Ethanol Fed Semi-Passive Bioreactors at the Leviathan Mine

Timothy K. Tsukamoto, Ph.D.

Glenn C. Miller, Ph.D.

Ms 199

University of Nevada,

Reno, NV 89557 USA

Three Types of Acidic Waters

	Weak	Moderate	Strong
pH	5-7	3-5	<2
Sulfate	<300	300-3000	>3000
Aluminum	<1	1-40	>40
Iron	<5	5-800	>800

Potential for Biological Treatment

- Weak AMD
  - Highly passive systems can work well, plugging and acidification potential is low
- Moderate AMD
  - Acidification and plugging of bioreactor likely unless some base is added and flushing of sludge is frequent; added alcohol helpful
- Stong AMD
  - Biological treatment highly problematic- acidification and plugging likely- lime use is best


Leviathan Mine Superfund Site

Comparison of the Leviathan Mine Aspen Seep with Discharge Objectives.

Values shown are maximum allowable/daily composite of three grab samples.

* Values calculated from 40 CFR 131.38 using hardness of 200 mg/L ($CaCO_3$)

Constituent	Aspen Seep	Discharge Objectives
pH	3.2	6.0-9.0 su
sulfate	1780	NA
Al	41	4.0/2.0
Fe	126	2.0/1.0
Ni	0.567	0.84/0.094*
Mn	21	NA
Cu	1.03	0.026/0.016*
Zn	0.786	0.21/0.21*
As	<0.05	0.34/0.15

The anaerobic sulfate-reducing treatment process

- The sulfate-reducing process can be described by the following equations:

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$$

$$2CH_2O + SO_4^{-2} + \rightarrow 2HCO_3^- + H_2S$$

H_2S (as S^{-2}) will then combine with a variety of divalent metals as metal sulfide precipitates:

$$S^{-2} + M^{2+} \rightarrow MS$$

Solubility products of various metal sulfides

Metal Sulfides	Solubility Product (18°C)
MnS	1.4×10^{-15}
FeS	3.7×10^{-18}
ZnS	1.2×10^{-23}
NiS	1.4×10^{-24}
CoS	3.0×10^{-26}
PbS	3.4×10^{-28}
CdS	3.6×10^{-29}
CuS	8.5×10^{-45}
HgS	4.0×10^{-52}

From CRC, 18^0C

Solubility of Fe^{+2} in the presence of sulfide

$FeS(s) = Fe^{2+} + S^{2-}$ $\quad pK_{s1} = 18.1$

$HS^{-} = S^{2-} + H^{+}$ $\quad pK = 13.9$

$H_2S = HS^{-} + H^{+}$ $\quad pK = 7.0$

$$[Fe^{+2}] = \frac{K_{s1}}{[S^{2-}]} = \frac{10^{-18.1}}{[S^{2-}]}$$

$$[Fe^{+2}] = \frac{10^{-18.1}\,(10^{13.9}[H^{+}] + 10^{20.9}[H^{+}]^{2})}{[S^{.} - II]_{tot}}$$

$[S^{.} - II]_{tot}$ = total sulfide

Iron concentrations at various pH values with 10^{-3} sulfide

pH	$[Fe^{+2}]$	Fe (mg/L)
4	6.3×10^{-3}	346
5	6.4×10^{-5}	3.5
6	6.9×10^{-7}	0.038
7	1.2×10^{-8}	0.00066
8	6.4×10^{-10}	0.0000034

Iron concentrations at various pH values with 10^{-4} M sulfide

pH	$[Fe^{+2}]$	Fe (mg/L)
4	6.3×10^{-2}	3460
5	6.4×10^{-4}	35
6	6.9×10^{-6}	0.38
7	1.2×10^{-7}	0.0066
8	6.4×10^{-9}	0.000034

Organic Substrates for Dissimilatory Sulfate Reducing Bacteria

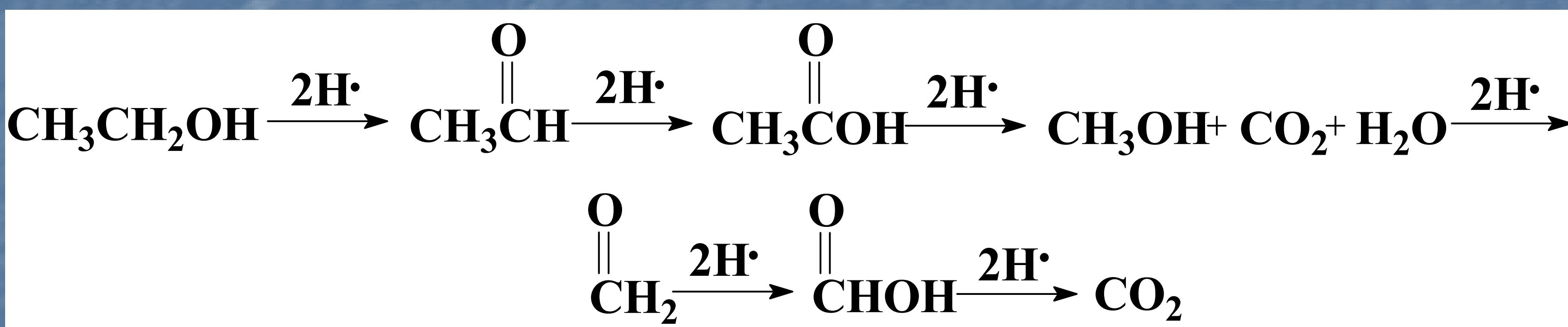
- Formate
- **Acetate**
- **Lactate**
- Pyruvate
- Malate
- Fumarate
- Succinate
- Alkanes
- Various sugars
- **Glycerol**
- **Methanol**
- **Ethanol**
- Propanol
- Butanol
- **Ethylene glycol**
- Propane diol
- Benzoate
- Phenols (many types)
- Others

Electron Accounting and Reducing Equivalents

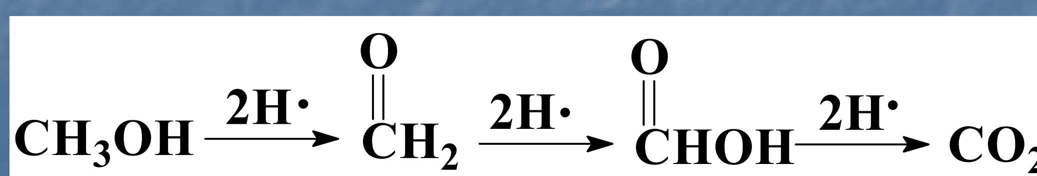
1. The reduction of sulfuric acid to sulfate requires 8 electrons.

$$H_2SO_4 \xrightarrow{2H\cdot} H_2SO_3 + H_2O \longrightarrow SO_2 \xrightarrow{2H\cdot} SO \xrightarrow{2H\cdot} S + H_2O \xrightarrow{2H\cdot} H_2S$$

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



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



Electron Accounting

One Mole of H_2S eliminates one mole of Fe^{2+}
If trying to remove 300 mg/L of Fe^{2+} (0.0054 M)

2. 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/1.5moles 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+}

Original Manure Substrate at the Leviathan Mine.

