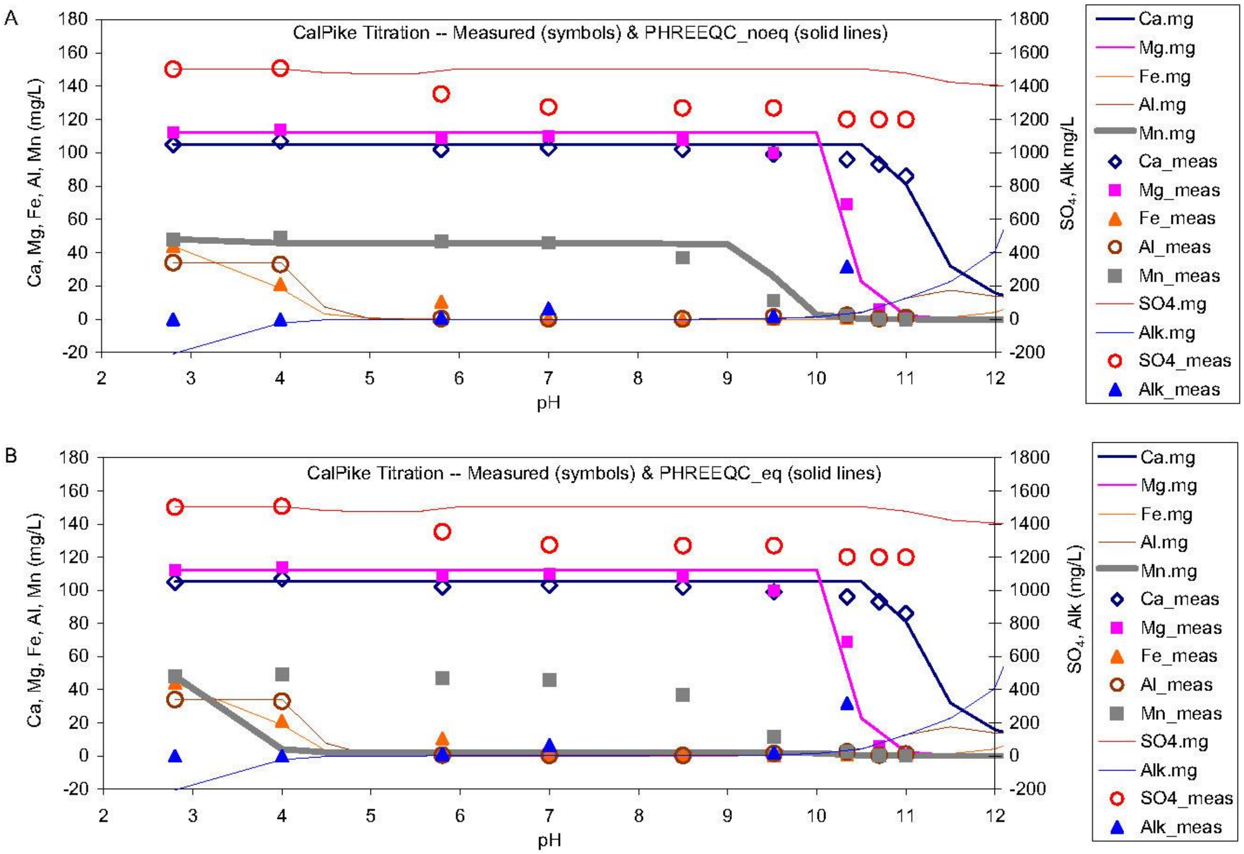

Figure 3. Data for measured (symbols) and simulated (solid lines) titration of "Cal Pike" effluent with NaOH at 16 °C: *A*, Simulated titration of "Cal Pike" effluent without gas exchange. *B*, Simulated titration of "Cal Pike" effluent after pre-aeration (initial O_2 and CO_2 equilibrated to atmospheric concentrations).

