



Evolution of Sulfate-reducing Bioreactors

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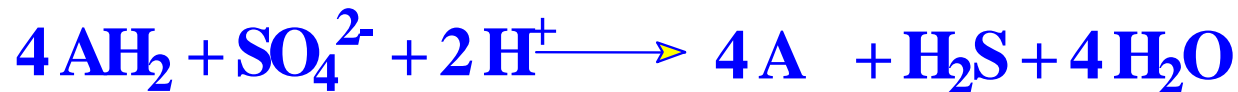
- Introduction
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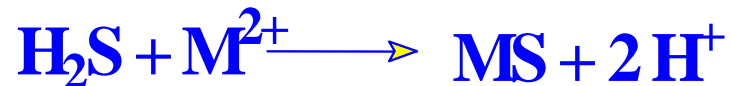
Introduction

Treatment Process Sulfate-reducing Bioreactors

Sulfate-reduction:



Sulfide Precipitation of Metals:





Introduction

Solubility Products for Metal Complexes

<u>Complex</u>	<u>K_{sp}</u>		<u>Complex</u>	<u>K_{sp}</u>
HgS	6.38×10^{-53}		Zn(OH) ₂	7.68×10^{-17}
Fe(OH) ₃	2.67×10^{-39}		Ni(OH) ₂	5.54×10^{-16}
CuS	1.28×10^{-36}		Cd(OH)₂	5.33×10^{-15}
CdS	1.4×10^{-29}		MnS	4.55×10^{-14}
PbS	8.81×10^{-29}		Mn(OH) ₂	2.04×10^{-13}
ZnS	2.91×10^{-25}		PbCO₃	1.48×10^{-13}
NiS	1.08×10^{-21}		CdCO₃	6.20×10^{-12}
Pb(OH)₂	1.4×10^{-20}		FeCO ₃	3.13×10^{-11}
FeS	1.57×10^{-19}		MnCO ₃	2.23×10^{-11}
Fe(OH) ₂	4.79×10^{-17}		NiCO ₃	1.45×10^{-7}

Types of Bioreactors

Passive Bioreactors:

- The carbon or energy source is part of the substrate.
- Once the degradable carbon sources are depleted, treatment efficiency falls off.
- Metals are precipitated within the matrix.
- Plugging and short circuiting leads to decreased treatment efficiency.



Types of Bioreactors

IWT Semi-Passive Bioreactors:

- The carbon source is added to the influent water
- The majority of the metals are precipitated outside of the bioreactor.
- Flushing built into the matrix.
- All three contribute to a longer lasting system

Original manure substrate at Leviathan Mine

- Down-flow reactor approximately 3ft deep.
- Ineffective at treating AMD after 1 year.
- The source of manure substrate for the column experiments that follow.





Original manure substrate at Leviathan Mine

	Six Weeks of Treatment		One Year of Treatment	
	7-27-93		7-1-94	
	Influent	Effluent	Influent	Effluent
pH (S.U.)	4.78	6.97	4.7	6.45
Temperature (C)	9.9	15.6	8.4	13.1
Alkalinity	-	1458.00	-	269
Al	41.0	<0.02	48	0.24
As	0.41	0.023	0.28	0.015
Fe	310	2.8	380	260
Ni	1.8	0.01	2.1	0.01
Sulfate	1690	1190	2070	1910

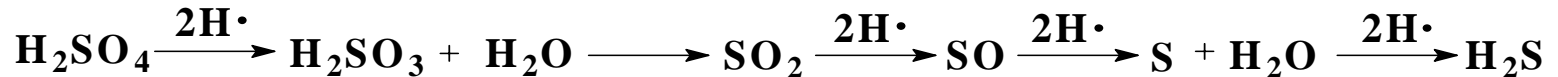
(mg/L unless specified differently)