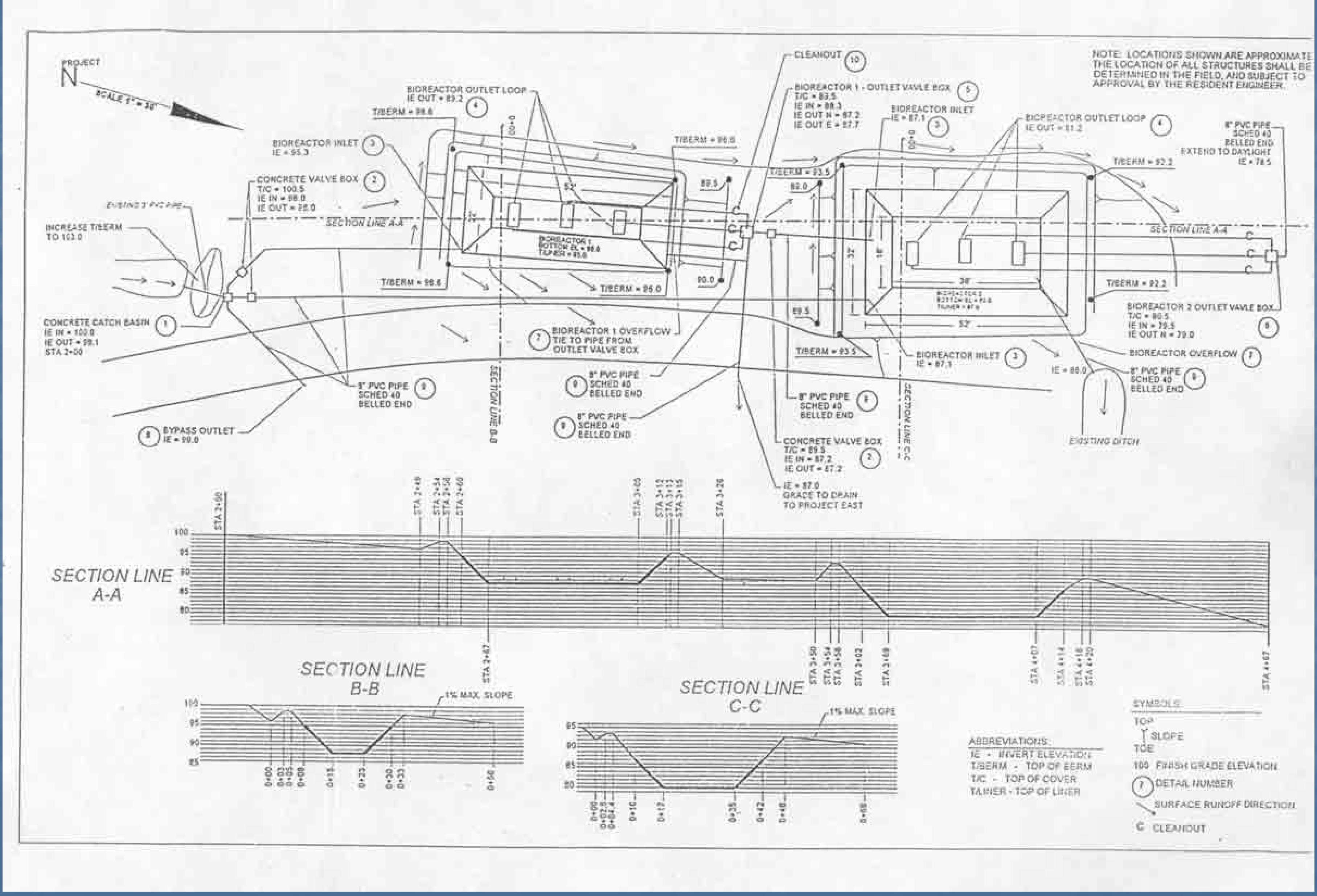
-down-flow reactor approximately 3ft deep.
-ineffective at treating AMD after 1 year.
-the source of manure substrate for the column experiments that follow.

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
- Designed to allow precipitates to be flushed from the cells

Aspen Seep

Leviathan Aspen Seep Schematics



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.

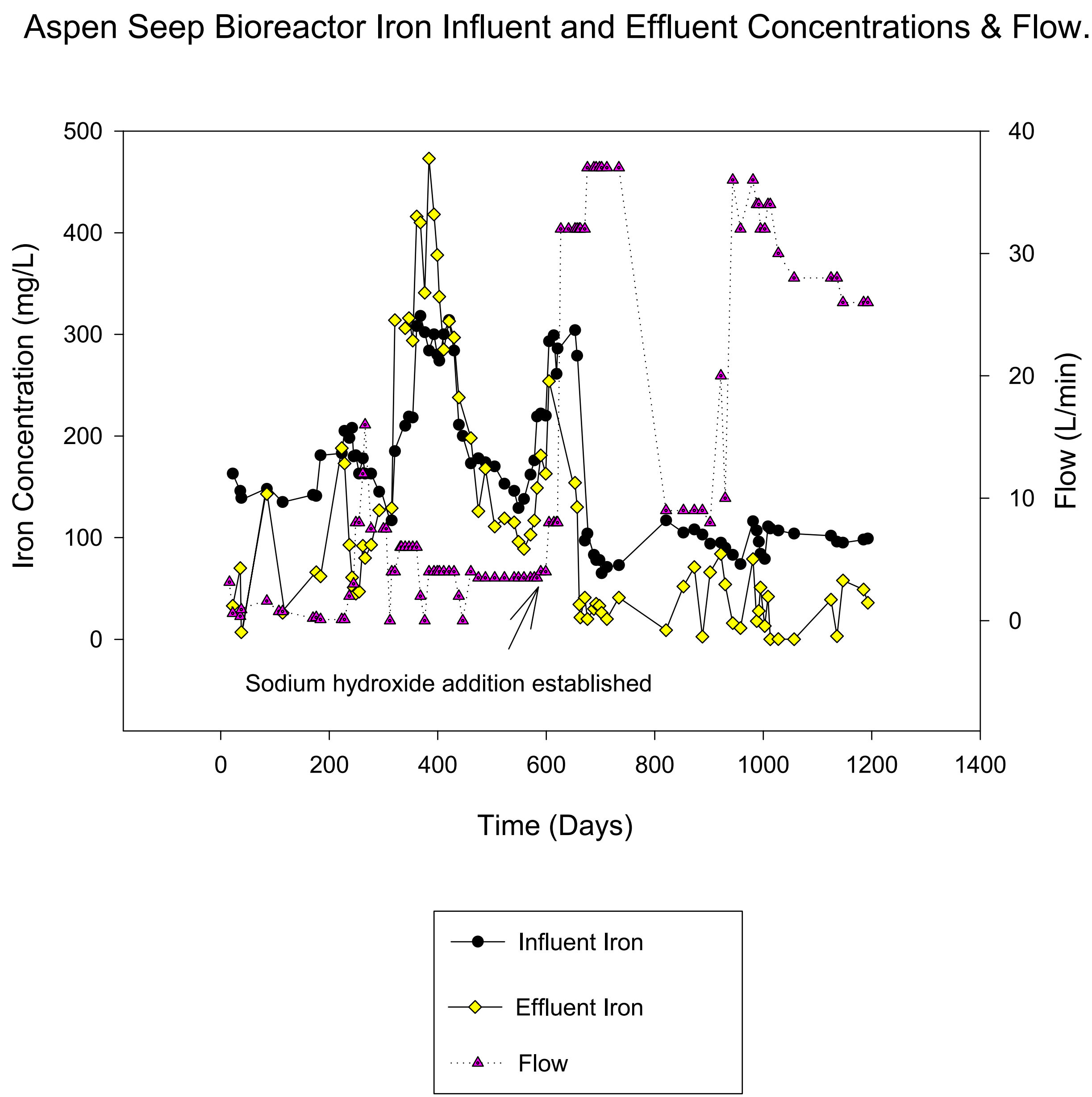
Precautions were taken to reduce oxide/ hydroxide precipitates from forming to reduce plugging

