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AN ENVIRONMENTAL SERVICES FIRM

Abiotic Aluminum and Sulfate Removal in Bench Scale Biochemical Reactors

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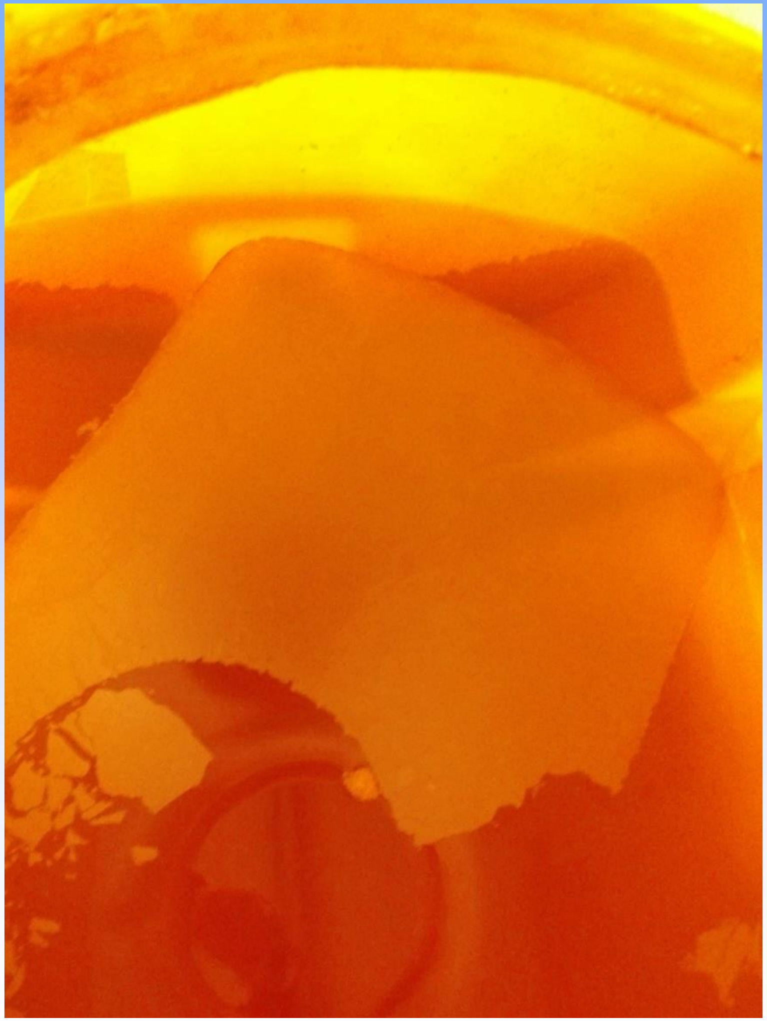
Acid Rock Drainage – Confidential Site



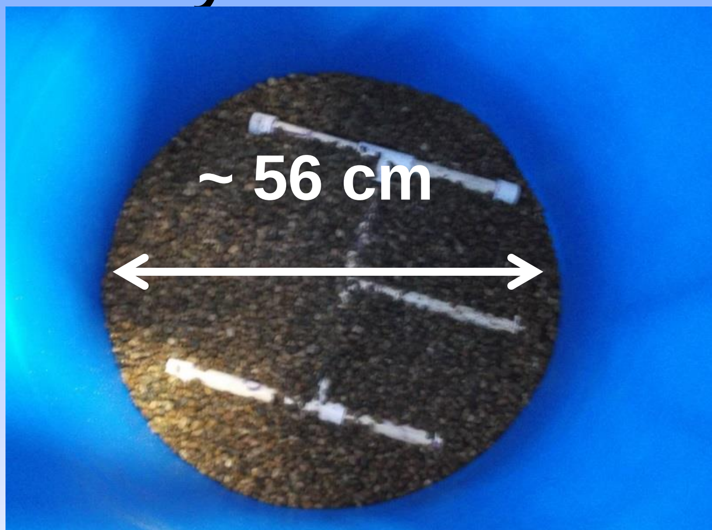
ARD Seep Chemistry

Flow is (thankfully) only 1 gpm [3.8 L/min]