Organic Substrates for Sulfate Reducing Bacteria

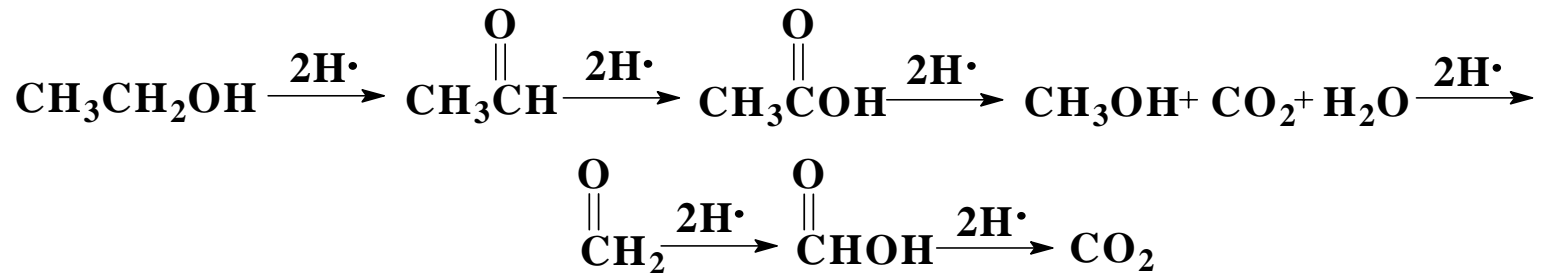
- Formate
- **Acetate**
- **Lactate**
- Pyruvate
- Malate
- Fumarate
- Succinate
- Alkanes
- Various sugars
- Glycerol
- **Methanol**
- **Ethanol**
- Propanol
- Butanol
- **Ethylene glycol**
- Propane diol
- Benzoate
- Phenols (many types)
- Others

Electron Accounting and Reducing Equivalents

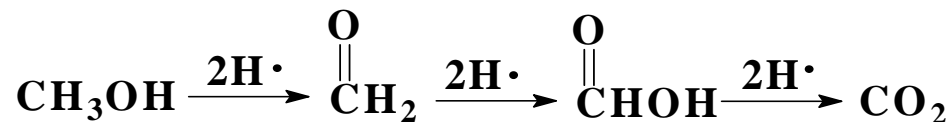
1. The reduction of sulfuric acid to sulfate requires 8 electrons.



2. The oxidation of ethanol to carbon dioxide involves 12 electrons.



3. The oxidation of methanol to carbon dioxide involves 6 electrons.



Electron Accounting and Reducing Equivalents

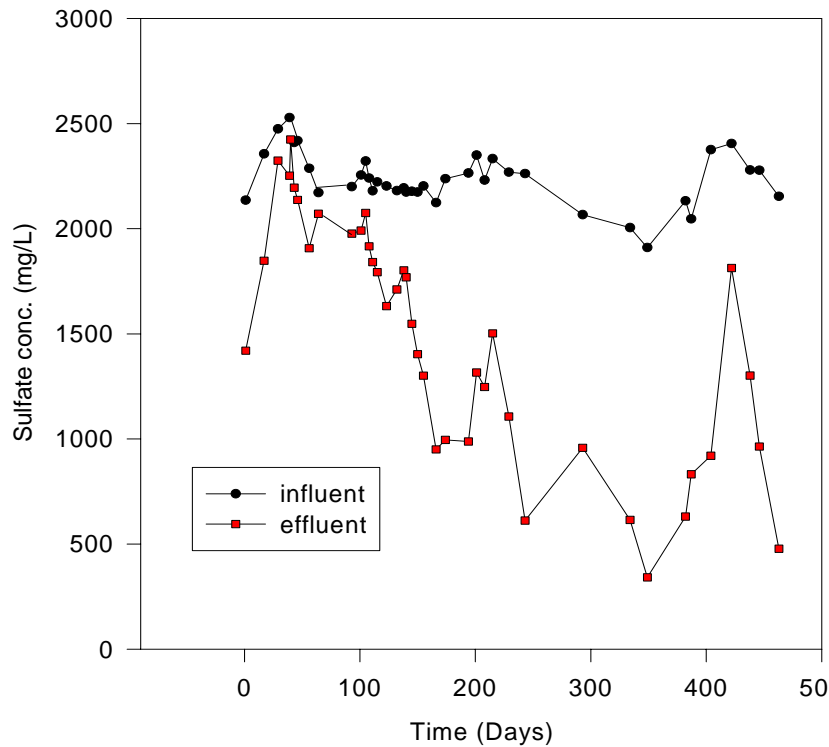
- One Mole of H_2S eliminates one mole of Fe^{2+}
 - If trying to remove 300 mg/L of Fe^{2+} (0.0054 M)
- ETHANOL:
- Ethanol can contribute 12 electrons per mole
 - Sulfate reduction requires 8 electrons per mole
 - To remove 0.0054 M Fe^{2+} , need to reduce 0.0054 M sulfate or 518 mg/L
 - One mole of ethanol reduces 1.5 moles sulfate
 - so 0.0054 M sulfate / 1.5 moles sulfate removed per ethanol = 0.0036 M ethanol needed
 - 0.0036 M ethanol = x (1 mole methanol) / 46.07 g/M
 - 166 mg/L ethanol required to remove 300 mg/L Fe^{2+}

