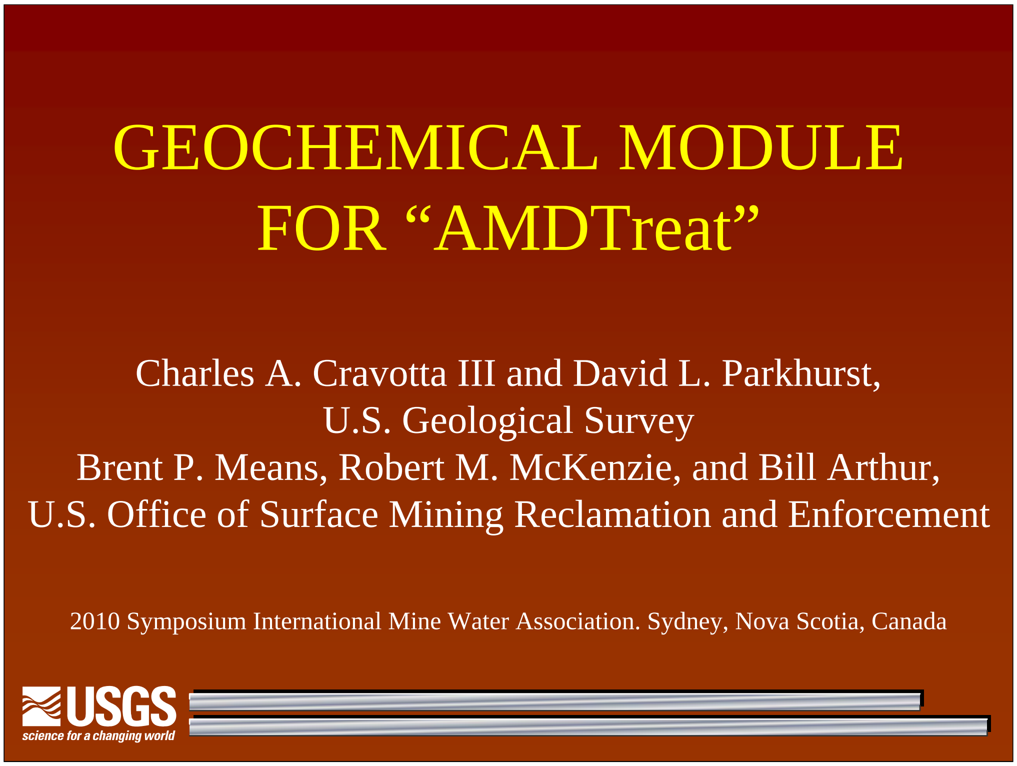
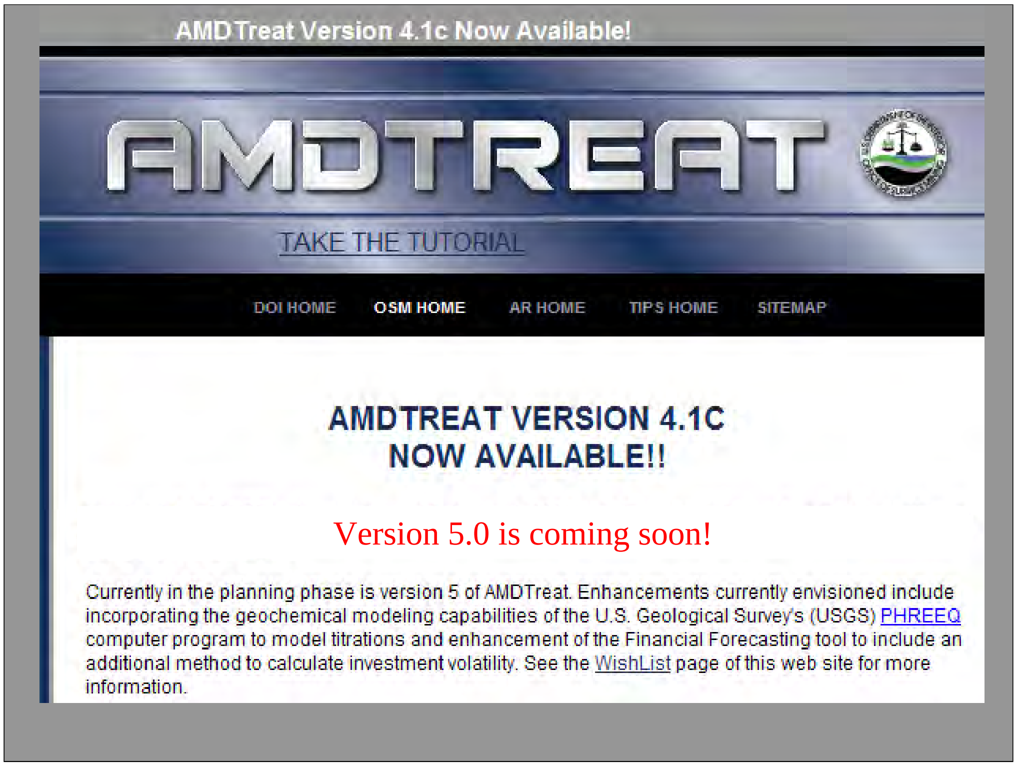


GEOCHEMICAL MODULE FOR “AMDTreat”

Charles A. Cravotta III and David L. Parkhurst,
U.S. Geological Survey
Brent P. Means, Robert M. McKenzie, and Bill Arthur,
U.S. Office of Surface Mining Reclamation and Enforcement

2010 Symposium International Mine Water Association. Sydney, Nova Scotia, Canada

ABSTRACT: 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 titration with industrial chemicals to accurately compute costs for treatment of net-acidic or net-alkaline mine drainage, such empirical 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 chemistry of 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 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.



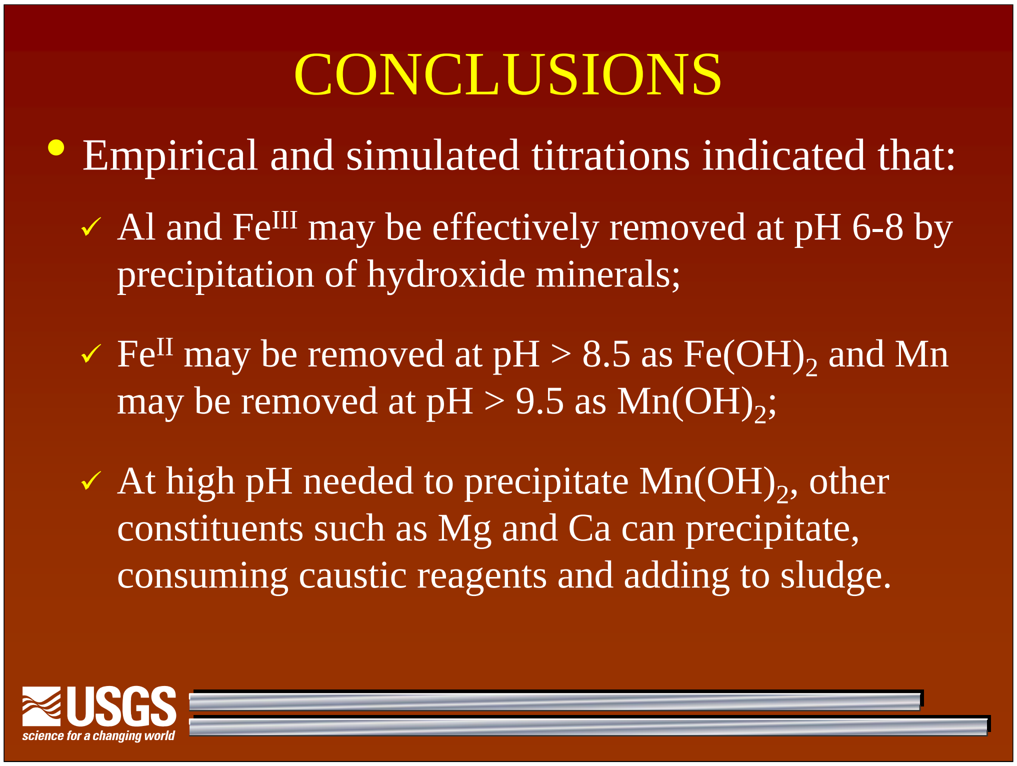
AMDTREAT VERSION 4.1C
NOW AVAILABLE!!

Version 5.0 is coming soon!

Currently in the planning phase is version 5 of AMDTreat. Enhancements currently envisioned include incorporating the geochemical modeling capabilities of the U.S. Geological Survey's (USGS) PHREEQ computer program to model titrations and enhancement of the Financial Forecasting tool to include an additional method to calculate investment volatility. See the WishList page of this web site for more information.

AMDTREAT UPGRADE: AMD TREATMENT COST ESTIMATE: The AMDTreat computer program is widely used to estimate costs for passive or active treatment of coal-mine drainage. For net acidic, metal-laden water, the caustic chemical requirement for active treatment is estimated as equivalent to the net acidity of the raw effluent. For net alkaline water with elevated Mn, AMDTreat wrongly indicates that no caustic chemical would be needed, even though caustic chemicals routinely are used to remove Mn from the effluent. Although AMDTreat can use results of titration with industrial chemicals to accurately compute costs for treatment of net-acidic or net-alkaline mine drainage, such empirical 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 chemistry of treated effluent, and (3) the volume of sludge produced by the treatment, a titration simulation is being developed using the geochemical program PHREEQC that will be coupled to AMDTreat.

This paper describes the development, evaluation, and potential utilization of the PHREEQC titration module for AMDTreat. In the near future, the PHREEQC titration routine will be coupled with AMDTreat to facilitate cost estimation for a wide variety of treatment scenarios.

