Chemistry, Design, and Operation of Limestone-based Passive Treatment Systems

By

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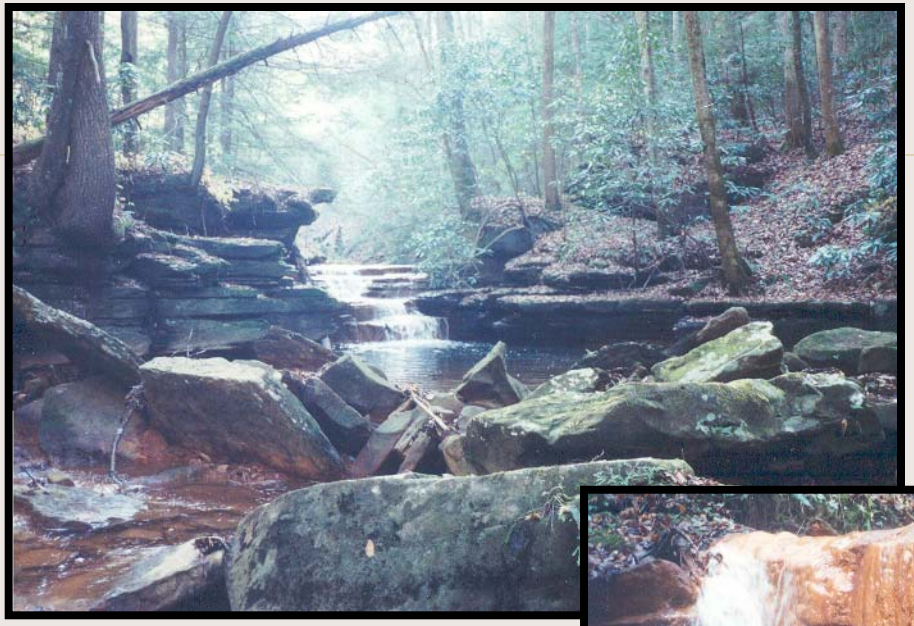
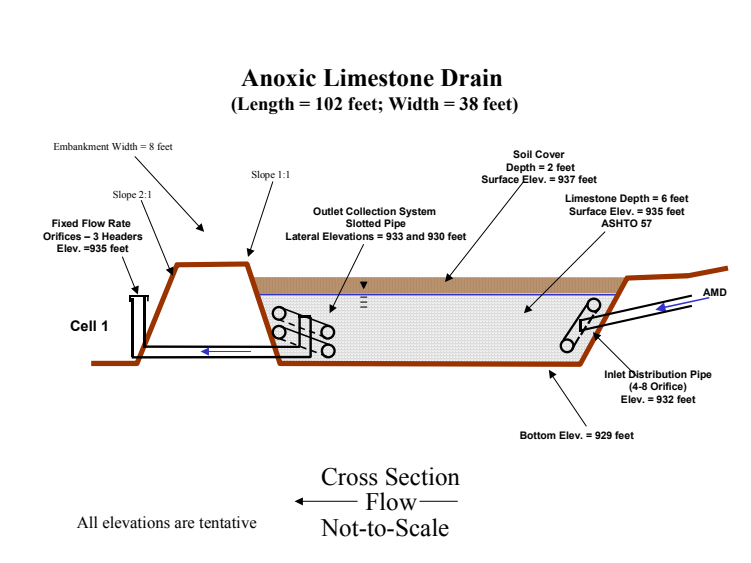


Anoxic Limestone Drains

Anoxic Limestone Drains

- **Advantages**
  - Low cost
  - Alkalinity -> 200-300 mg/L
  - Simple design
- **Disadvantages**
  - High acidity > 200 mg/L
  - Limits
    - Aluminum > 5 mg/L
    - No Ferric Iron > 2 mg/L
    - No Dissolved Oxygen
  - No Metal Removal
- **Sizing Guidance**
  - Current
    - 8-16 hours detention time
  - Proposed
    - Equilibrium & Kinetic-based Approach (MAEM-AKM)



Anaerobic Vertical Flow Wetland

Schrader Creek
Long Valley Run

East Br. Clarion River
Twomile Run

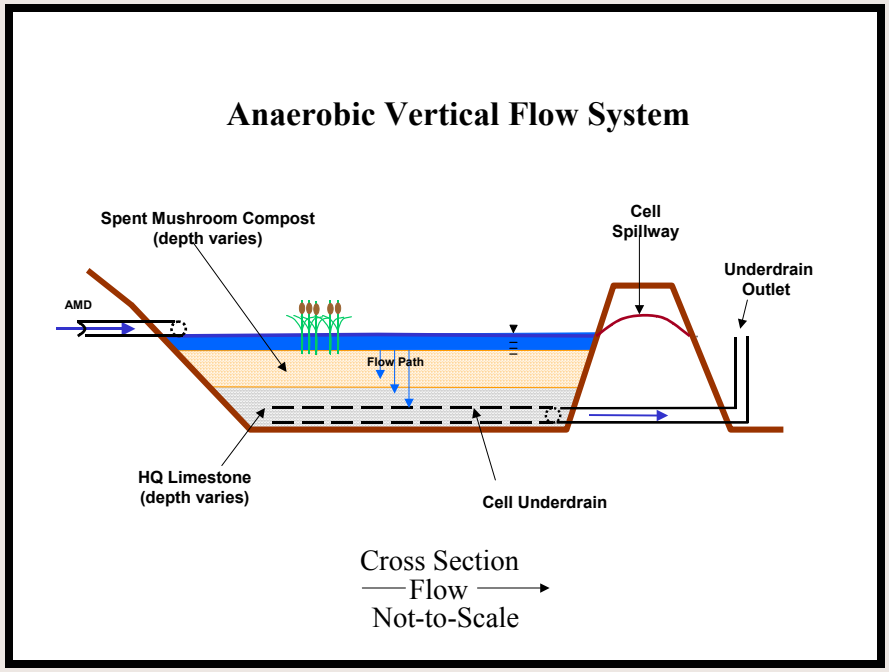
Anaerobic Vertical Flow Wetland

Little Mill Creek
Bog No. 1

Little Mill Creek
Filson No. 4

Anaerobic Vertical Flow Wetland

- **Advantages**
  - Accepts oxic discharges
  - Can treat high acidity
  - Not effected by high aluminum
  - Produces excess alkalinity
- **Disadvantages**
  - Effected by high iron loading
  - Poor manganese removal
  - Complex design
  - High capitol cost
- **Sizing Guidance**
  - Current
    - 8-16 hours detention time (limestone layer only)
  - Proposed
    - 25 GDM acidity removal
    - 125 gpm/acre