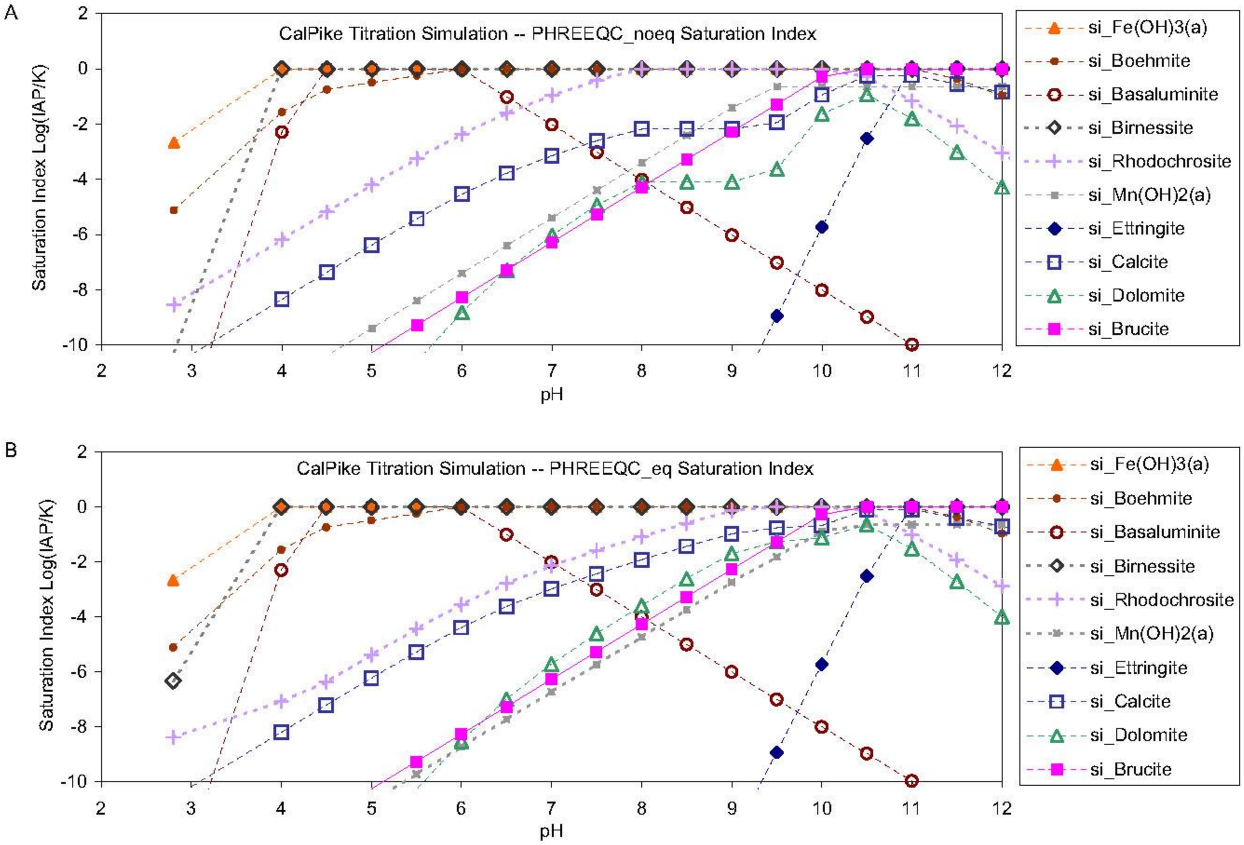

Figure 4. Saturation indices for minerals and other solids as a function of pH at 16 °C: .*A*, Simulated titration of “Cal Pike” effluent with NaOH, without gas exchange. B, Simulated titration of “Cal Pike” effluent with NaOH, after pre-aeration (initial O_2 and CO_2 equilibrated to atmospheric concentrations).

Titration with each of the chemicals listed in Table 1 was simulated for scenarios assuming no gas exchange with the atmosphere (_noeq) and limited gas exchange with the atmosphere (_eq). With the exception of manganese, the titrations without and with gas exchange produced similar results for Fe, Al, Na, Ca, Mg, or SO_4^{2-} (Fig. 3, Tables 3 and 4). Nearly complete removal of Fe without aeration at pH values less than 7 was simulated by the precipitation of $Fe(OH)_3$. Solubility control by this phase implies that Fe was already in the ferric oxidation state. In contrast, negligible removal of manganese was observed at pH values less than 9 (Fig. 3). The observed concentrations of Mn were approximately simulated without aeration by the precipitation of pyrochroite ($Mn(OH)_2$) (Fig. 3A, Table 3), but not by the scenario with pre-aeration (Fig. 3B, Table 4). For the pre-aeration simulation, the concentration of Mn was maintained at lower values than observed by the precipitation of birnessite (MnO_2), which implies that Mn was oxidized in the pre-aeration simulation. Although oxidation of Mn during the pre-aeration step is not realistic because of slow kinetics, comparing the results for the two titration simulations still could be informative.