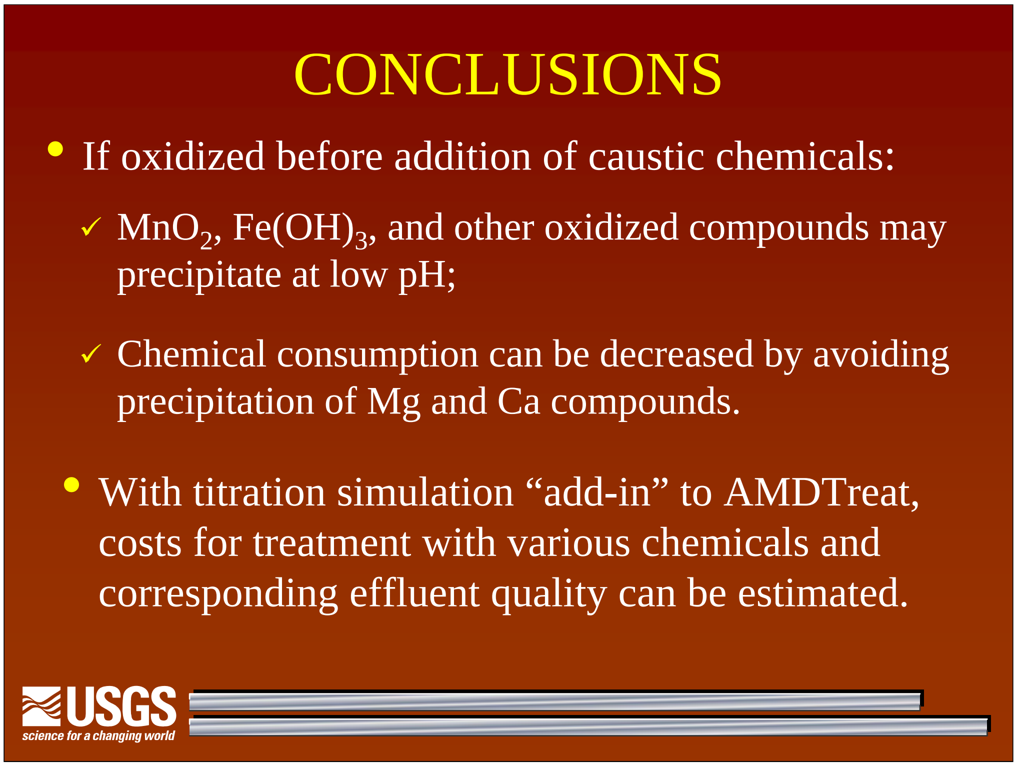


CONCLUSIONS

- Empirical and simulated titrations indicated that:
  - ✓ Al and Fe^{III} may be effectively removed at pH 6-8 by precipitation of hydroxide minerals;
  - ✓ Fe^{II} may be removed at pH > 8.5 as $Fe(OH)_2$ and Mn may be removed at pH > 9.5 as $Mn(OH)_2$;
  - ✓ At high pH needed to precipitate $Mn(OH)_2$, other constituents such as Mg and Ca can precipitate, consuming caustic reagents and adding to sludge.

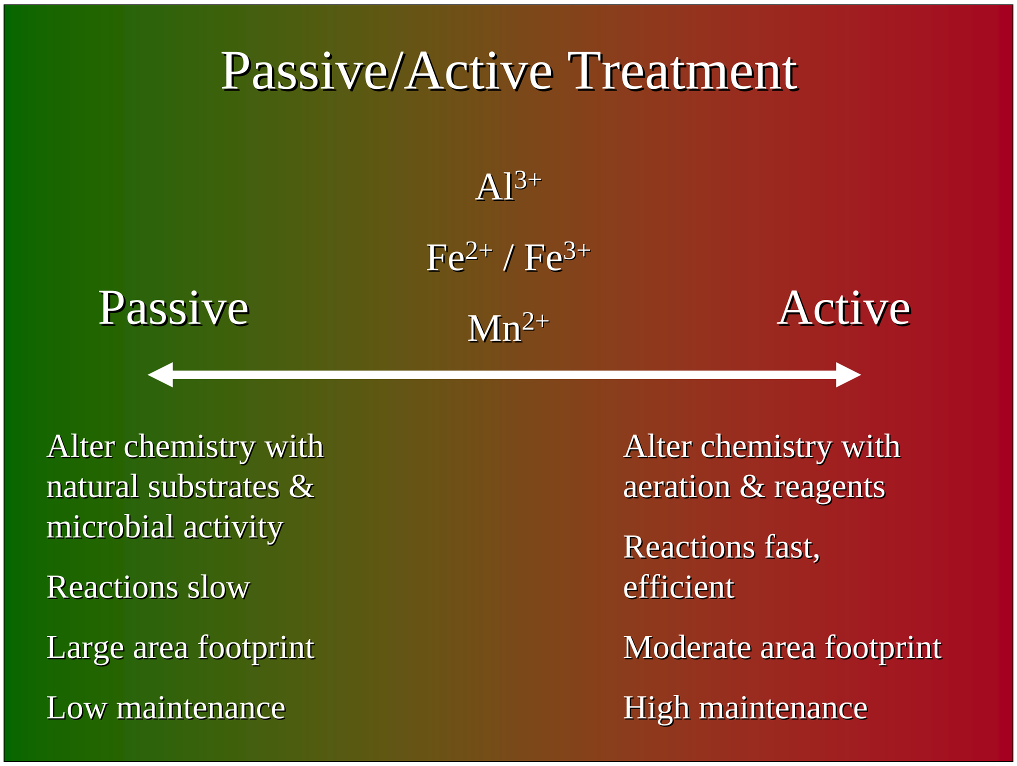
USGS
science for a changing world

CONCLUSIONS:



CONCLUSIONS

- If oxidized before addition of caustic chemicals:
  - ✓ MnO_2, $Fe(OH)_3$, and other oxidized compounds may precipitate at low pH;
  - ✓ Chemical consumption can be decreased by avoiding precipitation of Mg and Ca compounds.
- With titration simulation “add-in” to AMDTreat, costs for treatment with various chemicals and corresponding effluent quality can be estimated.



Passive/Active Treatment

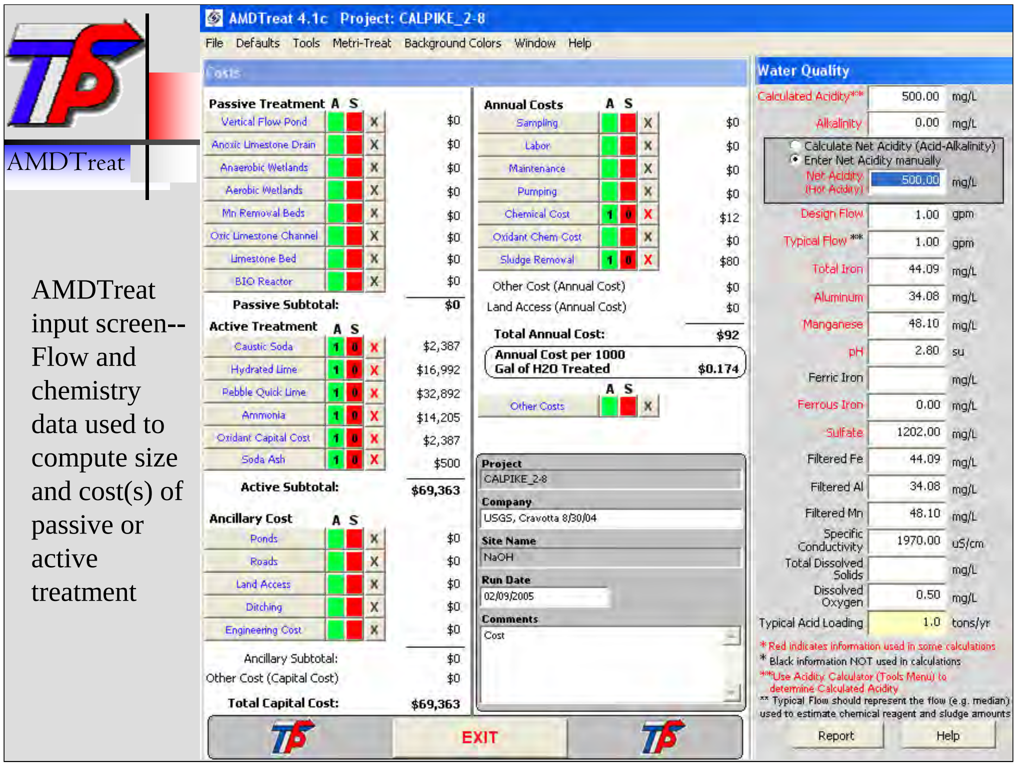
Al^{3+}

Fe^{2+} / Fe^{3+}

Mn^{2+}

Passive	Active
Alter chemistry with natural substrates & microbial activity	Alter chemistry with aeration & reagents
Reactions slow	Reactions fast, efficient
Large area footprint	Moderate area footprint
Low maintenance	High maintenance

PASSIVE/ACTIVE TREATMENT: Treatment of “acidic mine drainage” (AMD) may be necessary to neutralize acidity and remove dissolved and suspended metals. The conventional treatment for metal-laden effluent that has excess acidity involves the addition of strong alkaline (caustic) chemicals and, possibly, aeration with addition of polymers (Skousen and others, 1998). Although effective, this “active” treatment approach can be expensive because of the high cost of chemical reagents, operation, and maintenance. Alternative treatment methods for AMD include “passive” wetlands and limestone-based systems (Hedin and others, 1994; Skousen and others, 1998; Watzlaf and others, 2000). The “passive” treatment systems generally require little maintenance over their design life (typically 20 years) but are limited by slower rates of neutralization and contaminant removal and, consequently, may require larger land area than for conventional “active” treatments.



AMDTreat input screen--Flow and chemistry data used to compute size and cost(s) of passive or active treatment

Passive Treatment	A	S		
Vertical Flow Pond	🟩	🟥	X	$0
Anoxic Limestone Drain	🟩	🟥	X	$0
Anaerobic Wetlands	🟩	🟥	X	$0
Aerobic Wetlands	🟩	🟥	X	$0
Mn Removal Beds	🟩	🟥	X	$0
Oxic Limestone Channel	🟩	🟥	X	$0
Limestone Bed	🟩	🟥	X	$0
BIO Reactor	🟩	🟥	X	$0
Passive Subtotal:				**$0**

Active Treatment	A	S		
Caustic Soda	1	0	X	$2,387
Hydrated Lime	1	0	X	$16,992
Pebble Quick Lime	1	0	X	$32,892
Ammonia	1	0	X	$14,205
Oxidant Capital Cost	1	0	X	$2,387
Soda Ash	1	0	X	$500
Active Subtotal:				**$69,363**

Ancillary Cost	A	S		
Ponds	🟩	🟥	X	$0
Roads	🟩	🟥	X	$0
Land Access	🟩	🟥	X	$0
Ditching	🟩	🟥	X	$0
Engineering Cost	🟩	🟥	X	$0
Ancillary Subtotal:				$0
Other Cost (Capital Cost)				$0
Total Capital Cost:				**$69,363**

