ML/ARD Prediction
$FeCO_3$ and Low-Sulphide Materials

BC ARD Workshop 2005

Bruce Mattson,
Lorax Environmental Services

LORAX ENVIRONMENTAL

CONTENT

1. Carbonate Minerals
2. Leaching Behavior in Low Sulfur Humidity Cells
3. Fe carbonate issues as related to ARD Prediction – available NP
   - Fe hydrolysis
   - Carbonate Coatings
   - Dissolution Kinetics
4. Summary and Conclusions

LORAX ENVIRONMENTAL

Laboratory Artifacts to be Aware of when evaluating Site-Specific NP/AP Criteria for Low Sulphur Materials

1. Definition of Carbonate Molar Ratio -CMR
2. Results from 17 pH-neutral humidity cells
   - pH, sulphate, alkalinity and CMR
3. Lab Conditions vs. Field conditions
4. Summary and Conclusions

LORAX ENVIRONMENTAL

Definition & Application of CMR

- The depletion of neutralization potential (NP) in Humidity Cells is often assessed using the Carbonate Molar Ratio (CMR)
- CMR compares the concentration of alkali earth cations released by carbonate minerals to sulphate produced by sulphide oxidation in the HC leachate

$$CMR = [Ca] + [Mg] / [SO_4]$$

LORAX ENVIRONMENTAL

Primary CMR Assumption

- CMR assumes that Carbonate Dissolution is in direct response to Acidity produced from Sulphide Oxidation

Acid Generation (1):

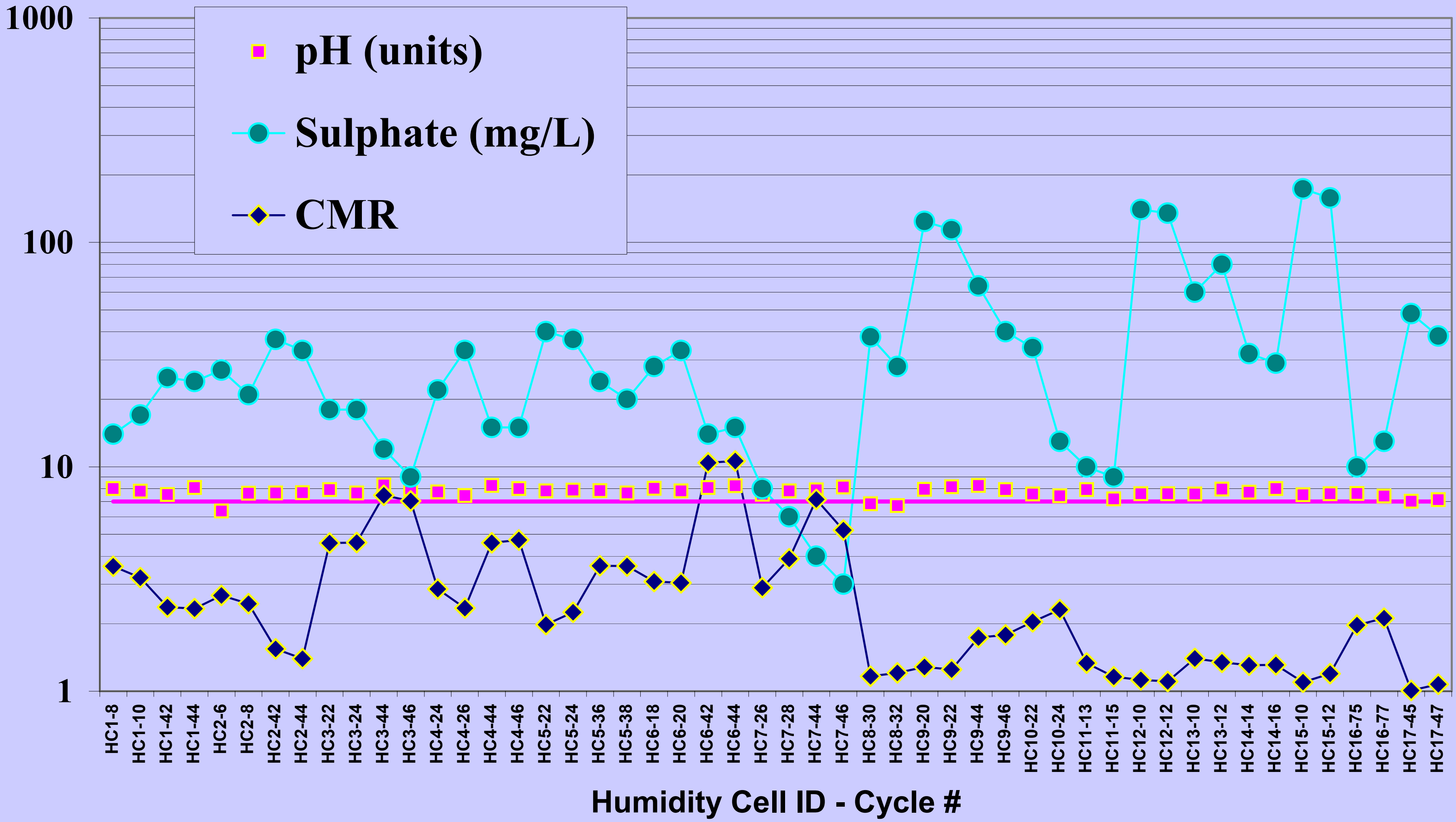
$$FeS_2 + {}^{15}\!/_4\, O_2 + {}^{7}\!/_2\, H_2O \Rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

