Alcohol Enhanced Sulfate-Reducing Bioreactors- Better Control of Microbial Activity and Sludge Management

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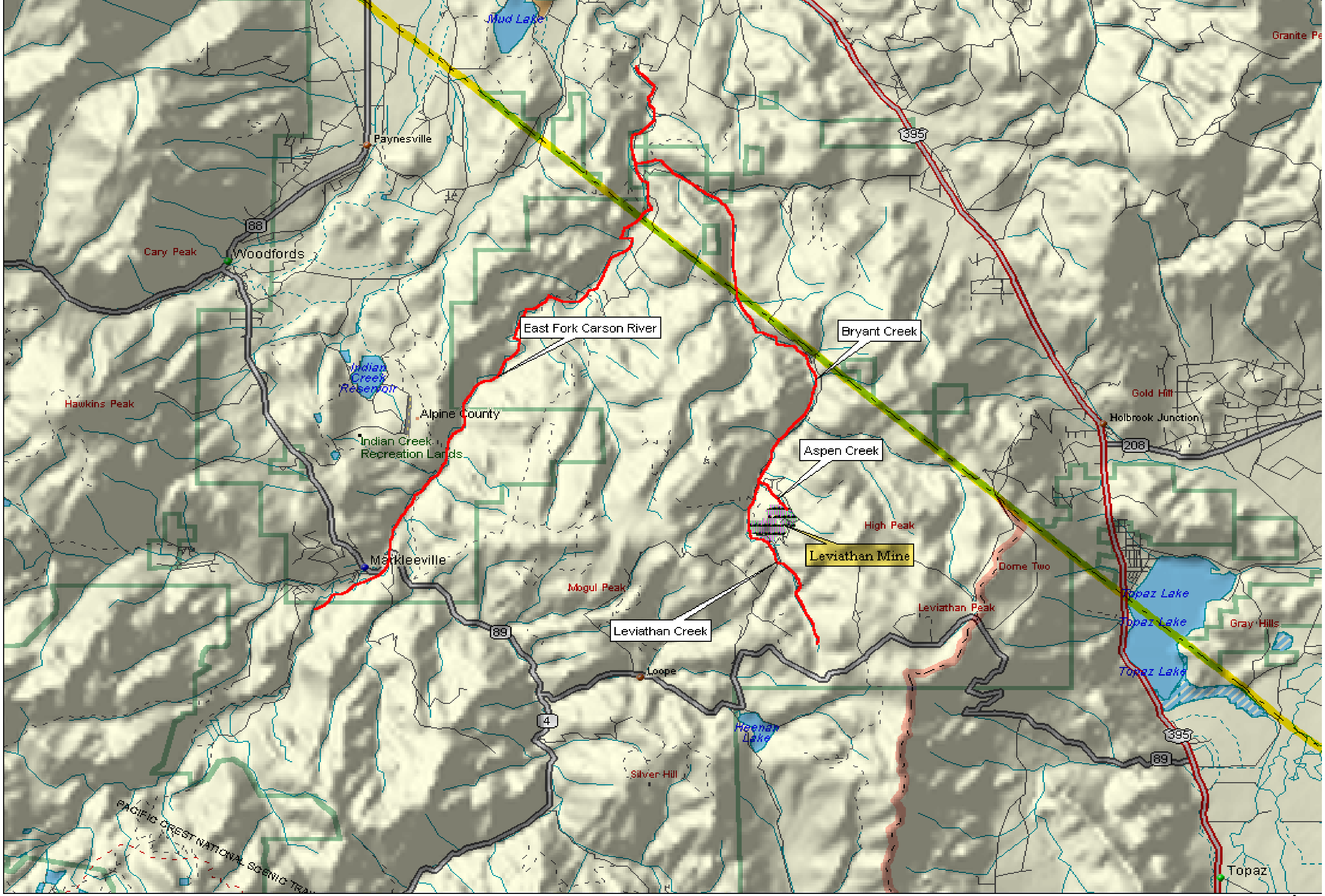

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Comparison of the Leviathan Mine Aspen Seep with Water Quality Standards.

MCL = primary maximum contaminant level
SMCL = secondary maximum contaminant level

constituent	Aspen Seep	Water Quality Standards
pH	3.2	6.5-8.5
sulfate	1780	400/500 MCL 250 SMCL
Al	41	0.05-0.2 SMCL
Fe	126	0.3 SMCL
Ni	0.567	0.1 MCL
Mn	21	0.05 SMCL
Cu	1.03	1.3 MCL 1.0 SMCL
Zn	0.786	5.0 SMCL
Co	0.37	-

Considerations for Bioreactor Use

- Treatment
    - -reliability - Is the system robust?
    - -water quality
- Sludge management
    - -quantity
    - -quality
- Sustainability
- Space availability
- Cost

Treatment Process

(general equations)

Sulfate-reduction and subsequent removal of metals by sulfide precipitation.

$$4\,AH_2 + SO_4^{2-} + 2\,H^+ \longrightarrow 4\,A^{2-} + H_2S + 4\,H_2O$$

$$(e.g.\ 2\,CH_2O + SO_4^{2-} + 2\,H^+ \longrightarrow 2\,CO_2 + H_2S + 2\,H_2O)\ pH < 7$$

and

$$H_2S + M^{2+} \longrightarrow MS + 2\,H^+$$

Solubility Products for Metal Complexes

Substance	K_{sp}		Substance	K_{sp}
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}		$PbCO_3$	1.48×10^{-13}
NiS	1.08×10^{-21}		$CdCO_3$	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}

Critical pH

- The critical pH is the threshold of precipitation. Precipitation of metal sulfides only occurs above the critical pH at specified metal and total sulfide concentration.
- The critical pH goes down when the total sulfide concentration increases at a fixed total Fe concentration.
- As pH increases with a fixed total sulfide concentration more Fe precipitates.