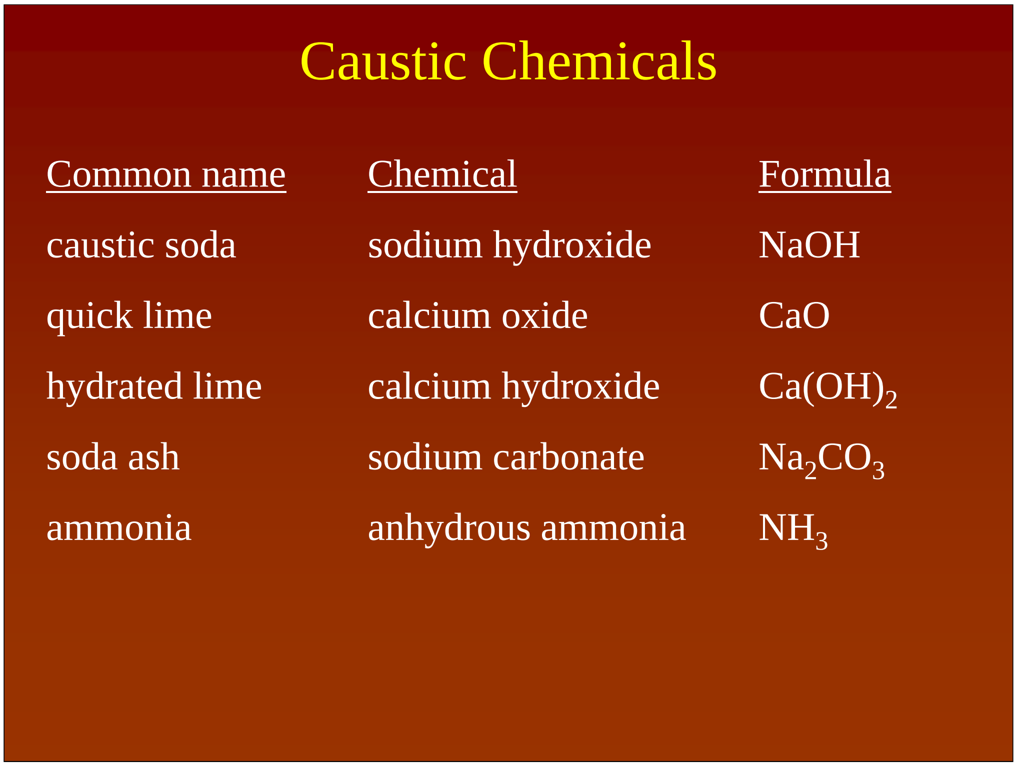
Annual Costs	A	S		
Sampling	🟩	🟥	X	$0
Labor	🟩	🟥	X	$0
Maintenance	🟩	🟥	X	$0
Pumping	🟩	🟥	X	$0
Chemical Cost	1	0	X	$12
Oxidant Chem Cost	🟩	🟥	X	$0
Sludge Removal	1	0	X	$80
Other Cost (Annual Cost)				$0
Land Access (Annual Cost)				$0
Total Annual Cost:				**$92**
Annual Cost per 1000 Gal of H20 Treated				**$0.174**
Other Costs	🟩	🟥	X	

Project
CALPIKE_2-8
Company
USGS, Cravotta 8/30/04
Site Name
NaOH
Run Date
02/09/2005
Comments
Cost

Water Quality		
Calculated Acidity**	500.00	mg/L
Alkalinity	0.00	mg/L
○ Calculate Net Acidity (Acid-Alkalinity) ● Enter Net Acidity manually		
Net Acidity (Hot Acidity)	500.00	mg/L
Design Flow	1.00	gpm
Typical Flow **	1.00	gpm
Total Iron	44.09	mg/L
Aluminum	34.08	mg/L
Manganese	48.10	mg/L
pH	2.80	su
Ferric Iron		mg/L
Ferrous Iron	0.00	mg/L
Sulfate	1202.00	mg/L
Filtered Fe	44.09	mg/L
Filtered Al	34.08	mg/L
Filtered Mn	48.10	mg/L
Specific Conductivity	1970.00	uS/cm
Total Dissolved Solids		mg/L
Dissolved Oxygen	0.50	mg/L
Typical Acid Loading	1.0	tons/yr

* Red indicates information used in some calculations
* Black information NOT used in calculations
**Use Acidity Calculator (Tools Menu) to determine Calculated Acidity
** Typical Flow should represent the flow (e.g. median) used to estimate chemical reagent and sludge amounts

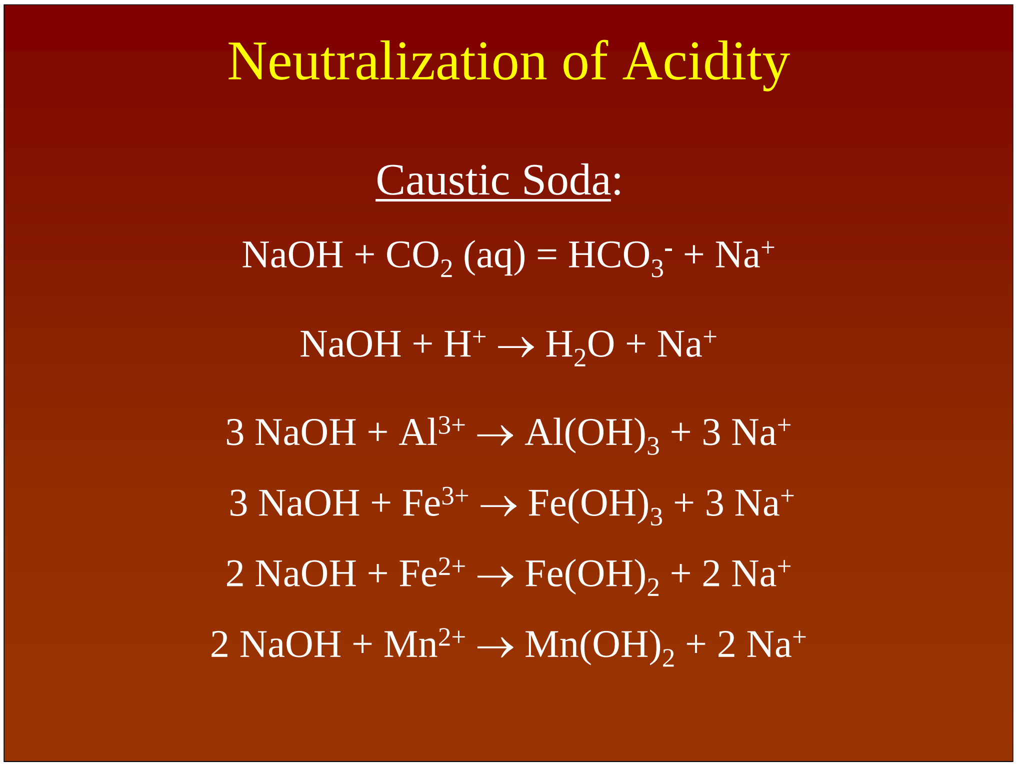
AMDTREAT INPUT SCREEN: Given input values for flow, alkalinity, acidity, metals, and sulfate, AMDTreat can be used compute costs for passive or active treatment strategies. However, because passive systems tend to be limited by kinetic factors (reactions slow), predicting effluent quality is difficult for passive treatments. In contrast, reactions tend to be faster and approach equilibrium conditions for active treatment with soluble chemicals. Thus, assuming geochemical equilibrium, active treatment with chemicals is simulated with PHREEQC. With added data for Ca, Mg, and Na, the PHREEQC titration “add-in” will permit the estimation of the chemical requirement to achieve a specific pH and the treated effluent composition. The PHREEQC titration routine will run in the background. A user will be able to select the target pH and evaluate simulated titration results for various chemicals.



Caustic Chemicals

Common name	Chemical	Formula
caustic soda	sodium hydroxide	$NaOH$
quick lime	calcium oxide	CaO
hydrated lime	calcium hydroxide	$Ca(OH)_2$
soda ash	sodium carbonate	Na_2CO_3
ammonia	anhydrous ammonia	NH_3

CAUSTIC CHEMICALS: 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 iron, manganese, aluminum, and other metals from discharges at active coal-mining operations (U.S. Environmental Protection Agency, 1983; Skousen et al., 1993, 2000). The treatment cost depends on the chemical used and increases with the quantities of chemical added and sludge produced.



Neutralization of Acidity

Caustic Soda:

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

$$NaOH + H^+ \rightarrow H_2O + Na^+$$

$$3\ NaOH + Al^{3+} \rightarrow Al(OH)_3 + 3\ Na^+$$

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

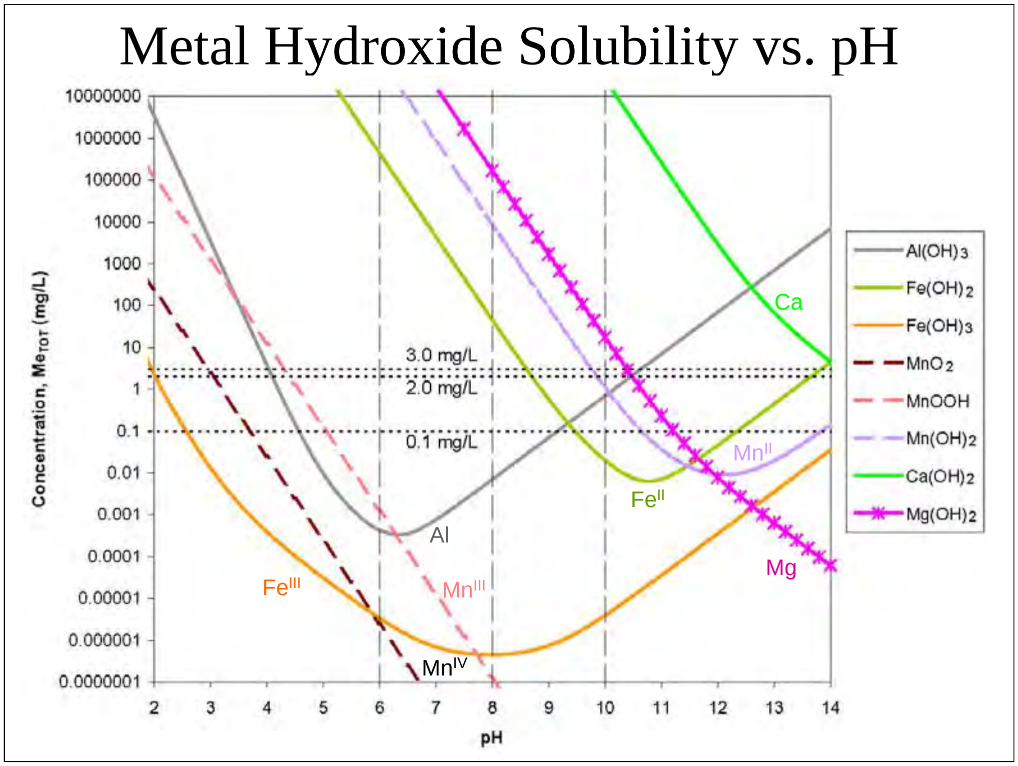
$$2\ NaOH + Fe^{2+} \rightarrow Fe(OH)_2 + 2\ Na^+$$

$$2\ NaOH + Mn^{2+} \rightarrow Mn(OH)_2 + 2\ Na^+$$

NEUTRALIZATION OF ACIDITY: The dissolved caustic agent will neutralize acidity associated with dissolved carbon dioxide (CO_2), protons (H^+), and dissolved metals such as aluminum (Al^{3+}), iron (Fe^{3+}, Fe^{2+}) and manganese (Mn^{2+}). Acidity associated with dissolved CO2 generally is considered temporary because aeration of AMD can promote the exsolution of CO_2, which initially causes pH to increase and the acidity (base requirement) to decrease. However, acidity associated with dissolved metals generally is not affected by aeration and requires the addition of base (caustic chemicals) for neutralization.