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

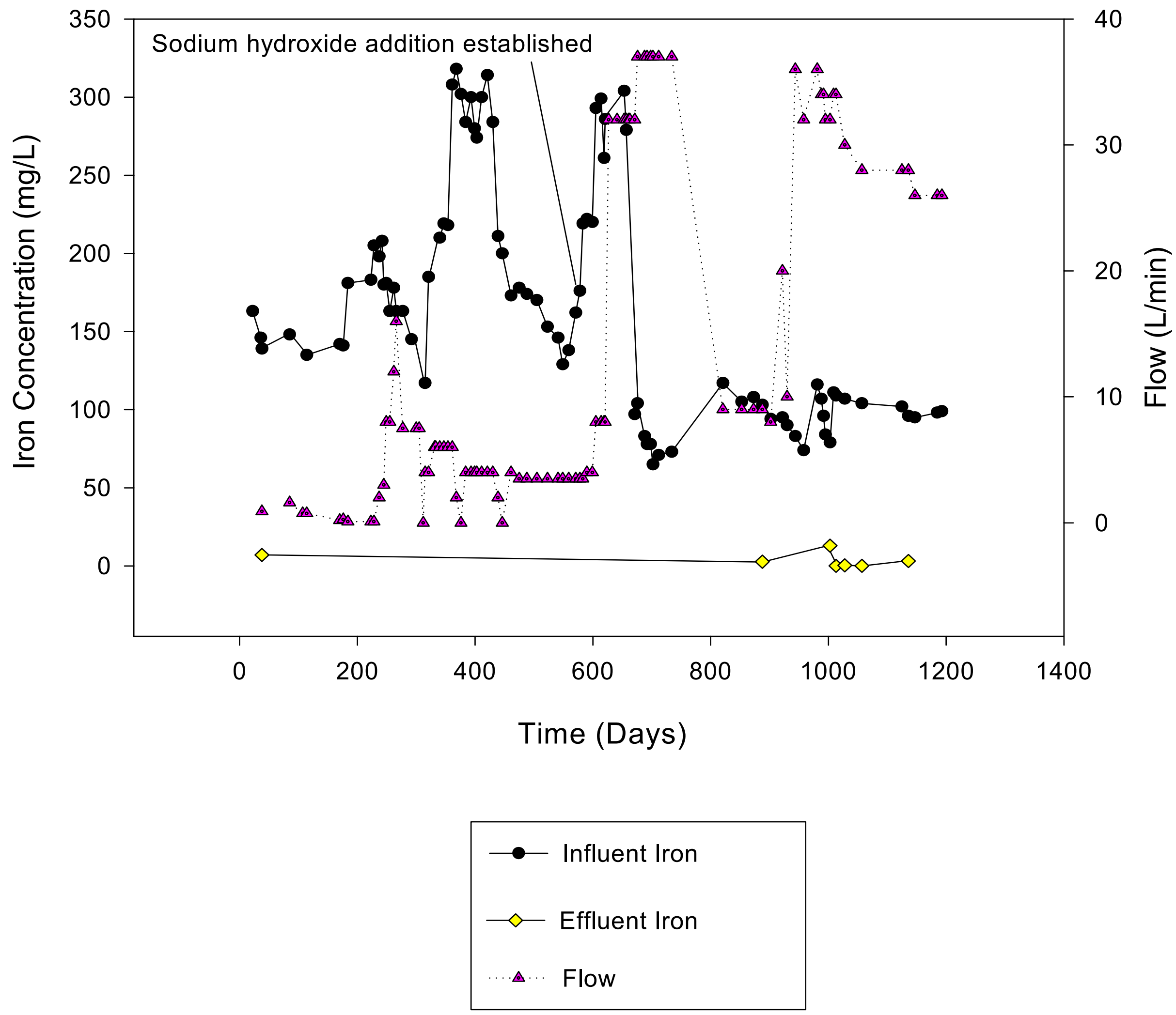
The second reactor consisted mainly of inert river rock.

Aspen Seep Bioreactor

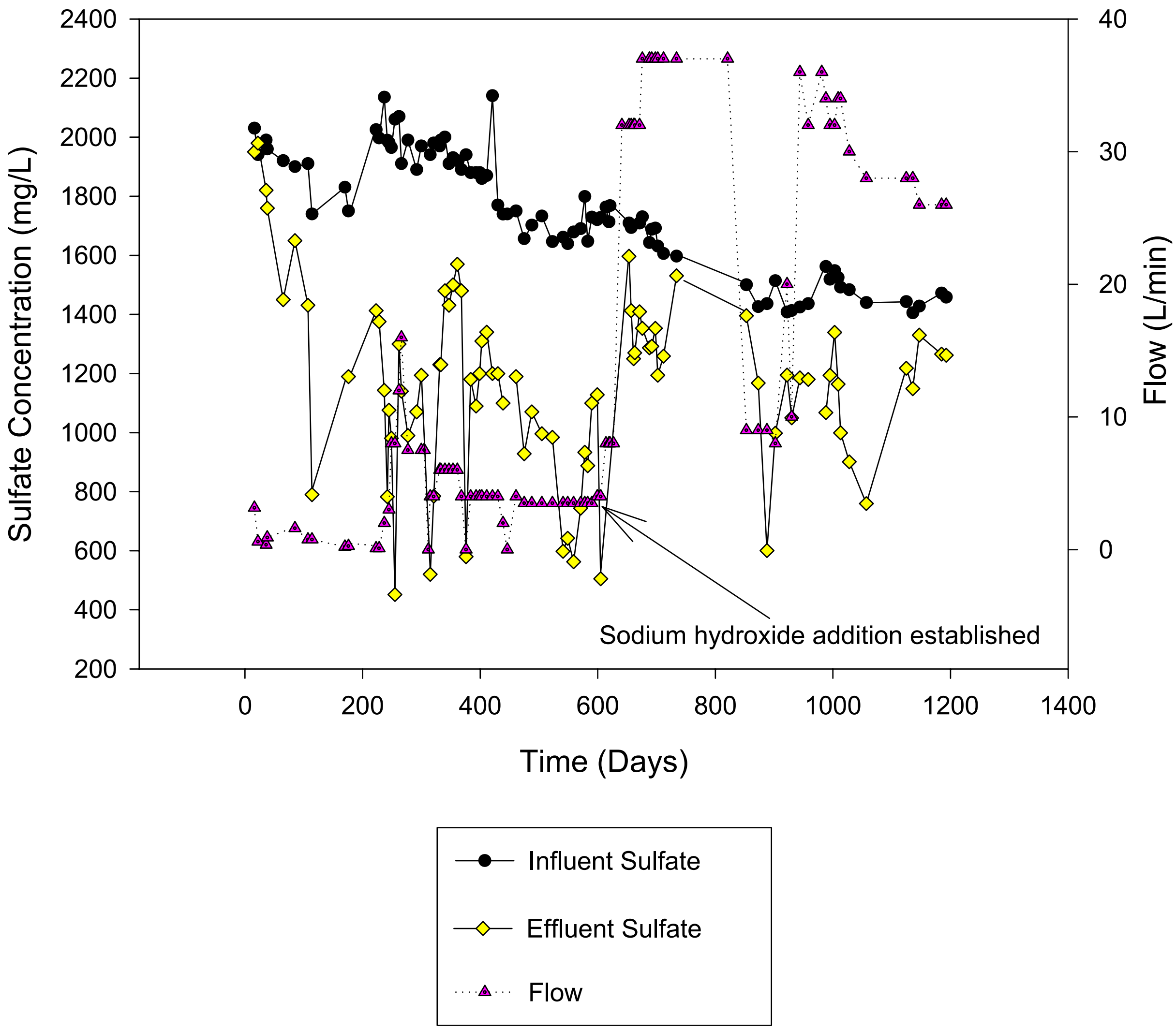
	Nickel (mg/L)	Copper (mg/L)	Zinc (mg/L)	Iron (mg/L)
Influent	0.14	0.28	1.75	83
Effluent	0.02	n.d.	n.d.	34
Effluent (settled)	0.02	n.d.	n.d.	0.7


Aspen Seep Bioreactor Iron Influent and Effluent Concentrations & Flow.
Iron Concentration (mg/L)
Flow (L/min)
Time (Days)
Sodium hydroxide addition established
500
400
300
200
100
0
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Influent Iron
Effluent Iron
Flow

Aspen Seep Bioreactor Iron Influent and Effluent Concentrations When pH > 6.5 in Effluent & Flow.