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

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

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

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

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

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

$[S\cdot - II]_{tot}$ = total sulfide

Substrates

- Typically utilize a substrate that contains the carbon source to generate anaerobic conditions and reduce sulfate.
  (e.g. sawdust, manure, mushroom compost)

- As the readily available carbon sources are depleted, treatment decreases.

Organic Substrates for Dissimilatory Sulfate Reducing Bacteria

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

Why an alcohol enhanced bioreactor?

- Better flow control
- Better management of reducing equivalents
- Easier ability to manage sludge
- Plugging easier to manage
- Smaller size required
- Requires delivery of alcohol

Sizing Bioreactors Based on Rate of Sulfate-Reduction

- Manure/wood/limestone: 0.3 moles of sulfate/m^3/day (Gusek, 2002)

- Alcohol enhanced: 1.5 moles of sulfate/m^3/day

Highly dependent on a variety of factors!

Electron Accounting and Reducing Equivalents

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

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

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

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

Amount of alcohol needed to remove 500 mg/L of sulfate

Alcohol	Electrons	gm/L AMD	mL/L AMD
Ethanol	12	0.16 gm/L	0.20 mL/L
Methanol	6	0.22 gm/L	0.28 mL/L
Ethylene Glycol	10	0.26 gm/L	0.23 mL/L

So to treat 32 L/min or 4.44 million gallons/year
you need ~ 890 gallons ethanol assuming 100% efficiency

In 1998 a Full Scale Bioreactor was Constructed at the Leviathan Mine

- 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 (gravity fed)
- Designed to allow precipitates to be flushed from the cells
- Utilized sequential reactors
- Some base needs to be added due to the low pH of Aspen Seep (pH 3.2)


