MINING
INFLUENCED WATERS
THEIR CHEMISTRY
& TREATMENT

Tom Wildeman
Colorado School of Mines, Golden, CO - USA
twildema@mines.edu

Flavio Vasconcelos
HidroGeo
Belo Horizonte, MG - Brasil

Belo Horizonte, 24 de Novembro de 2021

HidroGeo
Engenharia e Gestão de Projetos

- Most treatment methods have the same objectives the differences are:
  - In the time it takes for treatment
  - How mechanical is the treatment system
  - How much reactants require continuous human assistance to be added

- Other waters to treat besides ARD
- Other treatment methods to try besides hydroxide precipitation, sulfate reduction & aerobic oxidation.
- All the waters that you will see I have been asked to treat over the last 20 years.

Today, look at ARD, As, & Mn

DEFINITIONS:

- Mining Influenced Water: (MIW) Any water whose chemical composition has been affected by mining or mineral processing activities.
- Acid Rock Drainage: (ARD) A MIW that has mineral acidity.
- Passive Treatment: Any water treatment process that:
  - Utilizes common geochemical reactions typically assisted by microbes or plants,
  - Does not require the addition of chemical reagents, power and/or short term exchange of process media,
  - Functions without human intervention for long periods.

MIW TREATMENT OBJECTIVES:

- Acid Rock Drainage
  - Mineral Acidity, esp. Fe & Al
- Mineral Processing Waters
  - Usually cyanide & other anions of As & Se
- Marginal Waters
  - Circum-neutral with contaminants above aquatic standards
- Residual Waters
  - High total dissolved solids (TDS)

ACID ROCK DRAINAGE (ARD) in mg/L:

	Quartz Hill	JIC	Coal	Buckeye
pH	2.5	3.0	2.9	5.9
Al	60	20	36	21
Fe	750	1.8	180	580
Mn	80	1.2	50	20
Cu	55	0.12		0.03
Zn	150	0.20		0.24
Cd	0.80	0.003		
Pb	0.14			0.02
As	1.5	0.008		0.01
SO4	4000	184	2050	750

MINERAL PROCESSING WATER in mg/L

	Gilt Edge	Rain	Gold mine	Zn Proc
pH	9.0	8.0	8.6	5.5
Fe	470	0.05	0.5	0.60
Mn		0.47		187
Cu	78	3.3	8.3	0.024
Zn			0.06	657
Cd	0.09			1.9
As		0.09	20	
Se		0.2	0.05	
CN (Total)	230	4	~100	
SO4	300	400	1300	5800

MARGINAL WATERS in mg/L

	Westfork	Ferris Haggerty	Ni Mine	Rico
pH	7.9	6.6	7.1	7.0
Mn	0.01	0.03	0.37	0.66
Ni		0.05	7.5	0.01
Cu	0.02	20.6	0.015	
Zn	0.21	0.07	0.20	11.4
Cd	0.002	0.003	0.009	0.03
Pb	0.70			
SO4	63	48	1005	450
Alk.	156		33	595

RESIDUAL WATERS in mg/L:

	Wyoming	Coal	Oil Shale	Refinery
pH	8.2	7.1	7.9-8.8	7.8
Na	800	940	1000	180
K	92	3	743	82
Ca	260	290	47	160
Mg	34	100	33	170
Cl	1040	1000	69	350
SO4	900	1600	3000	600
Alk.	280	200	371	
TDS	3500	4200	5300	

MIW SUMMARY:

- Marginal waters are easily treated by passive methods
  - High flow may be an issue
- ARD & process waters can be treated by passive methods.
  - Chemical loading of cells may be an issue.
- Residual waters are very difficult to treat by any chemical method.
  - Billion dollar question is how to remove sulfate by an inexpensive method.

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METHODS FOR REMOVAL:

- Precipitation / Mineral Formation
  - Sulfides, Hydroxides, or Carbonates
- Adsorption –
  - Not as permanent,
  - Can be used for temporary removal
  - Can have adsorption onto organic or inorganic compounds
- Formation of Organic Compounds
  - Not as stable as inorganic precipitates

PRECIPITATION CONTROL BY pH

$$H_2O \Leftrightarrow H^+ (aq) + OH^- (aq)$$

$$H_2CO_3 (aq) \Leftrightarrow H^+ (aq) + HCO_3^- (aq)$$

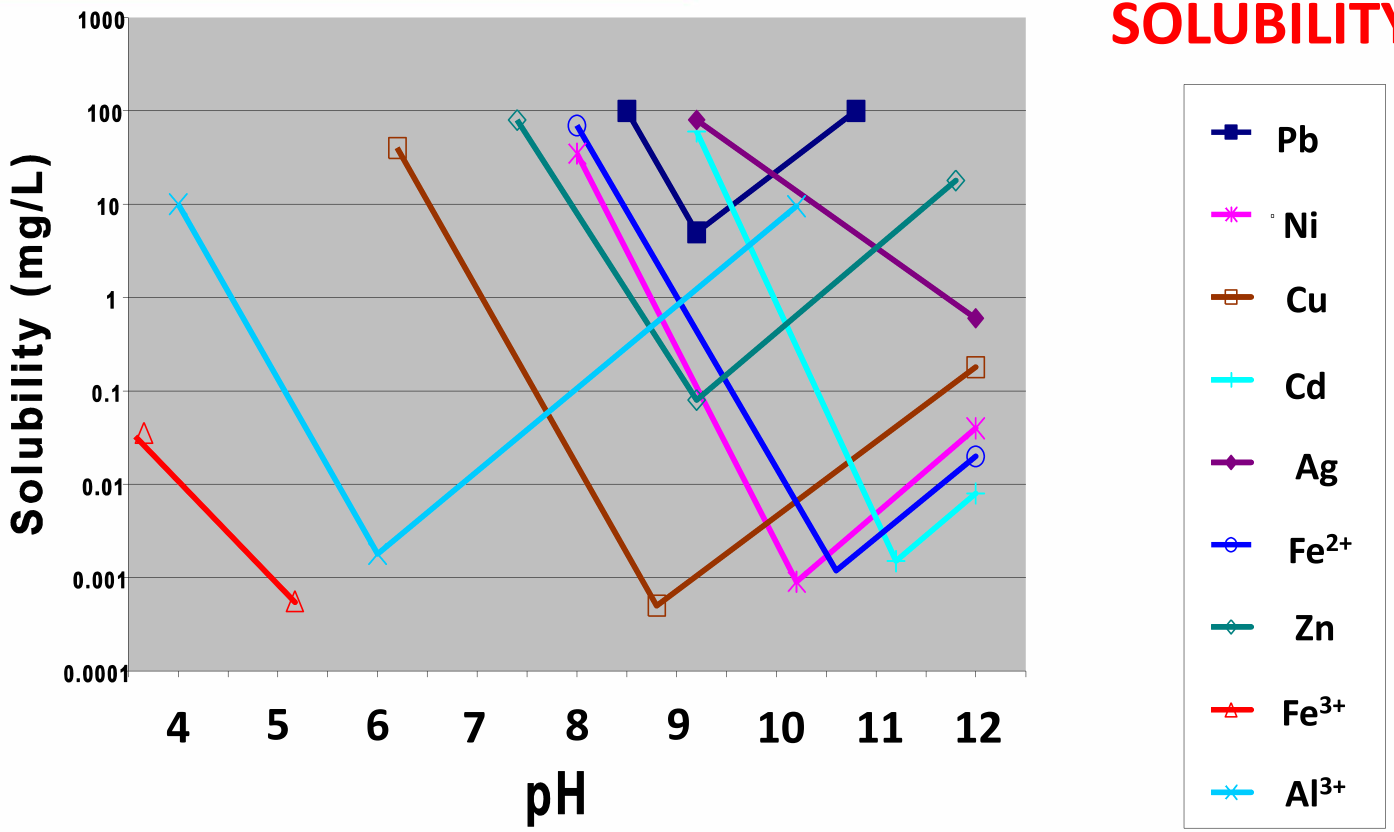
$$HCO_3^- (aq) \Leftrightarrow H^+ (aq) + CO_3^{-2} (aq)$$

$$H_2S (aq) \Leftrightarrow H^+ (aq) + HS^- (aq)$$

$$HS^- (aq) \Leftrightarrow H^+ (aq) + S^{-2} (aq)$$

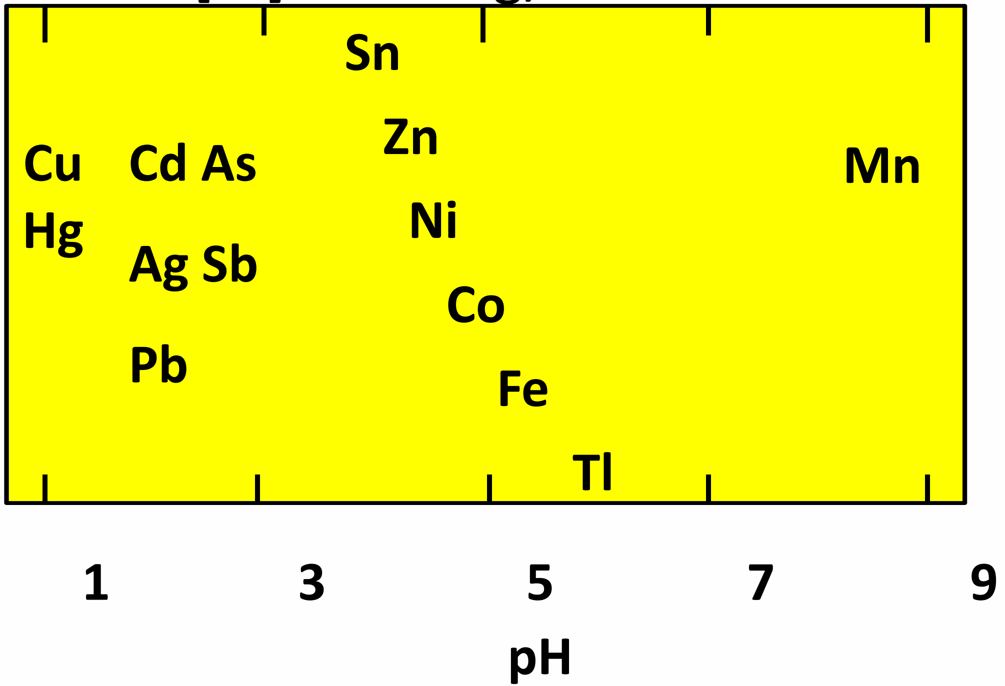
As pH increases, the anions become available