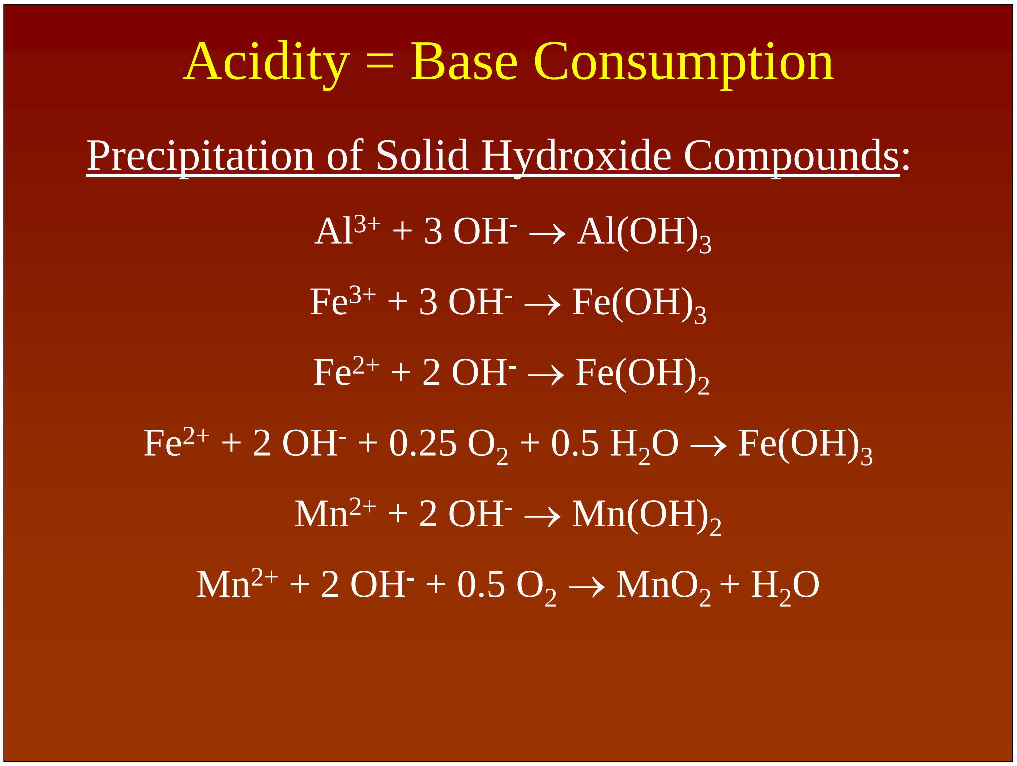
For example, as caustic soda (NaOH) is added to the effluent, the acidity associated with dissolved metals will be neutralized. Depending on the oxidation state of the dissolved metals, pH, and other characteristics of the solution, various solid hydroxide compounds may precipitate.

Similar neutralization reactions involving dissolved metals can be written for other caustic agents (CaO, $Ca(OH)_2$, Na_2CO_3, and NH_3) considering that the charge on the metal ion (+2, +3) 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+}).



METAL HYDROXIDE SOLUBILITIES: A plot of various metal hydroxide solubilities as a function of pH generally shows “amphoteric” characteristics of the metals, where the solubility minimum for each metal ion occurs at “intermediate” pH; dissolved metal concentrations may increase at lower or higher pH relative to the minimum. The solubility of hydrous Fe(II) oxide is significantly greater than oxidized Fe(III). Hence, AMD with pH <8 may contain substantial concentrations of dissolved Fe^{2+}; however, upon oxidation to Fe^{3+}, hydrous Fe(III) oxides tend to precipitate decreasing dissolved Fe concentrations. Likewise, the solubility of Mn(II) is greater than that of Mn(III-IV). Hence, hydrous oxides of Fe(III) and Al commonly form where AMD discharges or mixes with alkaline sources. Generally, most other have minimum solubilities at alkaline pH range (pH>9). Nevertheless, these metals are readily adsorbed by hydrous Fe(III), Al, and Mn(IV) oxides, reducing their concentrations below the solubility of their respective hydrous oxide compounds.

In addition to the precipitation of iron, manganese, and aluminum, compounds of magnesium (Mg(OH)2) and, to a lesser extent, calcium (CaCO3; Ca6Al2(SO4)3(OH)12.26H2O) may precipitate as the solution pH increases to alkaline values. 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 CO2 tend to buffer pH (Ott, 1988; Cravotta and Kirby, 2004).



Acidity = Base Consumption

Precipitation of Solid Hydroxide Compounds:

$$Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3$$

$$Fe^{3+} + 3\ OH^- \rightarrow Fe(OH)_3$$

$$Fe^{2+} + 2\ OH^- \rightarrow Fe(OH)_2$$

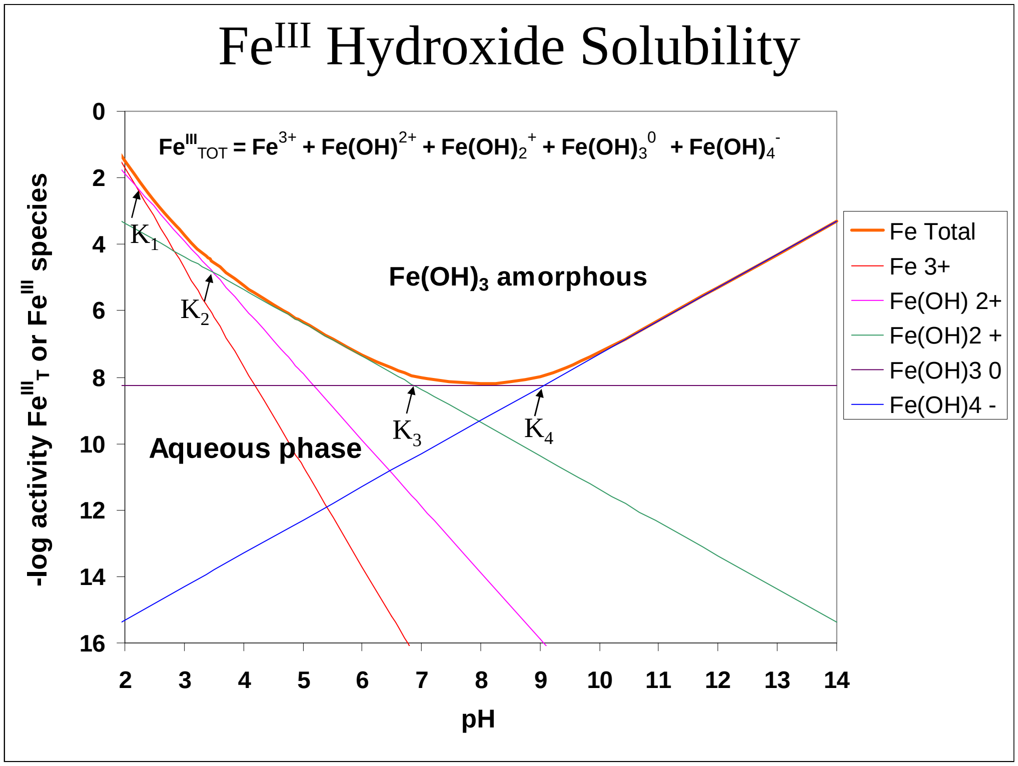
$$Fe^{2+} + 2\ OH^- + 0.25\ O_2 + 0.5\ H_2O \rightarrow Fe(OH)_3$$

$$Mn^{2+} + 2\ OH^- \rightarrow Mn(OH)_2$$

$$Mn^{2+} + 2\ OH^- + 0.5\ O_2 \rightarrow MnO_2 + H_2O$$

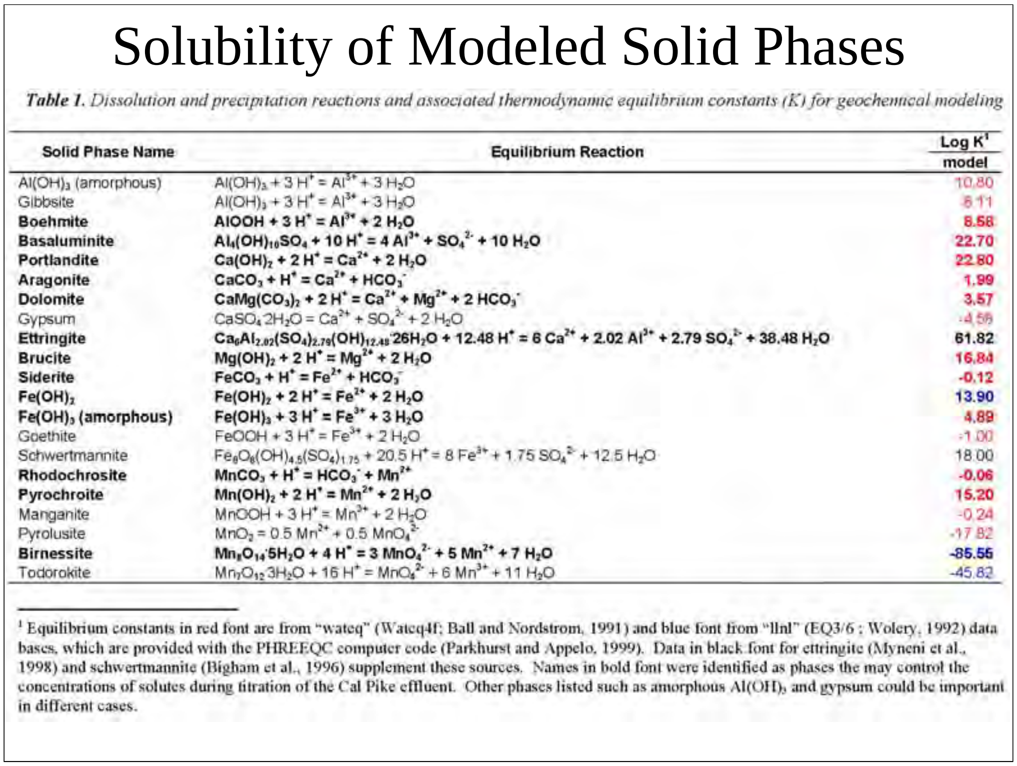
ACIDITY = BASE CONSUMPTION:

Precipitation of solid hydroxide compounds will occur when the solution becomes saturated with respect to the solid. Generally, base (OH^-) is added to increase pH beyond saturation to promote the removal of excess metals. Although the amount of base to precipitate the hydroxide solids is proportional to the concentration and charge of the dissolved metal, different solids have different solubilities. Specifically, 2 moles of OH^- are needed to neutralize the acidity associated with ferrous iron (Fe^{2+}), regardless of its precipitation as relatively soluble ferrous hydroxide ($Fe(OH)_2$) or insoluble ferric hydroxide ($Fe(OH)_3$). However, because $Fe(OH)_3$ tends to precipitate at lower pH than $Fe(OH)_2$, less base would be needed to precipitate the ferric form than the ferrous form. Likewise, less base is needed to precipitate oxidized forms of manganese (MnO_2) than the relatively soluble, unoxidized hydroxide ($Mn(OH)_2$)



FERRIC HYDROXIDE SOLUBILITY AND AQUEOUS SPECIES DISTRIBUTION: Fe(III) species distribution and solubility control by solid $Fe(OH)_3$. At equilibrium with solid $Fe(OH)_3$, the concentration of dissolved ferric iron will vary as a function of pH.