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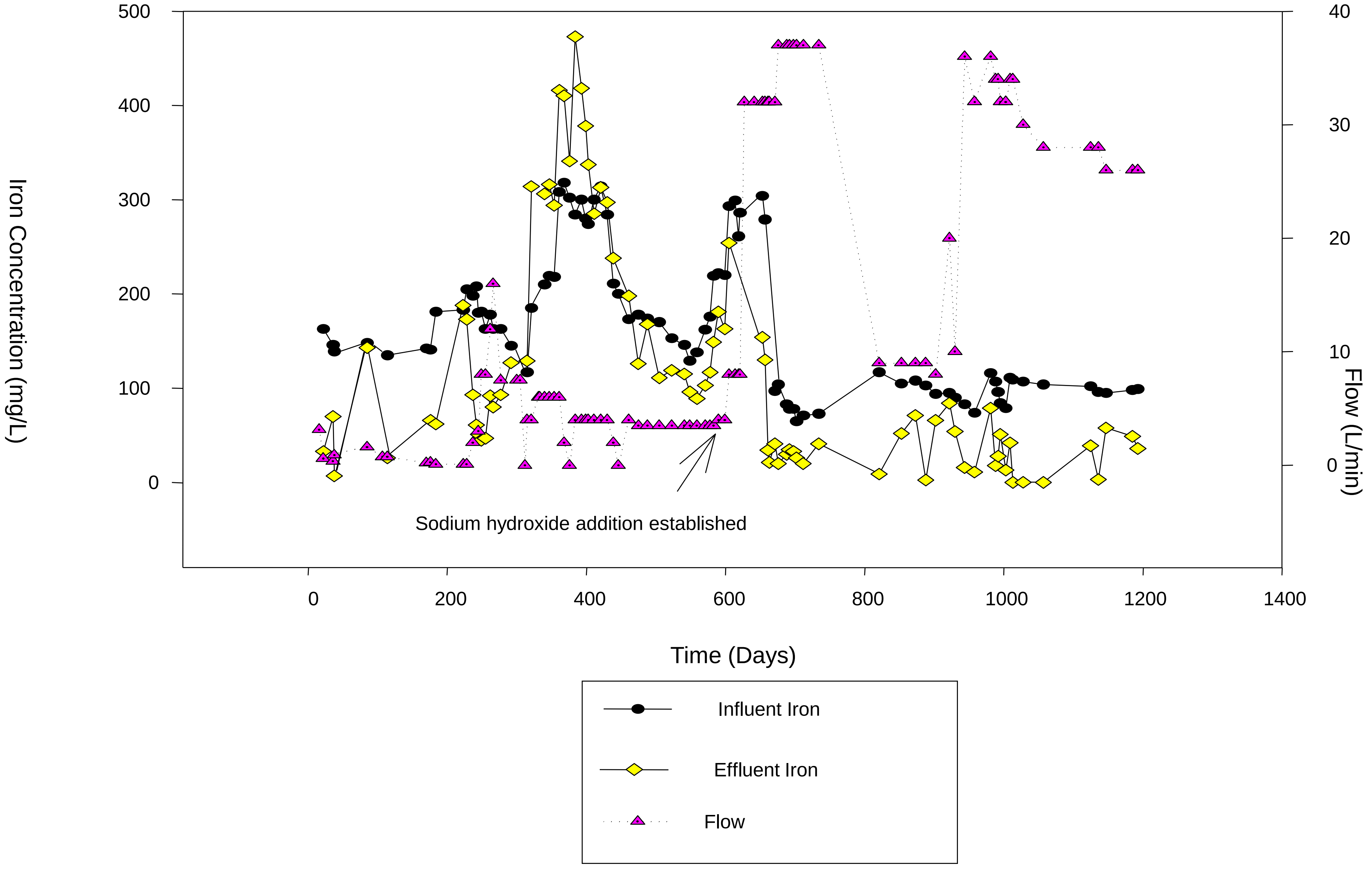
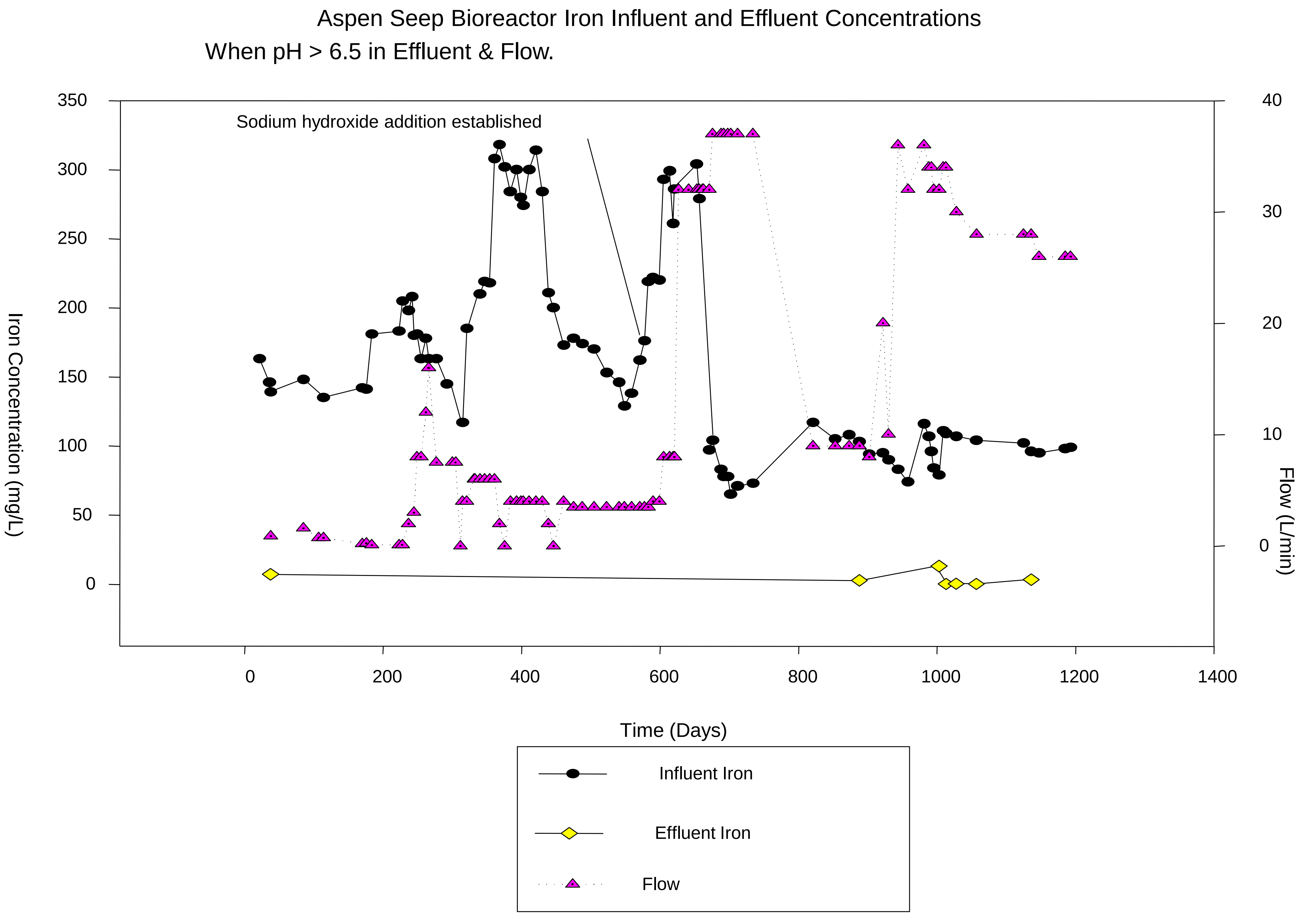
Aspen Creek Bioreactor