HYDROXIDE SOLUBILITY

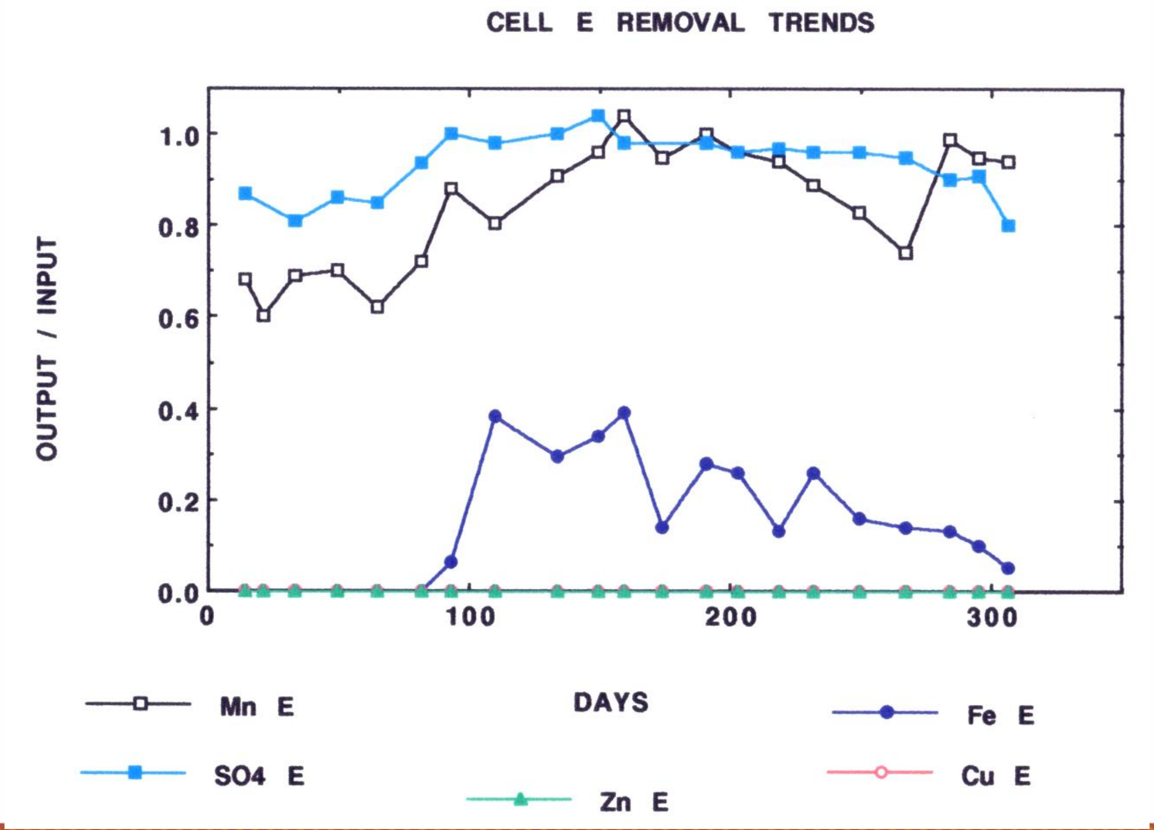


TOM'S ESTIMATE OF SULFIDE SOLUBILITIES

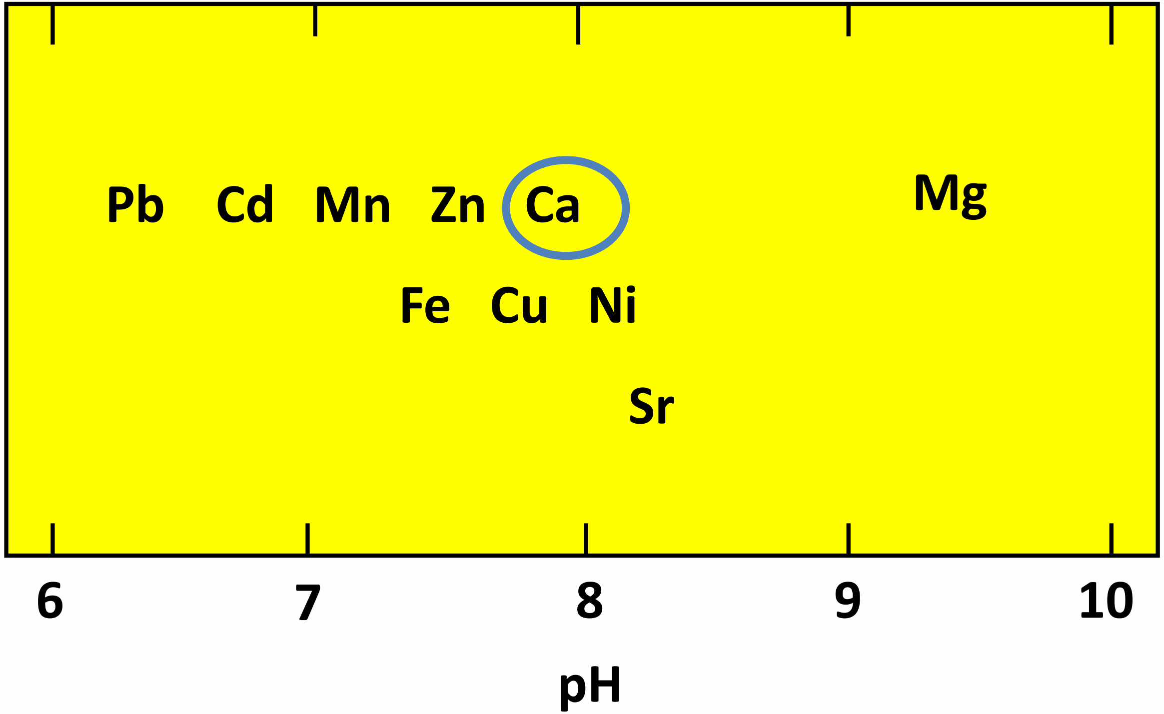
[M] < 1.0 mg/L



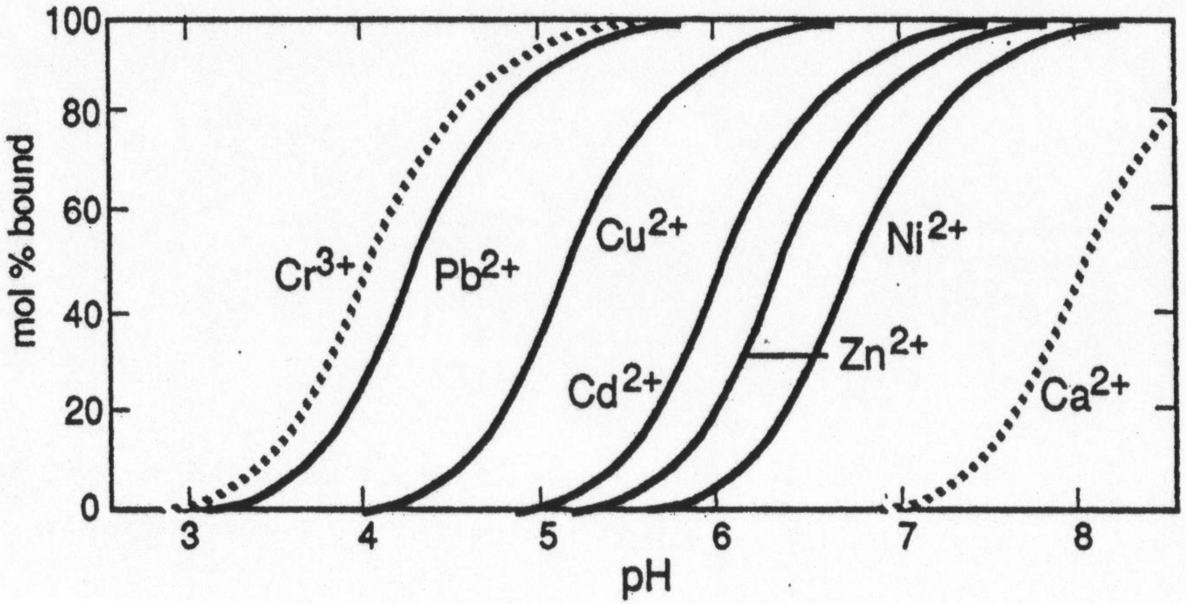
METAL REMOVAL BY SULFIDE PRECIPITATION



TOM'S ESTIMATE OF CARBONATE SOLUBILITIES [M] < 1.0 mg/L

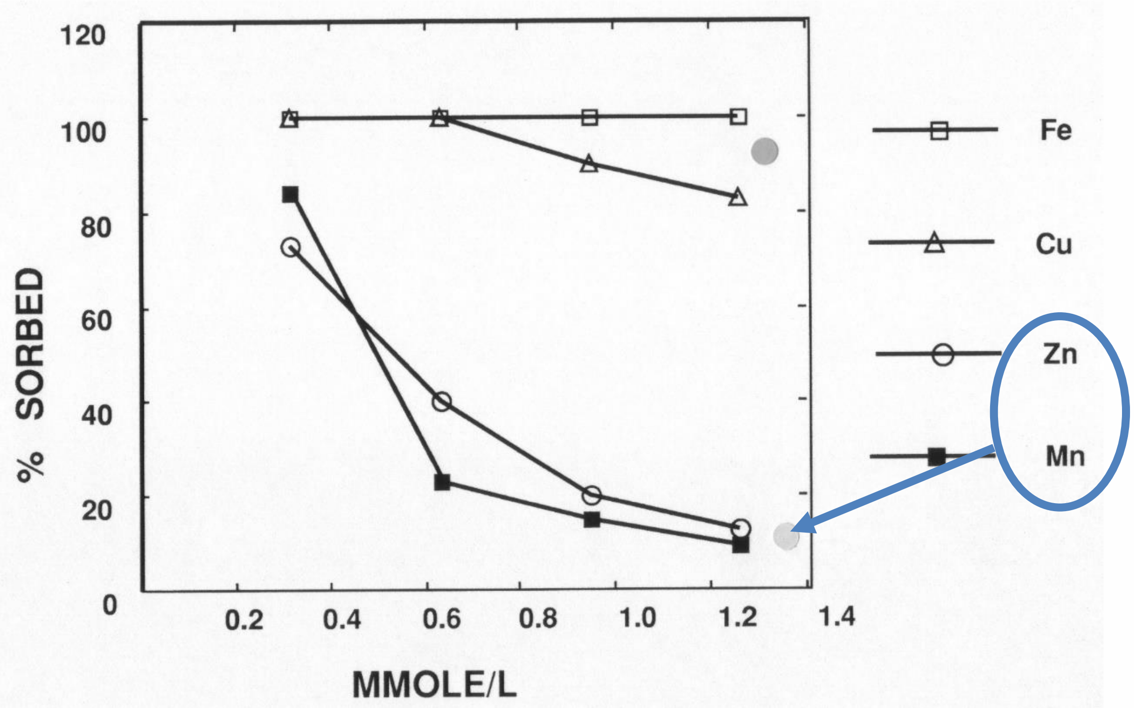


ADSORPTION ONTO $Al(OH)_3$



Hydroxide precipitation & adsorption sequence are comparable

COMPETITIVE ADSORPTION ONTO ORGANIC SUBSTRATE

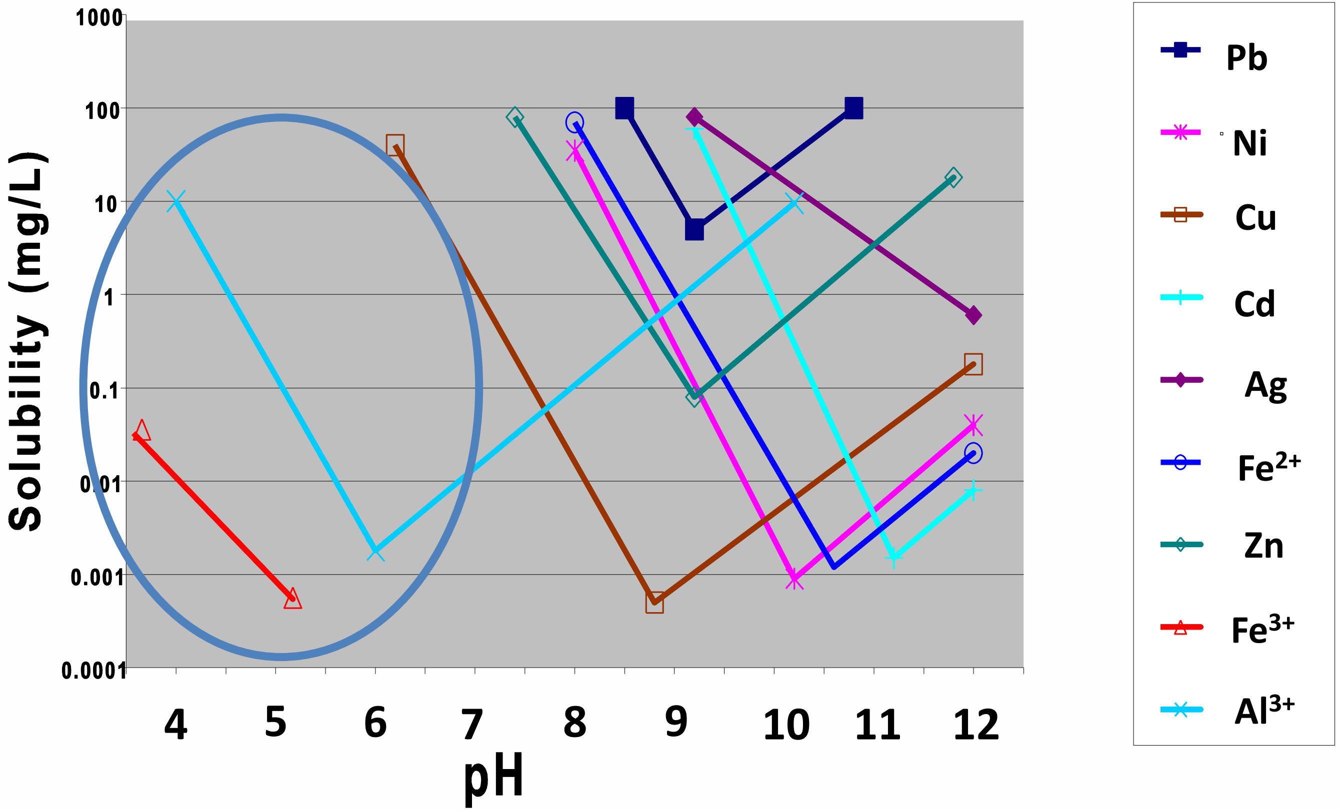


Adsorption is less permanent removal

SITUATIONS AGAINST REMOVAL

- Acid / Base Conditions
  - pH < 2: most cations are soluble
  - pH >11: As, Se, some cations are soluble