As pH increases to near neutral values, Fe^{+3}, $Fe(OH)^{+2}$, $Fe(OH)_2^+$, and $Fe(OH)_3^0$ species become progressively predominant, and the total dissolved iron concentration in equilibrium with the solid $Fe(OH)_3$ decreases. However, as pH increases into the alkaline range (>8) and $Fe(OH)_4^-$ becomes an important species, the equilibrium concentration of dissolved iron increases.



Solubility of Modeled Solid Phases

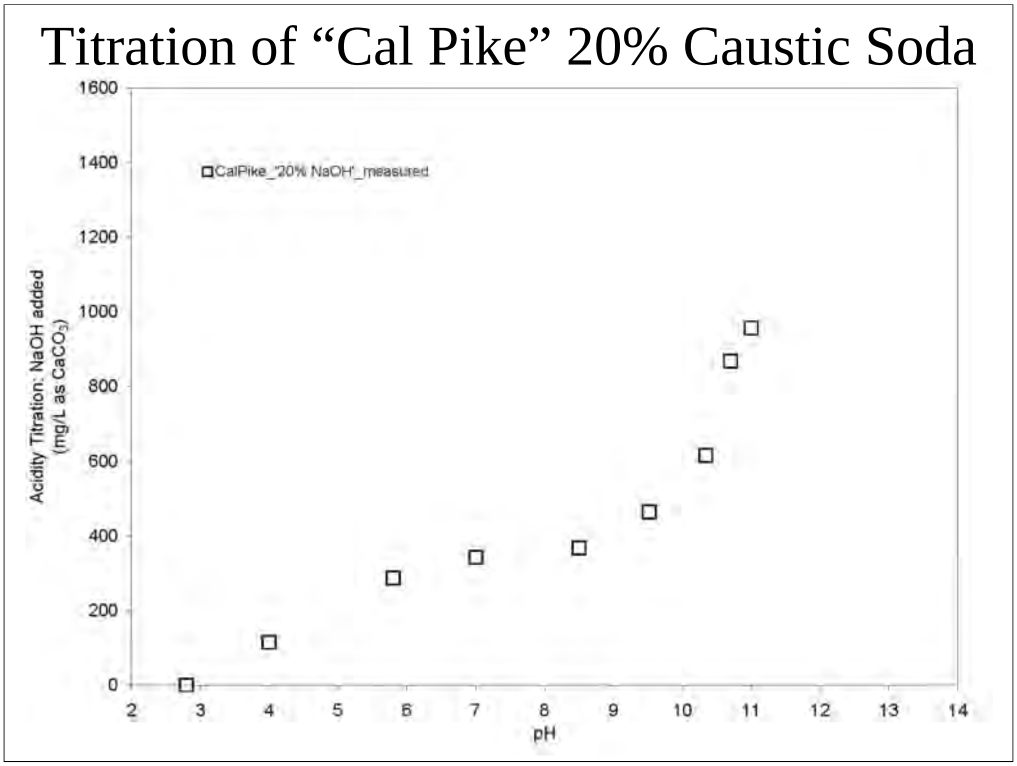
Table 1. *Dissolution and precipitation reactions and associated thermodynamic equilibrium constants (K) for geochemical modeling*

Solid Phase Name	Equilibrium Reaction	Log K[1] model
$Al(OH)_3$ (amorphous)	$Al(OH)_3 + 3 H^+ = Al^{3+} + 3 H_2O$	10.80
Gibbsite	$Al(OH)_3 + 3 H^+ = Al^{3+} + 3 H_2O$	8.11
Boehmite	$AlOOH + 3 H^+ = Al^{3+} + 2 H_2O$	8.58
Basaluminite	$Al_4(OH)_{10}SO_4 + 10 H^+ = 4 Al^{3+} + SO_4^{2-} + 10 H_2O$	22.70
Portlandite	$Ca(OH)_2 + 2 H^+ = Ca^{2+} + 2 H_2O$	22.80
Aragonite	$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	1.99
Dolomite	$CaMg(CO_3)_2 + 2 H^+ = Ca^{2+} + Mg^{2+} + 2 HCO_3^-$	3.57
Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2 H_2O$	-4.58
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
Brucite	$Mg(OH)_2 + 2 H^+ = Mg^{2+} + 2 H_2O$	16.84
Siderite	$FeCO_3 + H^+ = Fe^{2+} + HCO_3^-$	-0.12
$Fe(OH)_2$	$Fe(OH)_2 + 2 H^+ = Fe^{2+} + 2 H_2O$	13.90
$Fe(OH)_3$ (amorphous)	$Fe(OH)_3 + 3 H^+ = Fe^{3+} + 3 H_2O$	4.89
Goethite	$FeOOH + 3 H^+ = Fe^{3+} + 2 H_2O$	-1.00
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
Rhodochrosite	$MnCO_3 + H^+ = HCO_3^- + Mn^{2+}$	-0.06
Pyrochroite	$Mn(OH)_2 + 2 H^+ = Mn^{2+} + 2 H_2O$	15.20
Manganite	$MnOOH + 3 H^+ = Mn^{3+} + 2 H_2O$	-0.24
Pyrolusite	$MnO_2 = 0.5 Mn^{2+} + 0.5 MnO_4^{2-}$	-17.82
Birnessite	$Mn_8O_{14} \cdot 5H_2O + 4 H^+ = 3 MnO_4^{2-} + 5 Mn^{2+} + 7 H_2O$	-85.56
Todorokite	$Mn_7O_{12} \cdot 3H_2O + 16 H^+ = MnO_4^{2-} + 6 Mn^{3+} + 11 H_2O$	-45.82

---

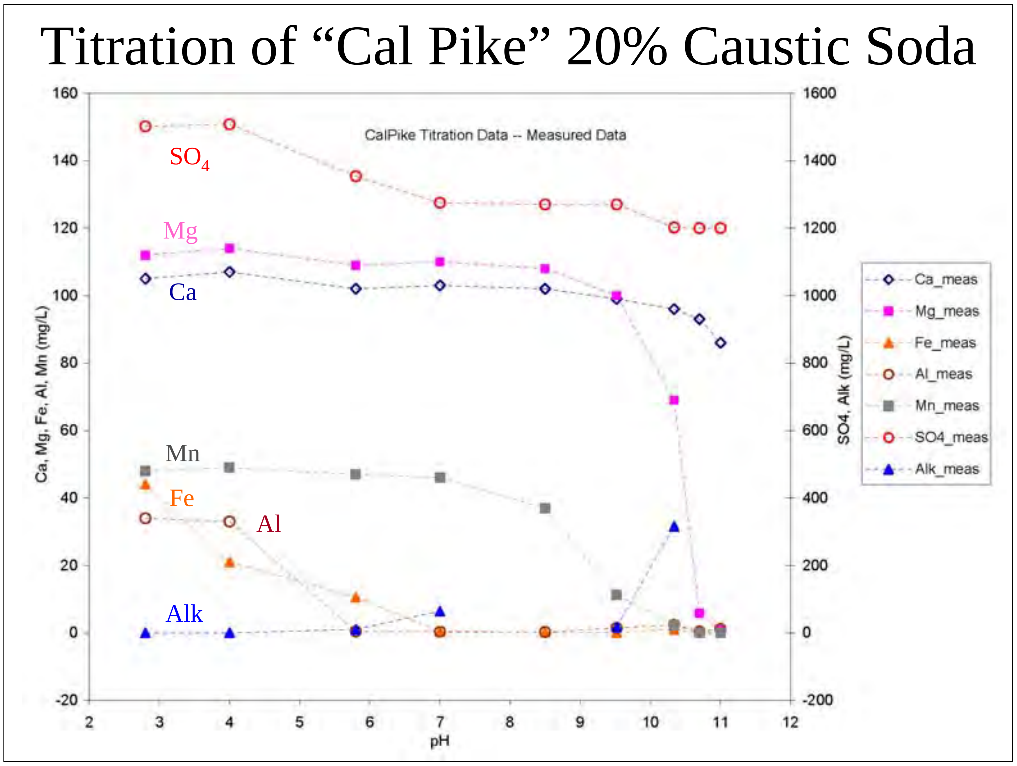
[1] Equilibrium constants in red font are from “wateq” (Wateq4f; Ball and Nordstrom, 1991) and blue font from “llnl” (EQ3/6 ; Wolery, 1992) data bases, which are provided with the PHREEQC computer code (Parkhurst and Appelo, 1999). Data in black font for ettringite (Myneni et al., 1998) and schwertmannite (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.

SOLUBILITY OF MODELED SOLID PHASES: Equilibrium constants in red font are from “wateq” (Wateq4f; Ball and Nordstrom, 1991) and blue font from “llnl” (EQ3/6 ; Wolery, 1992) data bases, which are provided with the PHREEQC computer code (Parkhurst and Appelo, 1999). Data in black font 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.


Titration of “Cal Pike” 20% Caustic Soda

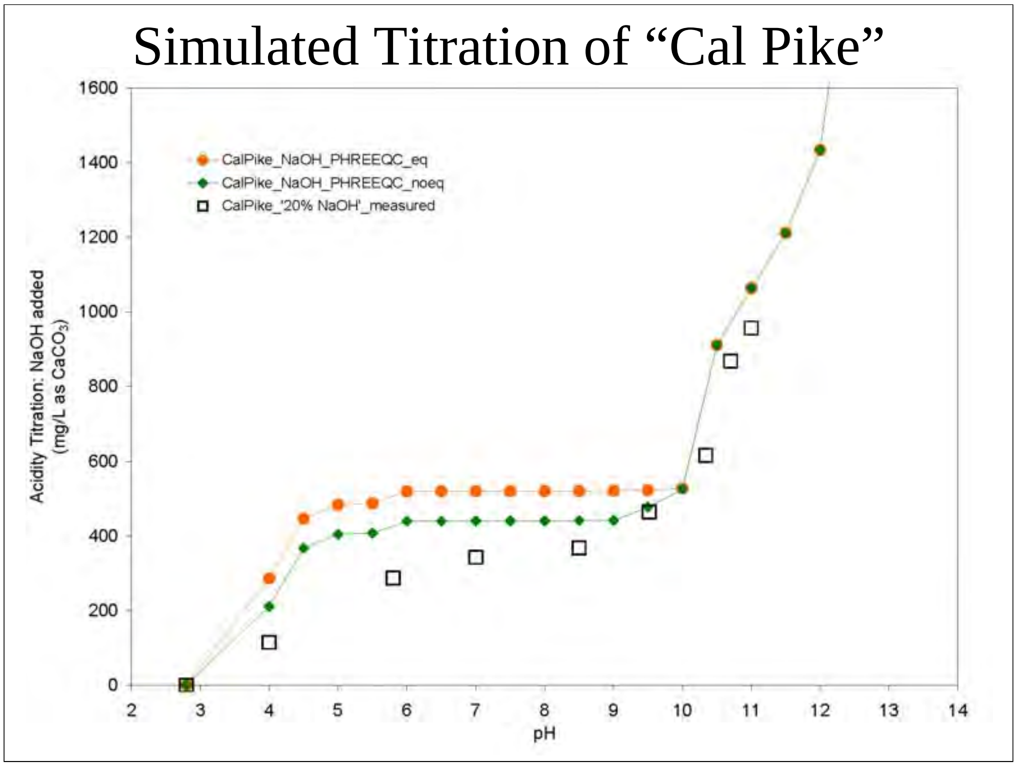
TITRATION: Empirical titrations of acidic, metal-laden effluent from the “Cal Pike” coal-mine site in western Pennsylvania were conducted in the field to document effects of on-site chemical treatment. A Hach Digital Titrator® was used with a cartridge that had been filled with industrial strength liquid caustic (6.1 N NaOH = “20 %” NaOH). Units on the Y-axis are expressed as mg/L CaCO3 by multiplying the quantity of NaOH added by 0.80 (2 * 40 g/mol / 100 g/mol).