Aspen Seep Bioreactor Influent and Effluent Sulfate Concentrations & Flow




MARK
Hertz

2003 Bioreactor Goals

- Improved flushing ability
- Larger rock matrix
- Improved water distribution
- Addition of pre-treatment pond for solids removal
- Improved sludge management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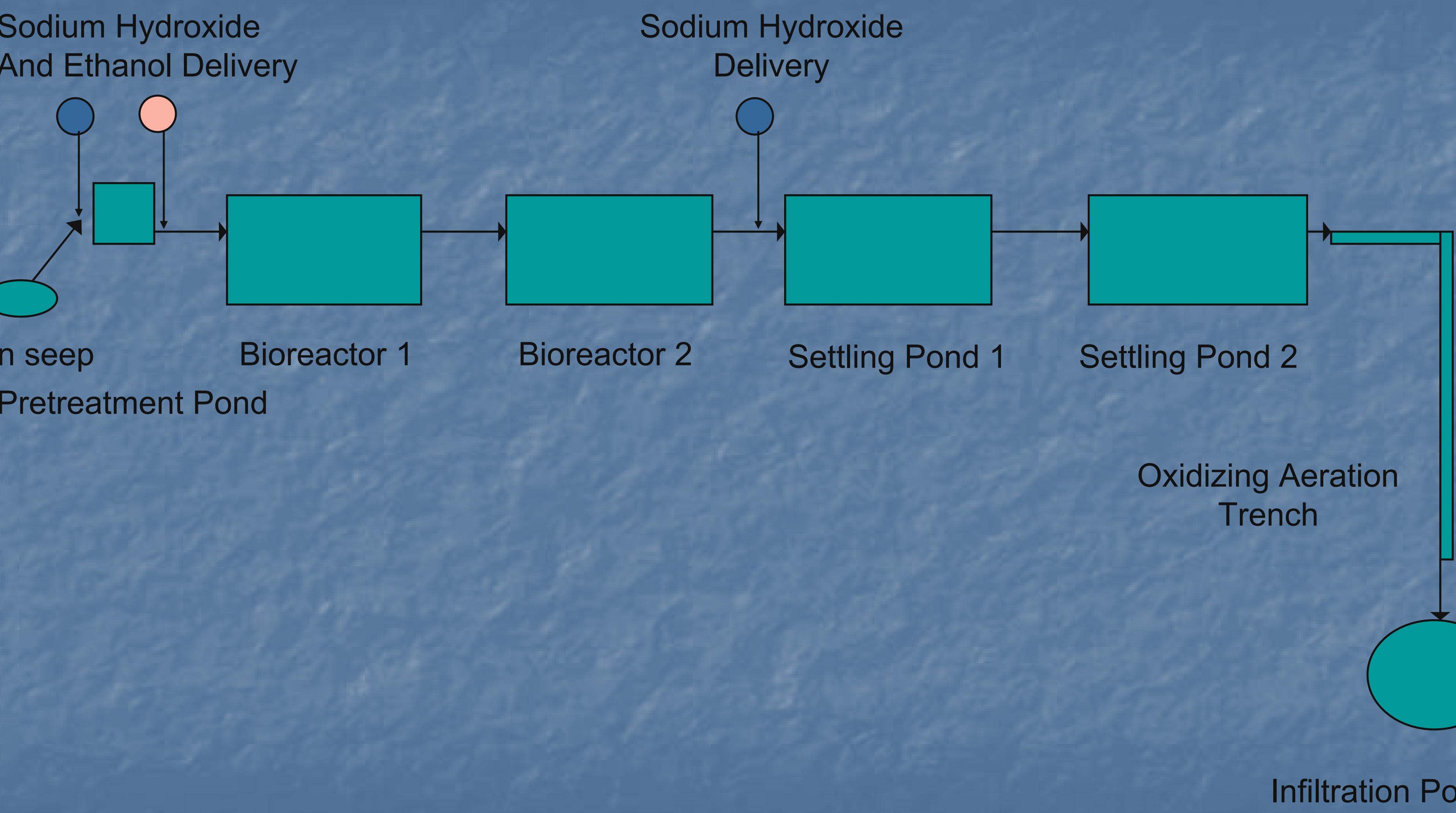
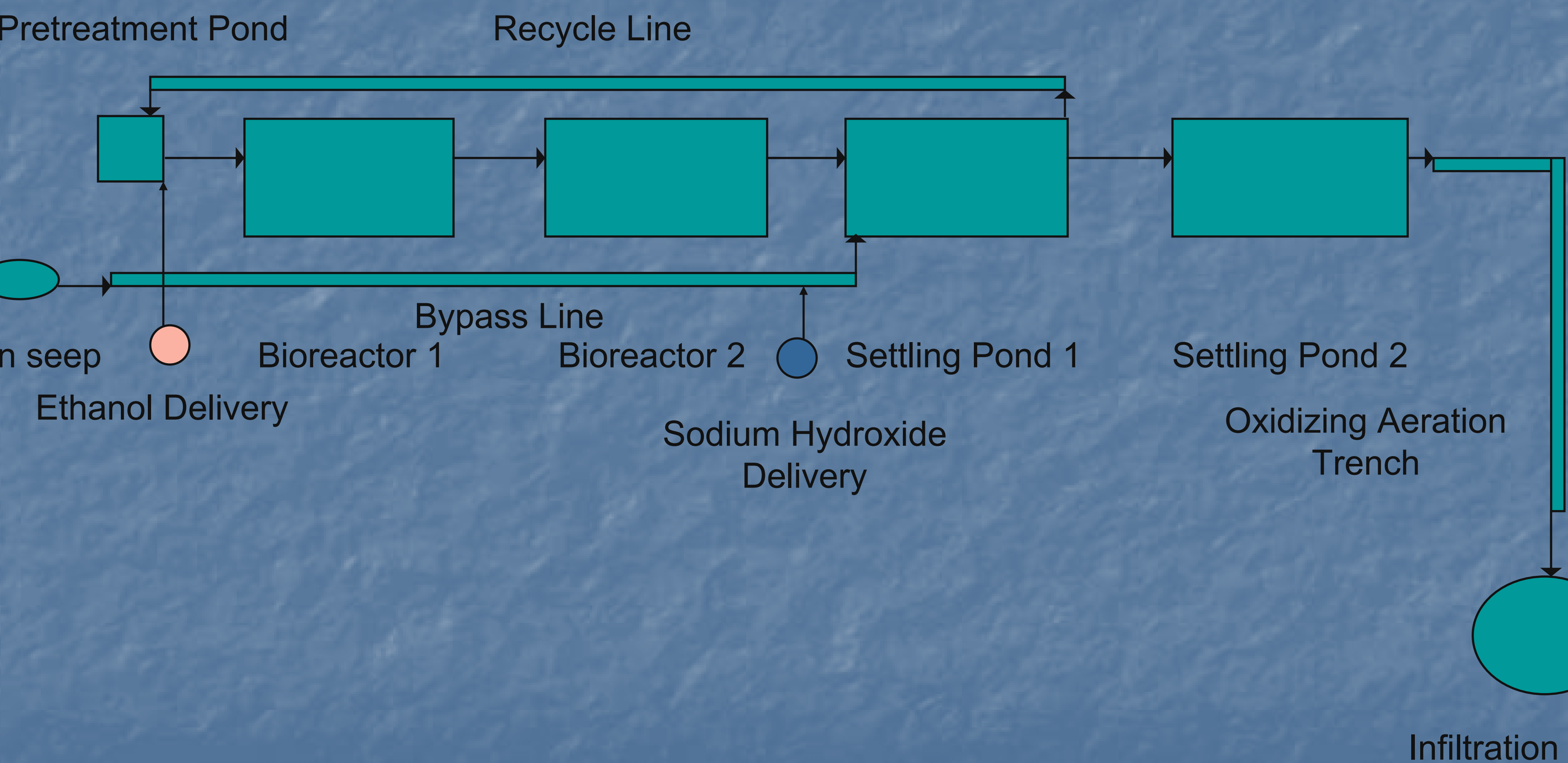
Designed Flow Schematics



onstituent	Aspen Seep	Bioreactor 1 effluent	Bioreactor 2 effluent	Discharge	Discharge objectives
H	3.17	4.70	4.77	7.19	6-9
O_4	1502	1307	1269	1222	NA
l	35	21	18	<0.1	4.0
e	107	69	65	1.9	2.0
i	0.40	0.26	0.21	0.06	.84
u	0.55	0.01	<0.01	<0.01	.026
n	0.74	0.08	0.04	0.02	.21