Table 3. Estimated quality of Cal Pike effluent treated with selected caustic chemicals to specified pH, under conditions with no gas exchange with atmosphere

Solute conc. (mg/L)	pH[a]	Treated to specified pH[b]										
	2.8	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
Caustic Soda (NaOH_noeq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.14	0.42
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.40	1.28	4.04	12.77
Mn	48.10	45.80	45.80	45.80	45.80	45.69	45.32	45.21	26.65	2.79	0.33	0.04
Na	200.4	402.7	402.8	402.9	402.9	403.0	403.3	403.6	419.9	442.0	618.8	689.1
Ca	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	81.2
Mg	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	22.7	2.4
SO4	1505.1	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1478.3
Alk	-206.8	0.1	0.4	0.5	0.7	0.7	0.7	1.7	4.9	14.5	41.8	127.1
Soda Ash (Na_2CO_3_noeq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.15	0.46
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.41	1.32	4.33	13.86
Mn	48.10	26.24	4.00	0.86	0.25	0.10	0.05	0.04	0.04	0.03	0.03	0.03
Na	200.4	459.1	526.2	584.8	782.2	871.4	893.9	923.4	1009.6	1295.5	2457.8	14210.0
Ca	105.2	105.2	105.2	105.2	35.3	4.2	0.4	0.0	0.0	0.0	0.0	0.0
Mg	112.2	112.2	112.2	112.2	69.8	51.0	48.7	48.4	48.4	48.4	48.4	18.2
SO4	1505.1	1505.1	1505.2	1505.2	1505.2	1505.2	1505.2	1505.2	1505.2	1505.2	1505.2	1505.3
Alk	-206.8	87.1	192.5	314.3	393.3	432.2	462.4	525.1	713.9	1340.7	3885.4	29373.0
Hydrated Lime ($Ca(OH)_2$_noeq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.13	0.41
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.40	1.27	1.33	0.09
Mn	48.10	45.80	45.80	45.80	45.80	45.68	45.32	45.21	25.94	2.71	0.30	0.04
Na	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.5	200.5
Ca	105.2	281.5	281.6	281.7	281.8	281.8	282.1	282.3	297.1	316.0	404.8	440.8
Mg	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	20.6	2.1
SO4	1505.1	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1344.4	1338.3
Alk	-206.8	0.1	0.4	0.5	0.7	0.7	0.8	1.8	5.0	14.8	22.5	35.8
Anhydrous Ammonia (NH_3_noeq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.14	0.41
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.40	1.27	4.01	12.55
Mn	48.10	45.81	45.81	45.81	45.81	45.69	45.33	45.21	26.40	2.76	0.32	0.04
Na	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.5	200.5
Ca	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.3	84.9
Mg	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	22.4	2.4
SO4	1505.1	1505.2	1505.2	1505.2	1505.2	1505.2	1505.2	1505.2	1505.2	1505.3	1505.5	1483.0
Alk	-206.8	0.2	0.7	1.5	3.7	10.3	31.1	97.9	333.6	1157.3	6282.8	23010.0

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[a] Untreated pH of 2.8 and associated water quality for Cal Pike effluent.

[b] Treatment to specified pH and associated water quality resulting from chemical reactions were simulated using PHREEQC (Parkhurst and Appelo, 1999). Simulations used the above data for pH and concentrations of solutes in the initial untreated effluent plus assumed dissolved oxygen of 0.5 mg/L and temperature of 16 ºC. Blue shading highlights the titration estimates to achieve pH 8.0 to 8.5 or 10.0 to 10.5.

Table 4. Estimated quality of Cal Pike effluent treated with selected caustic chemicals to specified pH, under conditions with initial gas exchange with atmosphere before chemical addition (pre-aerated)