The empirical titrations of the Cal Pike effluent with NaOH produced nonlinear changes in pH.


Titration of "Cal Pike" 20% Caustic Soda

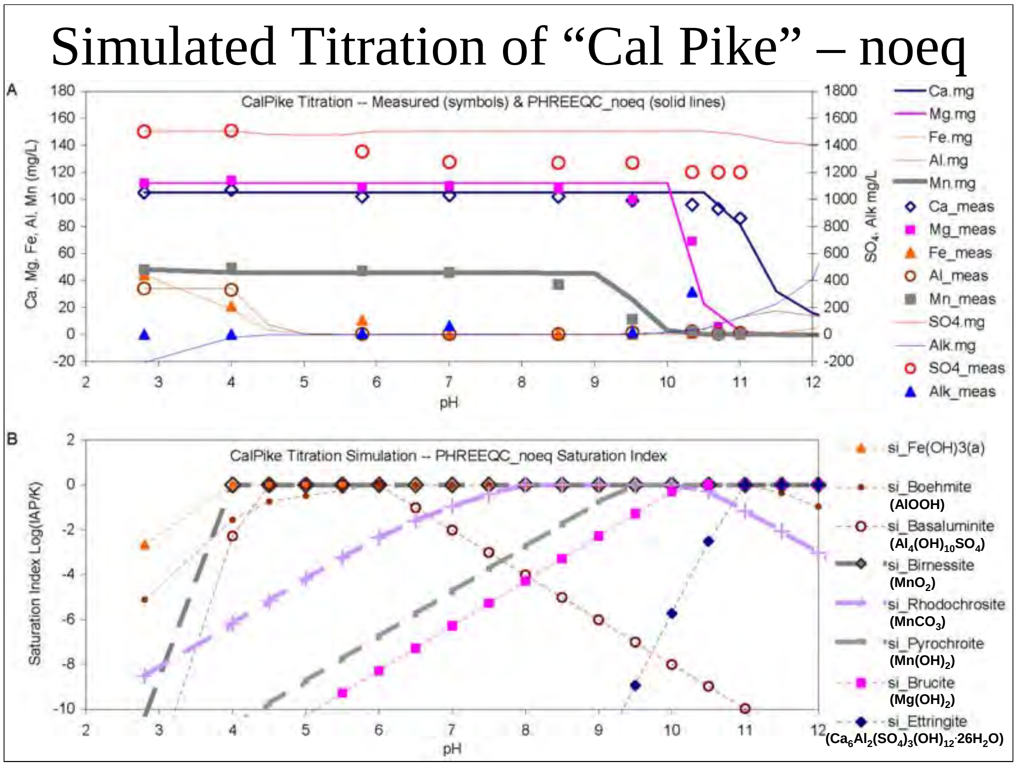
TITRATION OF CAL PIKE: To record changes in the chemical composition of the "Cal Pike" effluent during titration with industrial strength liquid caustic (6.1 N NaOH = "20 %" NaOH), filtered (0.45-µm pore size) effluent samples were collected at different pH endpoints and analyzed.

The untreated Cal Pike effluent had pH of 2.8 and elevated concentrations of dissolved constituents (Mg = 122.2 mg/L; Ca = 105.2 mg/L; Fe = 44.1 mg/L; Al = 34.1 mg/L; Mn = 48.1 mg/L; SO_4 = 1505 mg/L). As titration with caustic increased pH to 4.0 and then 5.8, the concentrations of dissolved Fe and Al decreased dramatically. Concentrations of dissolved Mn and other constituents remained relatively unchanged until pH was increased to alkaline values. At pH values greater than 8.5, concentrations of Mn and Mg began to decrease. At pH greater than 10, Mn was effectively removed, but a large fraction of Mg also precipitated. At pH greater than 10, concentrations of Ca^{2+} also began to decrease.



TITRATION: The titration curves revealed characteristic pH buffering (resistance to pH change) at pH of 3 to 5 and 9 to 12.

Two different titration scenarios were simulated. The lower curve (green diamond) was produced for the scenario without atmospheric exchange. The upper curve (orange circles) was produced for the scenario where the effluent was equilibrated with the atmosphere and dissolved Fe and Mn were oxidized prior to the addition of caustic chemicals. For the non-equilibrium scenario, Mn is not oxidized and thus does not react with base until pH greater than 9. However, for the atmospheric equilbrium scenario, Mn reacts with base at low pH. Note that at pH values greater than 10, the two simulations converge.

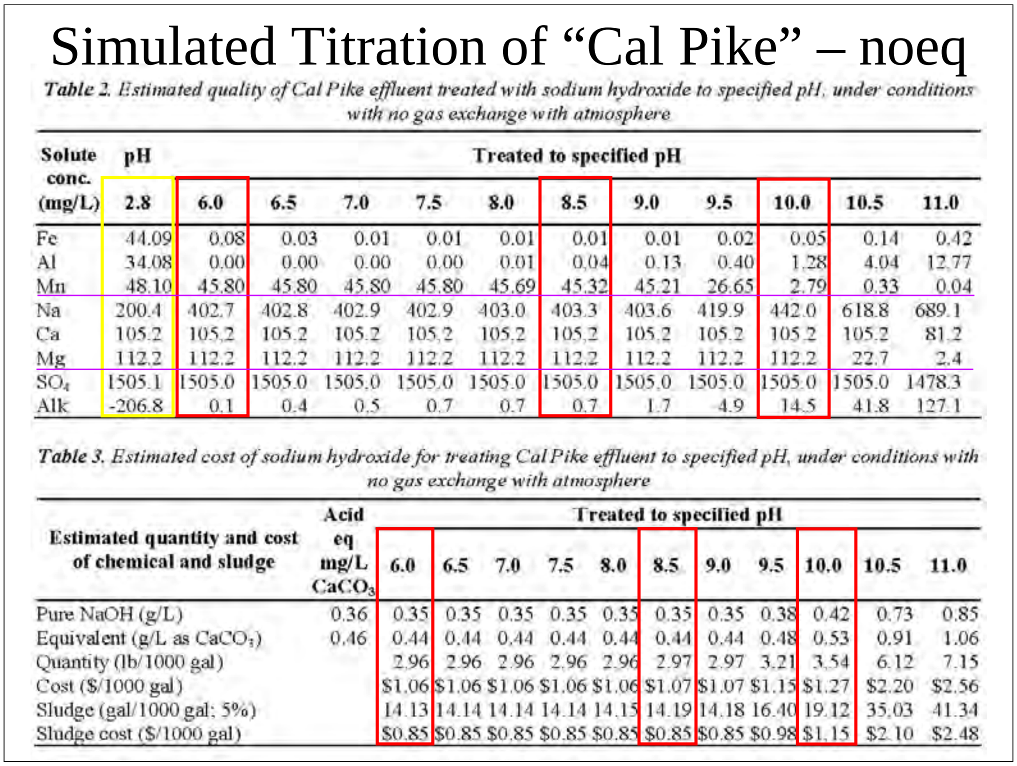


Simulated Titration of “Cal Pike” – noeq

SIMULATED TITRATION—To evaluate possible mineral precipitation reactions that could explain the changes in solute concentrations during the addition of caustic soda, the titration was simulated using PHREEQC. For the scenario illustrated, no gas exchange (unoxidized) was permitted. The top chart (A) shows data for the measured (symbols) and simulated (solid lines) titration of “Cal Pike” effluent with NaOH at 16 °C. The lower chart (B) shows saturation indices for selected minerals as a function of pH for simulated solutions.

Solid phases were identified for use in the titration simulations that yielded concentrations of solutes similar to the measured concentrations (A). The controlling phases phases were selected considering trends in measured concentrations of solutes and computed mineral saturation indices (SI) as a function of pH (B). 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.

Nearly complete removal of iron at pH values less than 7 was simulated by the precipitation of $Fe(OH)_3$. Solubility control by this phase implies that iron was already in the ferric oxidation state. In contrast, negligible removal of manganese was observed at pH values less than 9. The observed concentrations of manganese were approximately simulated without aeration by the precipitation of pyrochroite ($Mn(OH)_2$) at alkaline pH values. Basaluminite ($Al_4(OH)_{10}SO_4$) and boehmite (AlOOH) were considered likely controls of dissolved Al^{3+}. Decreased concentrations of Ca^{2+} were consistent with its solubility control by ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O$).



Simulated Titration of “Cal Pike” – noeq

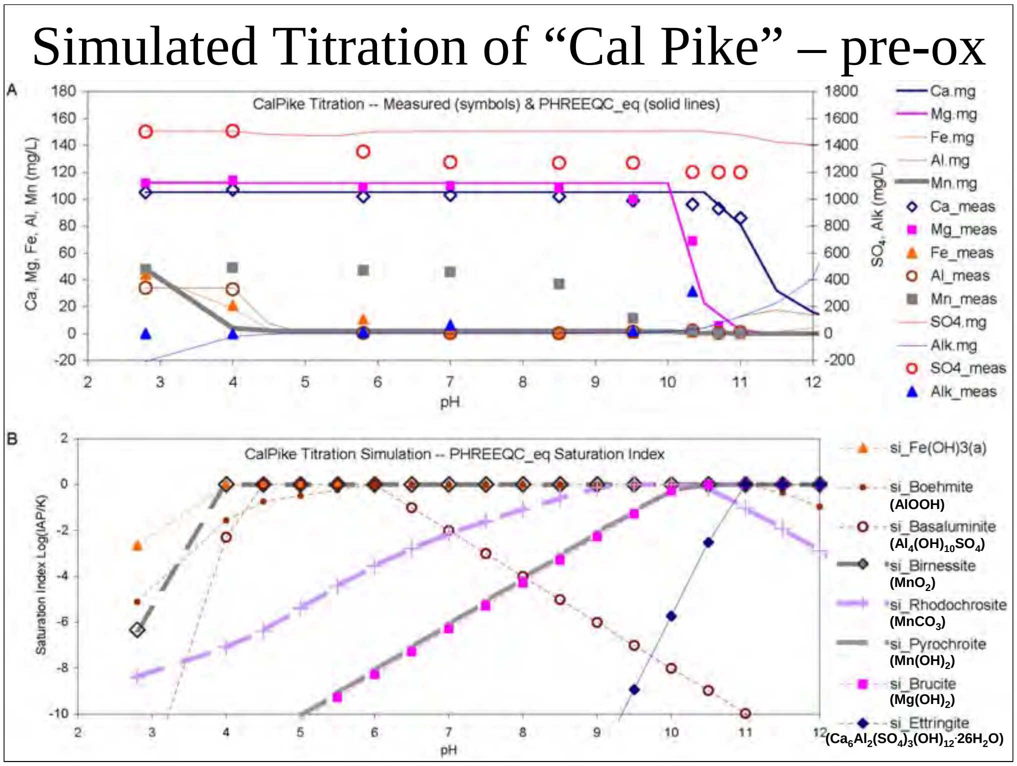
Table 2. Estimated quality of Cal Pike effluent treated with sodium hydroxide to specified pH, under conditions with no gas exchange with atmosphere

