ENHANCED SULFATE REDUCTION TREATMENT OF MINING-INFLUENCED WATER USING BIOCHEMICAL REACTORS

IMPACTS ON MERCURY SPECIATION

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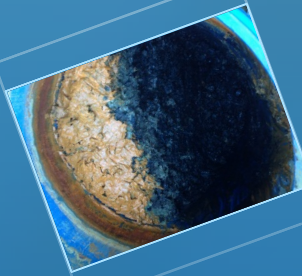
National Conference on Mining-Influenced Waters

Approaches for Characterization, Source Control and Treatment

Albuquerque, NM

August 13, 2014



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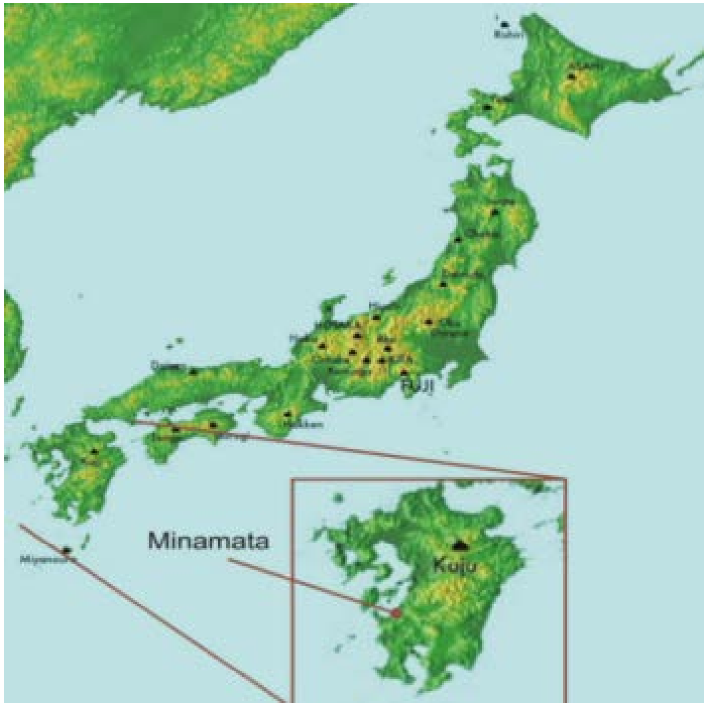
Presentation Objectives

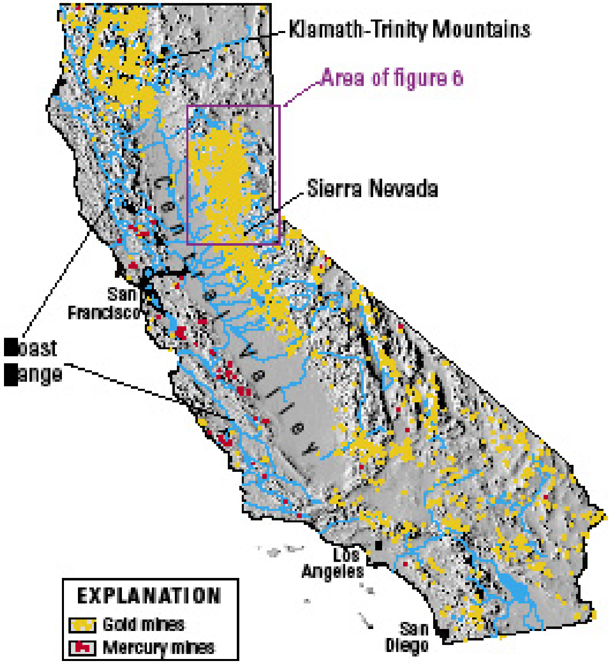
- Mercury in the Environment
  - Prevalence
  - How a Mole Hill Turns into a Mountain
- Biochemical Reactors – Mining Impacted Water
  - Formosa Treatability Study
  - ORD Bench Top Study
- General Conclusions
- Recommendations for Moving Forward