- Oxidation State
  - Low Oxidation State: Fe, Mn are soluble
  - High Oxidation State: U, Mo are soluble
  - Oxidation / Reduction reactions are often slow
- Formation of Complexes
  - Cyanides: Fe, Cu
  - Carbonates/ Hydroxides: Pb,

HYDROXIDE SOLUBILITY

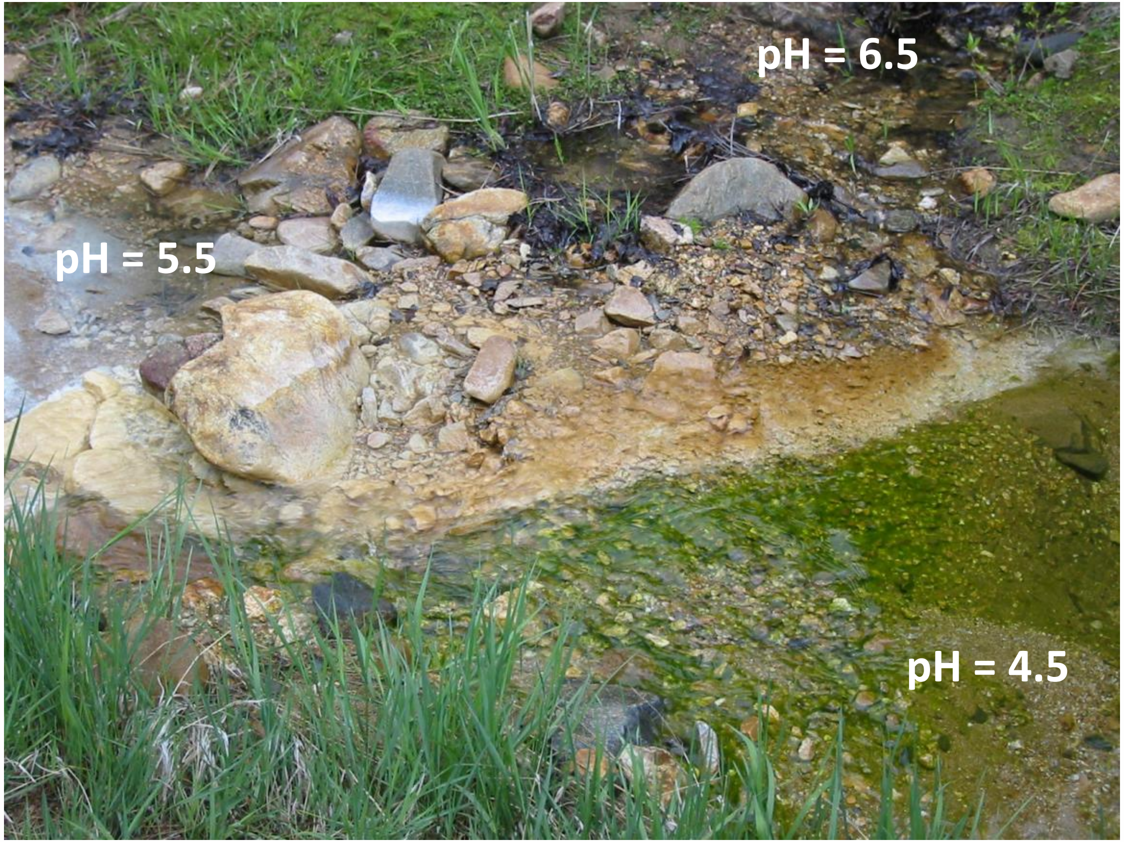


Mineral Acidity & Acid-Generating Reactions

Hydrolysis of metal cations

$$Fe^{3+} + 3\,H_2O \Leftrightarrow Fe(OH)_3 + 3\,H^+$$

$$Al^{3+} + 3\,H_2O \Leftrightarrow Al(OH)_3 + 3\,H^+$$



ALUMINUM PRECIPITATION

SOURCES OF ALKALINITY

ACTIVE

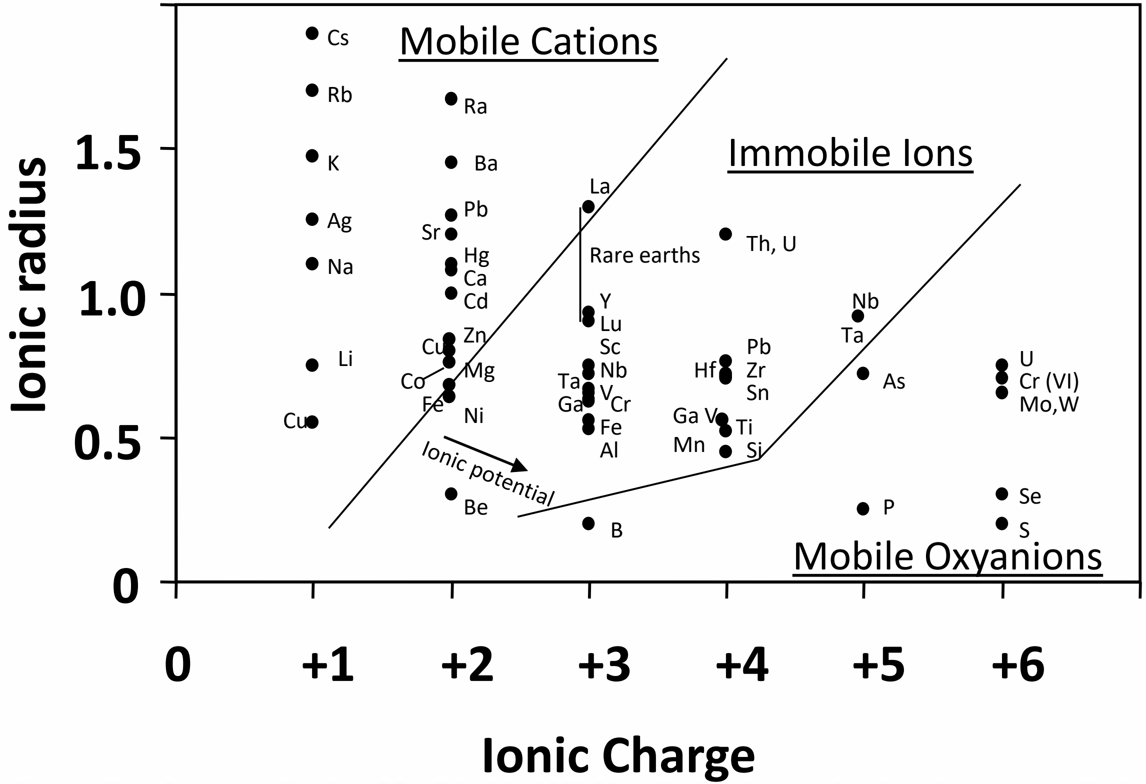
- Hydroxides: NaOH, $Ca(OH)_2$
- Carbonates: Na_2CO_3, $NaHCO_3$
- Ammonia