pH Effect

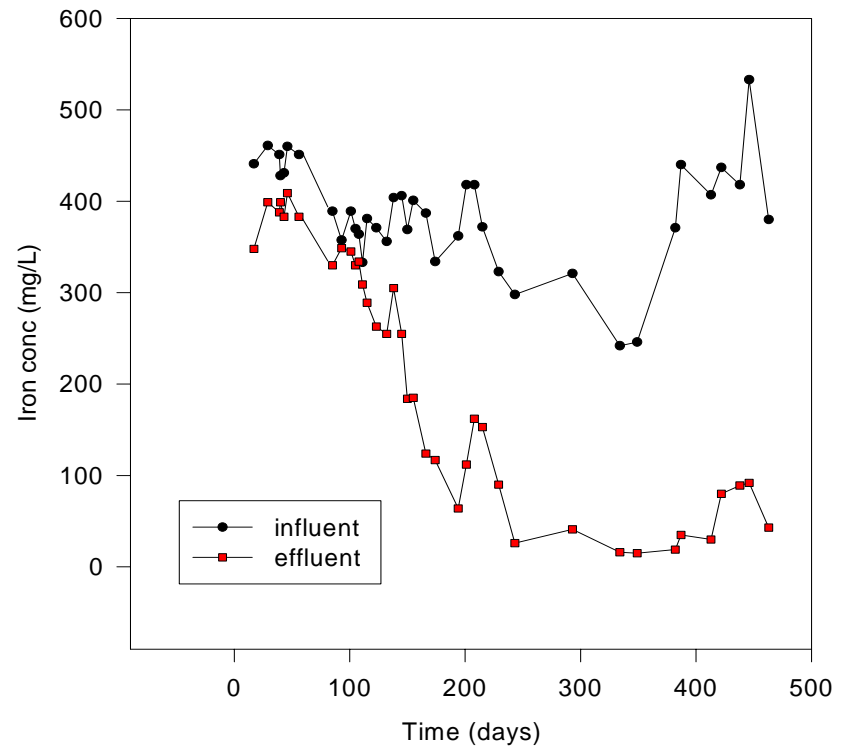
- The critical pH is the threshold of precipitation. Precipitation of metal sulfides only occurs above the critical pH at specified metal and sulfide concentration.
- The critical pH goes down when the sulfide concentration increases at a fixed total Fe concentration.
- At a higher pH and a fixed sulfide concentration, less total Fe exists in the solution and more Fe precipitates.
- The solubility of most of the divalent metal sulfides are at least 10 times lower than iron sulfide at the iron sulfide critical pH.