Solute conc. (mg/L)	pH[c] 2.8	Treated to specified pH[d]										
		6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
Caustic Soda (NaOH_eq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.14	0.42
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.40	1.28	4.04	12.77
Mn	48.10	2.10	2.10	2.10	2.10	2.10	2.10	2.10	1.80	1.57	0.33	0.04
Na	200.4	439.3	439.4	439.5	439.6	439.6	439.7	440.0	440.8	443.1	619.0	689.3
Ca	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	81.2
Mg	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	22.7	2.4
SO_4	1505.1	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1478.3
Alk	-206.8	0.2	0.5	0.7	0.9	1.0	1.4	2.4	5.3	14.7	42.2	127.6
Soda Ash (Na_2CO_3_eq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.15	0.45
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.41	1.33	4.37	13.61
Mn	48.10	2.10	2.10	0.75	0.23	0.09	0.05	0.04	0.04	0.03	0.03	0.03
Na	200.4	486.1	543.8	611.2	832.6	910.0	932.9	967.5	1070.0	1413.9	2858.7	16988.0
Ca	105.2	105.2	105.2	105.2	27.6	3.1	0.3	0.0	0.0	0.0	0.0	0.0
Mg	112.2	112.2	112.2	112.2	65.1	50.3	48.6	48.4	48.4	48.4	48.4	19.3
SO_4	1505.1	1505.1	1505.2	1505.2	1505.2	1505.3	1505.3	1505.3	1505.3	1505.3	1505.3	1505.4
Alk	-206.8	101.9	227.4	371.5	464.7	510.6	546.5	620.8	845.1	1598.2	4757.5	35419.0
Hydrated Lime ($Ca(OH)_2$_eq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.13	0.41
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.40	1.27	1.33	0.09
Mn	48.10	2.10	2.10	2.10	2.10	2.10	2.10	2.10	1.86	1.65	0.30	0.04
Na	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.5	200.5
Ca	105.2	313.4	313.6	313.7	313.7	313.8	313.8	314.1	314.8	316.9	404.8	440.8
Mg	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	20.6	2.1
SO_4	1505.1	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0	1344.4	1338.3
Alk	-206.8	0.2	0.5	0.7	0.9	1.0	1.4	2.5	5.5	15.1	22.5	35.8
Anhydrous Ammonia (NH_3_eq)												
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.14	0.41
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.40	1.27	4.01	12.55
Mn	48.10	2.10	2.10	2.10	2.10	2.10	2.10	2.10	1.79	1.56	0.33	0.04
Na	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.4	200.5	200.5
Ca	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	105.2	85.0
Mg	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	112.2	22.4	2.4
SO_4	1505.1	1505.3	1505.3	1505.3	1505.3	1505.3	1505.3	1505.3	1505.3	1505.3	1505.5	1483.0
Alk	-206.8	0.3	0.9	1.9	4.4	12.3	37.2	115.8	364.9	1162.6	6285.8	23018.0

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[c] Untreated pH of 2.8 and associated water quality for Cal Pike effluent.

[d] Treatment to specified pH and associated water quality resulting from chemical reactions were simulated using PHREEQC (Parkhurst and Appelo, 1999). Simulations used the above data for pH and concentrations of solutes in the initial untreated effluent plus assumed temperature of 16 ºC. To simulate pre-aeration, the dissolved oxygen was allowed to equilibrate with an atmospheric concentration of 21 volume percent before the addition of any caustic chemicals. Blue shading highlights the titration estimates to achieve pH 8.0 to 8.5 or 10.0 to 10.5.

Simulated solute concentrations as a function of pH for scenarios without and with pre-aeration (oxidation) were similar among NaOH, ammonia (NH_3), hydrated lime ($Ca(OH)_2$), (Tables 3 and 4), and quick lime[a] (CaO). Specific metals precipitated at consistent pH values. Similar concentrations of a solute as a function of pH imply that the pH was the critical factor controlling the concentration of the solute. In contrast, the simulated treatment with soda ash (Na_2CO_3) (Tables 3 and 4) and other carbonate phases ($NaHCO_3$, $CaCO_3$) produced pH and concentration trends that differed from the other caustic chemicals. Dissolution of soda ash created conditions that favored the precipitation of $FeCO_3$, $MnCO_3$, $CaCO_3$, and other carbonate minerals and resulted in decreases in the concentrations of divalent metals at near-neutral pH.

With the exception of treatment with Na_2CO_3, the titration simulations indicated that treatment using NaOH, $Ca(OH)_2$, CaO, or NH_3 under similar aeration scenarios could produce similar effluent characteristics. Nevertheless, different quantities of the chemicals could be needed to attain a specific pH value, and/or the costs to achieve the same end could differ. To evaluate the needed quantities and costs of different chemicals for treatment, a target pH of 10.0 to 10.5 or 8.0 to 8.5 may be considered (blue shaded cells in Tables 5 and 6). Because the latter pH range is approximately the endpoint for hot acidity titrations, it is a useful reference point to relate the chemical equivalents on the basis of the measured hot acidity or computed net acidity and the corresponding quantities of caustic chemicals computed by simulated titrations.