PASSIVE

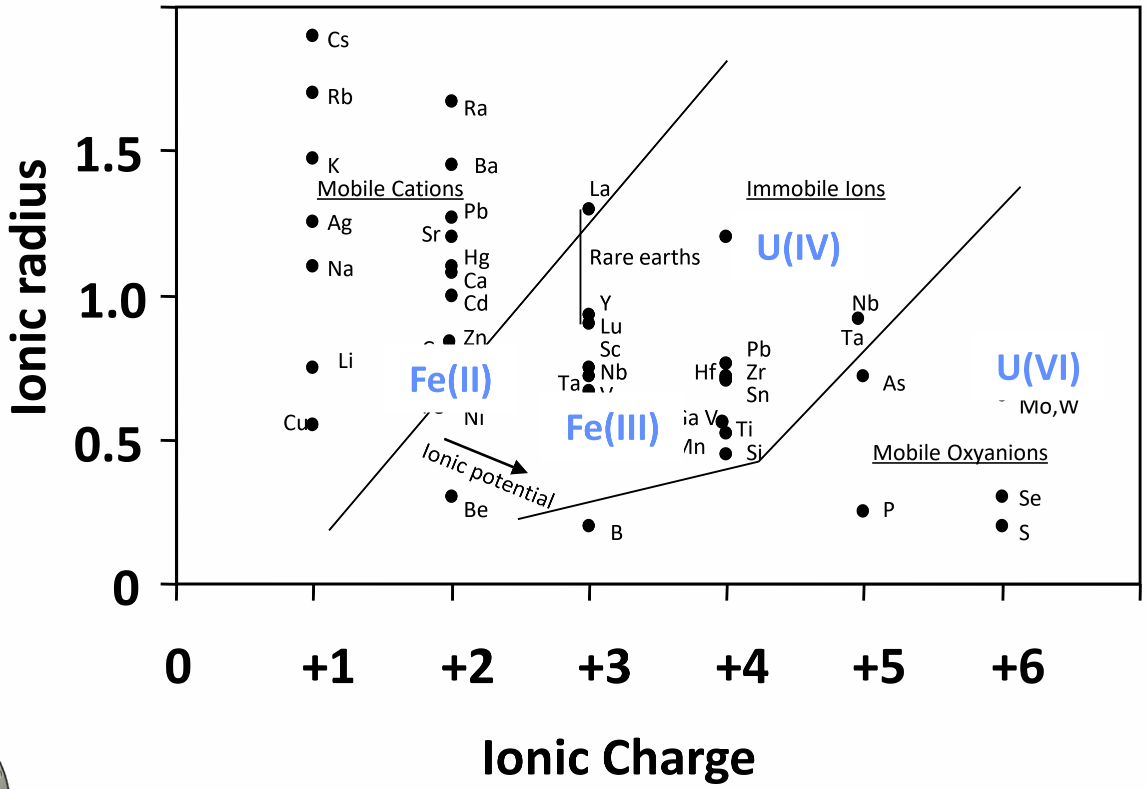
- Microbial (sulfate reducing bacteria)
  - $2\ H^+ + SO_4^= + 2\ \text{“}CH_2O\text{”} \rightarrow H_2S + 2\ HCO_3^-$
- Abiotic: slow liberation of $Ca(OH)_2$
  - Kiln Dust (cements)
  - Cement Clinker (may not cement)
- $CaCO_3$ (slow to dissolve)

MOBILITY & OXIDATION STATE

Courtesy of Rose, Hawkes, and Webb



MOBILITY & OXIDATION STATE



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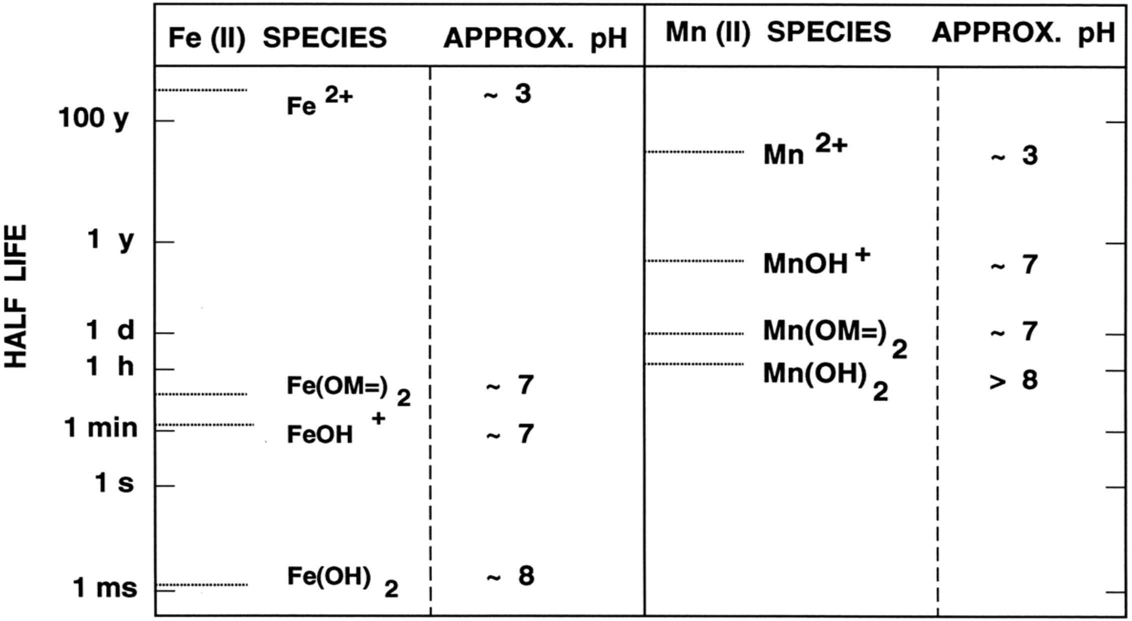
SCHOOL OF MINES
1874
COLORADO

Mn & Fe OXIDATION KINETICS

HALF-LIVES FOR OXYGENATION OF Fe(II) & Mn(II) SPECIES
(OM=) MEANS BOUND TO A METAL OXIDE SURFACE



From Wehrli & Stumm (1989)

SCHOOL OF MINES COLORADO 1874

HidroGeo Engenharia e Gestão de Projetos

Projeto Executivo para Tratamento Passivo do Efluente da Pilha de João Belo
Unidade Jacobina Mineração Comércio – BA   Yamana Gold

Best Professional paper in CBMinas, 2012. Belo Horizonte MG – Brasil.

HidroGeo
Engenharia e Gestão de Projetos

SCHOOL OF MINES 1874 COLORADO

ACID ROCK DRAINAGE (ARD) in mg/L

	Quartz Hill	Jacobina	Coal	Buckeye
pH	2.5	3.0	2.9	5.9
Al	60	20	36	21
Fe	750	1.8	180	580
Mn	80	1.2	50	20
Cu	55	0.12		0.03
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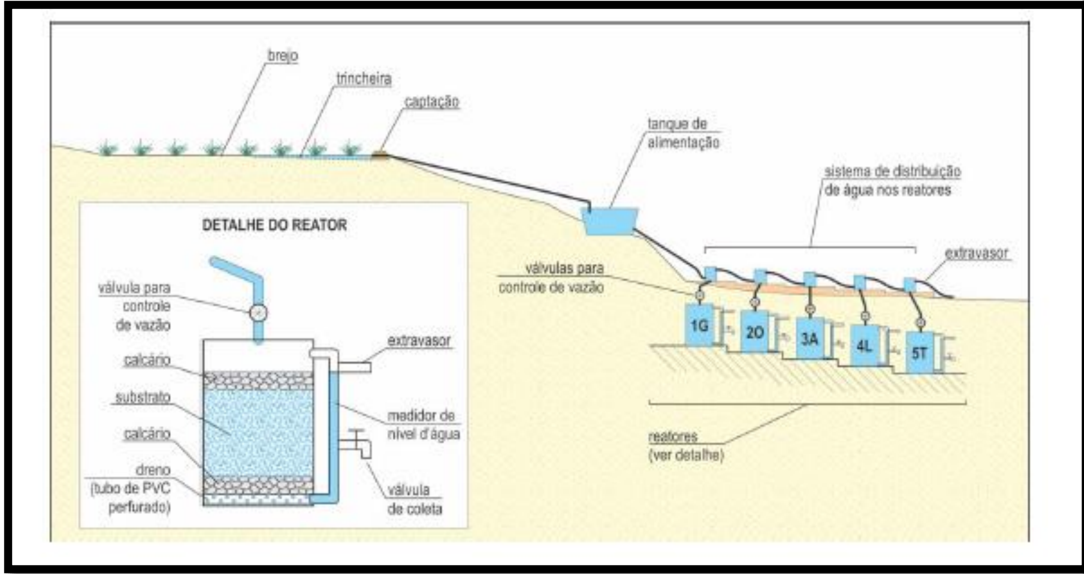
Cd	0.80	0.003		
Pb	0.14			0.02
As	1.5	0.008		0.01
SO4	4000	184	2050	750

Estudo em Escala Piloto:

Sistema de tratamento passivo em escala de bancada implantado na mina de Jacobina



(Fonte: Fregadolli, *et. al.*, 2012)