Neutralization (2):

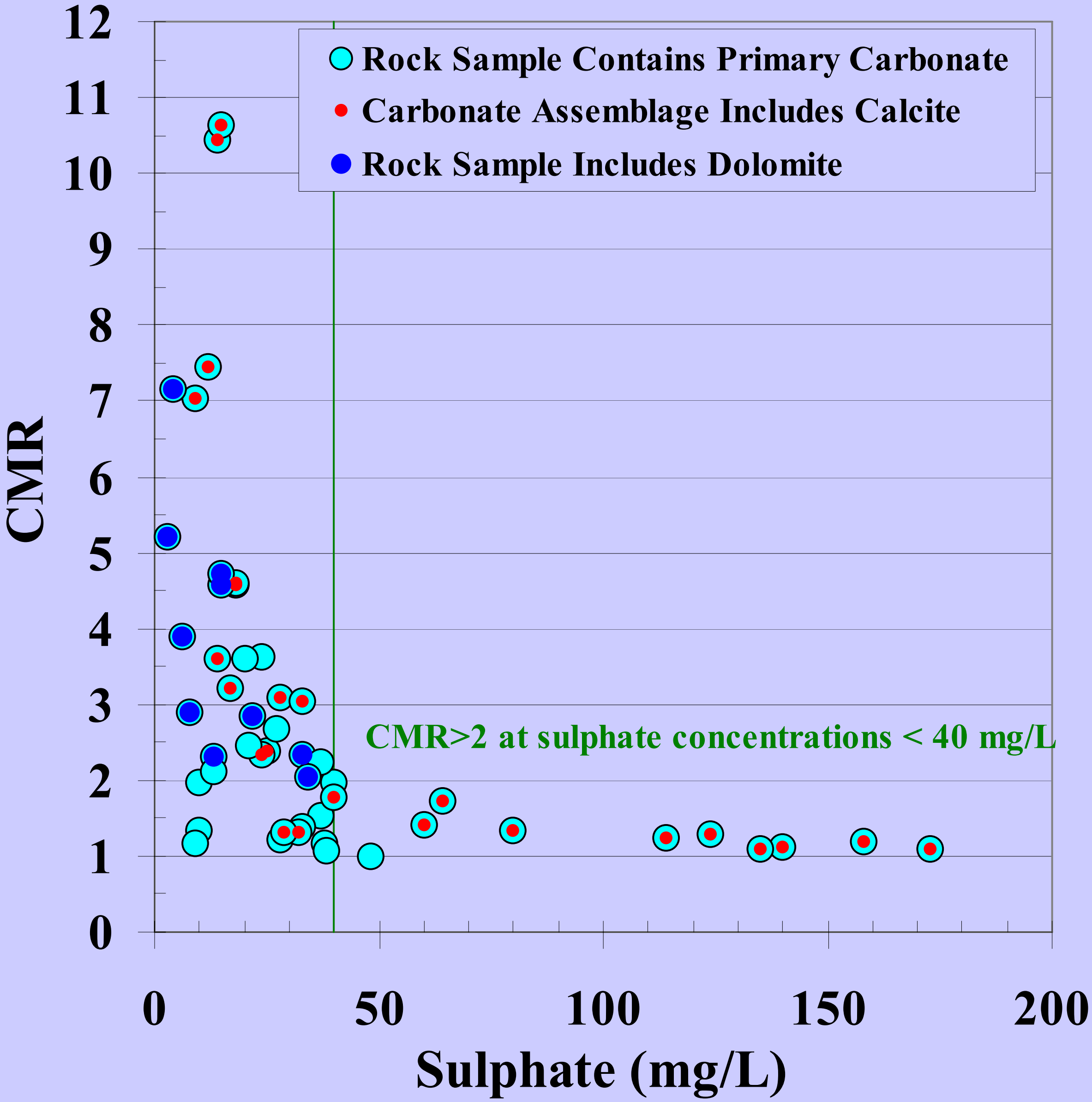
$$4\ CaCO_3 + 4H^+ \rightarrow 4Ca^{2+} + 4\ HCO_3^-$$