Results on the improvement of the manure bioreactor

Sulfate concentrations vs time for Leviathan underdrain site 4-3-97 to 7-10-98.



Iron concentrations vs time for Leviathan underdrain site 4-3-97 to 7-10-98.



1998 Aspen Seep Bioreactor

- Two Cell bioreactor
- Matrix consisted of wood chips in one cell and inert rock in the other
- Utilized a mixture of alcohols as the carbon source
- Some base needed to be added due to the low pH of Aspen Seep (pH 3.2)
- Designed to allow precipitates to be flushed from the cells

1998 Aspen Seep Bioreactor



The first pond (reactor) consisted mainly of wood chips.

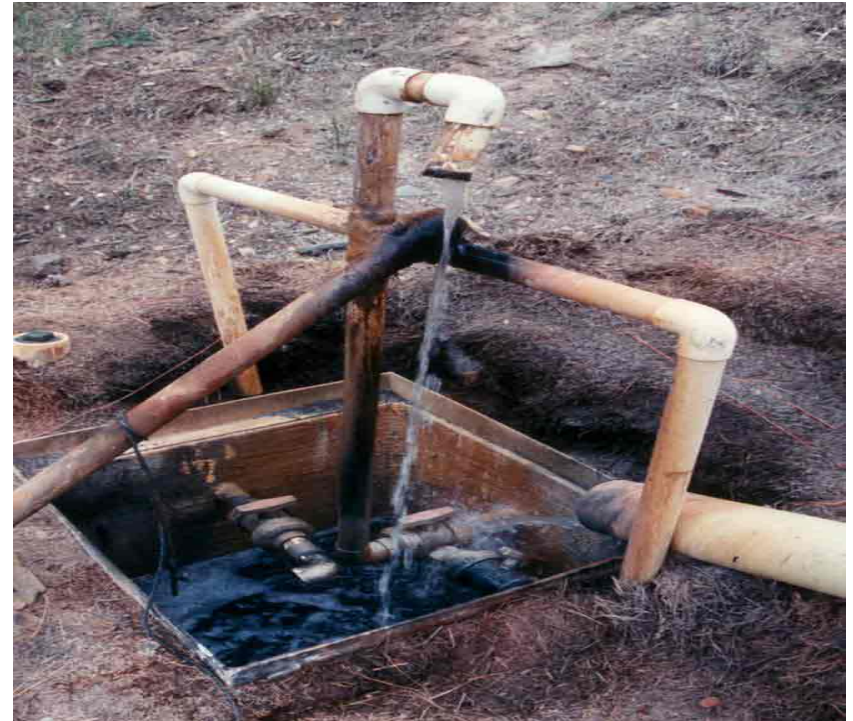


The second reactor consisted mainly of inert river rock.

1998 Aspen Seep Bioreactor



Flow was controlled into the reactor with a v-notch weiring device.



During operation flow was controlled out of the reactors with standpipes. Flushing was accomplished with valves.



1998 Aspen Seep Bioreactor Results






	Nickel (mg/L)	Copper (mg/L)	Zinc (mg/L)	Iron (mg/L)
Influent	0.14	0.28	1.75	83
Effluent	0.02	n.d.	n.d.	34
Effluent (settled)	0.02	n.d.	n.d.	0.7



1998 Aspen Seep Bioreactor Results

Problems Encountered

Solution

- | | | |
|---|--|--|
| 1. Depletion of carbon source |  | Addition of ethanol, methanol, and ethylene glycol |
| 2. Plugging of manure substrate |  | Rock substrate w/ large pore space |
| 3. pH too low for iron sulfide precipitation |  | Addition of caustic |
| 4. Build-up of iron sulfide precipitate |  | Flushing of pond and subsequent settling. Addition of settling tanks and Filtration bags |
| 5. Surface plugging due to iron oxide precipitation |  | Installation of a flushing zone At the front of pond 1. |



1998 Aspen Seep Bioreactor Results

Problems Encountered

- 6. Freezing of caustic
- 7. Plugging of base delivery valves



Solution

- Mix at appropriate concentrations
- Addition of filter and peristaltic pump

1998 Aspen Seep Bioreactor Results



The first pond.
Preferred flows and
oxidation.