Anthropogenic Point Source Impacts

Minamata Bay

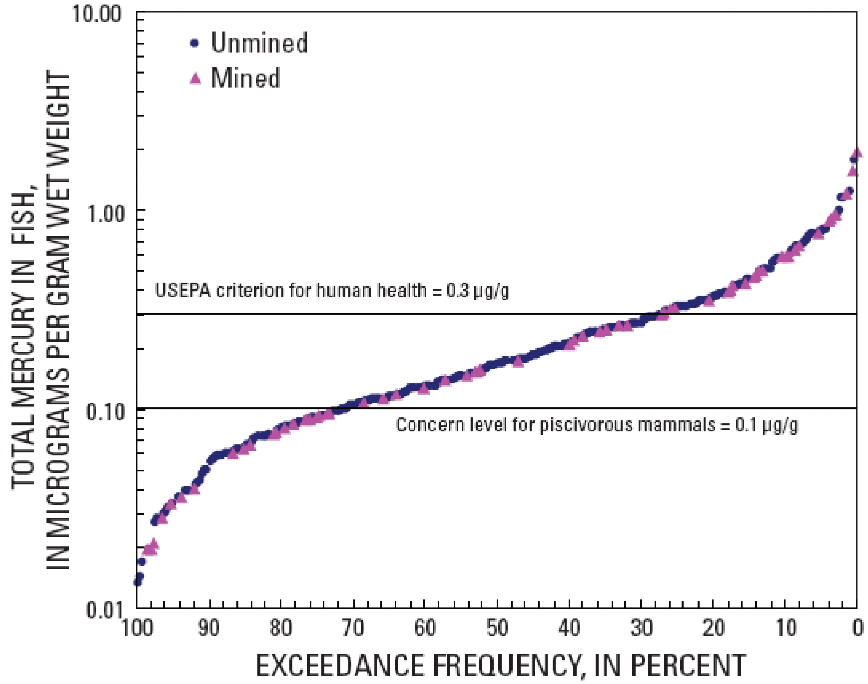


California Gold/Mercury Mines



Non-Point Source Impact

- 367 Stream Sites Sampled Across United States
- Sites with Fish Greater than 0.3 µg/g
  - 25% Exceedances
- Sites with Fish Greater than 0.6 µg/g
  - 10% Exceedances