Anaerobic Vertical Flow Wetland

Underdrain Outlet
Water Level &
Flow Control

Underdrain Piping
below organic layer
within limestone layer

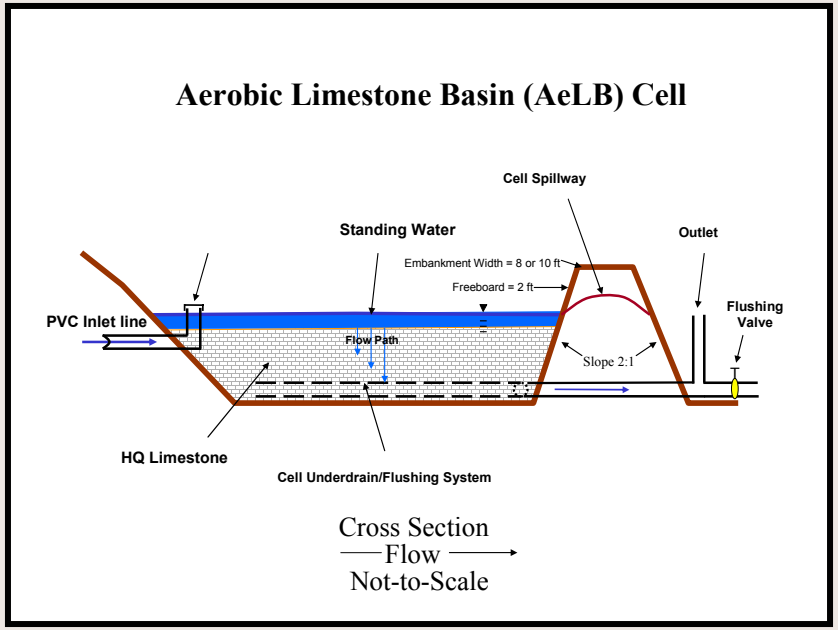
Limestone Basins & Beds

PA Turnpike Commission
Hickory Run

East Br. Clarion River
Twomile Run

Limestone Basins

- **Advantages**
  - Simple Design
  - Removes iron & aluminum
  - Removes acidity
  - Produces alkalinity
  - May remove manganese
- **Disadvantages**
  - Effected by coating
  - Potential clogging
  - No high metals (Fe & Al)
    Uncertain alkalinity generation
- **Sizing Guidance**
  - Current
    - 10-40 hours detention time
  - Proposed
    - Solubility & Kinetic-based



Background Chemistry

pH, Alkalinity, Acidity and the Carbonate System

Mine Drainage Waters

Parameter	Type 1	Type 2	Type 3
pH	5.2	3.2	4.2
Alkalinity (as mg/L $CaCO_3$)	25	0	0
(Hot) Acidity (as mg/L $CaCO_3$)	110	300	20
Iron (mg/L)	75	35	2.0
Manganese (mg/L)	3.0	3.0	2.0
Aluminum (mg/L)	<0.5	35	1.0
Calcium (mg/L)	150	150	10
Sulfate (mg/L)	1200	1200	100
Equilibrium Conditions with Limestone			
Alkalinity (as mg/L $CaCO_3$)	??	??	??
pH	??	??	??

Acidity & Alkalinity Definitions

Natural Waters:

Total Acidity = $[H^+] + 2[H_2CO_3^*] + [HCO_3^-] - [OH^-]$

$pH_{8.3}$ Acidity = $[H^+] + [H_2CO_3^*]$

$pH_{4.5\text{-}5.0}$ Alkalinity = $[HCO_3^-] + [CO_3^{2-}] + [OH^-]$

Carbon Dioxide Acidity = $[H_2CO_3^*]$

Mine Drainage Waters:

$pH_{8.3}$ Acidity = $[H^+] + [H_2CO_3^*] + 3[Al^{3+}] + 3[Fe^{3+}]$ ….

"Hot" or Net Acidity = $[H^+] + 3[Al^{3+}] + 3[Fe^{3+}] + 2[Fe^{2+}] + 2[Mn^{2+}]$….

- Alkalinity

$[H^+]_{acy}$: $50{,}000 \times 10^{-pH}$ = x mg/L as $CaCO_3$

$[Al^{3+}]_{acy}$: 1 mg Al/L = 5.6 mg/L as $CaCO_3$

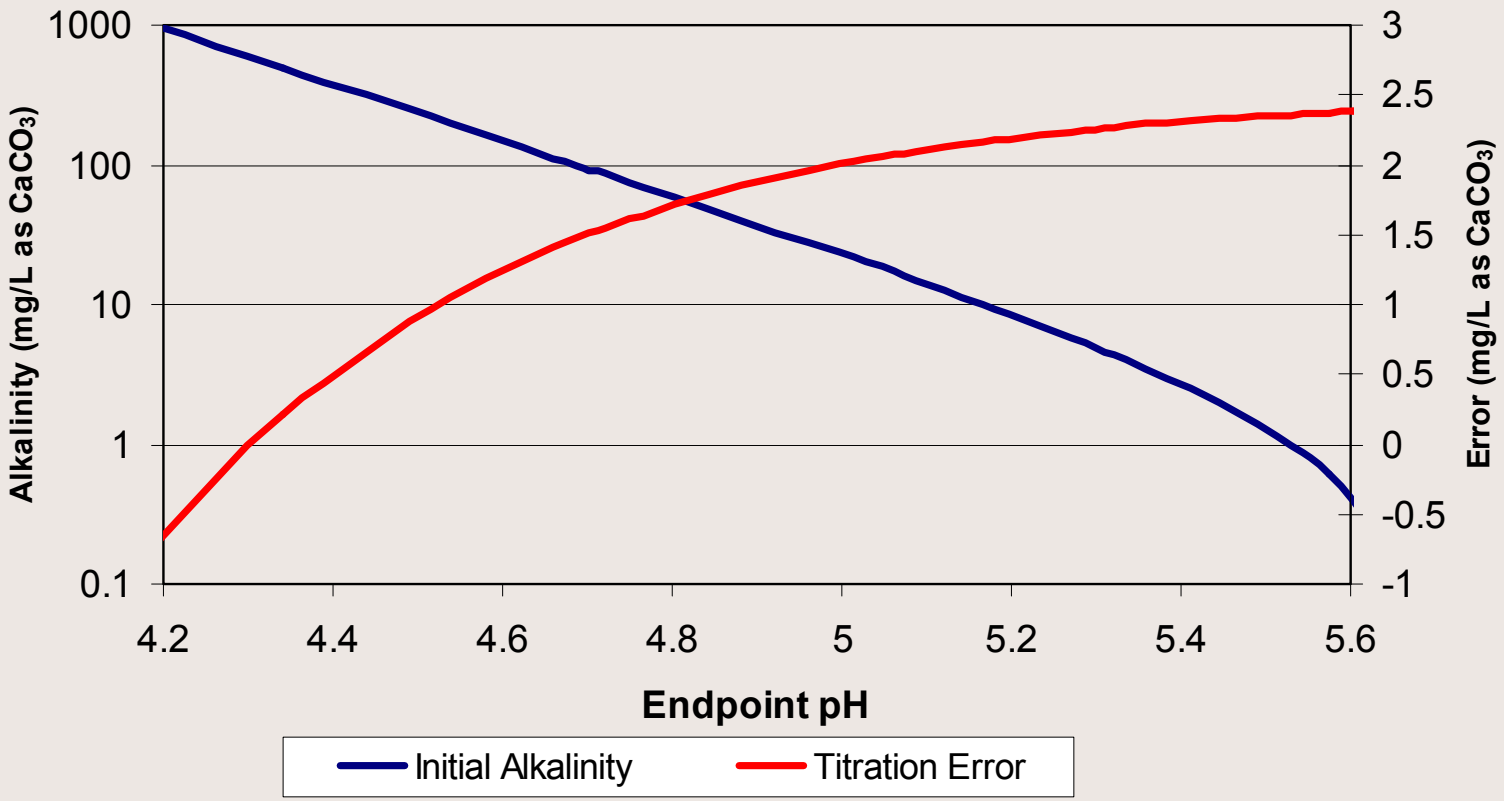
$[Fe^{3+}]_{acy}$: 1 mg Fe/L = 2.7 mg/L as $CaCO_3$