Materials Used in Pilot Reactors

	Reactors (amts. In weight percent)				
Substrate	**Gen**	**Fe1**	**Fe2**	**SB1**	**SB2**
Wood Dust	40	20	30	35	40
Limestone	30	30	25	30	30
Sugarcane Bagasse		10	10	15	20
Legume Vegetation	20		15	10	
Steel Dust		10	10		
Manure	10	10	10	10	10

Results (5 months)

			Reactors (Conc. In mg/L)				
Parameter	**Reg Limit**	**Intake**	**Gen**	**Fe1**	**Fe2**	**SB1**	**SB2**
Al	**0.10**	**20.7**	0.02	0.02	0.02	0.02	0.03
Fe	**0.30**	**1.44**	0.01	0.05	1.4	0.32	0.01
Mn	**0.10**	**1.95**	2.2	2.2	3.2	2.5	1.3
Cu	**0.009**	**0.15**	0.002	<0.001	0.001	0.001	<0.001
SO4	**250**	**209**	76	32	28	23	134
pH		**3.0**	7.5	7.1	6.9	7.0	7.4

Conclusions

All reactors met the treatment objectives of Al removal

Excellent production of alkalinity through sulfate reduction and limestone dissolution

Mn was not removed in fact it appeared to increase in all reactors

Zero valent iron (steel dust) was not effective

Final substrate would depend upon availability of materials

Passive As & Mn Removal in Neutral MIW

Tom Wildeman

Dept. of Chemistry & Geochemistry

Colorado School of Mines

USA

Flavio Vasconcelos

HidroGeo

Belo Horizonte, MG, Brasil

Outline

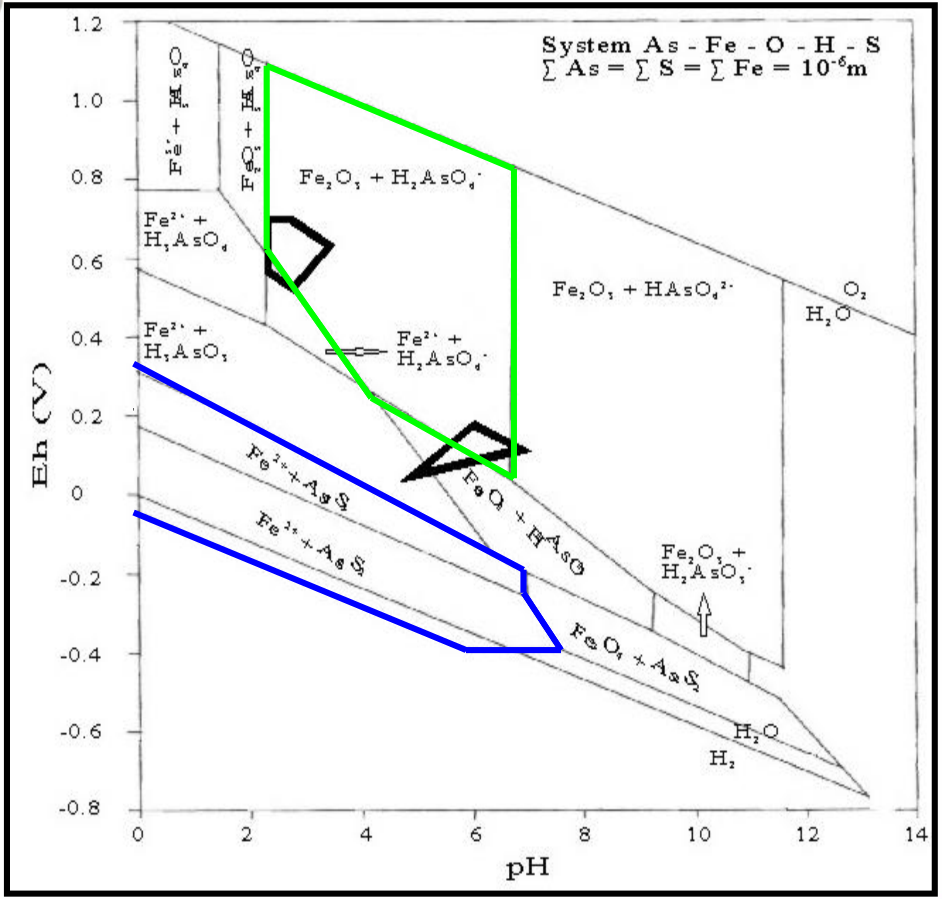
As & Mn Geochemistry

Experiment Descriptions

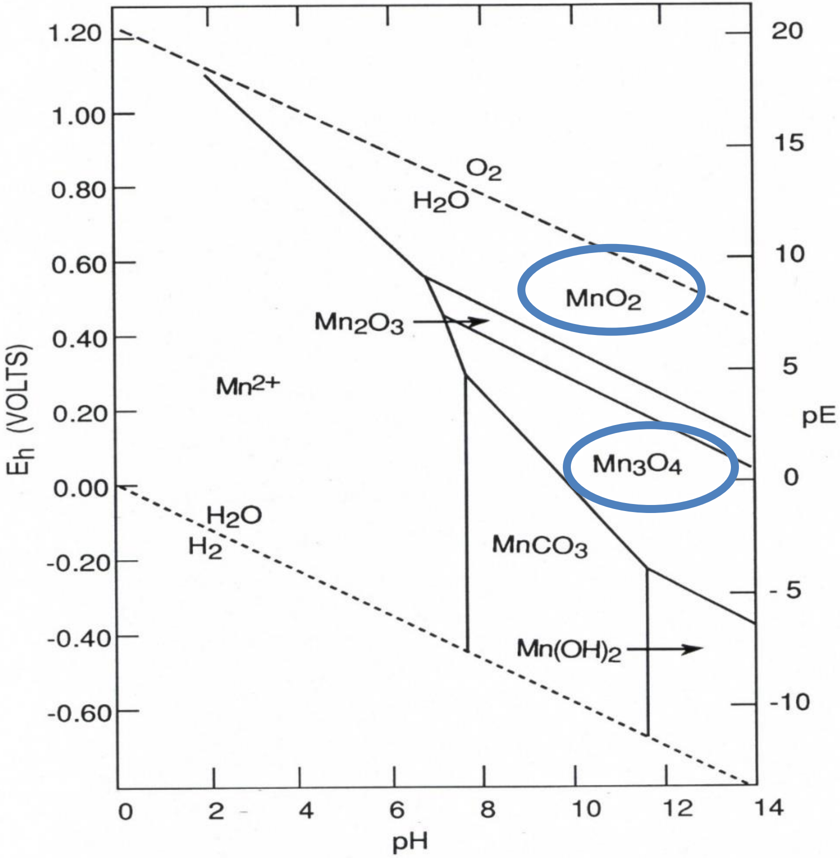
Results

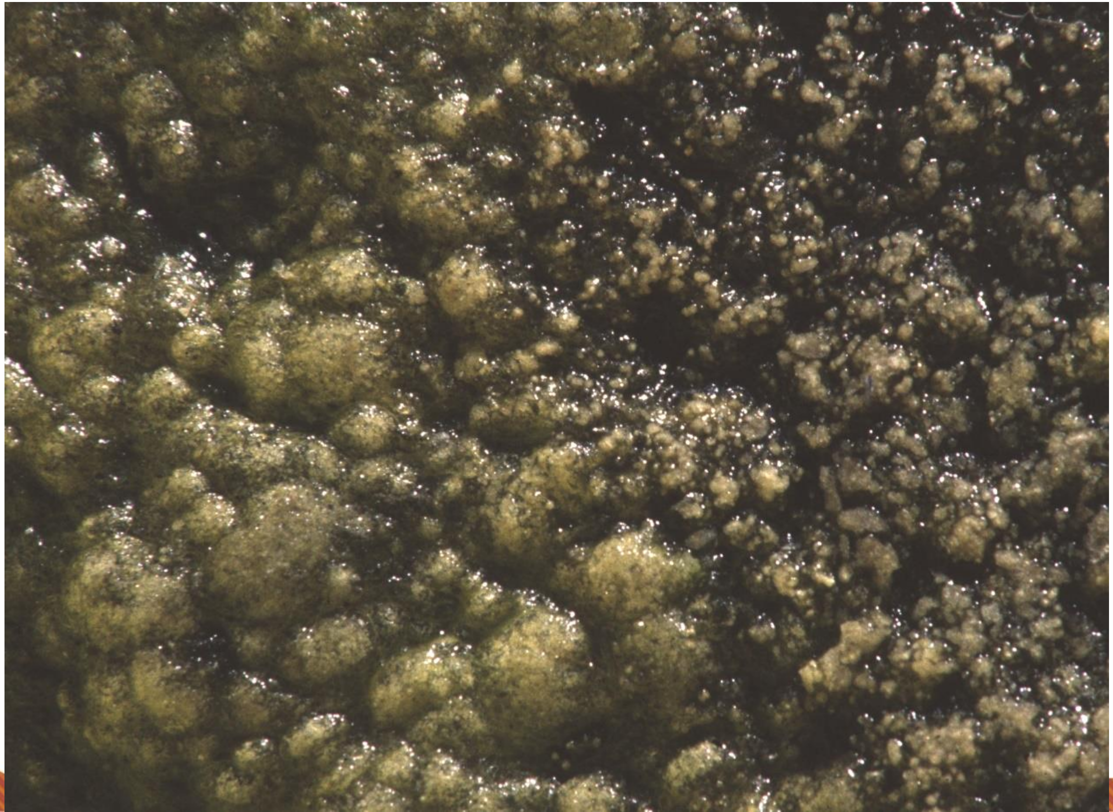
Conclusions

- **Eh vs. pH diagram:**
- **Fe, As and H_2O – system**:



- **Eh vs. pH diagram:**
- **Mn and H_2O – system:**





AEROBIC BENCH-SCALE TESTS

ALGAE CLOSE-UP

Water	Gold mine 1	Gold mine 2	Gold mine 3	Clear Creek	Reg. Limit
pH	6.8	6.3	7.1	6.9	
Al	0.03	0.03	0.06	0.05	0.10
As	2.1	0.2	0.03	BDL	0.01
Fe	0.01	0.05	0.003	BDL	0.30
Mn	0.14	0.13	5.0	0.003	0.10
SO4=	295	29	3400	78	250