To neutralize the net acidity of 460 mg/L as $CaCO_3$ for the Cal Pike effluent, an equivalent amount of 0.46 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 (Tables 5 and 6). Then, the quantity of industrial grade chemical, corrected for treatment efficiency and purity, was estimated for treatment of 1000 gallons (Table 5 and 6). Likewise, chemical requirements indicated by the simulated titrations to different pH endpoints were used to compute estimated treatment costs (Tables 5 and 6).

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[a] Quick lime results were nearly identical to those for hydrated lime, so are not reported.

Table 5. Estimated cost of selected caustic chemicals for treating Cal Pike effluent to specified pH, under conditions with no gas exchange with atmosphere

Estimated quantity and cost of chemical and sludge	Acid eq mg/L $CaCO_3$	Treated to specified pH[a]										
		6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
Caustic Soda (NaOH_noeq)												
Pure NaOH (g/L)	0.36	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.38	0.42	0.73	0.85
Equivalent (g/L as $CaCO_3$) [b]	0.46	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.48	0.53	0.91	1.06
Quantity (lb/1000 gal)[c]		2.96	2.96	2.96	2.96	2.96	2.97	2.97	3.21	3.54	6.12	7.15
Cost ($/1000 gal)[d]		$1.06	$1.06	$1.06	$1.06	$1.06	$1.07	$1.07	$1.15	$1.27	$2.20	$2.56
Sludge (gal/1000 gal; 5%)[e]		14.13	14.14	14.14	14.14	14.15	14.19	14.18	16.40	19.12	35.03	41.34
Sludge cost ($/1000 gal)[f]		$0.85	$0.85	$0.85	$0.85	$0.85	$0.85	$0.85	$0.98	$1.15	$2.10	$2.48
Soda Ash (Na_2CO_3_noeq)												
Pure Na_2CO_3 (g/L)	0.48	0.60	0.75	0.89	1.34	1.55	1.60	1.67	1.87	2.52	5.20	32.29
Equivalent (g/L as $CaCO_3$)	0.46	0.56	0.71	0.84	1.27	1.46	1.51	1.57	1.76	2.38	4.91	30.46
Quantity (lb/1000 gal)		8.36	10.52	12.42	18.80	21.68	22.40	23.36	26.14	35.38	72.93	452.56
Cost ($/1000 gal)		$1.17	$1.47	$1.74	$2.63	$3.04	$3.14	$3.27	$3.66	$4.95	$10.21	$63.36
Sludge (gal/1000 gal; 5%)		16.52	19.25	19.64	40.62	49.90	51.03	51.13	51.08	50.88	50.20	53.55
Sludge cost ($/1000 gal)		$0.99	$1.16	$1.18	$2.44	$2.99	$3.06	$3.07	$3.06	$3.05	$3.01	$3.21
Hydrated Lime ($Ca(OH)_2$_noeq)												
Pure $Ca(OH)_2$ (g/L)	0.34	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.35	0.39	0.82	0.90
Equivalent (g/L as $CaCO_3$)	0.46	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.48	0.53	1.11	1.21
Quantity (lb/1000 gal)		3.53	3.54	3.54	3.54	3.54	3.54	3.55	3.85	4.23	8.90	9.73
Cost ($/1000 gal)		$0.35	$0.35	$0.35	$0.35	$0.35	$0.35	$0.36	$0.39	$0.42	$0.89	$0.97
Sludge (gal/1000 gal; 10%)		7.06	7.07	7.07	7.07	7.07	7.09	7.09	8.24	9.56	18.01	19.81
Sludge cost ($/1000 gal)		$0.42	$0.42	$0.42	$0.42	$0.42	$0.43	$0.43	$0.49	$0.57	$1.08	$1.19
Anhydrous Ammonia (NH_3_noeq)												
Pure NH_3 (g/L)	0.16	0.15	0.15	0.15	0.15	0.15	0.16	0.18	0.27	0.57	2.44	8.15
Equivalent (g/L as $CaCO_3$)	0.46	0.44	0.44	0.44	0.44	0.45	0.47	0.54	0.81	1.67	7.16	23.98
Quantity (lb/1000 gal)		1.40	1.40	1.40	1.41	1.43	1.50	1.71	2.57	5.31	22.76	76.18
Cost ($/1000 gal)		$0.70	$0.70	$0.70	$0.71	$0.72	$0.75	$0.86	$1.28	$2.66	$11.38	$38.09
Sludge (gal/1000 gal; 5%)		14.12	14.13	14.13	14.13	14.14	14.18	14.18	16.42	19.12	35.10	40.68
Sludge cost ($/1000 gal)		$0.85	$0.85	$0.85	$0.85	$0.85	$0.85	$0.85	$0.99	$1.15	$2.11	$2.44

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[a] Treatment to specified pH was simulated using PHREEQC (Parkhurst and Appelo, 1999).