Bioaccumulation

Wood et al., 2013

100,000x

Algae

2-5x

Zooplankton

2-5x

Prey Fish

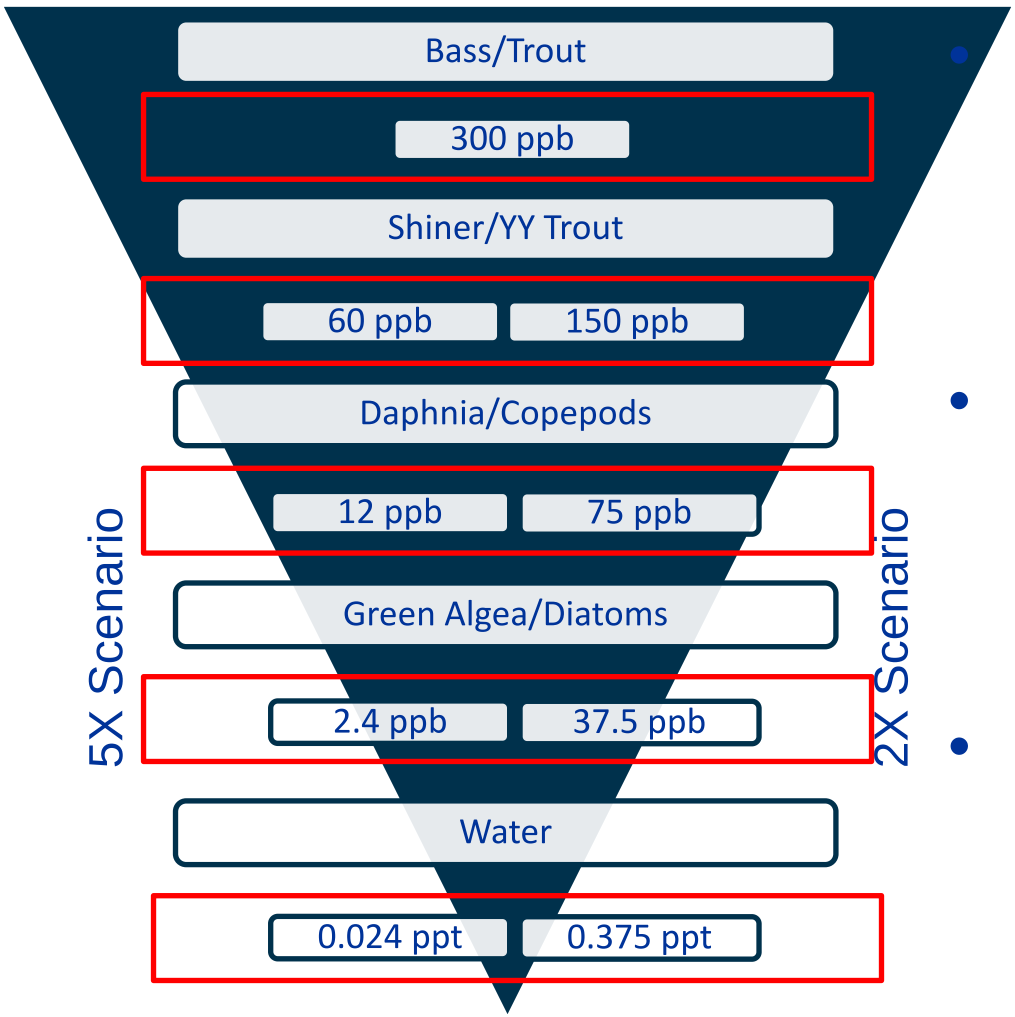
2-5x

Predator Fish

$$BAF = C_B / C_{DW}$$

- BAF = Bioaccumulation Factor (1/kg)
  - (Gobas and McCorquodale, 1992)
- C_B = Concentration in Biota or Particle (ng/kg)
- C_{DW} = Concentration Dissolved in Water (ng/L)

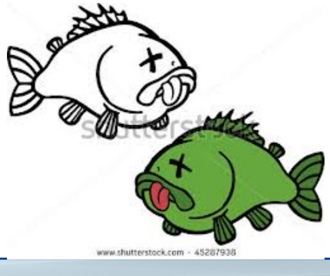
Working the Problem Backwards (MeHg)



- USGS: Mean, ng/L
  - All Sites: 0.19
  - Unmined: 0.2
  - Mined: 0.18
- Range, ng/L
  - All Sites: 4.11-ND
  - Unmined: 4.11 – ND
  - Mined : 2.02 – ND
- California Water Control Board:
  - 0.06 ng/L – Implementation Goal

Mine Impacted Water

- "Aqueous waste generated by ore extraction and processing, as well as mine drainage and tailings runoff." ~ITRC, 2013
- AMD: Sulfidic Rock in Contact with Surface Water and Oxygen
  - pH Decreases
  - Metals Dissolve



Biochemical Reactors

- BCRs are engineered systems that use an organic substrate (electron donor) to drive microbial and chemical reactions to reduce concentrations of metals, acidity, and sulfate in MIW.