- Assumes Ca^{2+} Eq.2 directly related to SO_4^{2-} Eq.1
- Material specific CMR value (kinetic test) is used as base for NP/AP Criterion (static test) that is used to segregate acid waste from non-acid waste
- [Ca]+[Mg]/[SO_4] extrapolated to establish site-specific NP/AP criteria (static test) to segregate mine waste
- Misinterpretation due to high volume of water used in the Humidity Cell Procedure that is not accounted for in the assumptions used to develop the CMR

17 Humidity Cells pH 6.3 - 8.3



CMR vs Sulphate



- Sulphide Oxidation produces > 40 mg/L SO_4 CMR values remain < 2.0
- At low sulphide oxidation rates (< 40 mg/L SO_4) CMR values may increase > 10
- Acid neutralization NOT responsible for elevated [Ca] and [Mg] relative to [SO_4]
- Dissolution of carbonate at low oxidation rates in direct response to the addition of deionized H_2O

Dissolution Effect of Deionized Water @ 22°C

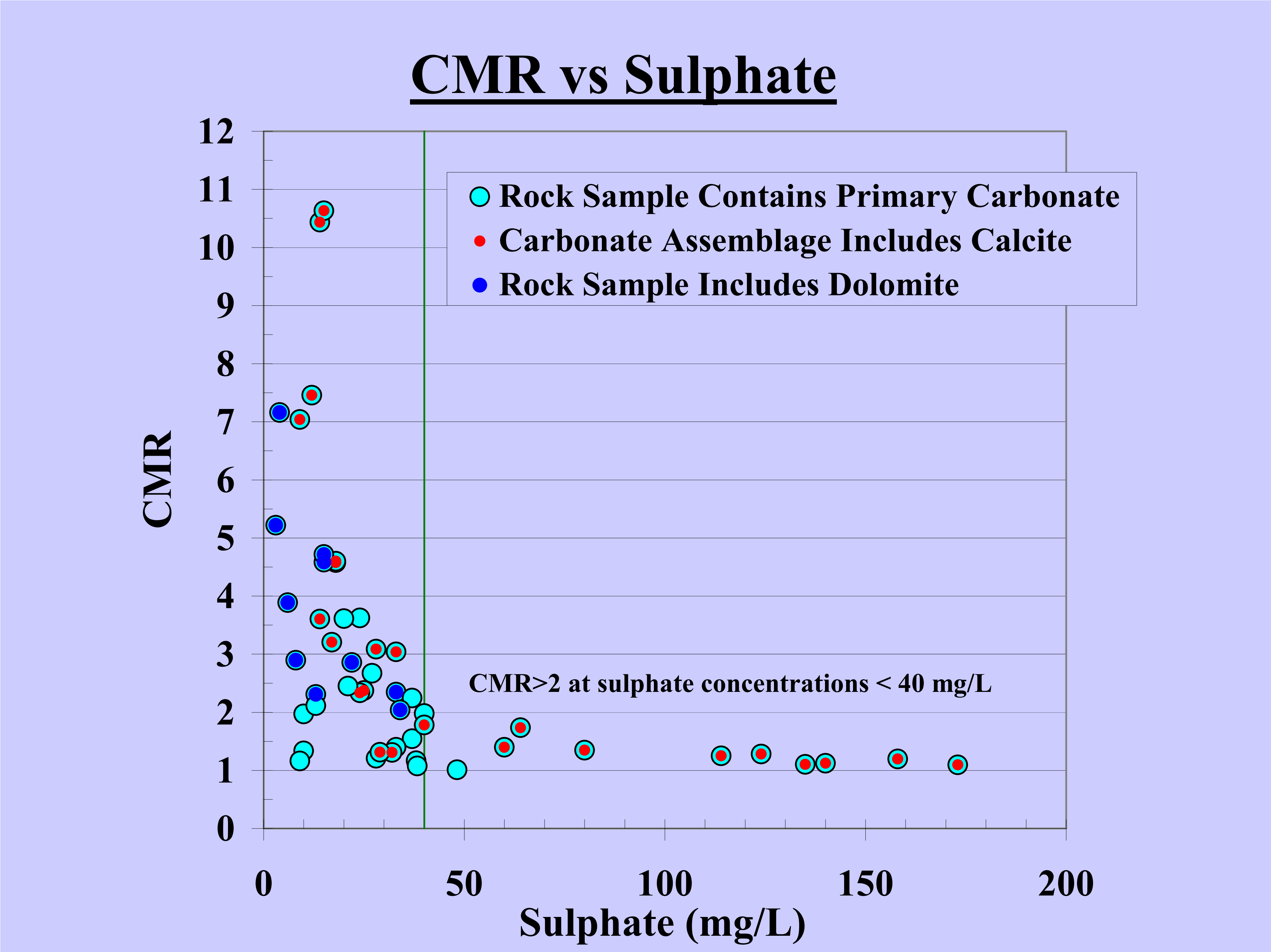
Process	Constraint	Ca^{2+} (mg/L)
Sulphide Oxidation	SO_4^{2-} = 20 mg/L	17
Water Dissolution	[Ca] at Sat. Index = 0.0	21

- At low sulphide acid production rates - 20 mg/L SO_4 >½ Ca^{2+} production attributed to natural open-system acidity
- Effect increases CMR up to 2 x
- Releases excess alkalinity