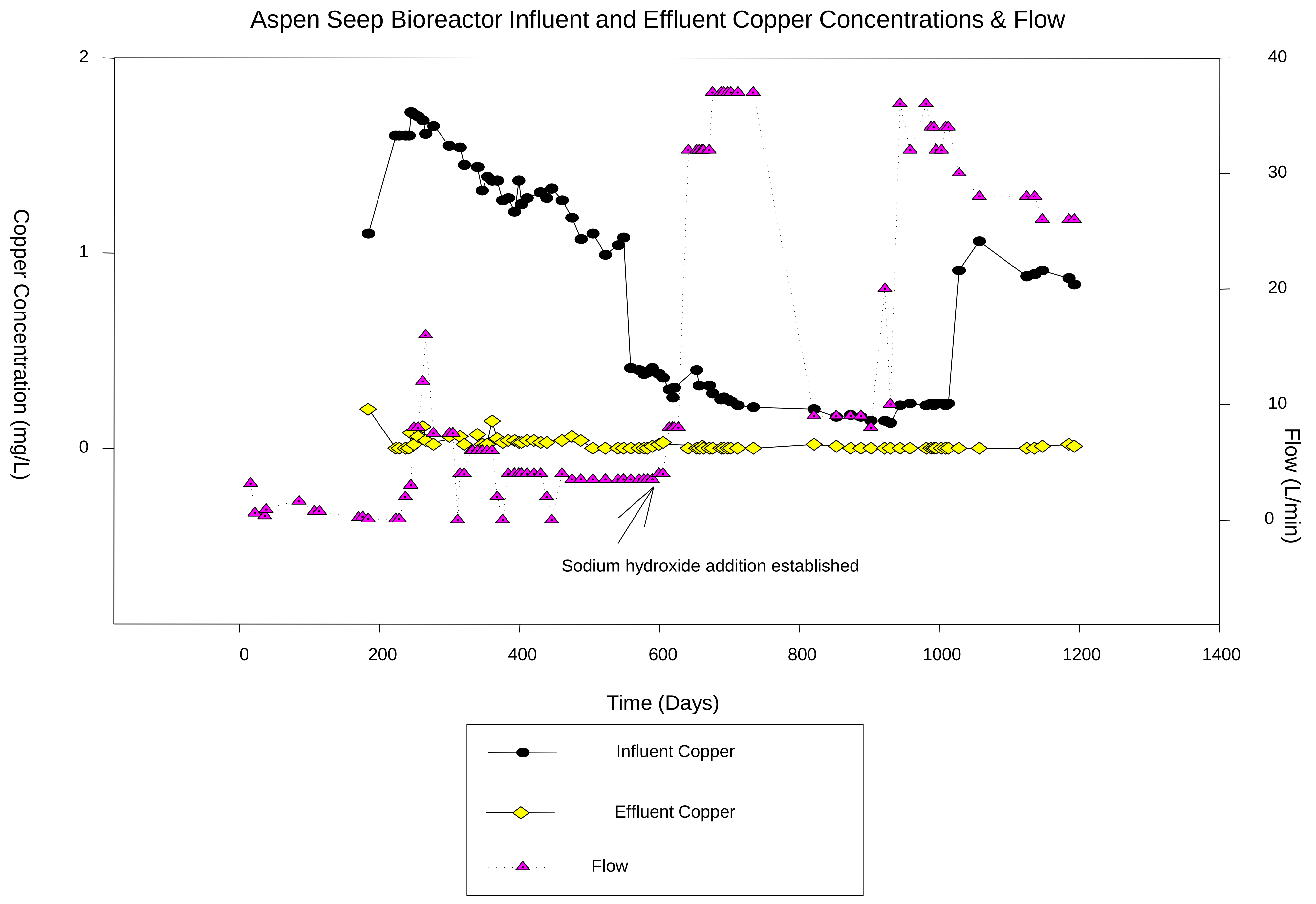
	Nickel (mg/L)	Copper (mg/L)	Zinc (mg/L)	Iron (mg/L)
Influent	0.14	0.28	1.75	83
Effluent	0.02	n.d.	n.d.	34
Effluent (settled)	0.02	n.d.	n.d.	0.7

Aspen Seep Bioreactor Iron Influent and Effluent Concentrations & Flow.