[b] Equivalent quantity of pure chemical in grams to treat 1 liter of solution is computed using $CaCO_3$ conversion factors in Table 1. The chemical equivalent for acidity of 460 mg/L as $CaCO_3$ is reported for comparison with estimated chemical quantities for treatment to specified pH. Blue shading highlights the acid equivalent estimate and titration estimates to achieve pH 8.0 to 8.5 or 10.0 to 10.5.

[c] Chemical quantity in pounds per 1,000 gallons is estimated using efficiency factor in Table 1.

[d] Cost is estimated using unit cost values and efficiency factors in Table 1. English units for quantities and costs are used for consistency with default settings of AMDTreat (U.S. Office of Surface Mining Reclamation and Enforcement, 2006).

[e] Sludge quantity is estimated assuming 5% or 10% solids concentration, as specified, for precipitated metal compounds ($Fe(OH)_3$, $Al(OH)_3$, $Mn(OH)_2$, $Mg(OH)_2$, $CaCO_3$), based on decrease in metal concentration (Table 4), plus unreacted chemical additive, based on the efficiency factor (Table 1).

[f] Sludge cost estimated by multiplying computed sludge volume by unit cost of $0.06/gal, which is default setting of AMDTreat (U.S. Office of Surface Mining Reclamation and Enforcement, 2006).

Table 6. Estimated cost of selected caustic chemicals for treating Cal Pike effluent to specified pH, under conditions with initial atmospheric equilibrium before chemical addition (pre-aerated)

Estimated quantity and cost of chemical and sludge	Acid eq mg/L $CaCO_3$	Treated to specified pH[a]										
		6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
Caustic Soda (NaOH_eq)												
Pure NaOH (g/L)	0.36	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.73	0.85
Equivalent (g/L as $CaCO_3$) [b]	0.46	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.53	0.91	1.06
Quantity (lb/1000 gal)[c]		3.46	3.47	3.47	3.47	3.47	3.47	3.48	3.49	3.52	6.07	7.09
Cost ($/1000 gal)[d]		$1.25	$1.25	$1.26	$1.26	$1.26	$1.26	$1.26	$1.26	$1.27	$2.20	$2.57
Sludge (gal/1000 gal; 5%)[e]		19.48	19.49	19.49	19.49	19.49	19.48	19.46	19.44	19.27	35.03	41.33
Sludge cost ($/1000 gal)[f]		$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.16	$2.10	$2.48
Soda Ash (Na_2CO_3_eq)												
Pure Na_2CO_3 (g/L)	0.48	0.66	0.79	0.95	1.46	1.64	1.69	1.77	2.00	2.80	6.13	38.69
Equivalent (g/L as $CaCO_3$)	0.46	0.62	0.75	0.89	1.37	1.54	1.59	1.67	1.89	2.64	5.78	36.50
Quantity (lb/1000 gal)		9.23	11.09	13.27	20.42	22.92	23.66	24.78	28.09	39.20	85.88	542.31
Cost ($/1000 gal)		$1.29	$1.55	$1.86	$2.86	$3.21	$3.31	$3.47	$3.93	$5.49	$12.02	$75.92
Sludge (gal/1000 gal; 5%)		19.48	19.48	19.65	42.91	50.23	51.07	51.13	51.08	50.88	50.20	53.41
Sludge cost ($/1000 gal)		$1.17	$1.17	$1.18	$2.57	$3.01	$3.06	$3.07	$3.06	$3.05	$3.01	$3.20
Hydrated Lime ($Ca(OH)_2$_eq)												
Pure $Ca(OH)_2$ (g/L)	0.34	0.38	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.82	0.90
Equivalent (g/L as $CaCO_3$)	0.46	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.53	1.11	1.21
Quantity (lb/1000 gal)		4.17	4.18	4.18	4.18	4.18	4.18	4.19	4.20	4.24	8.90	9.73
Cost ($/1000 gal)		$0.42	$0.42	$0.42	$0.42	$0.42	$0.42	$0.42	$0.42	$0.42	$0.89	$0.97
Sludge (gal/1000 gal; 10%)		9.74	9.74	9.74	9.74	9.74	9.74	9.73	9.71	9.63	18.01	19.81
Sludge cost ($/1000 gal)		$0.58	$0.58	$0.58	$0.58	$0.58	$0.58	$0.58	$0.58	$0.58	$1.08	$1.19
Anhydrous Ammonia (NH_3_eq)												
Pure NH_3 (g/L)	0.16	0.18	0.18	0.18	0.18	0.18	0.19	0.22	0.30	0.57	2.44	8.15
Equivalent (g/L as $CaCO_3$)	0.46	0.52	0.52	0.52	0.52	0.53	0.56	0.64	0.88	1.68	7.17	23.98
Quantity (lb/1000 gal)		1.65	1.66	1.66	1.67	1.69	1.77	2.02	2.81	5.33	22.77	76.20
Cost ($/1000 gal)		$0.83	$0.83	$0.83	$0.83	$0.85	$0.89	$1.01	$1.41	$2.67	$11.39	$38.10
Sludge (gal/1000 gal; 5%)		19.47	19.48	19.48	19.48	19.48	19.48	19.46	19.43	19.27	35.10	40.67
Sludge cost ($/1000 gal)		$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.16	$2.11	$2.44