$[Fe^{2+}]_{acy}$: 1 mg Fe/L = 1.8 mg/L as $CaCO_3$

$[Mn^{2+}]_{acy}$: 1 mg Mn/L = 1.8 mg/L as $CaCO_3$

Effects of Alkalinity on Endpoint pH

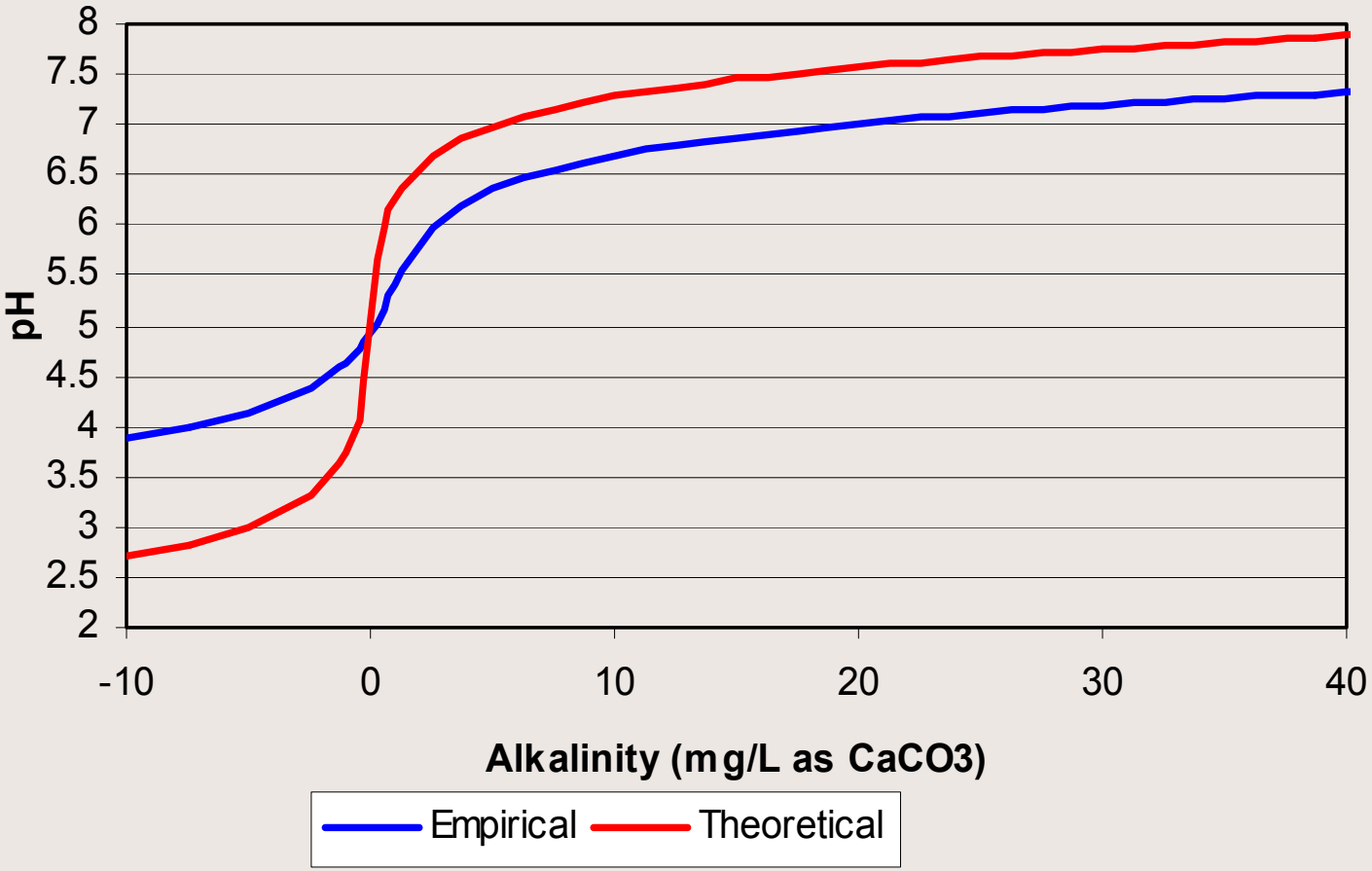
Potentiometric Titration @ 15-25°C



Note: Titration Error represents the increase in measured alkalinity when using a pH 4.3 endpoint versus the correct pH endpoint

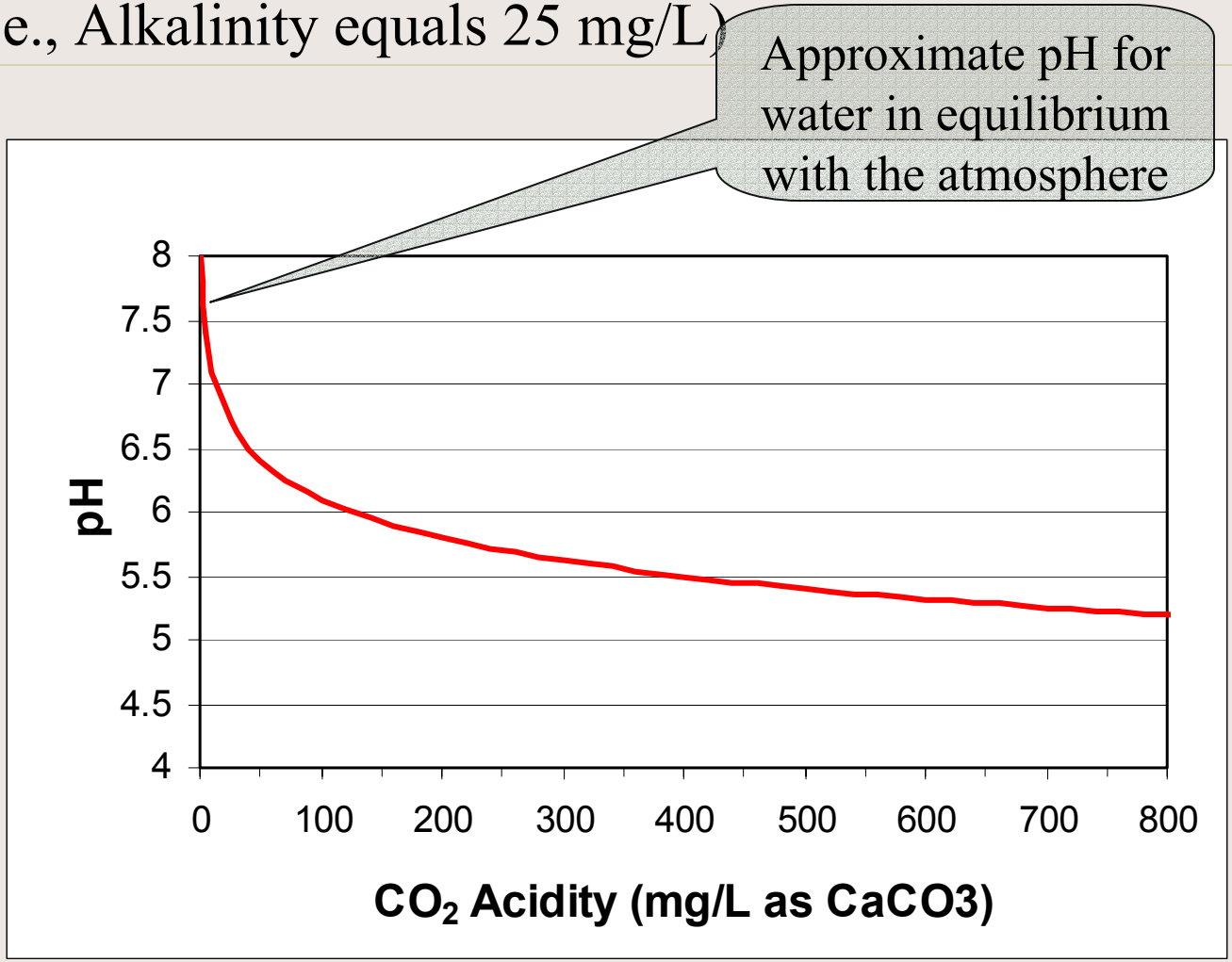
Alkalinity and pH Relationship in Open Systems; such as, Streams