Solute conc. (mg/L)	pH	Treated to specified pH										
	2.8	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
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
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	0.1	0.4	0.5	0.7	0.7	0.7	1.7	4.9	14.5	41.8	127.1

Table 3. Estimated cost of sodium hydroxide 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										
		6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
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 $CaCO_3$)	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)		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)		$1.06	$1.06	$1.06	$1.06	$1.06	$1.07	$1.07	$1.15	$1.27	$2.20	$2.56
Sludge (gal/1000 gal; 5%)		14.13	14.14	14.14	14.14	14.15	14.19	14.18	16.40	19.12	35.03	41.34
Sludge cost ($/1000 gal)		$0.85	$0.85	$0.85	$0.85	$0.85	$0.85	$0.85	$0.98	$1.15	$2.10	$2.48

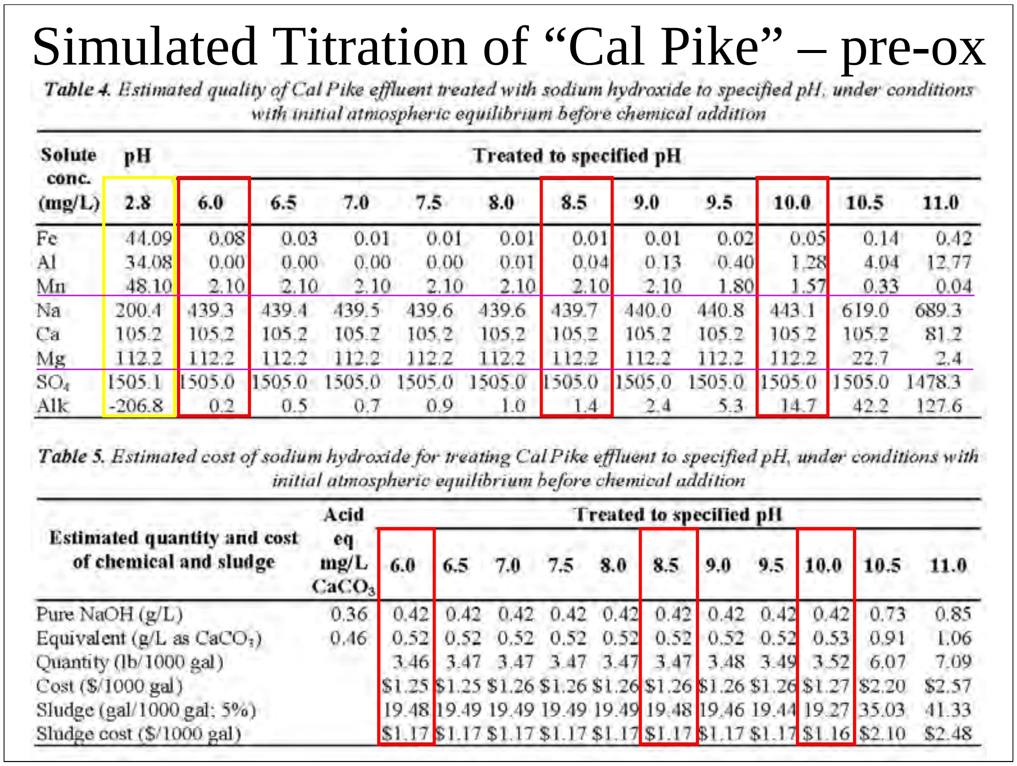
SIMULATED TITRATION—No gas exchange (unoxidized): Table 2 shows estimated composition of treated effluent to specific pH endpoints (same as previous graph) for conditions without oxidation of the effluent. Table 3 shows the corresponding amount and cost of caustic soda required to attain the specified pH. Costs for treatment to specific pH endpoints were computed using default values in AMDTreat for unit cost, purity, and efficiency of the specified chemical, and assuming a sludge density of 5 percent solids. The mass of solids in the sludge was computed assuming that the metals precipitated as hydroxide or carbonate compounds ($Fe(OH)_3$, $Al(OH)_3$, $Mn(OH)_2$, $Mg(OH)_2$, $CaCO_3$). Note that the added cost to treat from pH 6.0 to 8.5 is insignificant because the solute composition is relatively constant over this pH range. However, the cost increases greatly for treatment to pH 10 and greater values, needed to precipitate Mn as $Mn(OH)_2$ (pyrochroite). A large part of the increased cost to remove Mn results from the precipitation of Mg. The removal of Mg not only consumes chemical reagent, but it adds to the sludge volume and associated costs for sludge removal.



Simulated Titration of “Cal Pike” – pre-ox

SIMULATED TITRATION—To evaluate possible mineral precipitation reactions that could take place if the sample were completely oxidized before the addition of caustic soda, a second titration was simulated using PHREEQC. For the scenario illustrated, gas exchange (oxidized) was permitted. The top chart (A) shows data for the measured (symbols) and simulated (solid lines) titration of “Cal Pike” effluent with NaOH at 16 °C. The lower chart (B) shows saturation indices for selected minerals as a function of pH for simulated solutions.

With the exception of manganese, the titrations with gas exchange (oxidized sample) produced similar results for iron, aluminum, sodium, calcium, magnesium, or sulfate. The simulated concentrations of manganese decreased at low pH values because of the precipitation of birnessite (MnO_2). Not that the simulated concentration of Mn decreased to negligible values at pH values less than 5.



Simulated Titration of "Cal Pike" – pre-ox

Table 4. *Estimated quality of Cal Pike effluent treated with sodium hydroxide to specified pH, under conditions with initial atmospheric equilibrium before chemical addition*

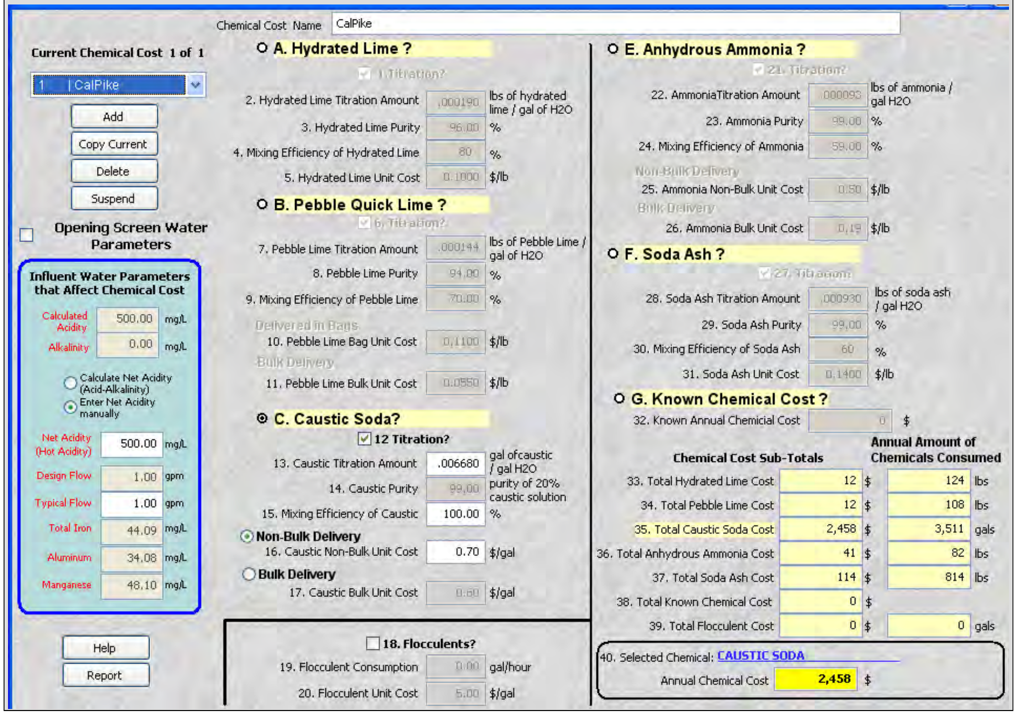
Solute conc. (mg/L)	**pH**	**Treated to specified pH**										
	2.8	**6.0**	**6.5**	**7.0**	**7.5**	**8.0**	**8.5**	**9.0**	**9.5**	**10.0**	**10.5**	**11.0**
Fe	44.09	0.08	0.03	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.14	0.42
Al	34.08	0.00	0.00	0.00	0.00	0.01	0.04	0.13	0.40	1.28	4.04	12.77
Mn	48.10	2.10	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

Table 5. *Estimated cost of sodium hydroxide for treating Cal Pike effluent to specified pH, under conditions with initial atmospheric equilibrium before chemical addition*

Estimated quantity and cost of chemical and sludge	**Acid eq mg/L $CaCO_3$**	**Treated to specified pH**										
		6.0	**6.5**	**7.0**	**7.5**	**8.0**	**8.5**	**9.0**	**9.5**	**10.0**	**10.5**	**11.0**
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 $CaCO_3$)	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)		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)		$1.25	$1.25	$1.26	$1.26	$1.26	$1.26	$1.26	$1.26	$1.27	$2.20	$2.57
Sludge (gal/1000 gal; 5%)		19.48	19.49	19.49	19.49	19.49	19.48	19.46	19.44	19.27	35.03	41.33
Sludge cost ($/1000 gal)		$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.17	$1.16	$2.10	$2.48

SIMULATED TITRATION—Gas exchange (oxidized): Table 4 shows estimated composition of treated effluent to specific pH endpoints (same as previous graph) for conditions where the effluent was oxidized before the addition of caustic soda. Table 5 shows the corresponding amount and cost of caustic soda required to attain the specified pH. In contrast with the previous simulation for unoxidized conditions, most of the Mn is removed at pH less than 6.0. Thus, addition of an oxidizing agent may be an appropriate alternative to treatment to high pH for removal of Mn. By removing Mn at lower pH values, less caustic chemical is used, and the sludge volume is decreased by avoiding the precipitation of $Mg(OH)_2$.

AMDTreat Chemical Cost Screen: PHREEQC titration will indicate "titration amount"



Chemical Cost Name: CalPike

Current Chemical Cost 1 of 1: 1 | CalPike

☐ Opening Screen Water Parameters

Influent Water Parameters that Affect Chemical Cost

Calculated Acidity: 500.00 mg/L
Alkalinity: 0.00 mg/L
○ Calculate Net Acidity (Acid-Alkalinity)
● Enter Net Acidity manually
Net Acidity (Hot Acidity): 500.00 mg/L
Design Flow: 1.00 gpm
Typical Flow: 1.00 gpm
Total Iron: 44.09 mg/L
Aluminum: 34.08 mg/L
Manganese: 48.10 mg/L

○ A. Hydrated Lime ?