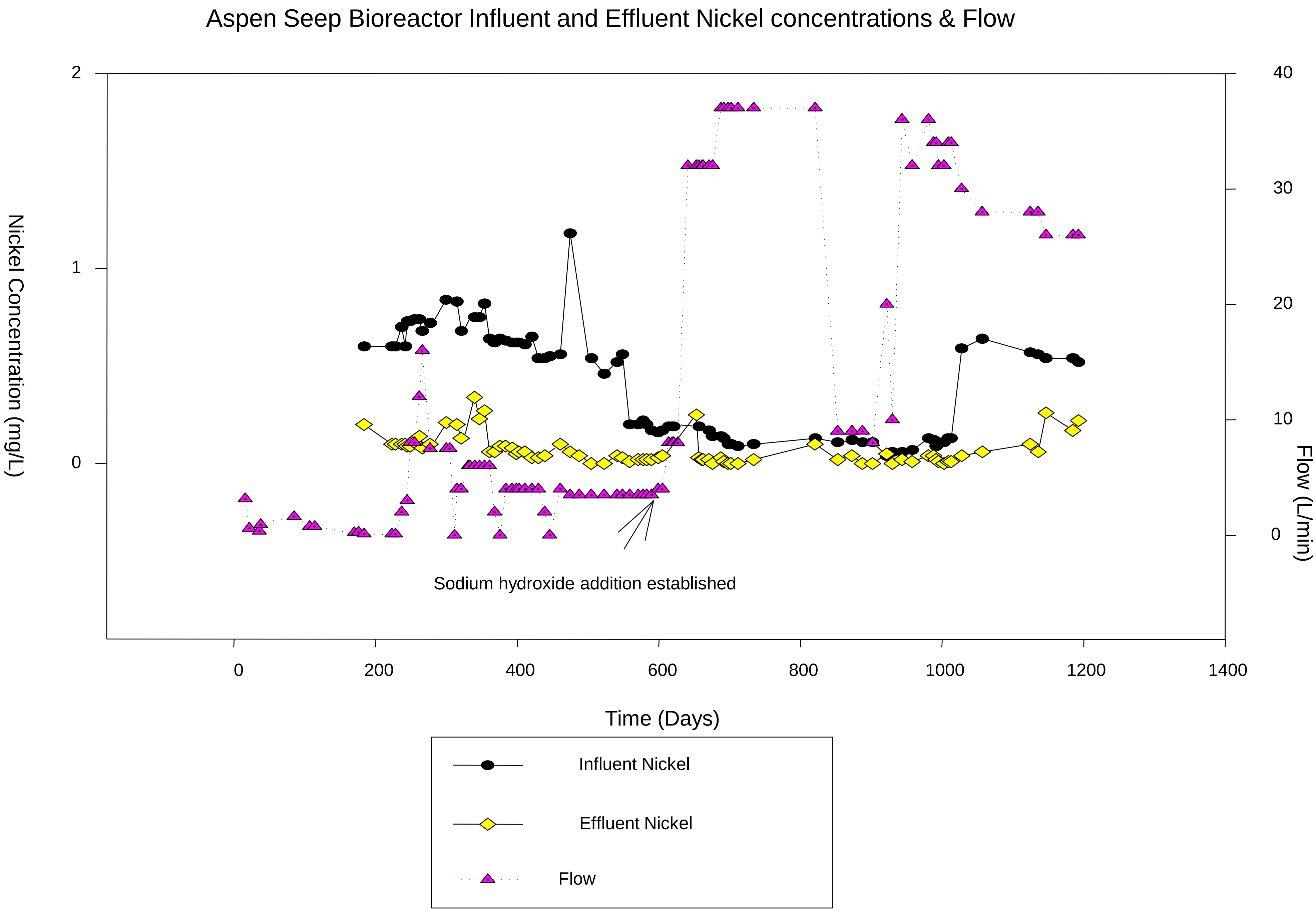




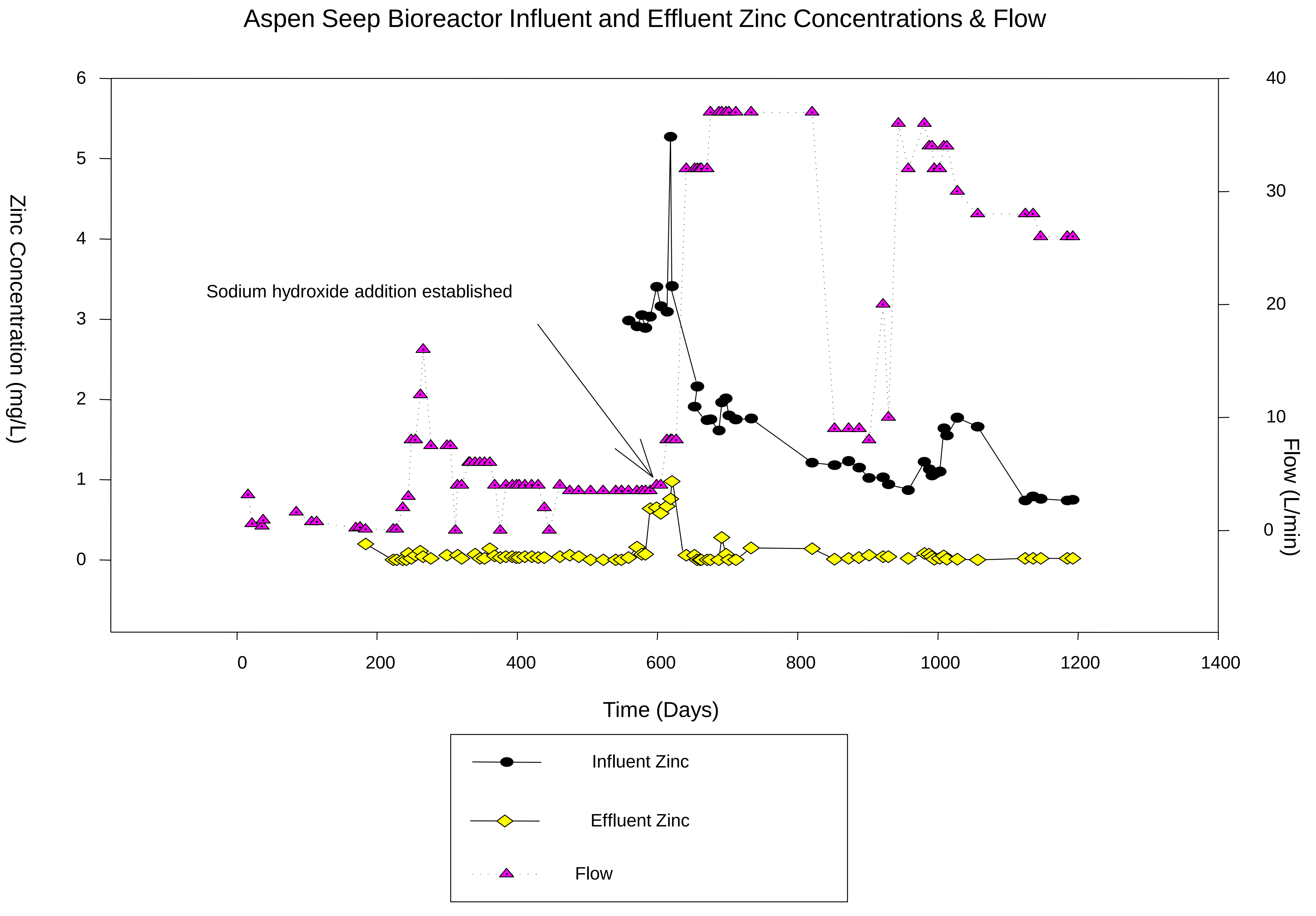
Aspen Seep Bioreactor Iron Influent and Effluent Concentrations
When pH > 6.5 in Effluent & Flow.
Sodium hydroxide addition established
Iron Concentration (mg/L)
350
300
250
200
150
100
50
0
Flow (L/min)
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Time (Days)
Influent Iron
Effluent Iron
Flow