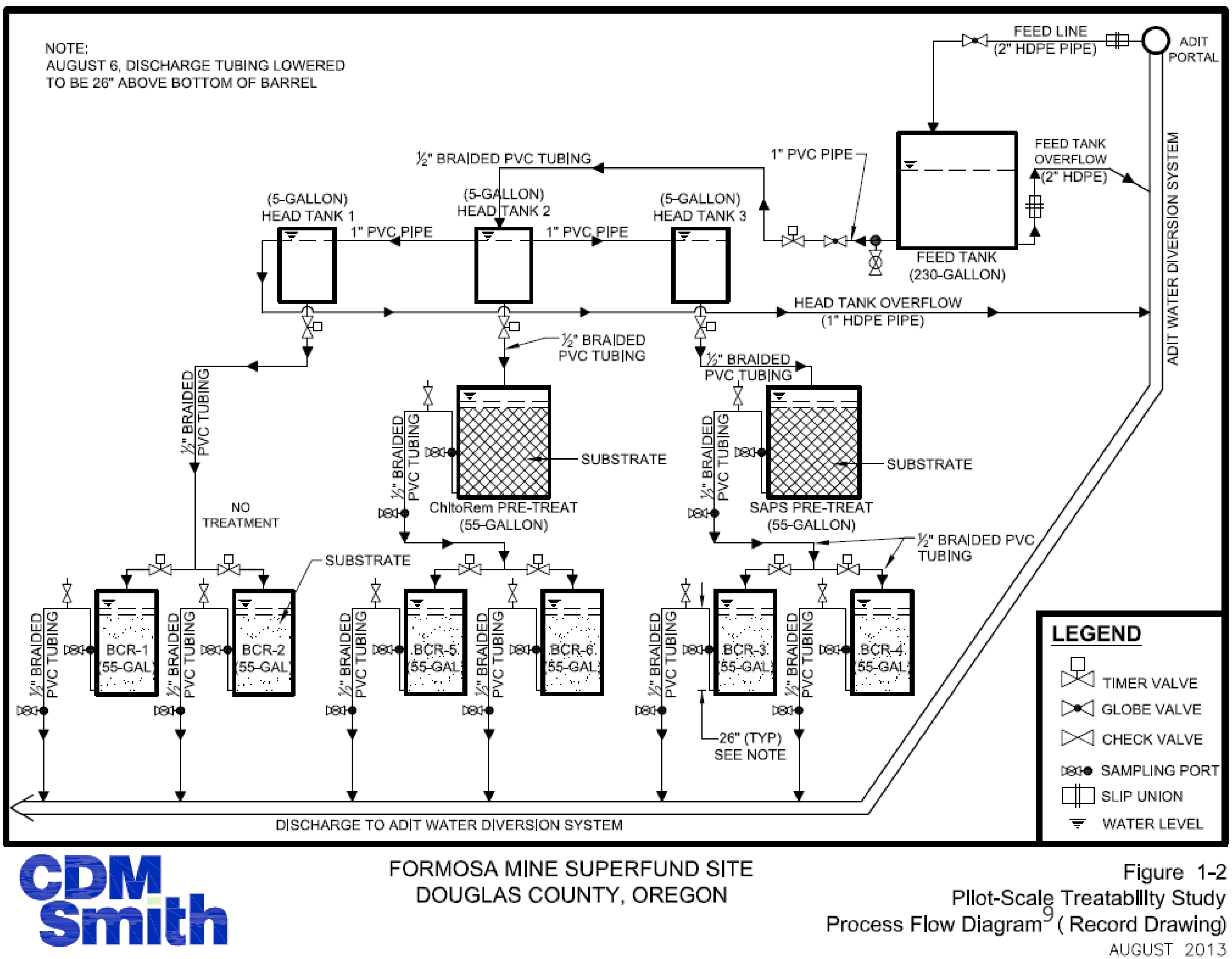
  - ChitoRem® SC-20
  - Woody Substrate/Manure Including Limestone

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

  - $S^{2-} + Me^{2+} \rightarrow MeS(s)$ and $HS^- + Me^{2+} \rightarrow MeS(s) + H^+$