The second pond.
Manure issues and
precipitation.



2003 Aspen Seep Bioreactor

- Improved flushing capability
- Improved flow distribution
- Improved matrix
- Addition of a pretreatment pond for solids removal
- Improved sludge capture

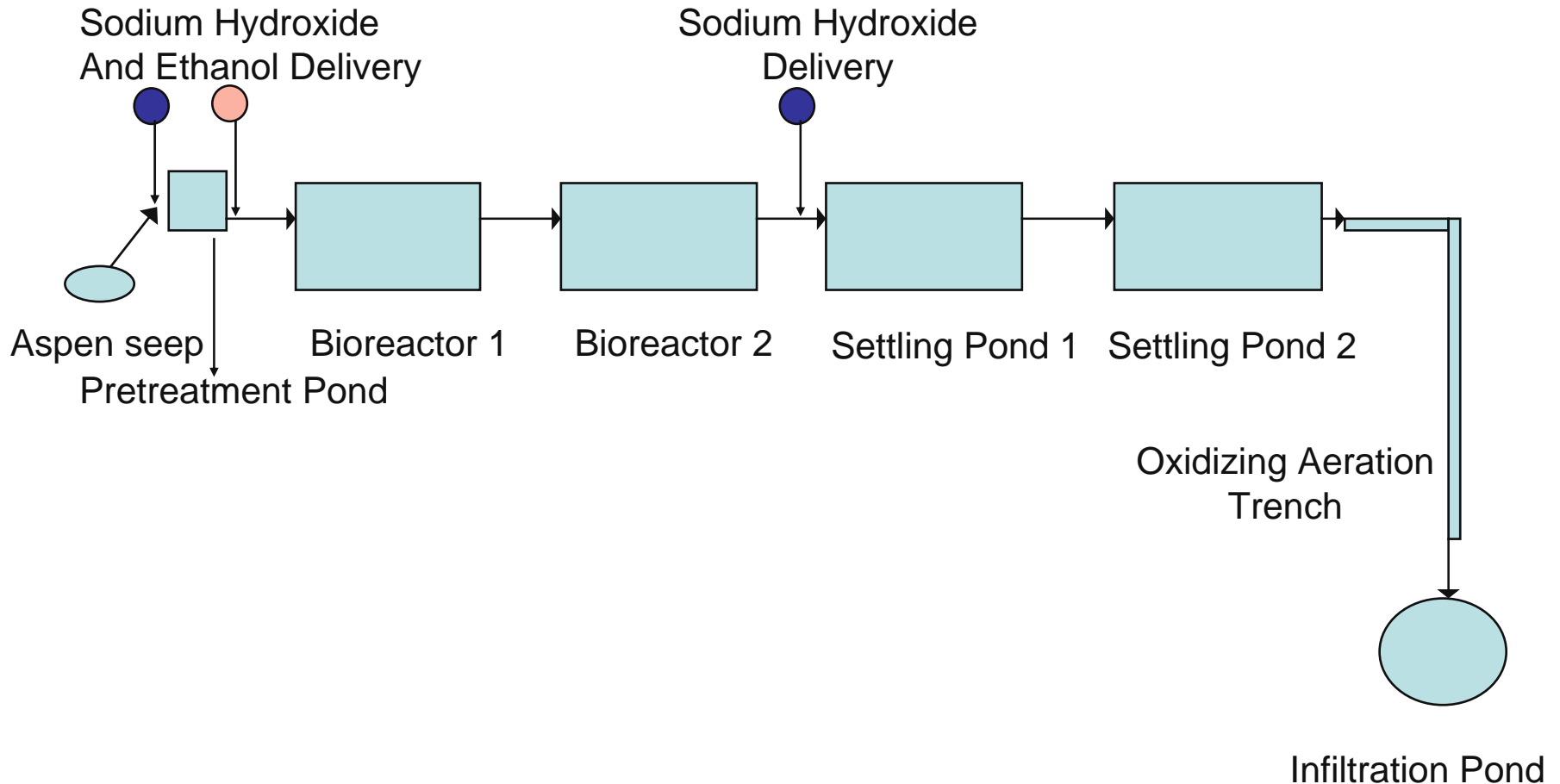
2003 Aspen Seep Bioreactor



Improved flushing capability

Improved matrix

2003 Aspen Seep Bioreactor schematic