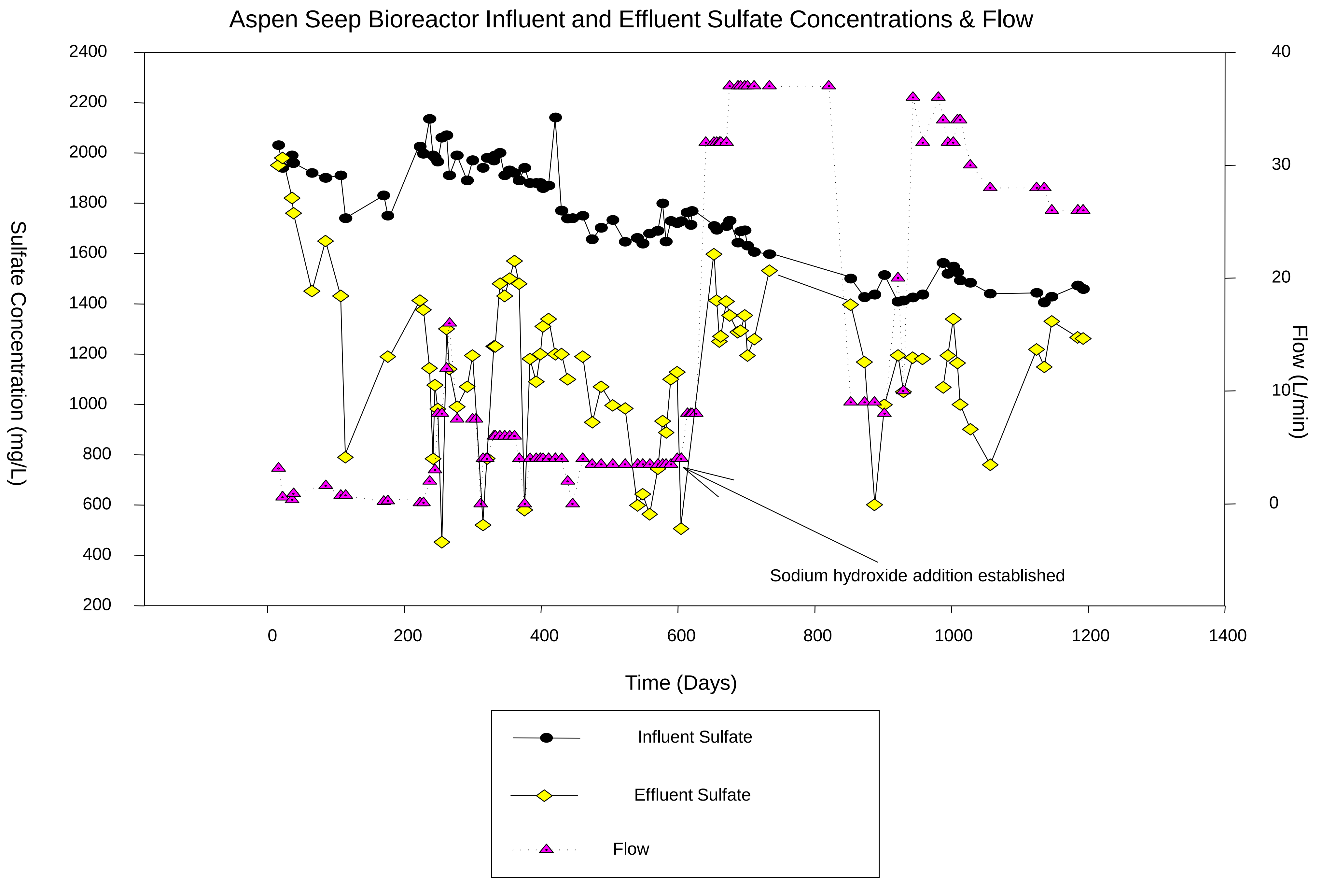


Aspen Seep Bioreactor Influent and Effluent Copper Concentrations & Flow
Copper Concentration (mg/L)
Flow (L/min)
Time (Days)
0
1
2
0
10
20
30
40
0
200
400
600
800
1000
1200
1400
Sodium hydroxide addition established
Influent Copper
Effluent Copper
Flow