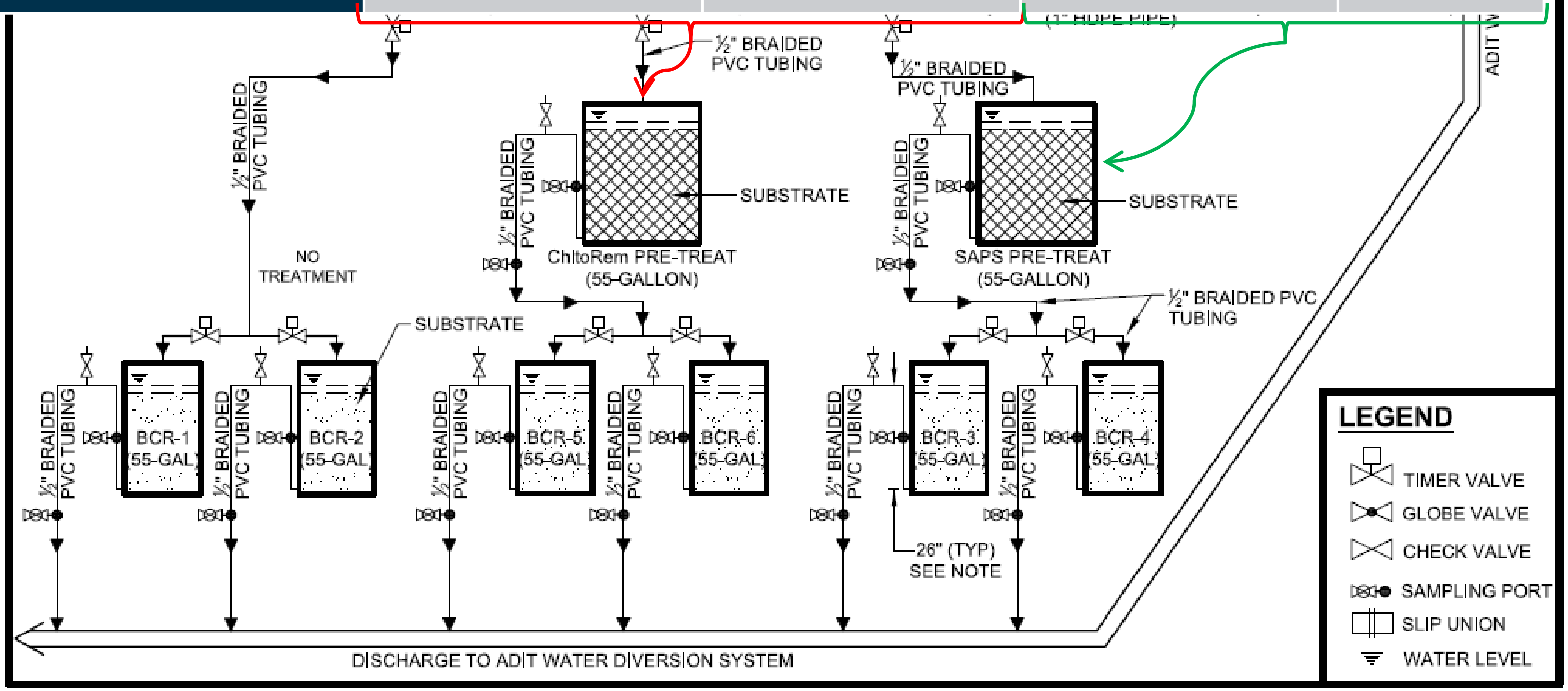
  - See Angela Frandsen's Talk; Section 10 @ 1:30 Today

Treatability Study Flow Diagram



Treatability Study Flow Diagram

Composition	Pre-Treatment ChitoRem®		Pre-Treatment SAPS	
	Substrate Mix (v/v Percent)	Volume (gallon)	Substrate Mix (v/v Percent)	Volume (gallon)
Compost	--	--	12.50	4.38
Fresh dairy manure	--	--	12.50	4.38
Limestone chips 3/4-inch to 1.5-inch	--	--	75.00	26.25
3/4-inch inert gravel	--	7.50	--	7.50
ChitoRem®	40	14.00	--	--
Construction sand	40	21.00	--	--
Inert pea gravel	20	7.00	--	--
Total	100	49.50	100.00%	42.51