2003 Aspen Seep Bioreactor Results

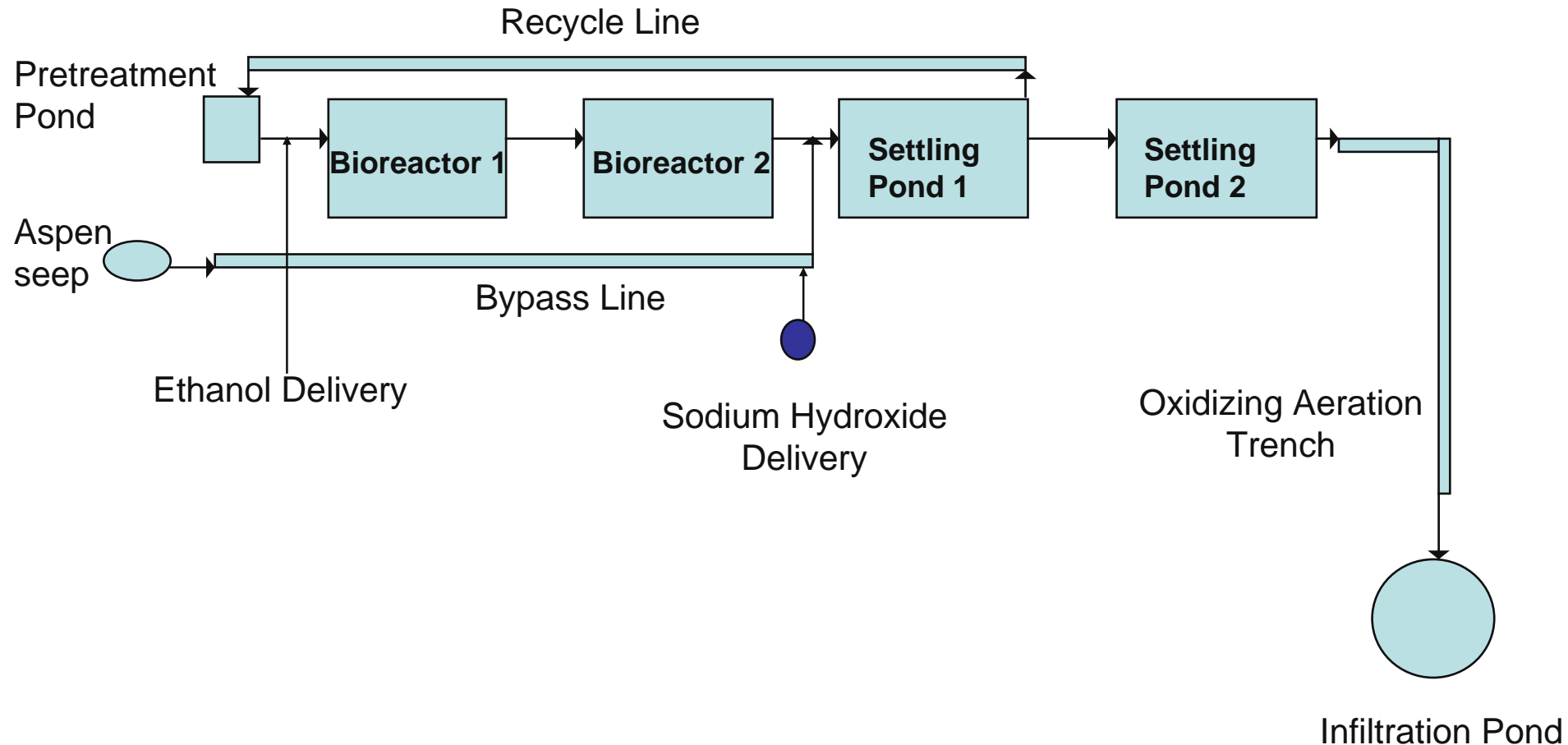
Constituent	Aspen Seep	Bioreactor 1 effluent	Bioreactor 2 effluent	Discharge	Discharge objectives
pH	3.17	4.70	4.77	7.19	6-9
SO ₄	1502	1307	1269	1222	NA
Al	35	21	18	<0.1	4.0
Fe	107	69	65	1.9	2.0
Ni	0.40	0.26	0.21	0.06	.84
Cu	0.55	0.01	<0.01	<0.01	.026
Zn	0.74	0.08	0.04	0.02	.21