Parameter	Raw MIW
pH	2.5
ORP (mv)	523
Conductivity ms	7.1
Sulfate (Lab 1) mg/L	9,480
Alkalinity mg/L	0
Aluminum mg/L	**932**
Calcium mg/L	310
Cadmium mg/L	0.47
Cobalt mg/L	7.3
Chromium mg/L	0.19
Copper mg/L	4.2
Iron mg/L	**348**
Potassium mg/L	0.87
Magnesium mg/L	213
Manganese mg/L	125
Nickel mg/L	4.95
Sulfate mg/L	6,245
Silicon mg/L	78.8
Zinc mg/L	24.4

Bench Scale BCRs

- Bottom drainage layer



- Three mixtures

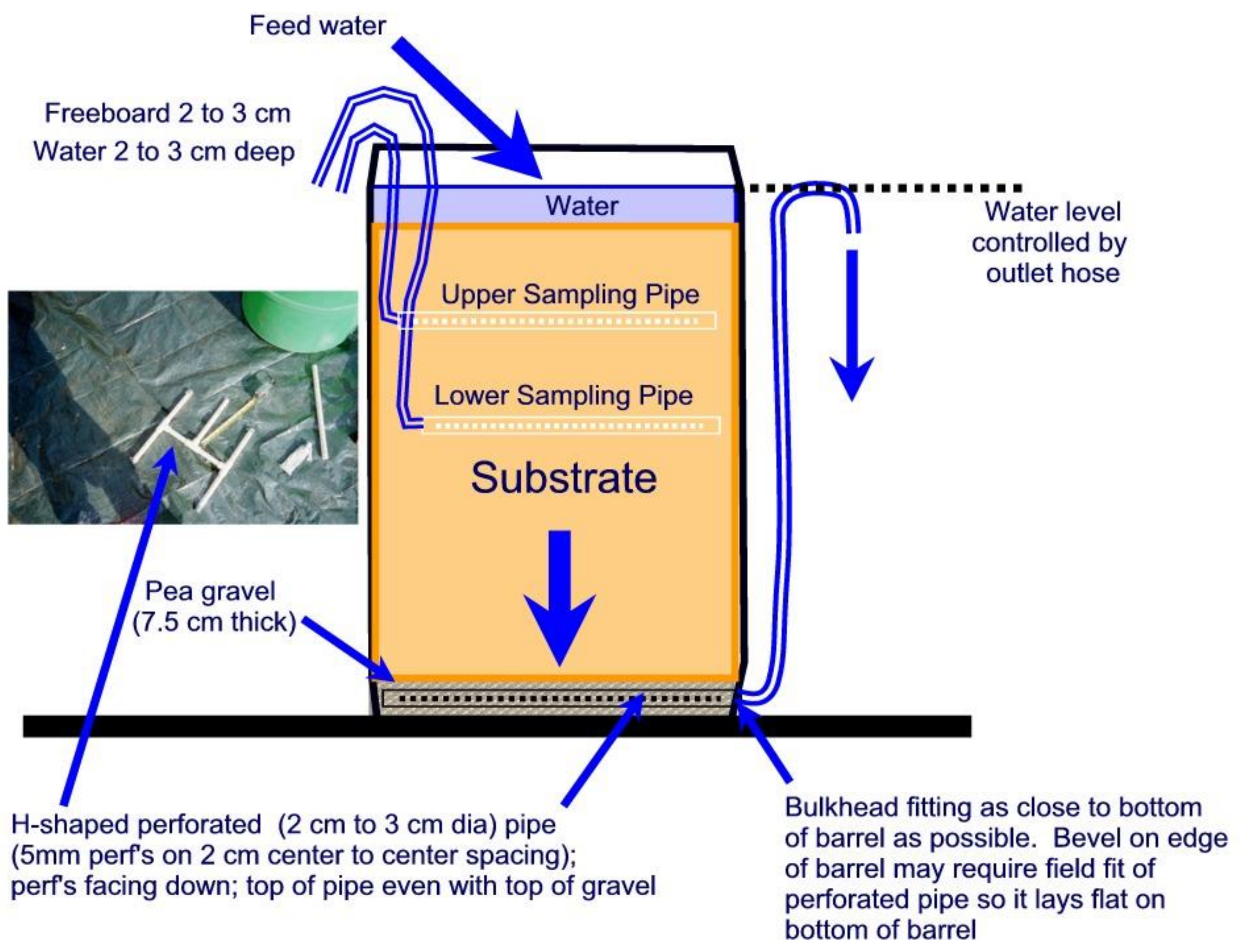
Test Mixtures & Flow

Material	Cell 1	Cell 2	Cell 3
Sawdust	0%	0%	10.0%
Wood Chips	64.5%	45%	49.5%
Limestone	25%	45%	30%
Wheat Straw	10%	9.5%	10%
Cow Manure	0.5%	0.5%	0.5%
Logic	*Low Limestone*	*High Limestone*	*Baseline*