Flow Schematics With Recycle



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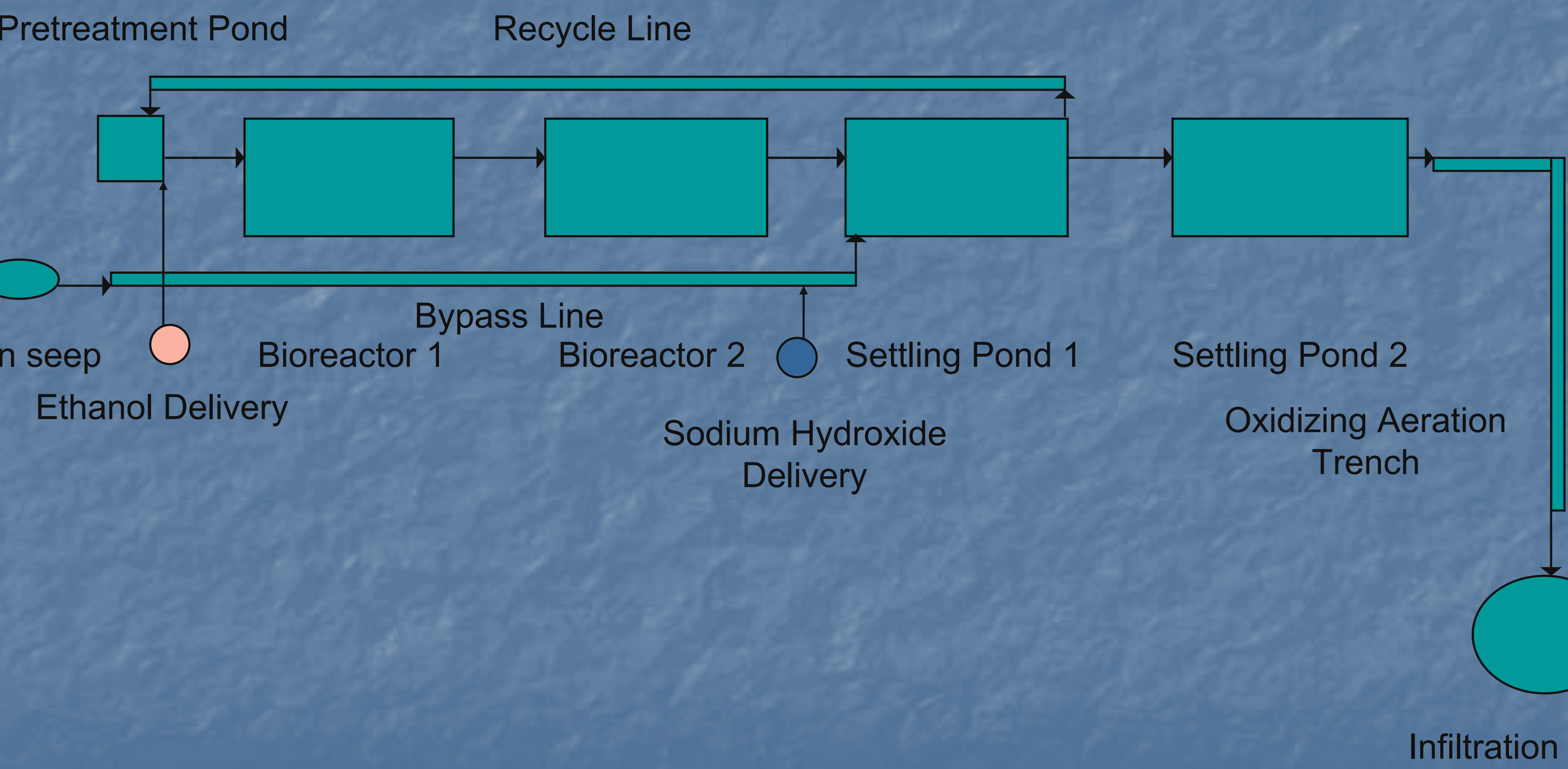
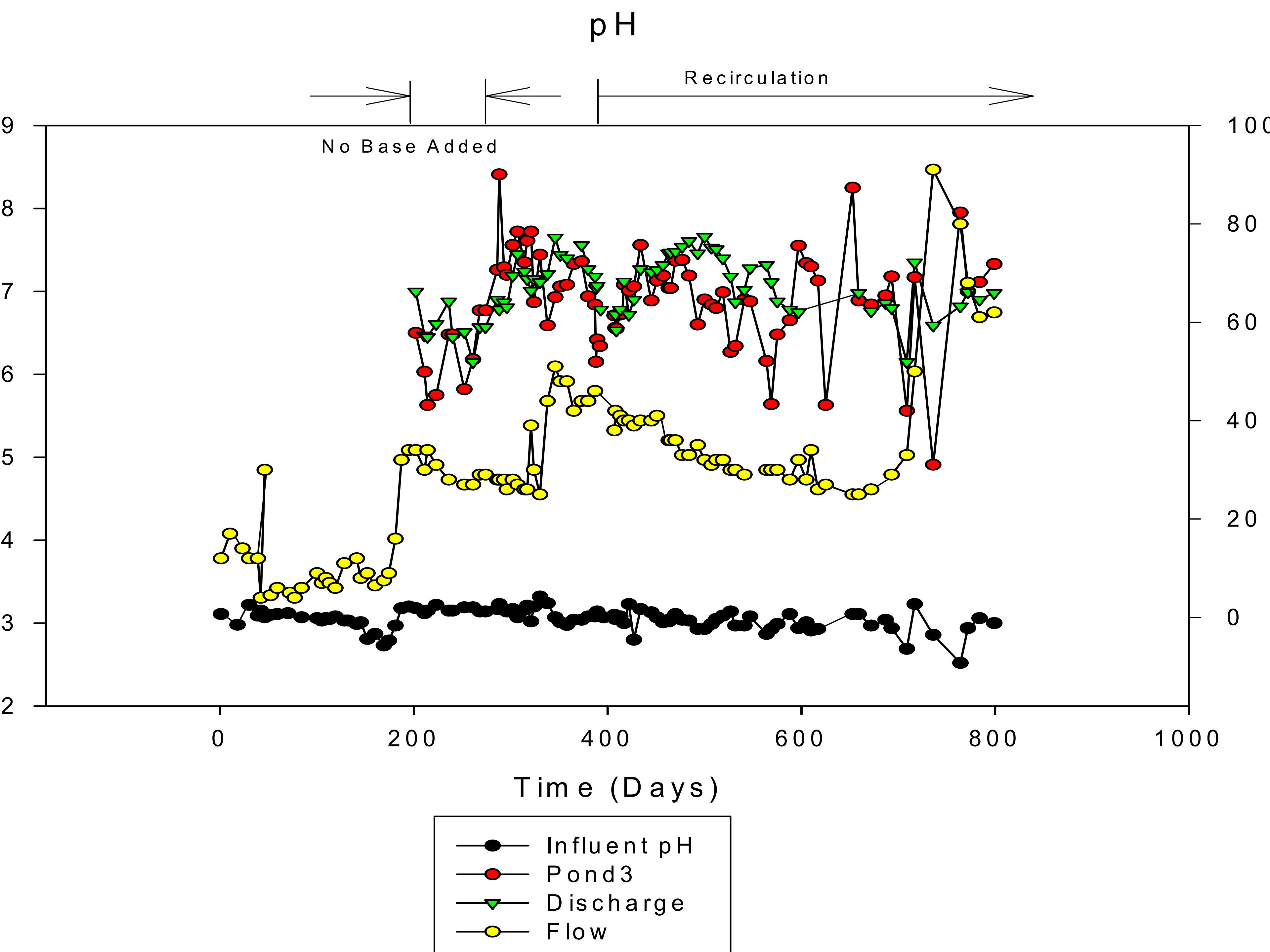
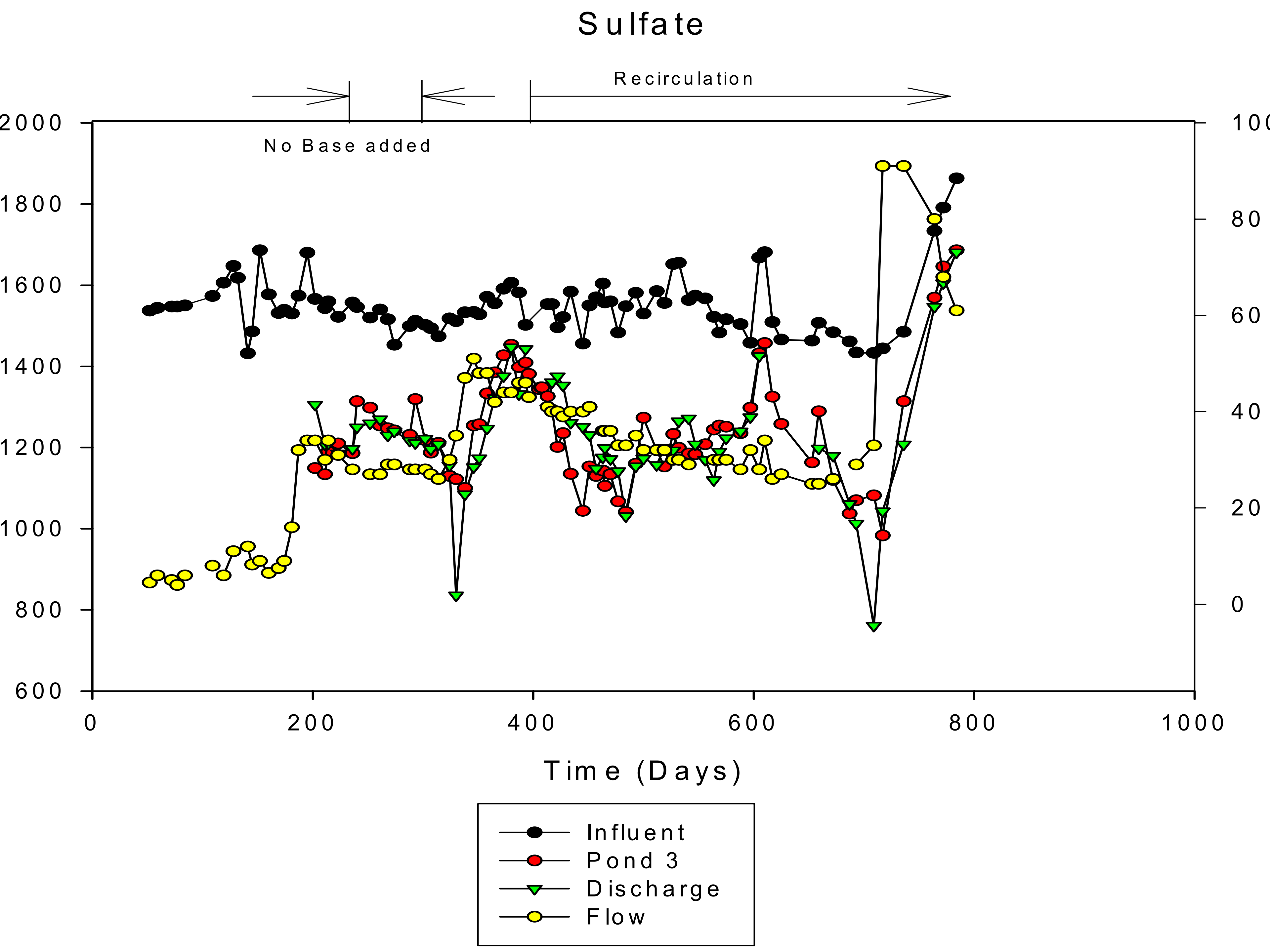
Flow Schematics With Recycle