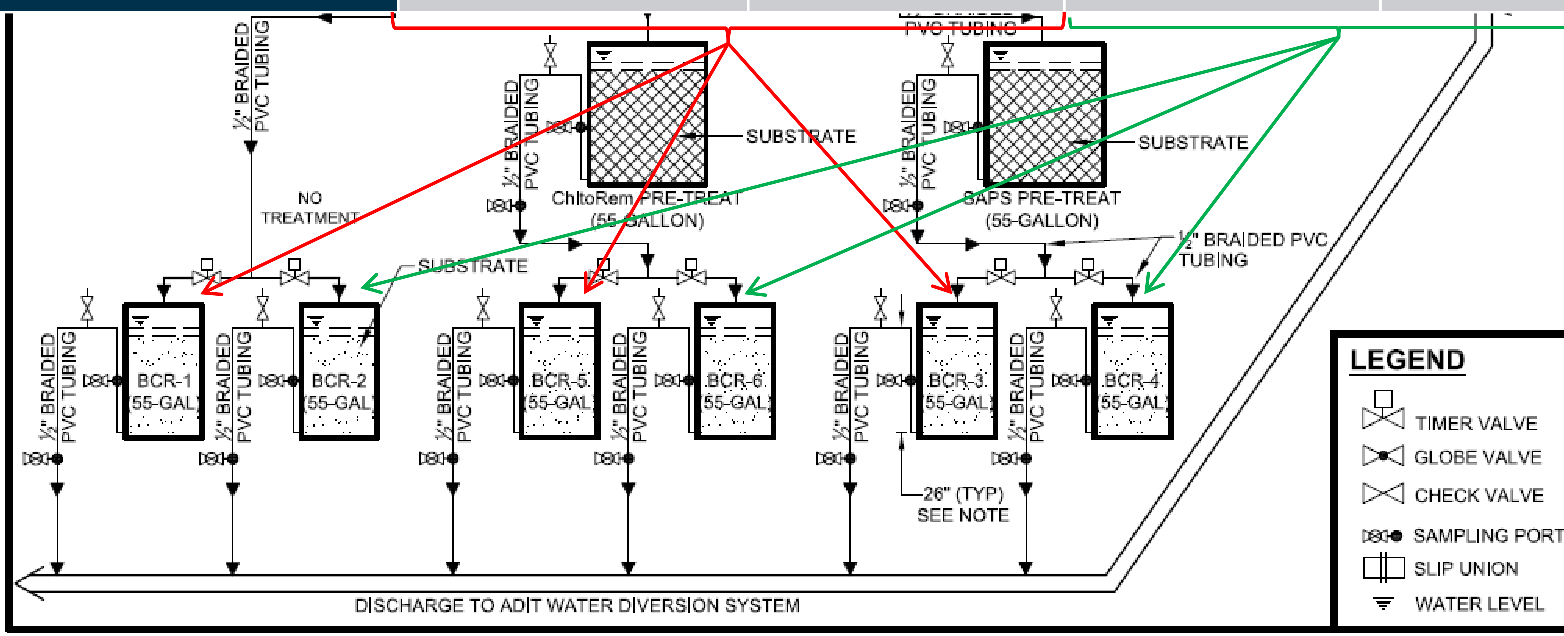


FORMOSA MINE SUPERFUND SITE
DOUGLAS COUNTY, OREGON

Figure 1-2
Pilot-Scale Treatability Study
Process Flow Diagram (Record Drawing)
AUGUST 2013

Treatability Study Flow Diagram

Composition	Woody Material Mixture		ChitoRem® and Sand Mixture	
	Substrate Mix (v/v Percent)	Volume (gallon)	Substrate Mix (v/v Percent)	Volume (gallon)
Sawdust	15.00	5.25	--	--
Wood chips	30.00	10.50	--	--
Compost	15.00	5.25	--	--
Fresh dairy manure	20.00	7.00	--	--
Limestone chips 3/4-inch to 1.5-inch	20.00	7.00	--	--
3/4-inch inert gravel	--	7.50	--	7.50
ChitoRem®	--	--	40.00	14.00
Construction sand	--	--	40.00	21.00
Inert pea gravel	--	--	20.00	7.00
Total	100.00	42.50	100.00	49.50