Aspen Seep Bioreactor Influent and Effluent Nickel concentrations & Flow
Nickel Concentration (mg/L)
Flow (L/min)
Time (Days)
2
1
0
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Sodium hydroxide addition established
Influent Nickel
Effluent Nickel
Flow


Aspen Seep Bioreactor Influent and Effluent Zinc Concentrations & Flow
Sodium hydroxide addition established
Zinc Concentration (mg/L)
Flow (L/min)
Time (Days)
0
1
2
3
4
5
6
10
20
30
40
200
400
600
800
1000
1200
1400
Influent Zinc
Effluent Zinc
Flow



Aspen Seep Bioreactor Influent and Effluent Sulfate Concentrations & Flow
Sulfate Concentration (mg/L)
Flow (L/min)
Time (Days)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Sodium hydroxide addition established
Influent Sulfate
Effluent Sulfate
Flow

Sludge Management

- Sludge generated from bioreactors contains precipitated metal sulfides, aluminum hydroxide, and calcium carbonate
- The sludge needs to be managed appropriately or will simply re-oxidize and potentially release metals

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

Comparison of STLC and TTLC standards with sludge sample results

Element	Tests	Standard	Sludge sample
Cu	**STLC(mg/L)**	**25**	**0.9**
	TTLC(mg/kg)	**2500**	**75**
Ni	**STLC(mg/L)**	**20**	**1.4**
	TTLC(mg/kg)	**2000**	**60**
Zn	**STLC(mg/L)**	**250**	**0.60**
	TTLC(mg/kg)	**5000**	**30**

Cost

Average flow for Aspen Seep: flow = 32 L/min

SO_4^{2-} = 2000 mg/L

Fe_T = 100 mg/L

required: ethanol = 1500 gallons/year or $3,000/year

sodium hydroxide = 3150 lbs or $2,000/year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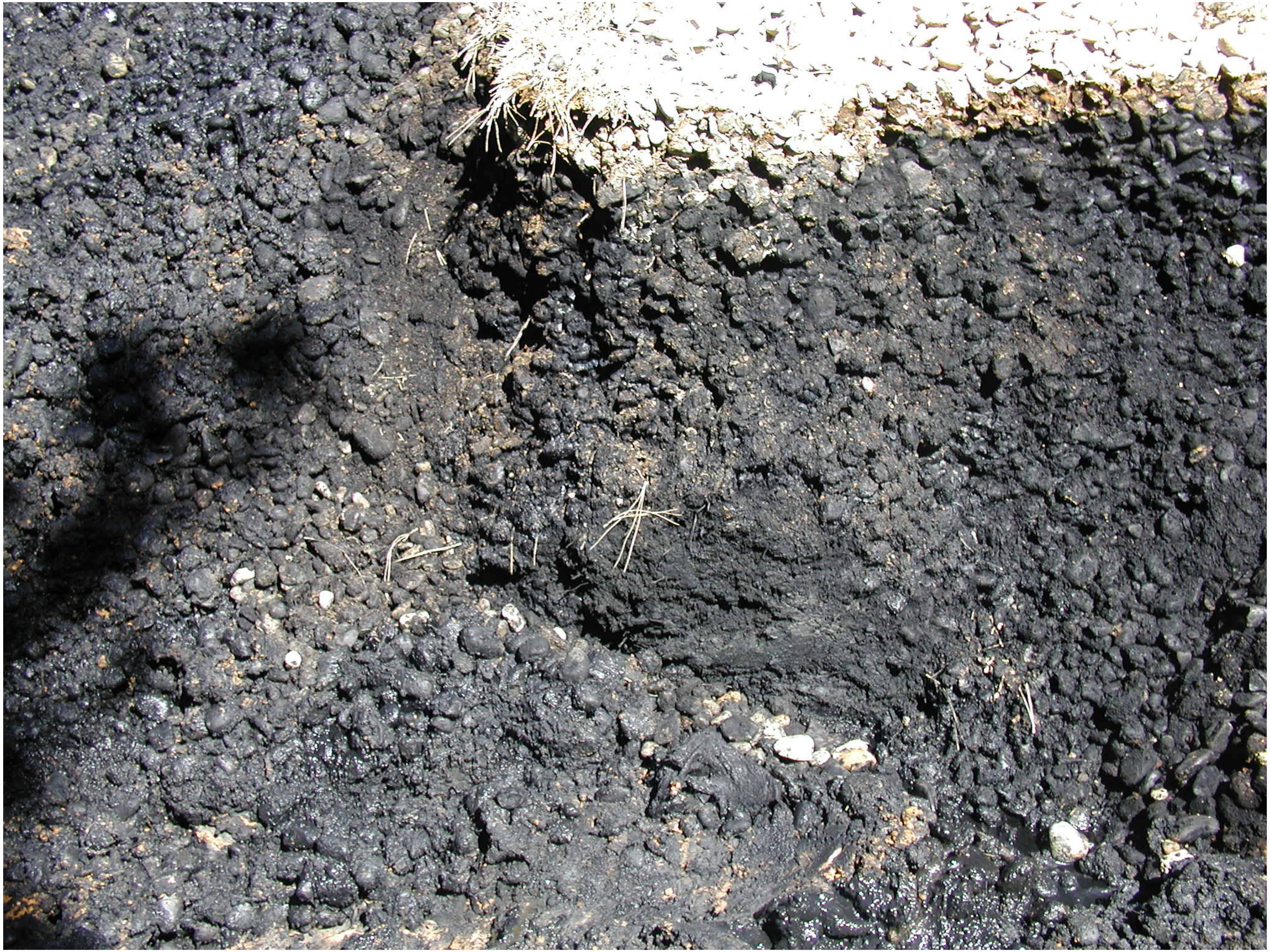