☑ 1. Titration?
2. Hydrated Lime Titration Amount: .000190 lbs of hydrated lime / gal of H2O
3. Hydrated Lime Purity: 96.00 %
4. Mixing Efficiency of Hydrated Lime: 80 %
5. Hydrated Lime Unit Cost: 0.1000 $/lb

○ B. Pebble Quick Lime ?

☑ 6. Titration?
7. Pebble Lime Titration Amount: .000144 lbs of Pebble Lime / gal of H2O
8. Pebble Lime Purity: 94.00 %
9. Mixing Efficiency of Pebble Lime: 70.00 %
Delivered in Bags
10. Pebble Lime Bag Unit Cost: 0.1100 $/lb
Bulk Delivery
11. Pebble Lime Bulk Unit Cost: 0.0550 $/lb

● C. Caustic Soda?

☑ 12 Titration?
13. Caustic Titration Amount: .006680 gal ofcaustic / gal H2O
14. Caustic Purity: 99.00 purity of 20% caustic solution
15. Mixing Efficiency of Caustic: 100.00 %
● Non-Bulk Delivery
16. Caustic Non-Bulk Unit Cost: 0.70 $/gal
○ Bulk Delivery
17. Caustic Bulk Unit Cost: 0.60 $/gal

☐ 18. Flocculents?
19. Flocculent Consumption: 0.00 gal/hour
20. Flocculent Unit Cost: 5.00 $/gal

○ E. Anhydrous Ammonia ?

☑ 21. Titration?
22. AmmoniaTitration Amount: .000093 lbs of ammonia / gal H2O
23. Ammonia Purity: 99.00 %
24. Mixing Efficiency of Ammonia: 59.00 %
Non-Bulk Delivery
25. Ammonia Non-Bulk Unit Cost: 0.50 $/lb
Bulk Delivery
26. Ammonia Bulk Unit Cost: 0.19 $/lb

○ F. Soda Ash ?

☑ 27. Titration?
28. Soda Ash Titration Amount: .000930 lbs of soda ash / gal H2O
29. Soda Ash Purity: 99.00 %
30. Mixing Efficiency of Soda Ash: 60 %
31. Soda Ash Unit Cost: 0.1400 $/lb

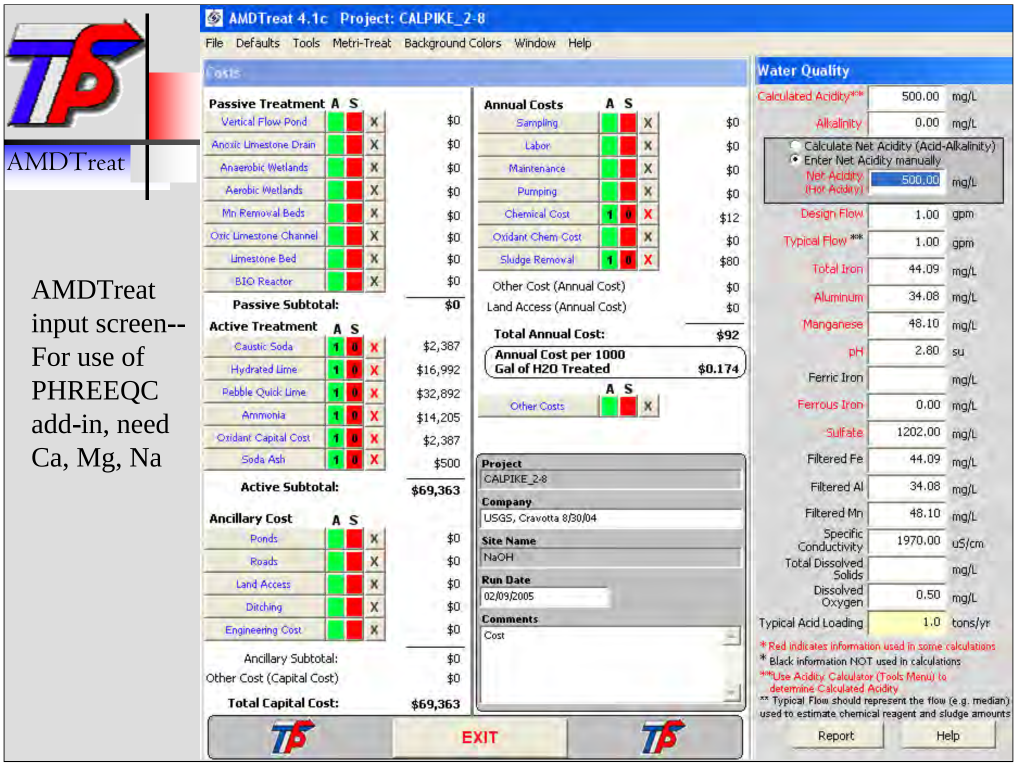
○ G. Known Chemical Cost ?

32. Known Annual Chemicial Cost: 0 $

	Chemical Cost Sub-Totals		Annual Amount of Chemicals Consumed	
33. Total Hydrated Lime Cost	12	$	124	lbs
34. Total Pebble Lime Cost	12	$	108	lbs
35. Total Caustic Soda Cost	2,458	$	3,511	gals
36. Total Anhydrous Ammonia Cost	41	$	82	lbs
37. Total Soda Ash Cost	114	$	814	lbs
38. Total Known Chemical Cost	0	$		
39. Total Flocculent Cost	0	$	0	gals

40. Selected Chemical: CAUSTIC SODA
Annual Chemical Cost: 2,458 $

TITRATION RESULT INPUT: The previous tables showed cost estimates using the simulated titration results and using unit values for chemical costs, purity, and efficiency as provided by AMDTreat. Users of AMDTreat may specify the chemical titration amount, plus choose other values for unit costs, chemical efficiency, and sludge density to vary estimates. Although this presentation showed results only for caustic soda (NaOH), simulations with different chemicals and aeration scenarios are described in the proceedings paper.



AMDTreat input screen-- For use of PHREEQC add-in, need Ca, Mg, Na

Passive Treatment	A	S	
Vertical Flow Pond			$0
Anoxic Limestone Drain			$0
Anaerobic Wetlands			$0
Aerobic Wetlands			$0
Mn Removal Beds			$0
Oxic Limestone Channel			$0
Limestone Bed			$0
BIO Reactor			$0
Passive Subtotal:			**$0**
Active Treatment	**A**	**S**	
Caustic Soda	1	0	$2,387
Hydrated Lime	1	0	$16,992
Pebble Quick Lime	1	0	$32,892
Ammonia	1	0	$14,205
Oxidant Capital Cost	1	0	$2,387
Soda Ash	1	0	$500
Active Subtotal:			**$69,363**
Ancillary Cost	**A**	**S**	
Ponds			$0
Roads			$0
Land Access			$0
Ditching			$0
Engineering Cost			$0
Ancillary Subtotal:			$0
Other Cost (Capital Cost)			$0
Total Capital Cost:			**$69,363**

Annual Costs	A	S	
Sampling			$0
Labor			$0
Maintenance			$0
Pumping			$0
Chemical Cost	1	0	$12
Oxidant Chem Cost			$0
Sludge Removal	1	0	$80
Other Cost (Annual Cost)			$0
Land Access (Annual Cost)			$0
Total Annual Cost:			**$92**
Annual Cost per 1000 Gal of H20 Treated			**$0.174**
Other Costs			

Project
CALPIKE_2-8
Company
USGS, Cravotta 8/30/04
Site Name
NaOH
Run Date
02/09/2005
Comments
Cost

Water Quality		
Calculated Acidity***	500.00	mg/L
Alkalinity	0.00	mg/L
○ Calculate Net Acidity (Acid-Alkalinity)		
● Enter Net Acidity manually		
Net Acidity (Hot Acidity)	500.00	mg/L
Design Flow	1.00	gpm
Typical Flow **	1.00	gpm
Total Iron	44.09	mg/L
Aluminum	34.08	mg/L
Manganese	48.10	mg/L
pH	2.80	su
Ferric Iron		mg/L
Ferrous Iron	0.00	mg/L
Sulfate	1202.00	mg/L
Filtered Fe	44.09	mg/L
Filtered Al	34.08	mg/L
Filtered Mn	48.10	mg/L
Specific Conductivity	1970.00	uS/cm
Total Dissolved Solids		mg/L
Dissolved Oxygen	0.50	mg/L
Typical Acid Loading	1.0	tons/yr

* Red indicates information used in some calculations
* Black information NOT used in calculations
***Use Acidity Calculator (Tools Menu) to determine Calculated Acidity
** Typical Flow should represent the flow (e.g. median) used to estimate chemical reagent and sludge amounts

AMDTREAT INPUT SCREEN: Current input parameters for AMDTreat include flow, alkalinity, acidity, metals, and sulfate. With added data for Ca, Mg, and Na, the PHREEQC titration “add-in” will permit the estimation of the chemical requirement to achieve a specific pH and the treated effluent composition. The PHREEQC titration routine will run in the background. A user will be able to select the target pH and evaluate simulated titration results for various chemicals.

AMD Treatment Cost Estimate

AMDTreat

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

AMDTREAT VERSION 4.1C DOWNLOAD

You must UNINSTALL previous versions of AMDTreat before installing the current release.

AMDTreat Version 4.1c - Eastern U.S. Download Site
Format: (33 mb).
Last updated: February 2008

Notes

When opening older file formats, version 4.x converts the (v.3.x) project files to version 4.x file formats. When saved, the program places the new files in an AMDTreat folder under the users My Documents folder. The v3.x files are unchanged and remain in their original location at the root of the C: drive in the C:\AMDTreat/Complete folder.

To install AMDTreat after downloading just go to the directory where you saved the downloaded file and double click on the file amdsetup4.exe or setup##.exe (e.g.,amdsetup4.exe). The program will install similar to other Windows applications.

AMDTreat is a 33 megabyte file. If you have difficulty downloading the file due to it's size, please contact the Development Team or call for AMDTreat technical support (Brent Means 717-782-4079 x18 or Bob McKenzie 412-937-2144).

Contact Info:

US Dept. of the Interior
Office of Surface Mining
Appalachian Region
3 Parkway Center
Pittsburgh, PA 15220
(412) 937-2804

getinfo@osmre.gov

This site last updated:
11/27/2006

Please send website comments and suggestions to
kbernhard@osmre.gov

AMD TREATMENT COST ESTIMATE: The AMDTreat computer program is widely used to estimate costs for passive or active treatment of coal-mine drainage. For net acidic, metal-laden water, the caustic chemical requirement for active treatment is estimated as equivalent to the net acidity of the raw effluent. For net alkaline water with elevated Mn, AMDTreat wrongly indicates that no caustic chemical would be needed, even though caustic chemicals routinely are used to remove Mn from the effluent. Although AMDTreat can use results of titration with industrial chemicals to accurately compute costs for treatment of net-acidic or net-alkaline mine drainage, such empirical 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 chemistry of treated effluent, and (3) the volume of sludge produced by the treatment, a titration simulation is being developed using the geochemical program PHREEQC that will be coupled to AMDTreat.