2003 Aspen Seep Bioreactor with Recycle Mode

- Sludge is precipitated outside of the bioreactor
 - a. Eliminates matrix plugging and short circuiting
 - b. Eliminates the need to replace matrix
- Higher pH within bioreactor results in more favorable conditions for sulfate reducing bacteria
 - a. pH is near neutral (reduces sulfide toxicity)
 - b. More activity per unit area

Recycle Mode schematic





Evolution

2003 Aspen Seep Bioreactor with Recycle Mode

Constituent	Aspen Seep	Bioreactor 1 effluent	Bioreactor 2 effluent	Discharge	Discharge objectives
pH	2.93	6.79	6.86	7.66	6-9
SO ₄	1530	1090	1080	1170	NA
Al	28	<0.5	<0.5	<0.5	4.0
Fe	99	0.16	0.13	0.04	2.0
Ni	0.50	0.15	0.05	0.1	0.84
Cu	0.62	0.02	0.01	0.01	0.026
Zn	0.73	0.02	0.02	0.06	0.21

2003 Aspen Seep Bioreactor with Recycle Mode



Inflow settlement pond 1.
High metals sulfide
concentration.



Inflow bioreactor 1.
Low metals, high sulfates.



Conclusions: Ideal Conditions and Limitations

- Flows treated dependant upon space availability
- Highly variable flows can affect O/M costs
- Low to moderate acidity, Fe < 800 mg/L
- Must have sulfate sufficient to remove metals
- Cold conditions increase acclimation time and reduce efficiency

Equity Silver Mine



- Four treatment reactors were constructed from 18" pipe.
- Columns were 15-20 ft in length (volume approximately 26 ft³ to 35 ft³)
- Reactors were fitted with standpipes and filled with manure ~20% and wood chips ~80%.
- Overall zinc was decreased by 97% to an average level of 0.34 mg/L for the 2001 season.
- Very cold conditions short summers.