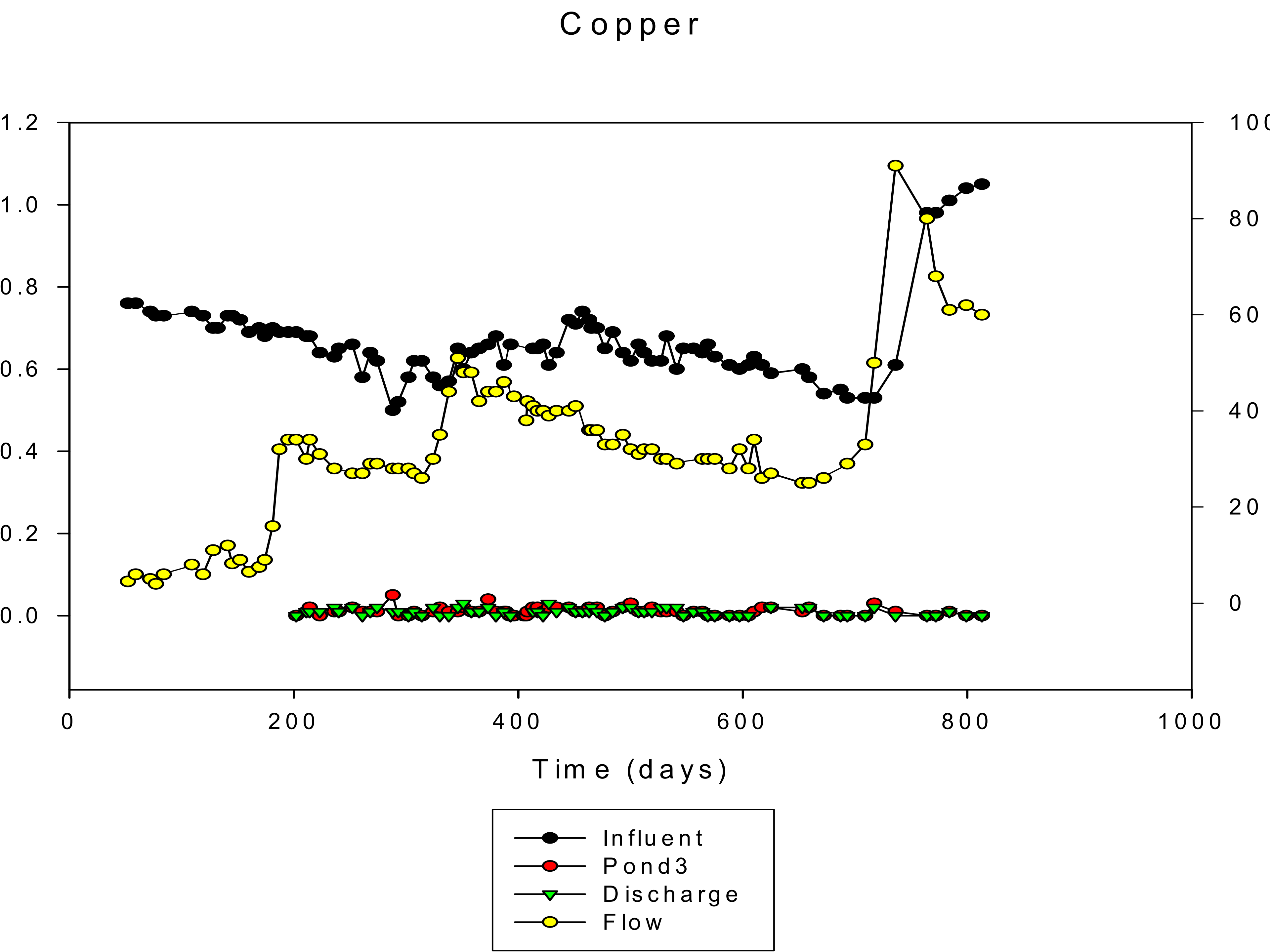


onstituent	Aspen Seep	Bioreactor 1 effluent	Bioreactor 2 effluent	Discharge	Discharge objectives
H	2.93	6.79	6.86	7.66	6-9
O_4	1530	1090	1080	1170	NA
l	28	<0.5	<0.5	<0.5	4.0
e	99	0.16	0.13	0.04	2.0
i	0.50	0.15	0.05	0.1	0.84
u	0.62	0.02	0.01	0.01	0.026
n	0.73	0.02	0.02	0.06	0.21