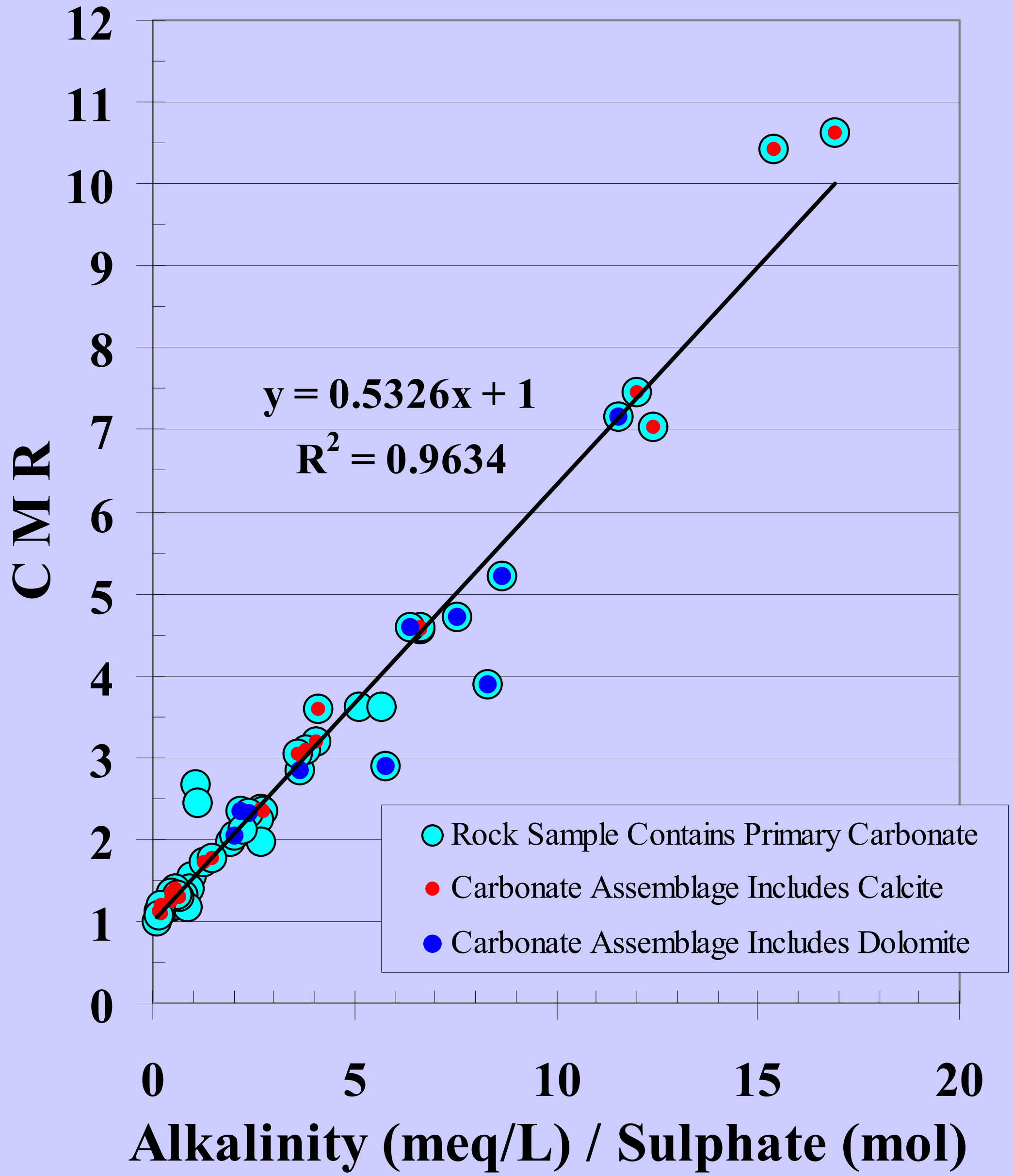
$$FeS_2 + {}^{15}\!/_4 O_2 + {}^{7}\!/_2 H_2O + 4CaCO_3 \longrightarrow Fe(OH)_3 + 2SO_4^{2-} + 4HCO_3^- + 4Ca^{2+}$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^-$$

LORAX ENVIRONMENTAL


CMR vs Sulphate
CMR
Sulphate (mg/L)
0
1
2
3
4
5
6
7
8
9
10
11
12
0
50
100
150
200
Rock Sample Contains Primary Carbonate
Carbonate Assemblage Includes Calcite
Rock Sample Includes Dolomite
CMR>2 at sulphate concentrations < 40 mg/L

Alkalinity/Sulphate to CMR Relationship



- Excess Alkalinity produced from water dissolution is directly related to the elevated CMR
- Alkalinity in dilute solutions associated with the reactivity of the carbonate mineral assemblage
- Dolomite can be sufficiently reactive to produce elevated CMR

Lab vs Field

- Is preferential dissolution effect observed in Laboratory applicable to Field Conditions?

Condition	Laboratory Humidity Cell or Column Test	Waste Rock Dump
Water to Solids Ratio	1:2 to 1:10	1:500 to > 1:1,000,000
Vertical Flow Path	10 cm to 1 m	10 m to 200 m
Contact Time	4 Hours to 1 Week	1 day to > 10 years

LORAX ENVIRONMENTAL

CMR Summary

- Three main factors affect Laboratory CMR
  1. Rate of sulphide oxidation;
  2. Water to solids mass ratio; and
  3. Solution alkalinity (carbonate reactivity)
- At low sulphide oxidation rates, carbonate dissolution in Humidity Cells is predominately in response to the volume of deionised water
- Laboratory phenomenon falsely elevates the measured rate of carbonate dissolution relative to sulphide oxidation