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[a] Treatment to specified pH was simulated using PHREEQC (Parkhurst and Appelo, 1999).

[b] Equivalent quantity of pure chemical in grams to treat 1 liter of solution is computed using $CaCO_3$ conversion factors in Table 1. The chemical equivalent for acidity of 460 mg/L as $CaCO_3$ is reported for comparison with estimated chemical quantities for treatment to specified pH. Blue shading highlights the acid equivalent estimate and titration estimates to achieve pH 8.0 to 8.5 or 10.0 to 10.5.

[c] Chemical quantity in pounds per 1,000 gallons is estimated using efficiency factor in Table 1.

[d] Cost is estimated using unit cost values and efficiency factors in Table 1. English units for quantities and costs are used for consistency with default settings of AMDTreat (U.S. Office of Surface Mining Reclamation and Enforcement, 2006).

[e] Sludge quantity is estimated assuming 5% or 10% solids concentration, as specified, for precipitated metal compounds ($Fe(OH)_3$, $Al(OH)_3$, $Mn(OH)_2$, $Mg(OH)_2$, $CaCO_3$), based on decrease in metal concentration (Table 4), plus unreacted chemical additive, based on the efficiency factor (Table 1).

[f] Sludge cost estimated by multiplying computed sludge volume by unit cost of $0.06/gal, which is default setting of AMDTreat (U.S. Office of Surface Mining Reclamation and Enforcement, 2006).

The equivalent quantities of NaOH, $Ca(OH)_2$, CaO, or NH_3 that were estimated on the basis of the net acidity (460 mg/L as $CaCO_3$) were similar to estimates on the basis of the titration simulations to target pH 8.0 or 8.5 without aeration (Table 5). However, without aeration (oxidation), Mn removal would not be expected until pH ~10 (Fig. 3, Table 3). In order to achieve a target pH of 10 necessary to remove Mn, without aeration, the titration simulations indicated that approximately 10 to 15 percent greater quantities of the caustic chemicals would be needed than were estimated as net acidity equivalents.

To achieve a target pH 10, approximately the same quantity of a given caustic chemical would be needed with or without pre-aeration (Tables 5 and 6). Nevertheless, treatment to this high pH may not be necessary if the dissolved Mn and Fe^{2+} were oxidized before the addition of caustic chemicals. The pre-aeration simulation indicated removal of iron as $Fe(OH)_3$ and manganese as MnO_2 may be possible at low pH (Fig. 3; Table 4). Although oxidation of manganese may not actually be achieved by pre-aeration because of slow kinetics, pre-treatment with an oxidizing agent such as ozone, hydrogen peroxide, or potassium permanganate could be considered (Skousen et al., 1993; Sato and Robbins, 2000). With oxidation (indicated by pre-aeration simulation), the estimated caustic chemical quantities for treatment to pH 8.0 to 8.5 were less than those estimated to achieve manganese removal at pH 10 without aeration (Table 6). Although the same amounts of Mn and Fe ultimately are removed under each of these treatment scenarios, treatment of an oxidized solution at pH 8.0 to 8.5 avoids precipitation of Mg and Ca and thus uses a smaller quantity of caustic chemicals than treatment of an unoxidized solution to pH 10. Because of the simulated precipitation of Mg as $Mg(OH)_2$, the estimated sludge volume nearly doubled from pH 9.5 to 10.5 (Tables 5 and 6). The inadvertent precipitation of Mg not only adds to the sludge volume but consumes caustic chemicals, which increase costs for the operation and maintenance of treatment systems. Thus, some practitioners have argued that the cost of treatment to remove Mn is not warranted, requiring high pH and/or oxidizing agents, and that treatment to a lower pH, such as 8.0, would consume less caustic chemical, remove Al and Fe, and, prolong the viability of treatment trust funds (Kleinmann and Watzlaf, 1986; Means and Hilton, 2004).