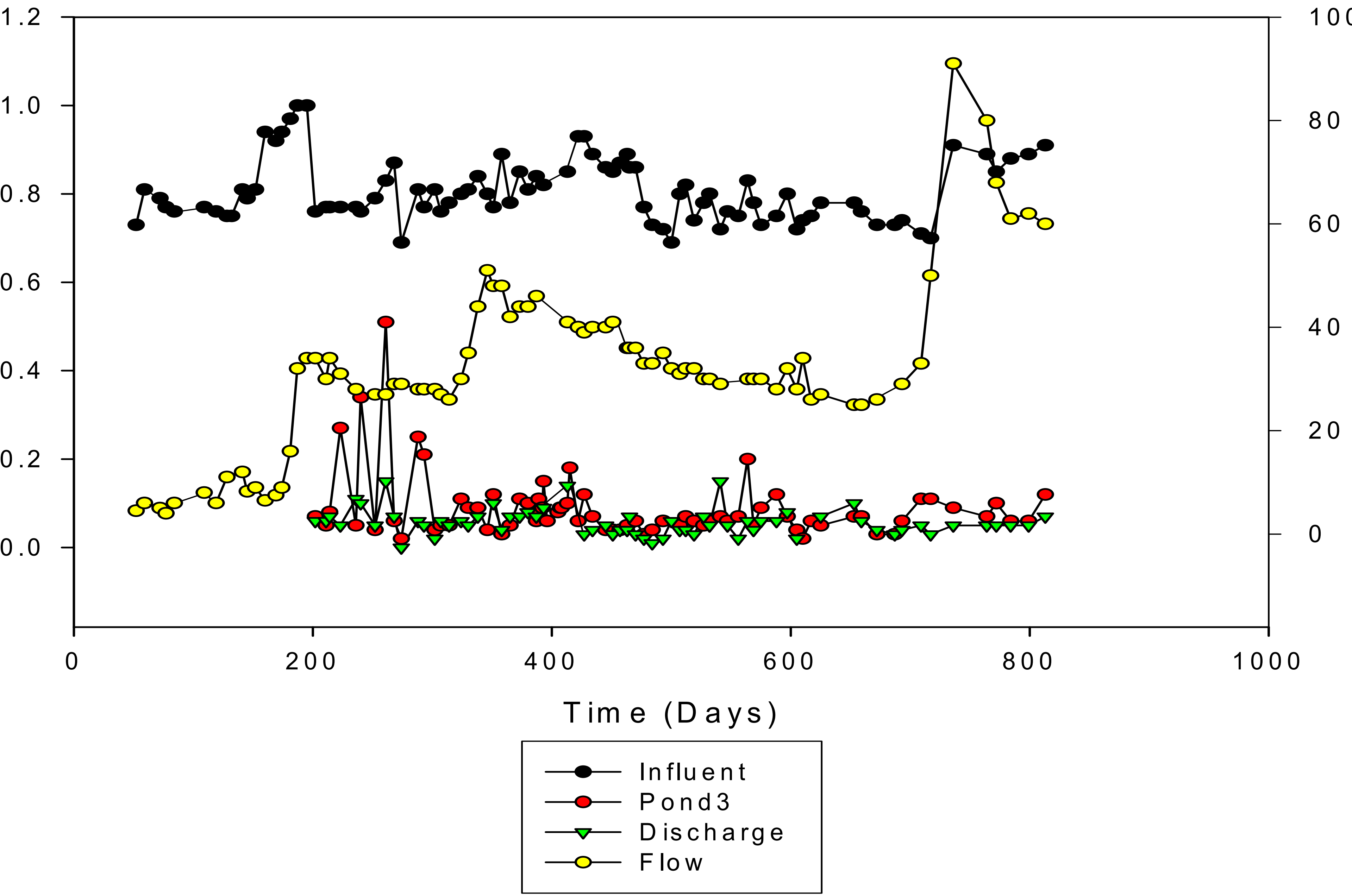
pH
Recirculation
No Base Added
9
8
7
6
5
4
3
2
100
80
60
40
20
0
0
200
400
600
800
1000
Time (Days)
Influent pH
Pond3
Discharge
Flow


Sulfate
Recirculation
No Base added
2000
1800
1600
1400
1200
1000
800
600
100
80
60
40
20
0
0
200
400
600
800
1000
Time (Days)
Influent
Pond 3
Discharge
Flow

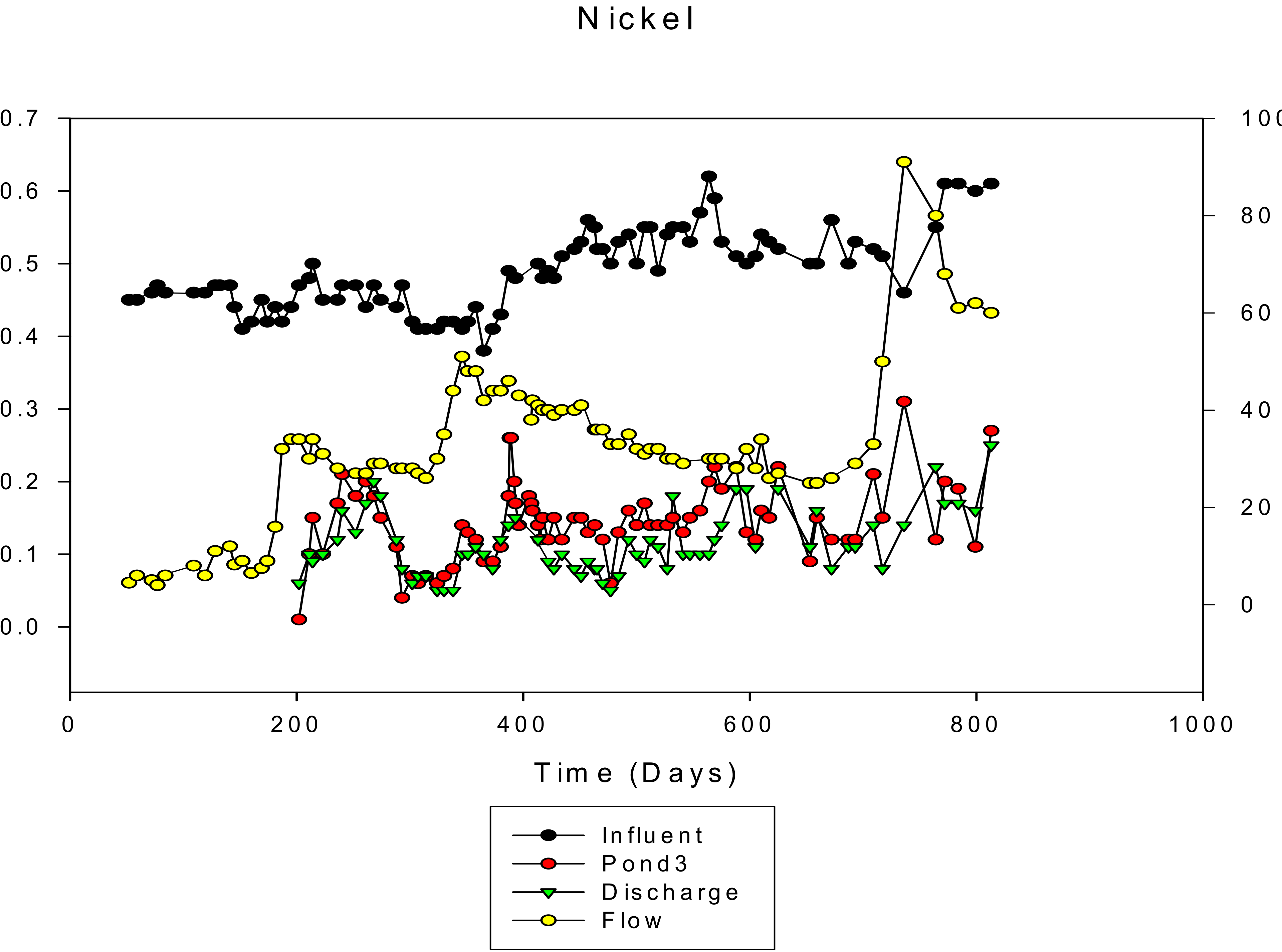


Copper
1.2
1.0
0.8
0.6
0.4
0.2
0.0
100
80
60
40
20
0
0
200
400
600
800
1000
Time (days)
Influent
Pond3
Discharge
Flow