FORMOSA MINE SUPERFUND SITE
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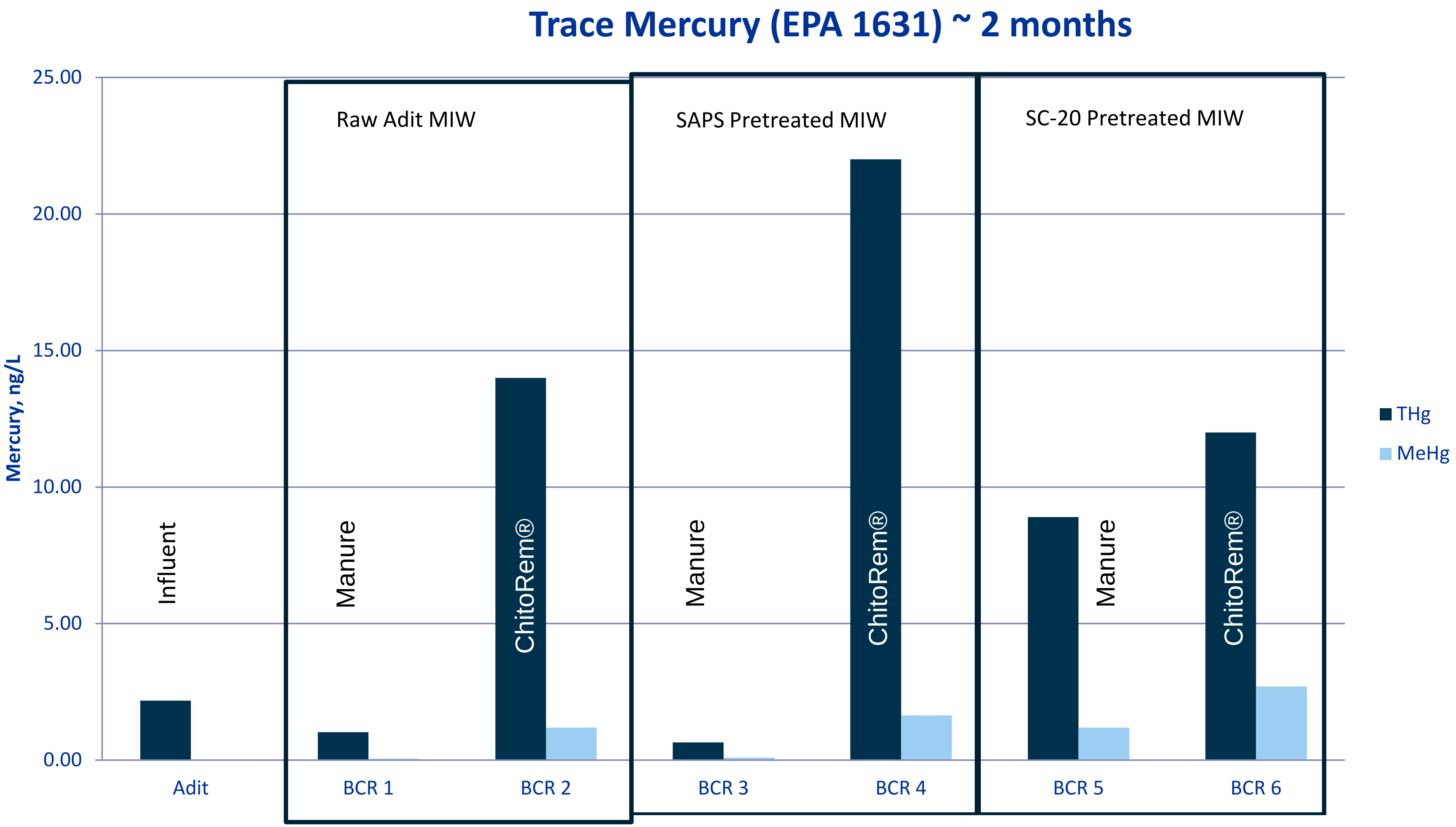