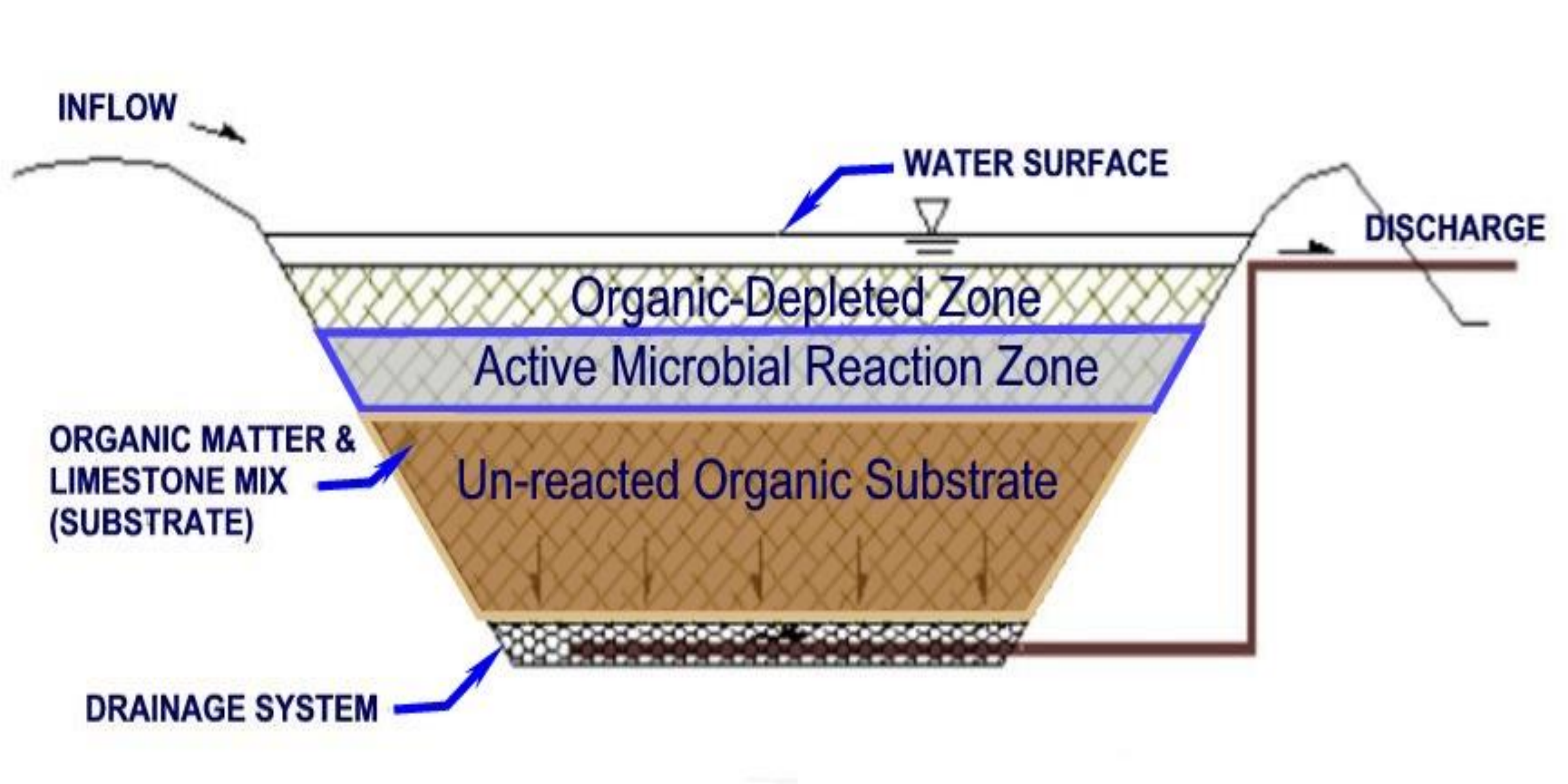
Bench Flow rate: 1.2 liters/day; HRT about 94 days