(i.e., in equilibrium with the atmosphere)



Alkalinity and pH Relationship in Closed Systems; such as, Groundwater & Deep Mines

(i.e., Alkalinity equals 25 mg/L)



Calculation of CO_2 Acidity

$$m_{H2CO3} = 10^{-pH} \times \gamma_{HCO3-} \times m_{HCO3-} / K_1 \times \gamma_{H2CO3}$$

$$P_{CO2} = m_{H2CO3} \times \gamma_{H2CO3} / a_{H2O} \times K_H$$

$$CO_2 \text{ Acidity (mg/L } CaCO_3)] = m_{H2CO3} \times 1 \text{ mole } CaCO_3/1 \text{ mole } H_2CO_3 \times 1{,}000 \text{ mM/M} \times 100 \text{ mg } CaCO_3/\text{mM } CaCO_3$$

where:

m_i = *molar concentration*

$Log\ (\gamma_{H2CO3}) = 0.1 \times I$

$Log\ (\gamma_i) = -A \times z^2 \times I^{0.5} / (1 + B \times a_o \times I^{0.5})$

$a_{H2O} = 1 + (0.026 \times I)$

$A = 1824830 \times (\varepsilon \times T)^{-1.5}$

$B = 50.3 \times (\varepsilon \times T)^{-0.5}$

a_o = Ion Size Parameter ($a_o = 4$ for HCO_3^- ; $a_o = 4$ for Ca^{2+})

$I = ½\ \Sigma C_i Z_i^2$ or $\approx 10^{-4.796} \times$ Conductivity (µS)

T = Temperature (°K) = (°C + 273.16)

$\varepsilon = 87.74 - (0.4008 \times T) + (0.0009398 \times T^2) - (0.00000141 \times T^3)$

$Log\ K_H = 108.3865 + (0.01985 \times T) - (6919.53/T) - (40.4515 \times \log T) + 669365/T^2)$

$Log\ K_1 = -356.3094 + (0.06092 \times T) + (21834/T) + (126.83 \times \log T) - 1684915/T^2)$

Simplified Calculation of CO_2 Acidity

$$CO_2\ Acidity_{(mg/L\ CaCO_3)} = Alkalinity_{(mg/L\ CaCO_3)} \times 2 \times 10^{-pH} \div 10^{-6.4}$$

For No Alkalinity Type Waters (i.e. pH < 4.5) CO_2 Acidity must be measured by:

1) Normal Acidity Titration to pH 8.3 and with subtraction of Al and Fe^{3+} (i.e., hydolyzable metals) acidity; or
2) Dissolved Inorganic Carbon Analysis

Calcite Dissolution

Solubility & Kinetics

Calcite Dissolution Reactions

$$CaCO_{3(s)} + H^{+} \rightarrow Ca^{2+} + HCO^{3-} \quad (1)$$

$$CaCO_{3(s)} + H_2CO_3^{*} \rightarrow Ca^{2+} + 2HCO_3^{-} \quad (2)$$

$$CaCO_{3(s)} + H_2O \rightarrow Ca^{2+} + HCO_3^{-} + OH^{-} \quad (3)$$

The dissolution mechanism(s) depend on the characteristics of the water solution in contact with the limestone and may involve one, two or a progression of all three.

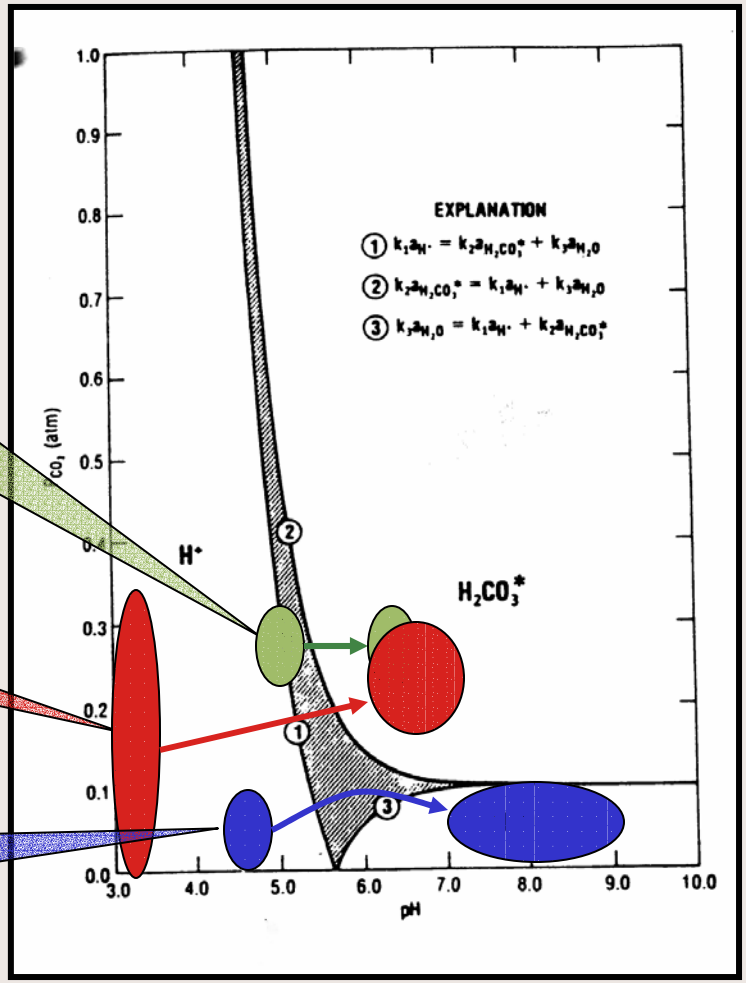
Calcium Carbonate (i.e., limestone) Dissolution Solubility

Examples of reaction progression and final pH based on solubility

Type 1
Slightly Acidic pH (~5-6), High CO_2 Acidity (100 to 600 mg/L)

Type 2
Highly Acidic pH (< 4), with low or high CO_2 Acidity, and high hydrolyzable metals (Al and Fe^{3+})

Type 3
Acidic pH with low CO_2 Acidity and low hydrolyzable metals



Brezonik, P.L. 1994. Chemical Kinetics and Process Dynamics in Aquatic Systems. Lewis Publishers, Ann Arbor, MI. 754p.