Experiment 1

Clear Creek Water

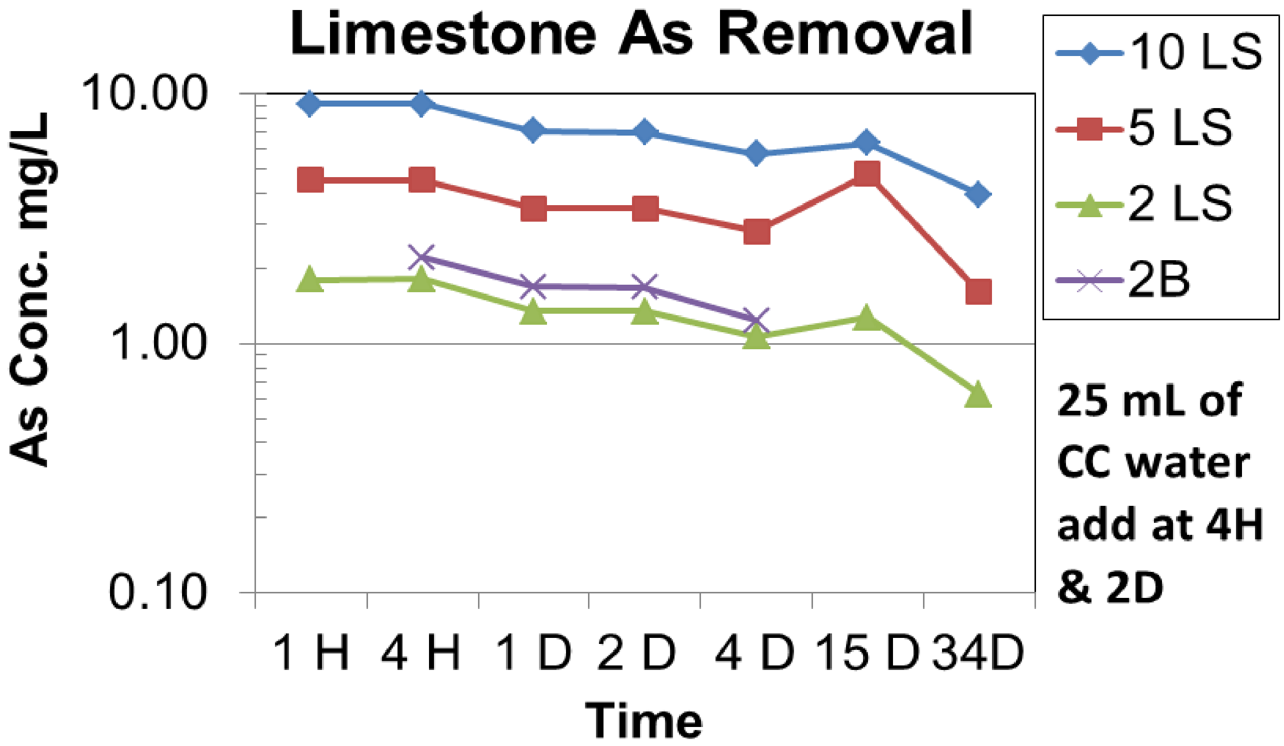
2, 5, & 10 mg/L As

Limestone

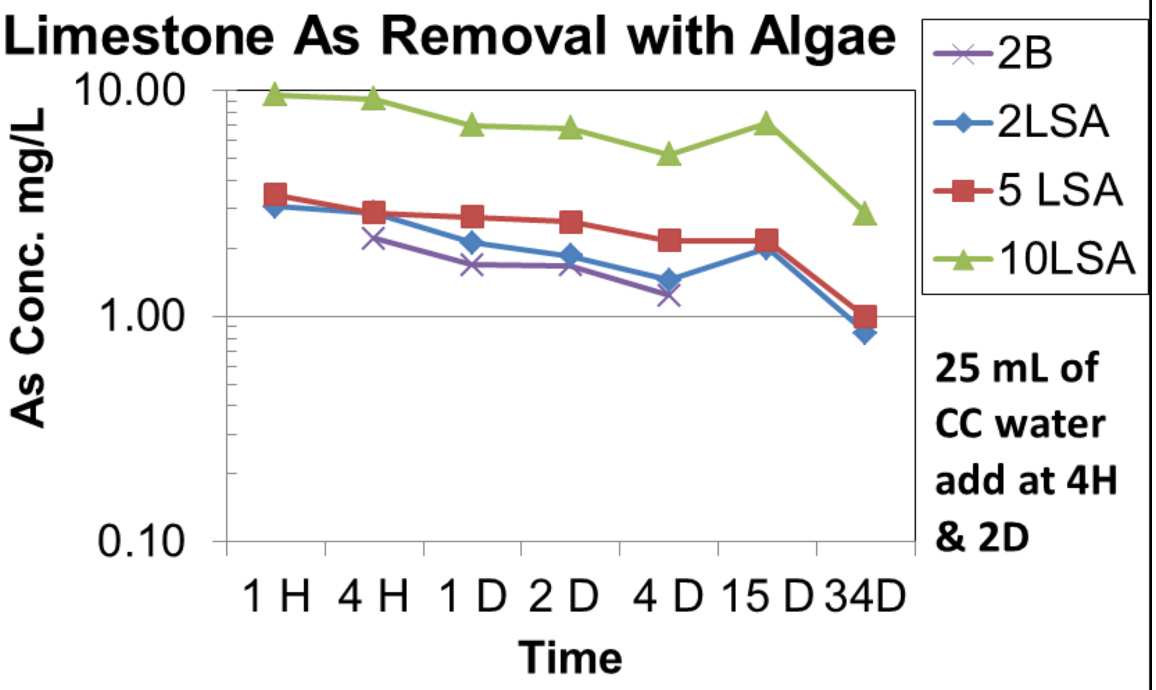
Limestone plus Algae

34 Days

Can limestone remove arsenic?



25 mL of CC water add at 4H & 2D



25 mL of CC water add at 4H & 2D

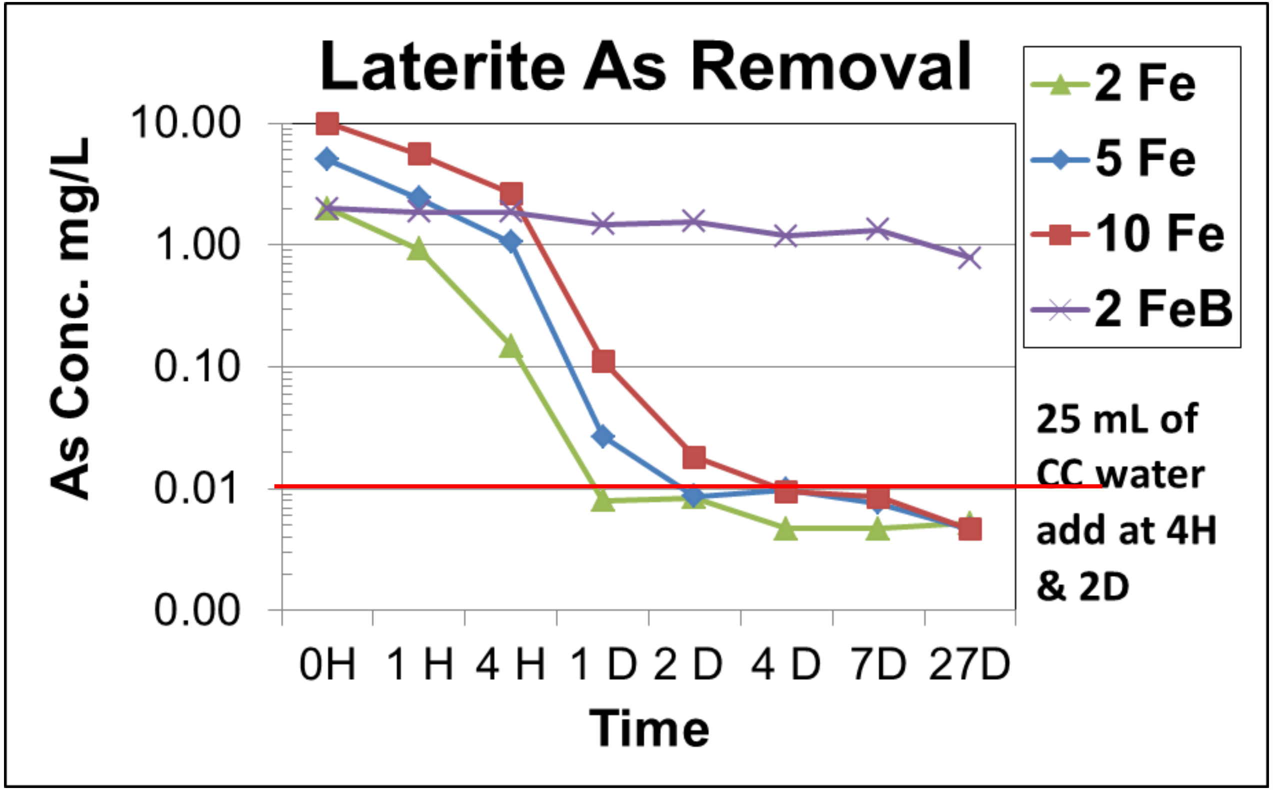
No arsenic removal with limestone nor with limestone & algae

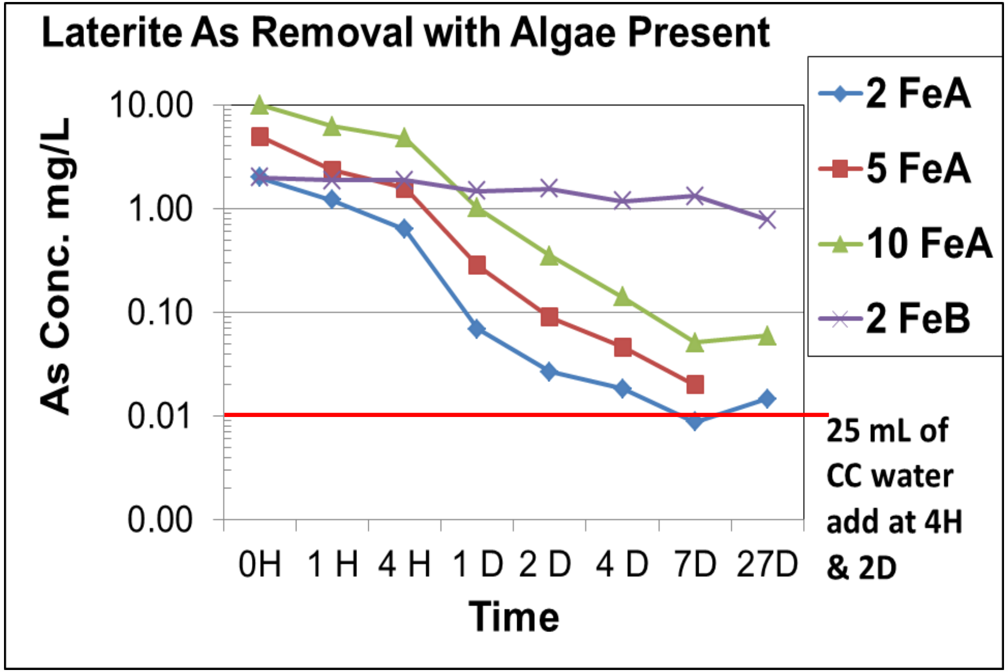
Experiment 2

- Clear Creek Water
- 2, 5, & 10 mg/L As
- Laterite from Minas Gerais
- Laterite plus Algae
- 27 Days

Is laterite removal of arsenic reasonable?