In contrast with the simulated treatment of the Cal Pike effluent with NaOH, $Ca(OH)_2$, CaO, or NH_3, the simulated treatments with Na_2CO_3 and $NaHCO_3$ indicated the potential for removal of Mn, Mg, Ca, and other divalent metals as $MnCO_3$, $CaCO_3$, $CaMg(CO_3)_2$, and other carbonates. The precipitation of carbonates was indicated at pH values near neutral (7.0 to 8.0). As a consequence of the precipitation of Ca, Mg, and other carbonates, the estimated sludge volumes at pH 8.0 were 2.5 to 5 times greater than the sludge volumes estimated for non-carbonate chemical treatments (Tables 5 and 6). Thus, soda ash and other carbonate based agents may have limited usefulness, mainly for treatment of effluents with high concentrations of manganese and low concentrations of Ca and Mg.

The simulated titration of mine drainage with different caustic chemicals was of a general nature. The simulations were not intended to describe kinetics of chemical reactions, mixing, particle formation and settling, and other dynamic processes within an active treatment system. The simulated titration to a specified pH assumed equilibrium conditions would be achieved among solid phases and aqueous species, and that dissolved gases would have no exchange or limited exchange with the atmosphere (pre-aeration). Actual conditions for titrations or treatment systems may be intermediate of these conditions. 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 Pacek, 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^{2+} and Fe^{2+} (Hem and Lind, 1983; Kirby et al., 2009). The consideration of these kinetic factors may be possible with more advanced geochemical models that consider residence time as an additional variable.

Conclusions

The Cal Pike effluent had greater concentrations of acidity and metals and lower concentrations of dissolved CO_2 compared to a majority of effluents from legacy coal mines in Pennsylvania. Chemical addition during titration of the Cal Pike effluent increased pH values and led to decreases in metals concentrations that were consistent with solubility controls of Fe, Al, Mn, and Mg by hydroxide and/or carbonate minerals.

The empirical and simulated titrations indicated that the addition of caustic chemicals to increase pH to values near-neutral (6 to 8) can be effective for removal of Al and Fe^{3+} from acidic, metal-laden effluent. The titration simulations indicated that manganese may be removed as $Mn(OH)_2$ at pH 10, without aeration, or as MnO_2 or related compounds at low pH if oxidation is completed before the addition of caustic chemicals. Treatment to pH values less than or equal to 8.5 may be effective for removing Al, Fe, and Mn, while avoiding the unnecessary precipitation of Mg and Ca. The quantities of chemicals needed for treatment and the volume of sludge produced can be reduced accordingly. However, oxidation of Mn and Fe^{2+}can be slow. Thus; kinetic factors need to be considered to accurately simulate treatment strategies for removal of Mn and Fe^{2+} under oxidizing conditions.

The simulated titration results for chemical requirements and corresponding effluent quality (pH and solute concentrations) and sludge volumes can be used with or in place of empirical titration data to evaluate potential costs for alternative treatment strategies with AMDTreat. Additional empirical titration data can be evaluated to refine the titration modeling approach. Specifically, simulations could be considered for the titration of various net-acidic effluents and net-alkaline effluents with a range of compositions. After refinement, possibly including other solid phases or oxidation kinetics, the PHREEQC titration simulation will be coupled as an add-in module to AMDTreat. The concept is for the PHREEQC titration simulation to be called by AMDTreat to run in the background. A user of AMDTreat would need to provide the required water-quality data on the input screen of AMDTreat, but would not need to understand geochemical modeling. Given chemical input data currently required for AMDTreat, plus values for calcium, magnesium, and redox state (dissolved oxygen, iron speciation, or redox potential), the PHREEQC treatment titration simulations will indicate an approximate quantity of caustic chemicals to achieve specified pH values and the corresponding dissolved chemical concentrations remaining in treated effluent. A new “titration model” screen would be displayed by AMDTreat summarizing the results of the PHREEQC subroutine such as Tables 3-4 of this paper. The user will be able to consider these results for treatment to different pH values with various caustic chemicals, and then specify the chemical type and quantity to achieve the desired pH in the active treatment screen of AMDTreat.

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