Calculation of Maximum Alkalinity

Calculation of Maximum Alkalinity (A_{max}):

$$A_{max} = [(m_{Ca2+\ solubility} - m_{Ca2+\ Initial}) \times 100] + A_o$$

A_{max} = maximum alkalinity in mg/L as $CaCO_3$ *A_o* = initial *alkalinity in mg/L as $CaCO_3$*

Calculation of Calcium Solubility:

$$m_{Ca+2} = [(P_{CO2} \times K_H \times K_1 \times K_{arg})/(K_2 \times \gamma_{HCO3-} \times \gamma_{Ca2+})]^{1/3}$$

Calculation of P_{CO2}:

$$P_{CO2} = m_{H2CO3} \times \gamma_{H2CO3} / a_{H2O} \times K_H$$

$$m_{H2CO3} = 10^{-pH} \times \gamma_{HCO3-} \times m_{HCO3-} / K_1 \times \gamma_{H2CO3}$$

where:

m_i = molar concentration **T** = Temperature (°K) = (°C + 273.16)

Log (γ_{H2CO3})= $0.1 \times I$ $a_{H2O} = 1 + (0.026 \times I)$ ***Log*** $(\gamma_i) = -A \times z^2 \times I^{0.5}/(1 + B \times a_o \times I^{0.5})$

$A = 1824830 \times (\varepsilon \times T)^{-1.5}$ *$B = 50.3 \times (\varepsilon \times T)^{-0.5}$* $\mathbf{a_o}$ = Ion Size Parameter (a_o = 4 for HCO_3^- ; a_o = 4 for Ca^{2+})

I = $\frac{1}{2} \Sigma C_i Z_i^2$ or $\approx 10^{-4.796} \times$ Conductivity (µS)

$\varepsilon = 87.74 - (0.4008 \times T) + (0.0009398 \times T^2) - (0.00000141 \times T^3)$

Log $K_H = 108.3865 + (0.01985 \times T) - (6919.53/T) - (40.4515 \times \log T) + (669365/T^2)$

Log $K_1 = +356.3094 + (0.06092 \times T) - (21834/T) - (126.83 \times \log T) + (1684915/T^2)$

Log $K_2 = +107.8871 + (0.03253 \times T) - (5159.8/T) - (38.925 \times \log T) + (563714/T^2)$

Log $K_{arg} = -171.9773 - (0.077993 \times T) + (2903.29/T) + (71.595 \times \log T)$

Calculation of Maximum Alkalinity

Calculation of Maximum Alkalinity (A_{max}):

$$A_{max} = [(m_{Ca2+\ solubility} - m_{Ca2+\ Initial}) \times 100] + A_o$$

A_{max} = *maximum alkalinity in mg/L as* $CaCO_3$ A_o = initial *alkalinity in mg/L as* $CaCO_3$

Calculation of Calcium Solubility:

$$m_{Ca+2} = [(P_{CO2} \times K_H \times K_1 \times K_{arg})/(K_2 \times \gamma_{HCO3-} \times \gamma_{Ca2+})]^{1/3}$$

Calculation of P_{CO2}:

$$P_{CO2} = m_{H2CO3} \times \gamma_{H2CO3} / a_{H2O} \times K_H$$

$$m_{H2CO3} = 10^{-pH} \times \gamma_{HCO3-} \times m_{HCO3-} / K_1 \times \gamma_{H2CO3}$$

where: (@ T=12°C and Cond. = 2000 μS)

m_i = ***molar concentration*** **T** = Temperature (°K) = (°C + 273.16)

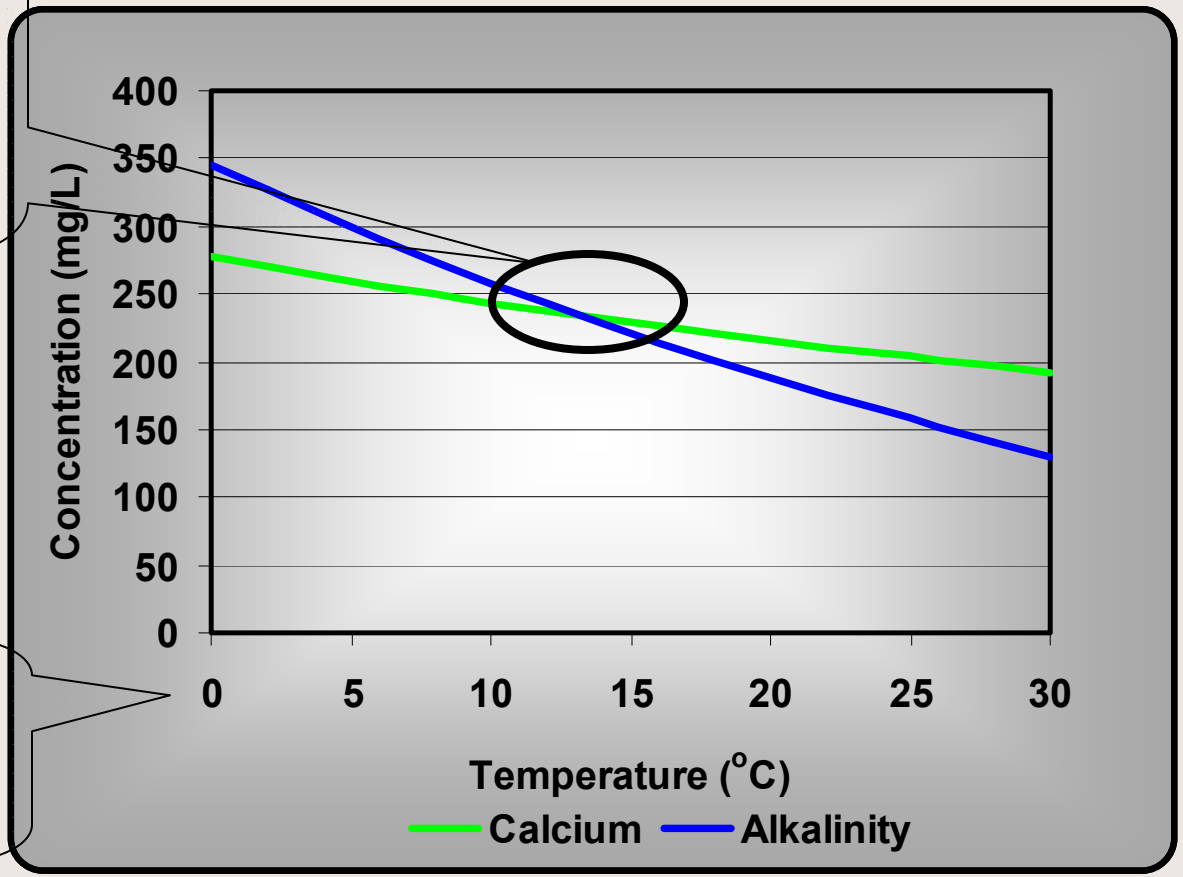
γ_{H2CO3} = **1.007** a_{H2O} =0.9992 γ_{HCO3-} = ***0.846*** γ_{Ca2+} = ***0.543***

Log K_H = –1.26 ***Log*** K_1 = -6.44 ***Log*** K_2 = -10.46 ***Log*** K_{arg} = -8.26

Type 1 Mine Drainage Discharge

Effects of Temperature (Enthalpy) on Solubility

Typically not a factor over the narrow temperatures encountered in Type 1 discharges