LORAX ENVIRONMENTAL

Carbonate Minerals

- There are ~ 60 carbonate minerals
- Most Common Carbonate Mineral is Calcite [$CaCO_3$]
- Major cation composition in the most common carbonate minerals are Ca, Mg, Fe, Mn
- Extensive substitution and solid solution between mineral end-members
- Other metals form carbonates including Sr, Zn, Cd, Co, Ba & Ni but are rare relative to the Ca, Mg, Fe and Mn carbonates

LORAX ENVIRONMENTAL

Carbonate Endmember Solid Solution

Calcite Group		Dolomite Group
Calcite $CaCO_3$	Siderite $FeCO_3$	Dolomite $CaMg(CO_3)_2$
Magnesium Calcite $Ca_xMg_{1-x}(CO_3)$	Magnesite $MgCO_3$	Ankerite $Ca(MgFeMn)(CO_3)_2$
	Rhodochrosite $MnCO_3$	

Siderite – $(Fe_{0.7}Mg_{0.1}Ca_{0.1})CO_3$

LORAX ENVIRONMENTAL

Three Issues - Fe Carb Neutralization

1. Fe^{2+} released during iron carbonate dissolution may hydrolyse in oxic environment – produce acidity
2. Fe hydrolysis products re-precipitate on the carbonate – coat mineral surface
3. Fe carbonate dissolution kinetics are slower than that of calcite

LORAX ENVIRONMENTAL

Carbonate Dissolution

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2CO_3^{2-} + 2H^+$$

CO_3 & H^+ form carbonate alkalinity – pH dependent

Theoretical equilibrium pH = 8.3 (PHREEQC)

$$FeCO_3 + CO_2 + 4H_2O \longrightarrow Fe(OH)_3 + 2CO_3^{2-} + 5H^+ + e^-$$

Fe^{2+} ultimately hydrolyses to form ferrihydrite – releases acidity

End member siderite buffers at lower pH values than calcite

Actual pH will be system dependent (pore water chemistry, PCO_2, reaction kinetics)

Although lower pH, this reaction neutralizes acidity and produces some buffering capacity

LORAX ENVIRONMENTAL

Neutralization Potential (NP) Measurement from Rock Samples

- Rock samples may contain
  - a mixture of Ca and Fe/Mn carbonate minerals and/or
  - Fe carbonate minerals of non-endmember composition

Two Traditional NP Measurements

- CaNP calculated from inorganic C content
  – Assumes all C is in the form of Calcite ($CaCO_3$)
- Sobek Bulk NP
  – measured via rapid high-temperature titration

Neither method fully accounts for the Fe Hydrolysis reaction

LORAX ENVIRONMENTAL

Accounting for Fe Hydrolysis

1. Correct the CaNP value based on the stoichiometry of the carbonate minerals

   - Stoichiomtry determined using detailed mineral techniques to measure cation composition with microprobe or estimate composition from EDS spectra data

   - The fraction of the cation composition comprised of Alkaline Earth Metals are used to calculate the available NP.

Eg. $(Fe_{0.7}Mg_{0.2}Ca_{0.1})CO_3$

$$Available\ NP = CaNP(0.1_{Ca} + 0.2_{Mg})$$

LORAX ENVIRONMENTAL

Accounting for Fe Hydrolysis

2. Conduct a modification of the USEPA NP determination through the addition of hydrogen peroxide as outlined in MEND Report 1.16.1c