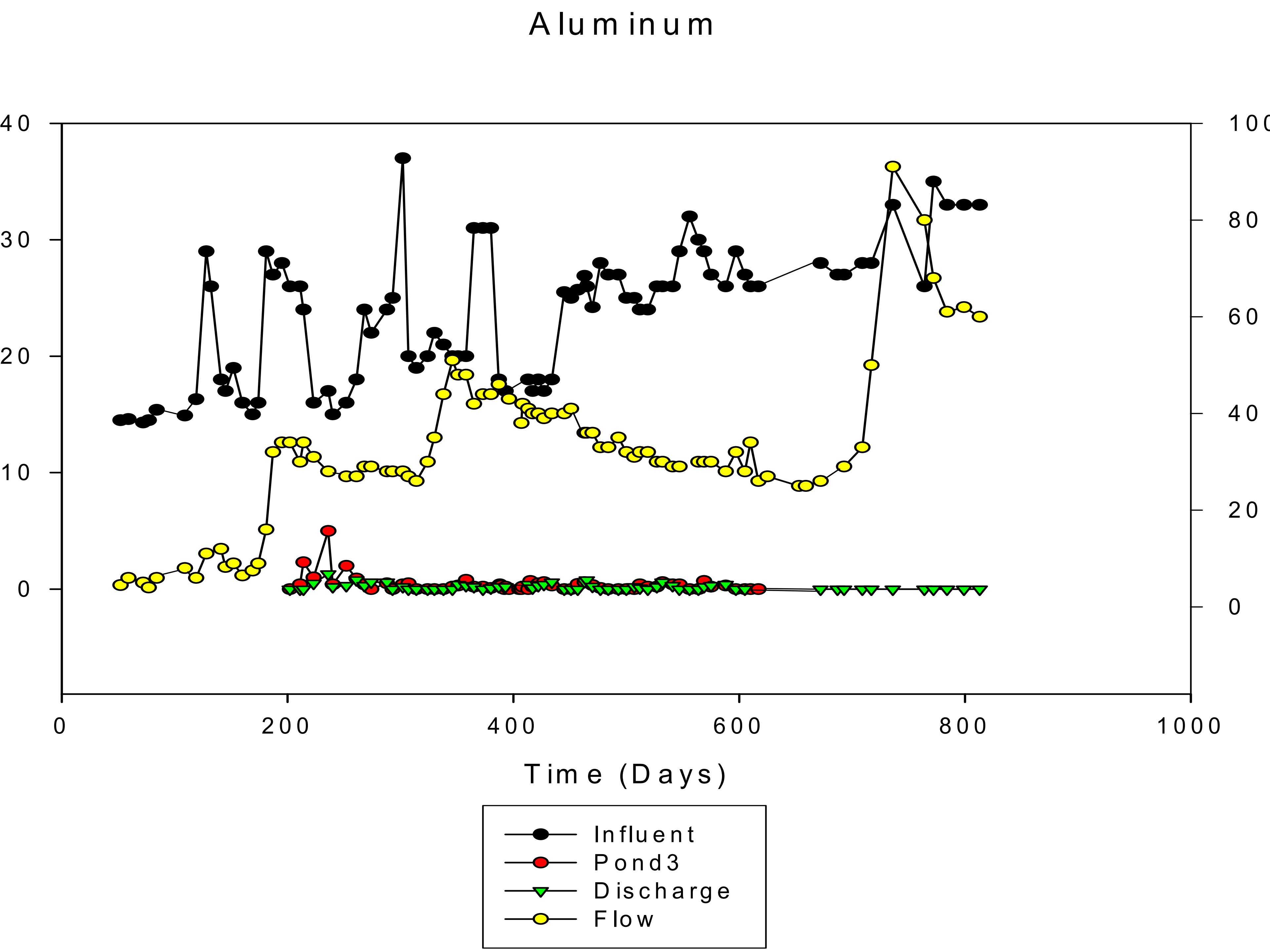
Zinc



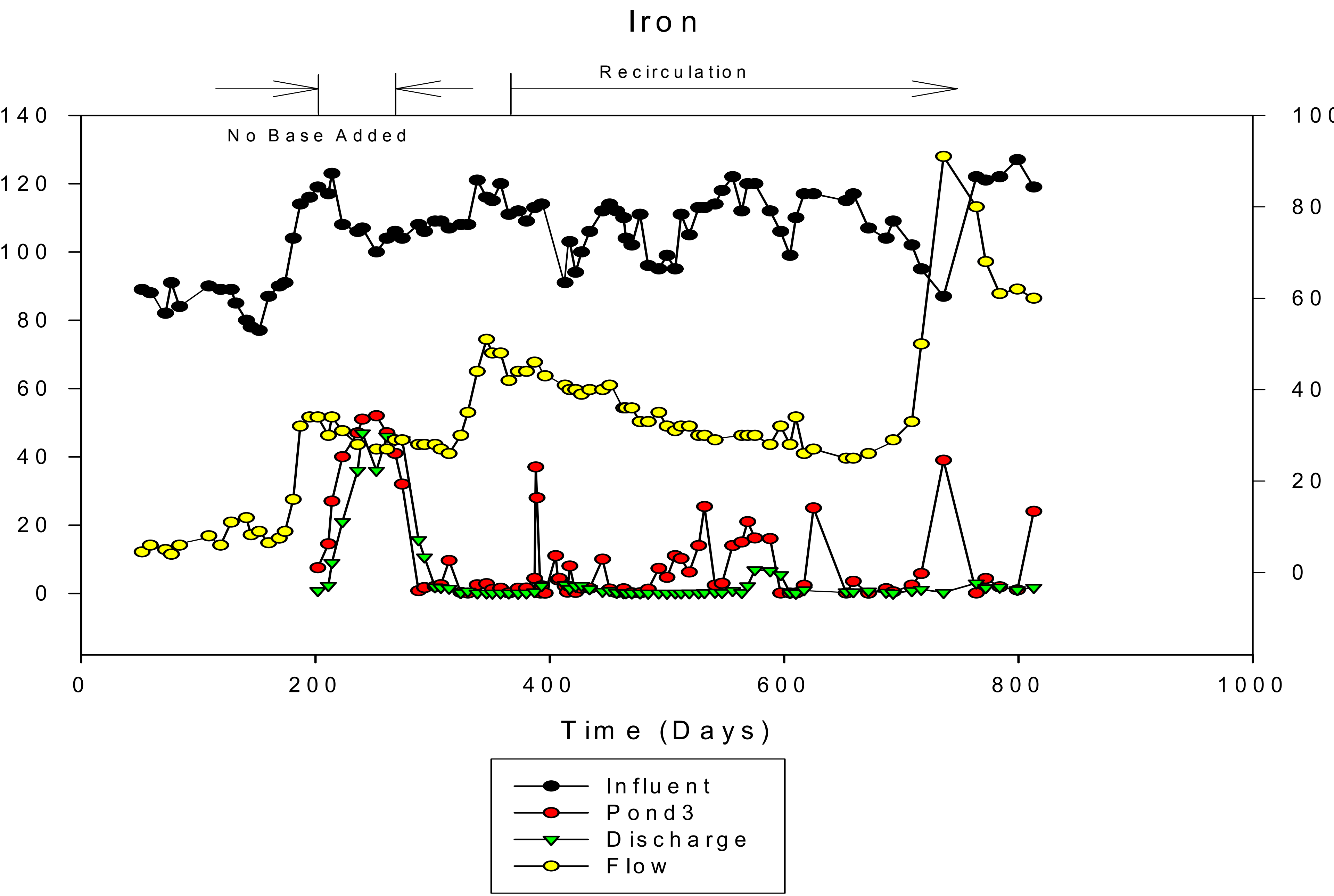
1.2
1.0
0.8
0.6
0.4
0.2
0.0
100
80
60
40
20
0
0
200
400
600
800
1000
Time (Days)
Influent
Pond3
Discharge
Flow



Nickel
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
100
80
60
40
20
0
0
200
400
600
800
1000
Time (Days)
Influent
Pond3
Discharge
Flow



Aluminum
40
30
20
10
0
100
80
60
40
20
0
0
200
400
600
800
1000
Time (Days)
Influent
Pond3
Discharge
Flow



Iron
Recirculation
No Base Added
140
120
100
80
60
40
20
0
100
80
60
40
20
0
0
200
400
600
800
1000
Time (Days)
Influent
Pond3
Discharge
Flow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Metal content of the sludge (dry basis)

Element	Concentration (mg/g)
Fe	225.9
Mn	6.23
Zn	1.34
Cu	0.86
Ni	0.75
Ca	49.10
Al	49.50
Na	3.30
Mg	9.70


Sodium
Carbonate

Cost

- Dependant upon chemistry (acidity and metals) and flow.
- Capital Costs- $50,000 to $1,000,000 could be higher if flows are extremely high and site conditions are challenging
- Maintenance Cost-

  - Personnel- 2 to 4 visits per month

  - Alcohol- variable @ Leviathan ~ $ 0.54/1000 gallons treated

  - Base – variable @ Leviathan ~ $0.47/1000 gallons treated

  - Recirculation energy cost ~ 0-$6000/year ($6,000 @ leviathan, diesel currently used)

  - other yearly maintenance - variable @ Leviathan ~ $10,000/year

Lessons Learned

- Either use the bioreactor as a sulfide generation system with sludge generated in an open pond or have an efficient sludge flushing system
- Avoid valves or piping systems that can (will) plug
- Sodium hydroxide addition is required (at least for the present), pH of effluent needs to be close to 7 for good iron removal
- Many alcohols will work- ethanol is our choice (for now)
- Sludge management requires seeking opportunities
- There is no magic bullet for AMD treatment- Even though alcohol enhanced bioreactors can be less than lime treatment, management and monitoring still required
- Recycle appears to work well

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