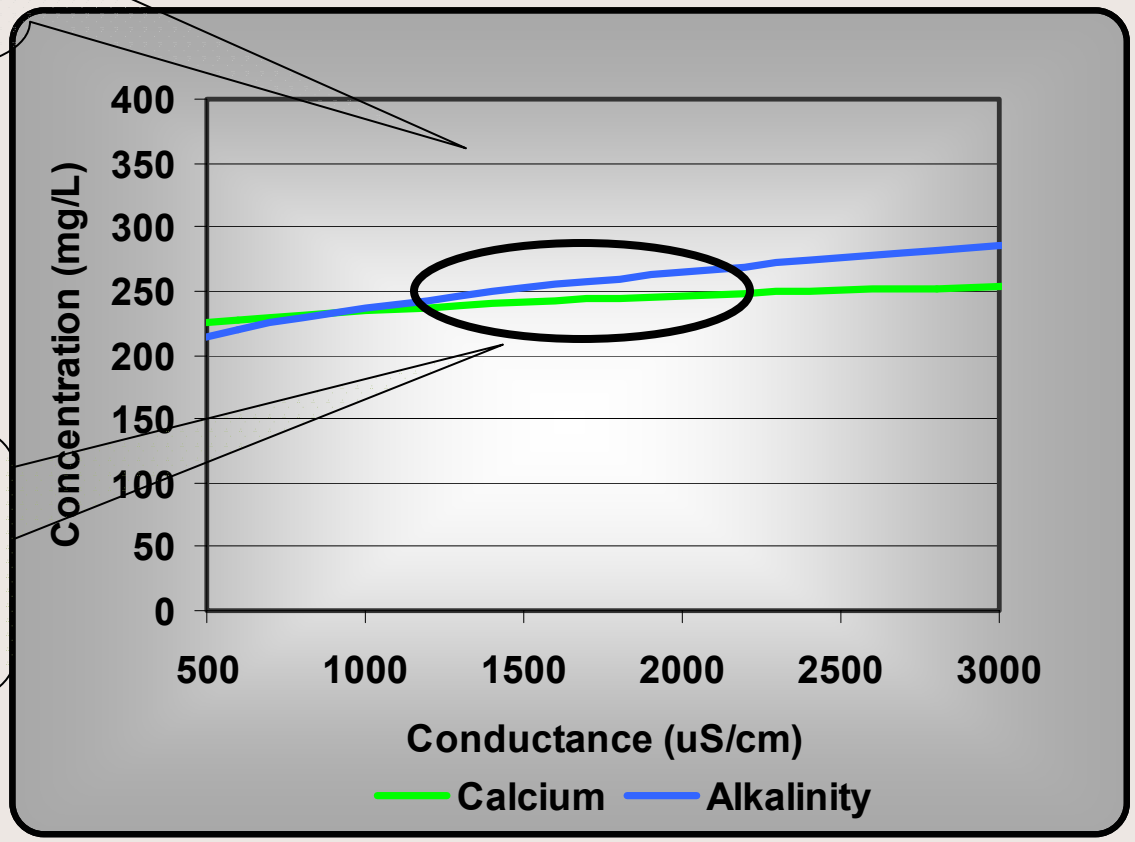


Increasing temperature decreases the solubility and alkalinity

Type 1 Mine Drainage Discharge

Effects of Conductivity (Ionic Strength) on Solubility

Increasing conductivity (or salts in the water) increases the solubility



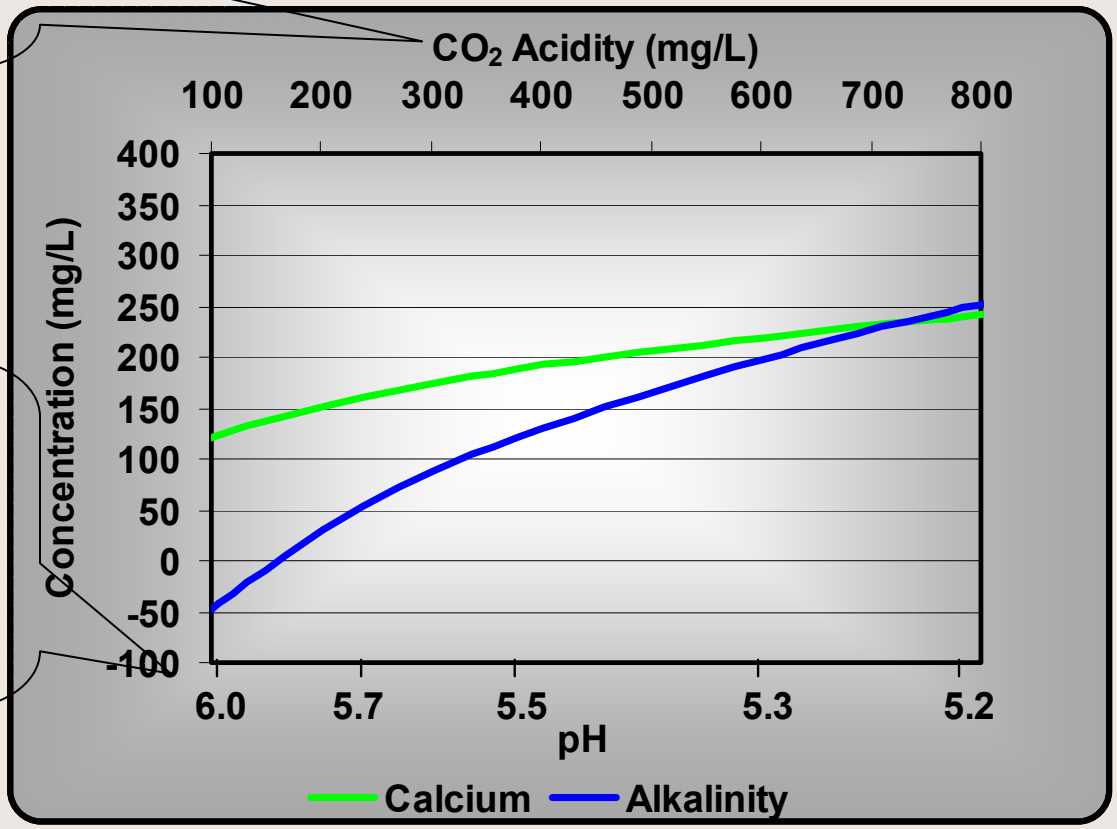
Will only have a 10-20% affect on alkalinity, because most Type 1 discharges are high conductivity

Type 1 Mine Drainage Discharge

Effects of Carbon Dioxide Acidity (P_{CO2}) on Solubility

Increasing carbon dioxide acidity increases the solubility

This scale shows the affects of carbon dioxide acidity on initial pH. Also shows the importance of measuring pH accurately



Mine Drainage Waters

Parameter	Type 1	Type 2	Type 3
pH	5.2	3.2	4.2
Alkalinity (as mg/L $CaCO_3$)	25	0	0
(Hot) Acidity (as mg/L $CaCO_3$)	110	300	20
Iron (mg/L)	75	35	2.0
Manganese (mg/L)	3.0	3.0	2.0
Aluminum (mg/L)	<0.5	35	1.0
Calcium (mg/L)	150	150	10
Sulfate (mg/L)	1200	1200	100
Equilibrium Conditions with Limestone			
Alkalinity (as mg/L $CaCO_3$)	**245**	**>250**	**40**
pH	**6.4**	**<7**	**8.2**