Bench Scale BCRs

Multiple Sampling Ports



Anaerobic Biochemical Reactors (BCRs)



PLANTS ARE NOT REQUIRED FOR A BCR

Anaerobic Biochemical Reactors (BCRs)

AKA

Vertical Flow Reactors
or

Sulfate Reducing
Bioreactors (SRBRs)

Aluminum and heavy metal removal, selenium removal, de-nitrification, pH adjustment, alkalinity & hardness addition

Biochemical Reactor Chemistry

$$SO_4^{-2} + 2\ CH_2O \rightarrow HS^- + 2HCO_3^- + H^+$$

(Sulfate reduction and neutralization by bacteria)

REDUCING/ ANAEROBIC CONDITIONS

$$Zn^{+2} + HS^- \rightarrow ZnS\ (s) + H^+$$

(Sulfide precipitation)

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

(Limestone dissolution)

$$Fe^{+3} + 3\ H_2O \rightarrow Fe(OH)_3\ (s) + 3\ H^+$$

(Hydroxide precipitation)

Aluminum Behavior

Al^{3+} + $3H_2O$ => $Al(OH)_3$ (Gibbsite) + $3H^+$

(problematic due to sludge buildup)

Conditions within BCRs are favorable for aluminum hydroxysulfate precipitation (examples):

$3Al^{3+} + K^+ + 6H_2O + 2SO_4^{2-} \Rightarrow KAl_3(OH)_6(SO_4)_2$ (Alunite) + $6H^+$

$6Ca^{2+} + 2Al^{3+} + 38H_2O + 3SO_4^{2-} \Rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{:}26H_2O$ (Ettringite) + $12H^+$

Thomas, R.C. 2002. *Passive Treatment of Low pH, Ferric Iron-Dominated Acid Rock Drainage*. Doctoral Thesis. University of Georgia.

Other Aluminum Possibilities

- Hydrobasaluminite $Al_4(SO_4)(OH)10 \bullet 12\text{-}36(H_2O)$
- **Basaluminite $Al_4(SO_4)(OH)10 \bullet 5(H_2O)$**
- Aluminite $Al_2(SO_4)(OH)_4 \bullet 7(H_2O)$
- Kaolinite $Al_2Si_2O_5(OH)_4$
- Silvialite $(Ca,Na)_4Al_6Si_6O_{24}(SO_4,CO_3)$

Ratio of aluminum to sulfate varies from 6 Al to 1 SO_4 (Silvialite) to 0.67 Al to 1 SO_4 (Ettringite)

Loading and Removal Calcs

Parameter	Raw MIW	BCR Effluent	In Moles/day	Out Moles/day	Gain/ (-Loss)	Limestone %
pH	2.5	6.5				
ORP	523	63				
Conductivity ms	7.1	6.07				
Sulfate (A) mg/L	9,480	2,770	0.12???	0.03	0.084??	
Alkalinity mg/L	0	1,060				
Aluminum mg/L	932	0.26	0.04	0.00001	0.042	
Calcium mg/L	**310**	**690**	**0.01**	**0.02**	**-0.011**	**78%**
Cadmium mg/L	0.47	0.0004	0.00001	0.00000	0.00001	
Cobalt mg/L	7.3	2.0	0.00015	0.00004	0.00011	
Chromium mg/L	0.19	0.0003	0.000004	0.000000	0.00000	
Copper mg/L	4.2	0.0080	0.0001	0.0000	0.00008	
Iron mg/L	348	1.3	0.01	0.00	0.0074	
Potassium mg/L	0.87	1075	0.00	0.03	-0.033	
Magnesium mg/L	**213**	**312**	**0.01**	**0.02**	**-0.005**	**22%**
Manganese mg/L	125	113	0.00	0.00	0.00025	
Nickel mg/L	4.95	0.60	0.00	0.00	0.00009	
Sulfate (B) mg/L	**6,245**	**2,725**	0.08	0.03	0.044	
Silicon mg/L	78.8	10.7	0.00	0.00	0.00290	
Zinc mg/L	24.4	0.25	0.00	0.00	0.00044	