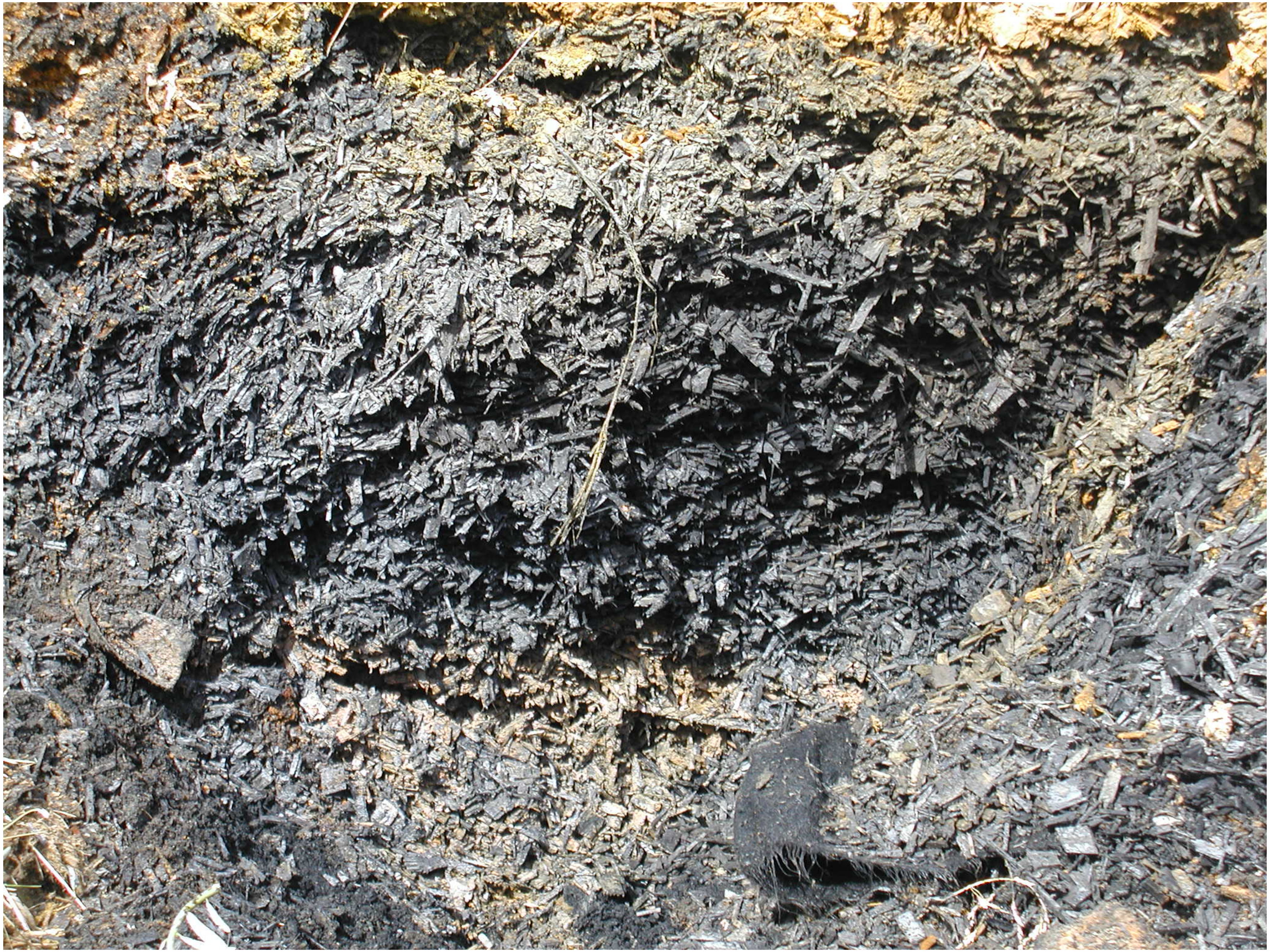

Vital Features of Alcohol Enhanced Bioreactor

-Flushing capability

-Proper influent and effluent pH

-Elimination of ponding on the surface

-Stable flow control of alcohol and base

- Sludge capture and management