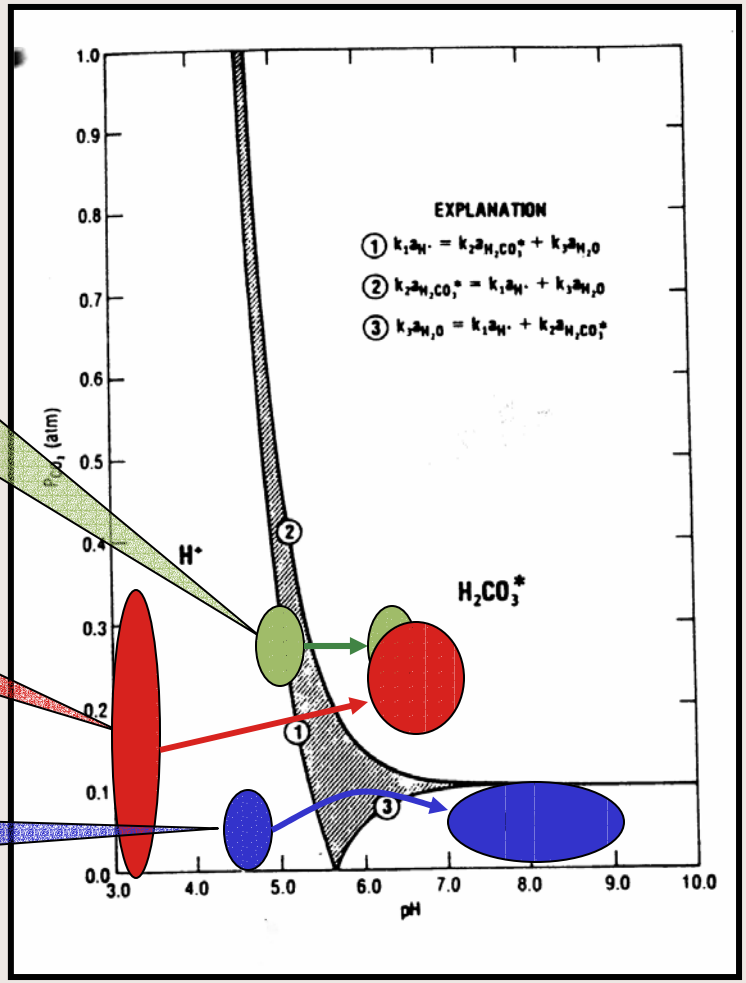
Calcium Carbonate (i.e., limestone) Dissolution Kinetics

Examples of reaction progression and final pH based on solubility

Type 1
Dominated H_2CO_3 Reaction Rate

Type 2
A combined H^+ and H_2CO_3 Reaction Rate

Type 3
Dominated by H_2O Reaction Rate



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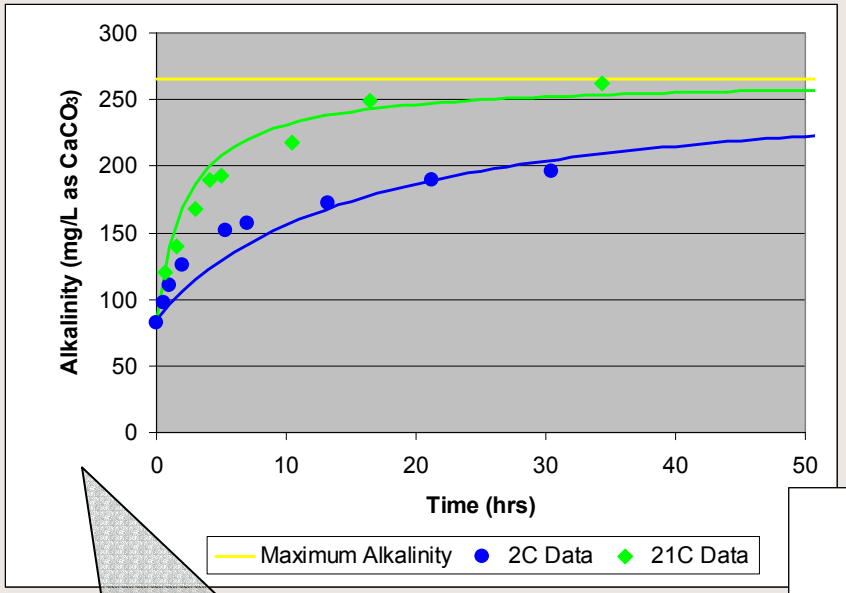
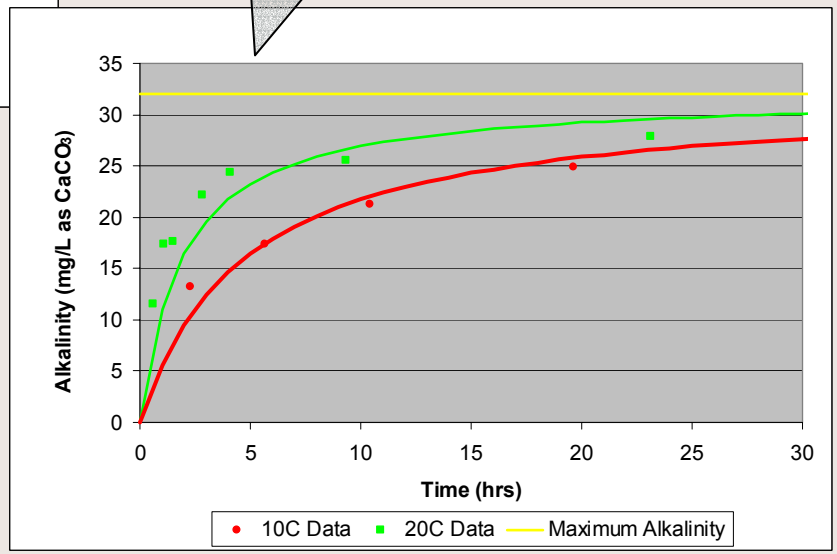
Effects of Temperature on Reaction Rate

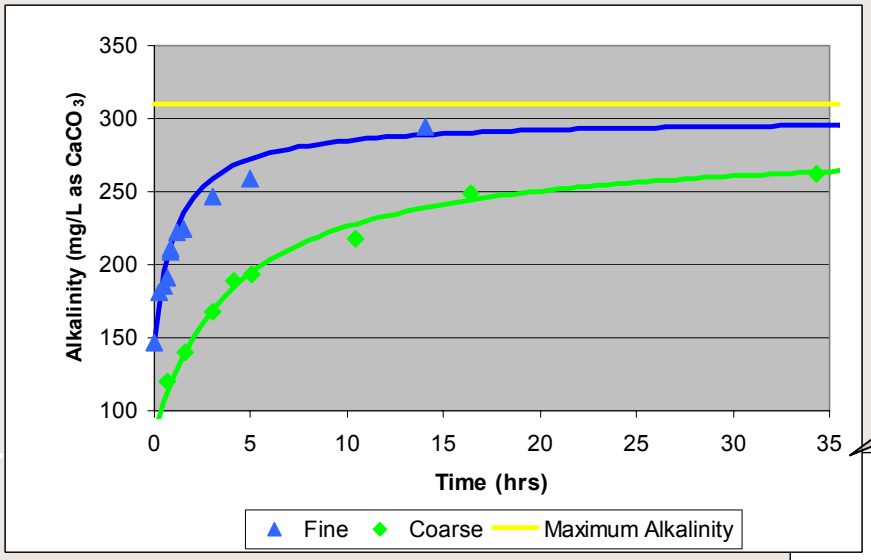


Type 3 AMD Discharge
Temperature change doubled the alkalinity generations rate
Final pH = 8.2