Estimating Substrate Longevity

- Limestone
  - $CaCO_3$ and
  - $MgCO_3$
- Available organic matter (carbon)
  - Wood Chips
  - Sawdust
  - Straw
  - Manure

Sulfate reduction problem

- Sulfate reduction is used for estimating carbon longevity: 2 moles “available” carbon needed to reduce 1 mole of sulfate
- Aluminum precipitation in hydroxysulfate phase will sequester sulfate ABIOTICALLY
- Introduced bias suggests too much sulfate reduction and reduced carbon longevity – a correction factor is needed.

How much sulfate is removed Abiotically?

- Calcium is typically used for estimating limestone longevity

$$(Ca_{in} - Ca_{out} = Ca_{gain})$$

- Limestone Longevity (f) Ca_{gain}
- Aluminum precipitation in hydroxysulfate phase could sequester calcium
- Introduced bias suggests falsely extended limestone longevity

Could we be making Ettringite?

$$6Ca^{2+} + 2Al^{3+} + 38H_2O + 3SO_4^{2-}$$

=>

$$Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O + 12H^+$$

Loading and Removal Calcs

So let's assume that the Al concentration is about 878 mg/L and the flow is 1.2 L/day. Assume it's all removed.

That's 0.039 moles of Al/day.

Now, if we look at the calcium and say the effluent is 690 mg/L and the influent is 310 mg/L, that's a gain of 380 mg/L or about ***0.0114 moles Ca/day.***

Loading and Removal Calcs (cont.)

*So carrying this further, the 0.039 moles of Al/day would need 0.117 (or 3 * 0.039)moles of calcium/day to solely create Ettringite.*

The calcium would stay sequestered in the substrate… But now the apparent calcium consumption would be 0.117 + 0.0114 = 0.128 moles/day.

This is quite a bit more than the 0.0114 observed – about ***11 times more****!*

Partial Conclusion

We are not likely to be making mostly Ettringite purely on stoichiometry (we might be making some other mineral that involves calcium sequestration);

Basaluminite (which doesn't involve calcium) might be a better bet for most of the hydroxysulfate precipitates

Loading and Removal Calcs (cont.)

If we abiotically remove aluminum by forming aluminum hydroxy sulfate (Basaluminite), that means we'll be removing 1 mole of sulfate for every 4 moles of aluminum via this mechanism.

Call this the limestone-aluminum "correction" factor for sulfate removal/organic matter consumption rate.

Adjusted Organic Longevity

Material	Cell 1	Cell 2	Cell 3
Organic Total	75%	55%	70%
Kg OM avail	4.9	4.6	5.0
TOC losses	*0.46 g/d*	*0.50 g/d*	*0.37 g/d*
Aluminum-Adjusted OM Life	*15 yrs?*	*13.8 yrs?*	*19.5 yrs?*
Unadjusted OM Life	*~7yrs?*	*~6 yrs?*	*~10 yrs?*
Cell Design Logic	*Low Limestone*	*High Limestone*	*Baseline*

Loading and Removal Calcs (cont.)

For limestone longevity, we've typically assumed that for every mole of calcium liberated (in the effluent), that was a mole of calcium carbonate consumed in the limestone.

It might be better to use magnesium gain (more conservative) to estimate limestone dissolution

Limestone Longevity

Material	Cell 1	Cell 2	Cell 3
Limestone	25%	45%	30%
Kg Calcite	8.3	19.3	11.0
Kg Dolomite	2.3	5.4	3.1
Calcite (Ca) Based	*42 yrs*	*85 yrs*	*49 yrs*
Dolomite (Mg) Based	*22 yrs*	*56 yrs*	*38 yrs*
Cell Design Logic	*Low Limestone*	*High Limestone*	*Baseline*

CONCLUSIONS

- Aluminum precipitation in a hydroxysulfate phase will sequester sulfate abiotically, but the minerals that form are unknown
- This reaction can sequester calcium
- Developing an aluminum correction factor for OM longevity is tricky
- Using *magnesium* is better than using calcium for estimating limestone dissolution rates in high aluminum situations

Thank You

IF YOU'RE NOT PART OF THE *SOLUTION*, YOU'RE

PART OF THE *PRECIPITATE*

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