Fe 5
Fe 10


Laterite As Removal
As Conc. mg/L
10.00
1.00
0.10
0.01
0.00
0H
1 H
4 H
1 D
2 D
4 D
7D
27D
Time
2 Fe
5 Fe
10 Fe
2 FeB
25 mL of CC water add at 4H & 2D

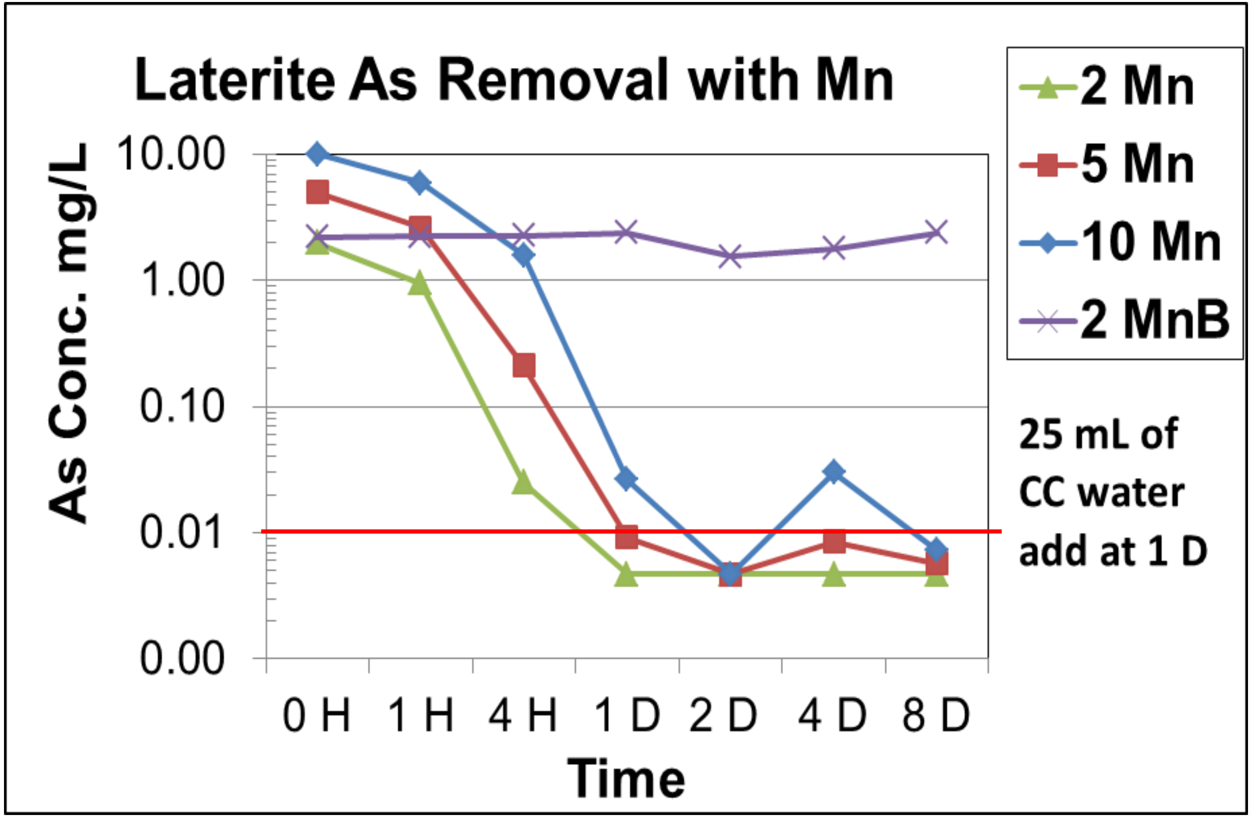

Laterite As Removal with Algae Present
As Conc. mg/L
10.00
1.00
0.10
0.01
0.00
0H
1 H
4 H
1 D
2 D
4 D
7D
27D
Time
2 FeA
5 FeA
10 FeA
2 FeB
25 mL of CC water add at 4H & 2D

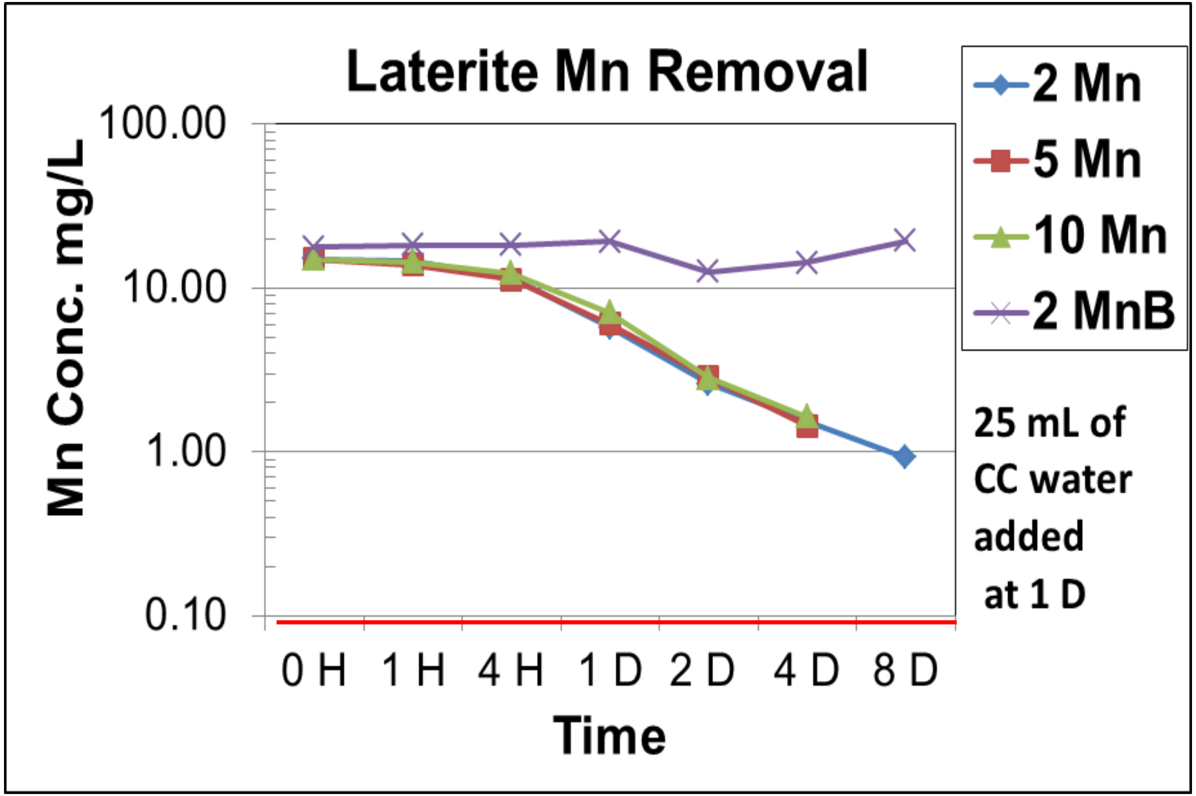
- Arsenic removal to below 0.010 mg/L in 2 days
- Algae impairs arsenic removal

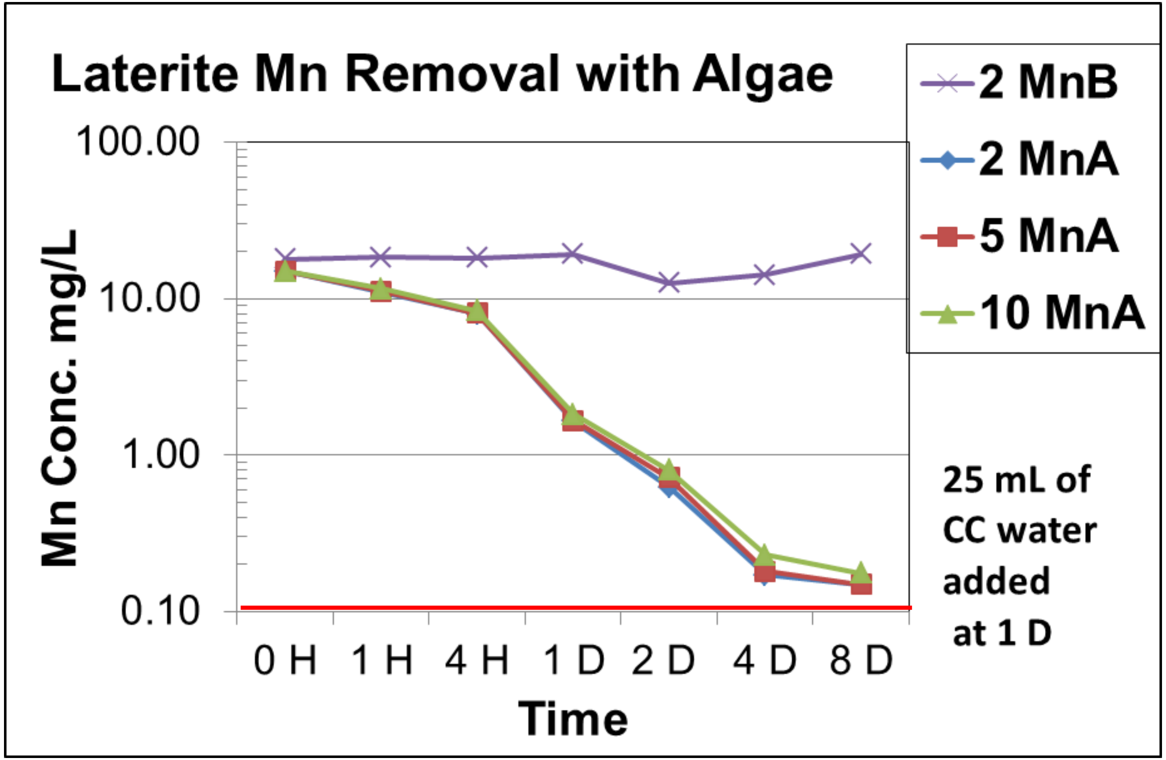
Experiment 3

- Clear Creek Water
- 2, 5, & 10 mg/L As
- Laterite
- Laterite plus Algae
- 15 mg/L Mn in all flasks
- 8 days

Does manganese interfere with arsenic removal?