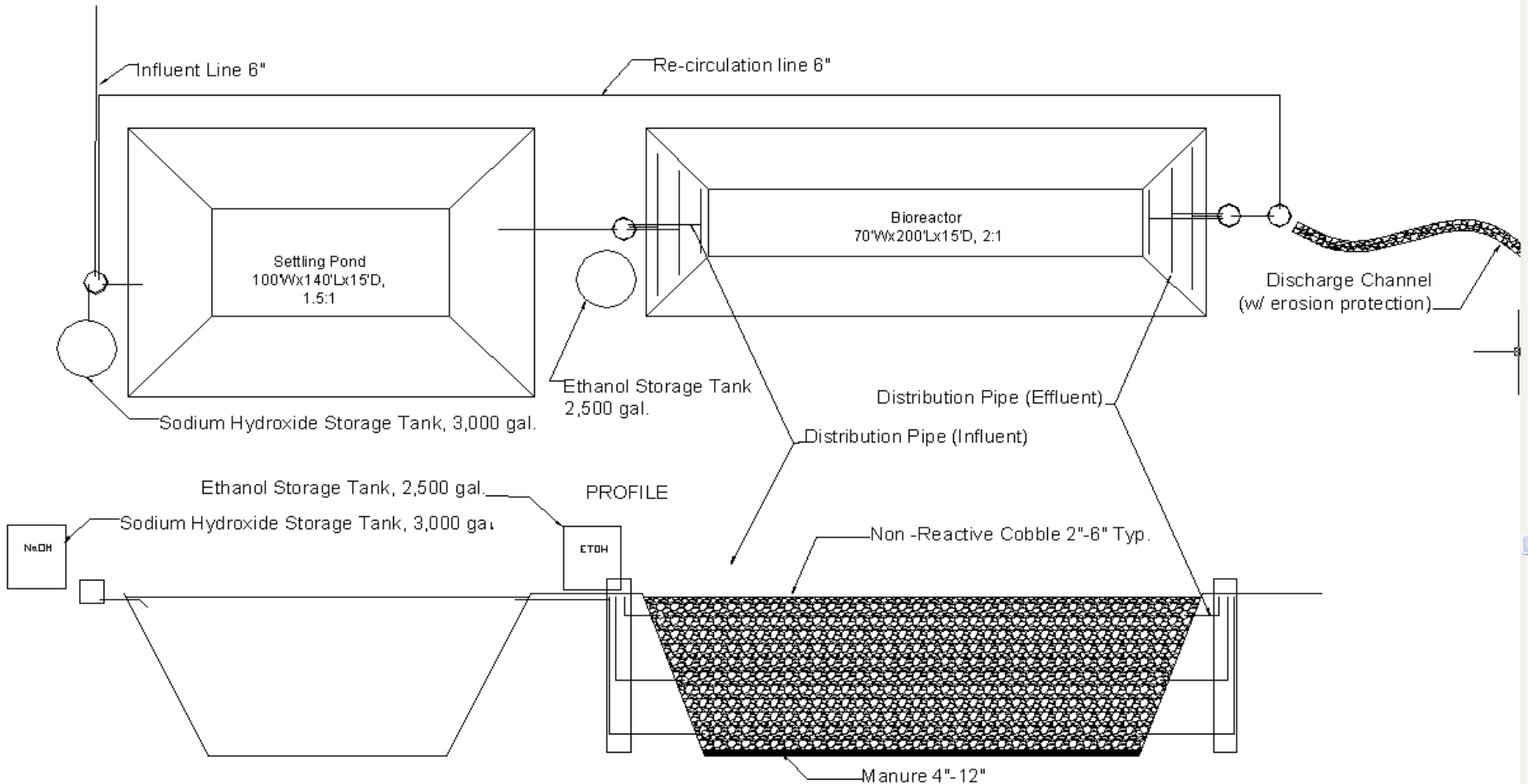
Rio Tinto Bioreactor

- Very high metals concentrations and acidity
- Lime precipitation more cost-effective at this site



Nacimiento Mine

PLAN VIEW





Other projects

Sulfate Removal



- Reverse osmosis very expensive still have the brine to deal with.
- Mix Ferric hydroxide sludge from RCTS with bioreactor effluent that contains sulfide.
- Ferric iron reacts with sulfide to produce elemental sulfur.
- The reduced iron can then react with sulfide generating ferrous sulfide.
- 2 moles of sulfate removal for every mole of iron added.



Questions

Thanks again!