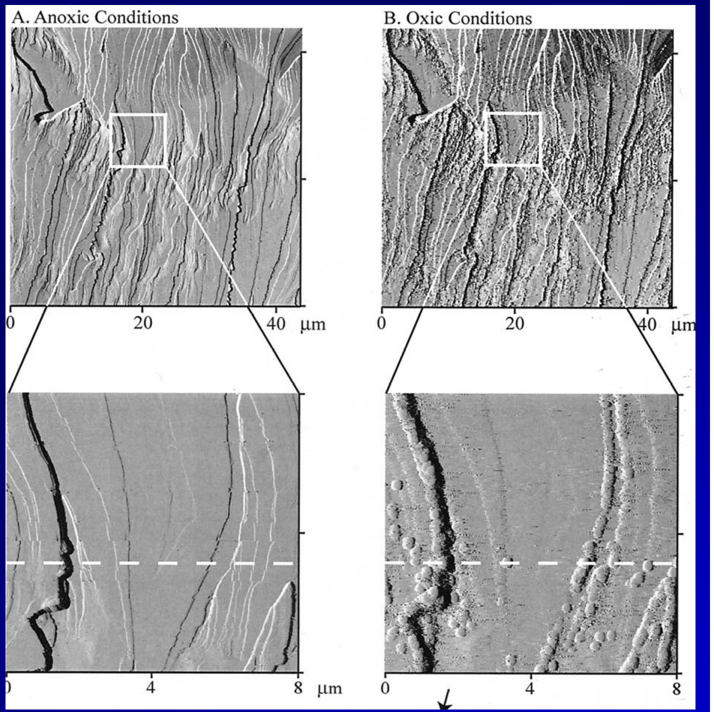
    - Method ensures the complete hydrolysis of Fe and these NP measurements closely reproduce the alkaline earth cation fraction of the carbonate mineral (Jambor et al 2003)

Both methods provide a conservative estimate of the available NP which discounts the buffering capacity of Fe carbonates

Why use a conservative approach?

Carbonate Coatings

- Under oxic pH-neutral conditions secondary minerals (Fe or Mn) may precipitate on carbonate mineral surfaces (Al et al 2000, Duckworth & Martin, 2004)
- Accumulation of the coatings diminish porewater-mineral interactions and lower carbonate dissolution rates
- Fe Carbonates are likely most susceptible to this phenomenon due to the proximity of the Fe source



From Duckworth & Martin 2004

LORAX ENVIRONMENTAL

Fe-Carbonate Dissolution Rates

- In the absence of secondary mineral coatings, calcite dissolution rates are 2 to 3 orders of magnitude greater than Fe-carbonate or dolomite

Mineral	**Dissolution Rate at pH 7.0**
Calcite $CaCO_3$	$10^{-9.5}$ (mol/cm^2/s)
Dolomite $CaMg(CO_3)_2$	$10^{-11.5}$ (mol/cm^2/s)
Rhodochrosite $MnCO_3$	10^{-12} (mol/cm^2/s)
Siderite $FeCO_3$	$10^{-12.5}$ (mol/cm^2/s)

- Calcite may be depleted more rapidly than Fe-Carbonate due to the formation of excess alkalinity during high flushing events
- Fe-Carbonate more efficient at increasing pH per mole of carbonate dissolved but produces less alkalinity
- Mine Waste systems that have Fe-carbonates in close proximity to the acidity source, may require a lower NP/AP criteria

LORAX ENVIRONMENTAL

Summary and Conclusions

- Fe hydrolysis decreases the bulk NP of Fe Carbonates and may lower the pH of Fe Carbonate buffered systems
- Fe hydrolysis produces coatings on the carbonate mineral surface that may prevent a portion of the total carbonate from dissolving and buffering pH
- Fe carbonates (particularly ankerite) may be more efficient than calcite at buffering acidic systems on a CaMg mole-release basis
- ARD Prediction from Fe-carbonate material should account for these 3 phenomena

LORAX ENVIRONMENTAL

References

Al T.A., C.J. Martin, D.W. Blowes 2000 Carboante-mineral/water interactions in sulfide-rich mine tailings Geochimica et Cosmochimica Acta, Vol 64 pp. 3933-3948

Duckworth O.W., S.T. Martin 2004 Role of molecular oxygen in the dissolution of siderite and rhodochrosite Geochimica et Cosmochimica Acta Vol 68. pp. 607-621

Jambor J.L., J.E.Dutrizac, M.Raudsep, L.A.Groate 2003 Effect of peroxide on neutralization potential values of siderite and other carbonate minerals. Journal of Environmental Quality Vol. 32 pp 2373-2378.

LORAX ENVIRONMENTAL