Laterite As Removal with Mn
2 Mn
5 Mn
10 Mn
2 MnB
As Conc. mg/L
10.00
1.00
0.10
0.01
0.00
0 H
1 H
4 H
1 D
2 D
4 D
8 D
Time
25 mL of
CC water
add at 1 D

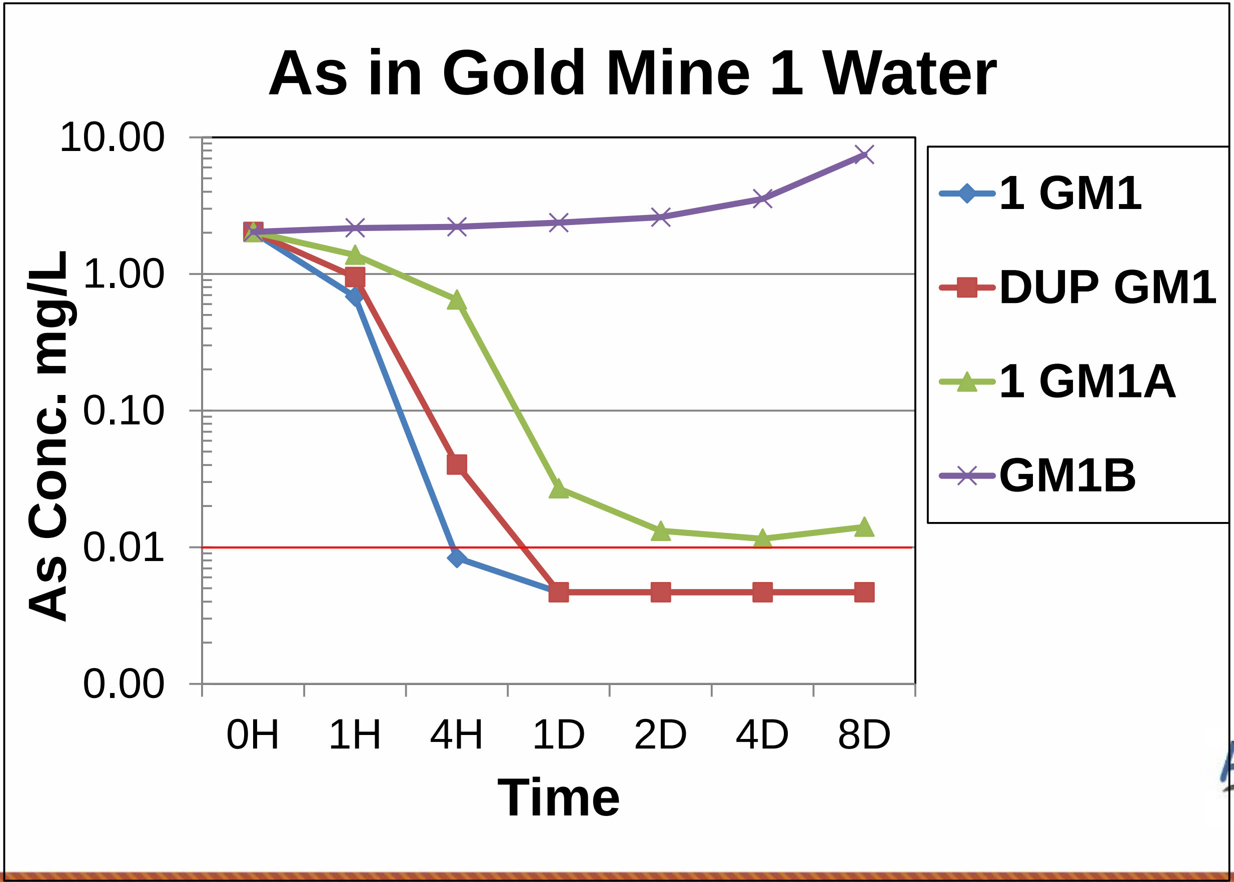

Laterite Mn Removal
Mn Conc. mg/L
100.00
10.00
1.00
0.10
0 H
1 H
4 H
1 D
2 D
4 D
8 D
Time
2 Mn
5 Mn
10 Mn
2 MnB
25 mL of CC water added at 1 D

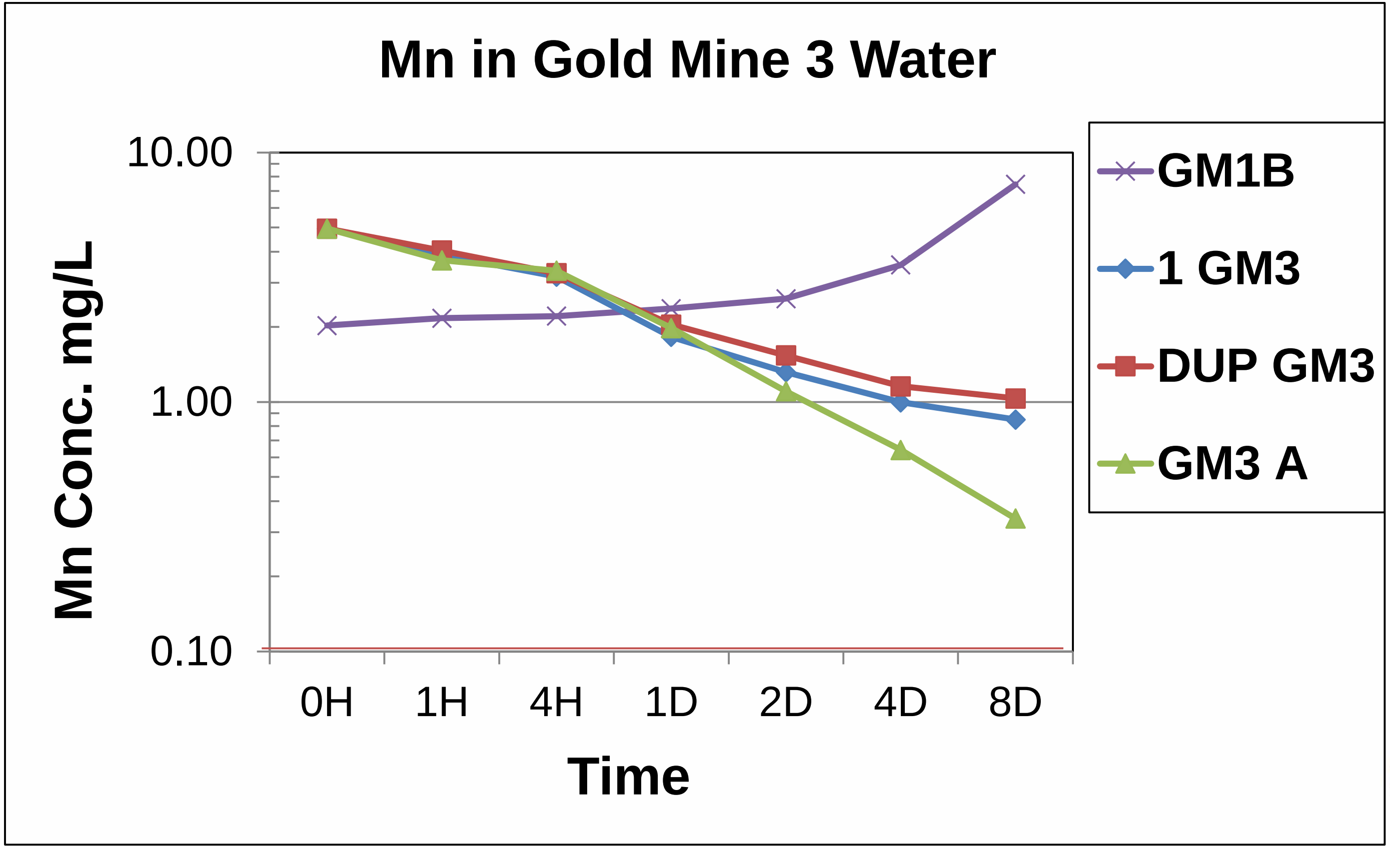

Laterite Mn Removal with Algae
2 MnB
2 MnA
5 MnA
10 MnA
100.00
10.00
1.00
0.10
Mn Conc. mg/L
0 H
1 H
4 H
1 D
2 D
4 D
8 D
Time
25 mL of
CC water
added
at 1 D

- With laterite, As and Mn removal act independently
- Laterite removes most of the manganese
- The removal of arsenic within 2 days is confirmed
- Algae retards As removal but promotes Mn removal

Experiment 4

- Gold Mine 1 Water (2 mg/L As)
- Gold Mine 3 Water (5 mg/L Mn, 0.03 mg/L As, 3400 mg/L $SO_4^{=}$)
- Laterite
- Laterite plus Algae
- 8 days


As in Gold Mine 1 Water
As Conc. mg/L
10.00
1.00
0.10
0.01
0.00
0H
1H
4H
1D
2D
4D
8D
Time
1 GM1
DUP GM1
1 GM1A
GM1B


Mn in Gold Mine 3 Water
10.00
1.00
0.10
Mn Conc. mg/L
0H
1H
4H
1D
2D
4D
8D
Time
GM1B
1 GM3
DUP GM3
GM3 A

Using real mine waters, arsenic and manganese removal is confirmed

Removal of manganese using laterite is slow (over 8 days)

Conclusions

- Arsenic removal by laterite is promising
- The usual method of Mn removal by limestone and algae is confirmed.
- Using laterite, removal of Mn independent of As removal occurs but it is slow.
- Using laterite, algae is a detriment to As removal.

MUITO OBRIGADO!