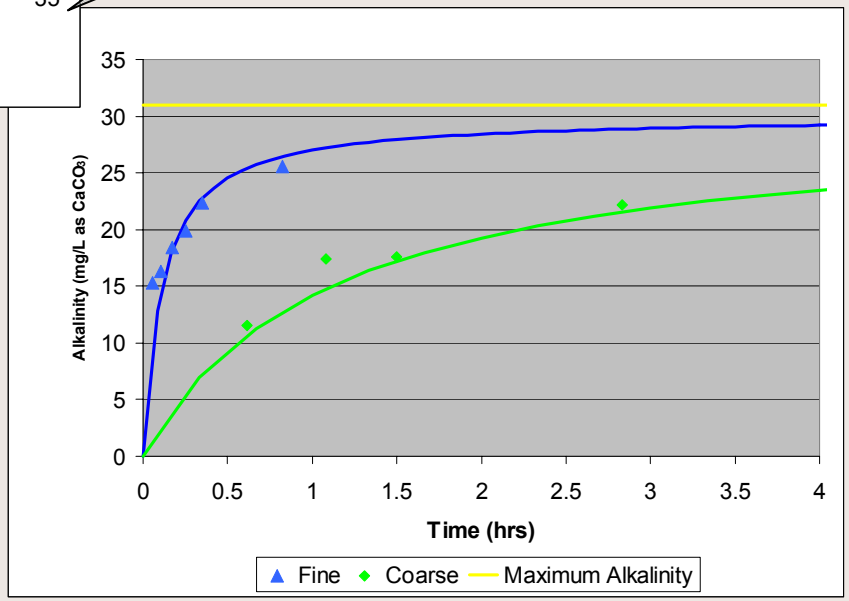
Type 1 AMD Discharge
Temperature change more than doubled the alkalinity generations rate
Final pH = 6.6



Effects of Limestone Surface Area on Reaction Rate



The size of the limestone used strongly affects the alkalinity generations rate



Alkalinity Kinetic Model (AKM)

Kinetic Equation:

$$A_t = A_{max} - [(A_{Max} - A_o)^{-1} + (k \times SA \times t)]^{-1}$$

where:

A_t – *Alkalinity at any time (t)*

A_o – *Alkalinity at initial time (t=0)*

A_{max} – *Maximum alkalinity ($t = \infty$)*

$k = 2^{nd}$ *Order Reaction Rate*

Type 1 $k_{@12C} = 10^{-6.95}$ *m/min* *Type 2* $k_{@12C} = 10^{-6.00}$ *m/min*

SA = *Surface Area* $(m^2/m^3) = 0.0003 \times d^2 \times (100/d)^3$

t – time in minutes

d = Nominal Diameter in cm

$pk_{T2} = pK_{T1} - [(E_a/19.15) \times ((T_2 - T_1)/(T_2 \times T_1))]$

E_a = *Activation Energy*

Type 1 $E_a = 67.5$ *KJ/mole* *Type 2* $E_a = 90.6$ *KJ/mole*

Anoxic Limestone Drain (ALD)
and Limestone Beds

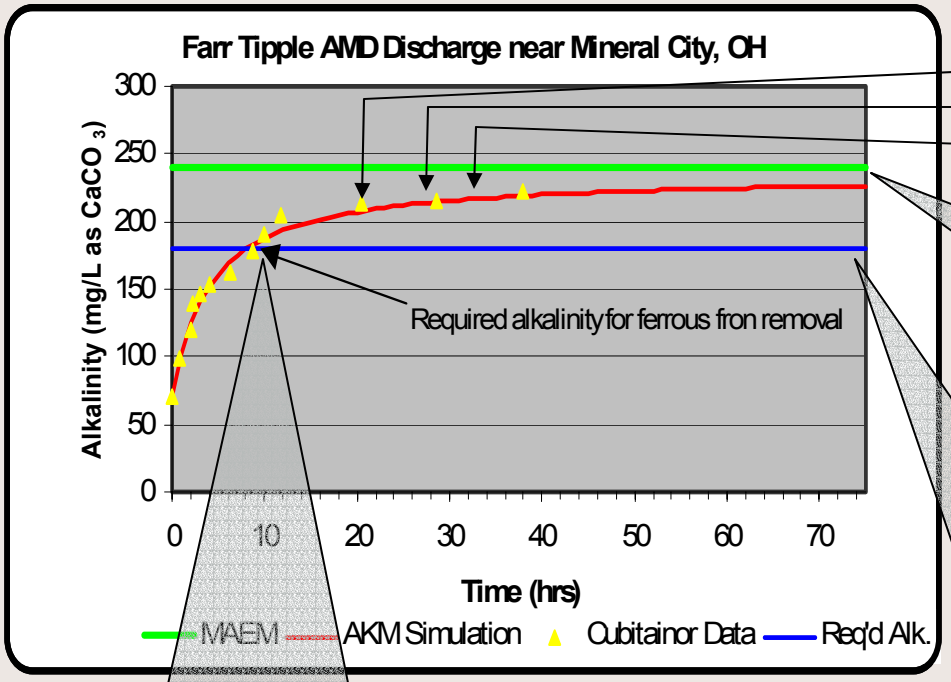
For Alkalinity Generation and Treatment of Type 1 & 3 AMD Waters

Basis for Detention Sizing Approach Using MAEM-AKM & IAD

A Procedure for ALD Detention Time Estimation

1) **ALD Design Limitations**
   1) AMD Discharge Must Be Anoxic!
   2) Aluminum < 1 mg/L, pH>5, DO<0.5mg/L
2) **Conduct MAEM-AKM and/or Cubitainor Study**
3) **Determine Required Alkalinity**
   1) IAD = Iron Alkalinity Demand
   2) IAD (mg/L $CaCO_3$) = 1.8 mg/L $CaCO_3$/mg/L Fe^{2+} × Total Iron (mg/L) × 1.25 (FOS)
4) **Determine Required Detention Time (hours) = DTR**
5) **Determine Required Longevity Volume (e.g., 25 years) =RV**
   1) Volume (ft^3) = Flow (gpm)× Maximum Alkalinity × 3.8 L/gal × 525,600 min/yr × X yrs ÷ 0.9 ÷ 1,000,000 mg/kg × 2.204 lbs/kg ÷ 90 lbs/ft^3
   2) Volume (ft^3) = Flow (gpm)× Maximum Alkalinity × 1.35
   3) Longevity Detention Time (DTL) = Volume ×7.5 gal/ft^3÷ 2 ÷ Flow÷ 60 min/hr
6) **Estimate Total ALD Detention Time**
   1) Total DT = DTR + DTL

Graphical Examples of ALD Sizing



1st Iteration

2nd Iteration

3rd Iteration

MAEM

Max. Alkalinity = 245 mg/L $CaCO_3$

Required Alkalinity = 190 mg/L $CaCO_3$

IAD = 90 mg/L × 1.7 × 1.25

IAD = 190 mg/L $CaCO_3$

Total DT = DTR + DTL = 9.5 hrs + 20.5 hrs = 30 hrs