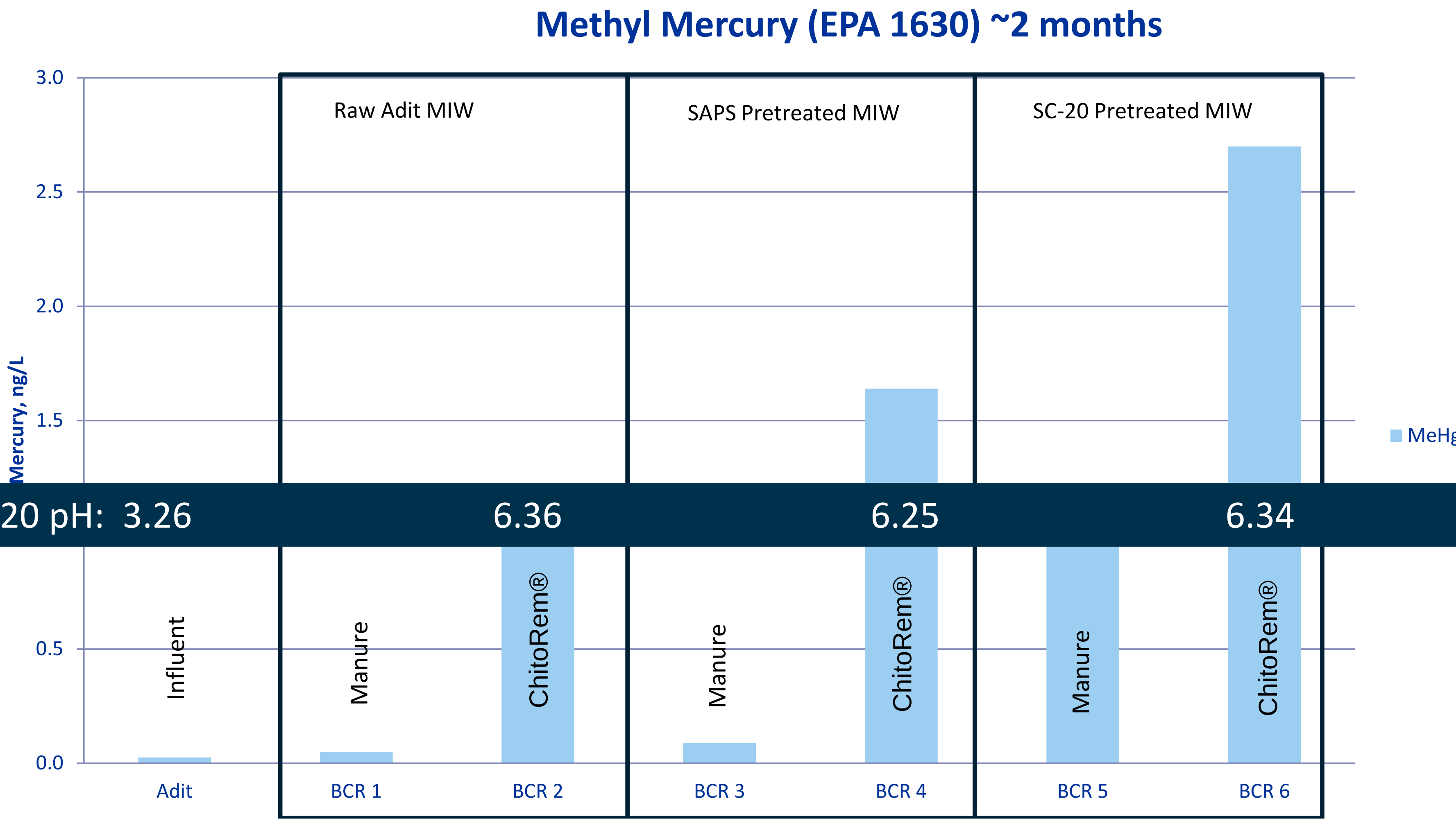
Figure 1-2
Pilot-Scale Treatability Study
Process Flow Diagram (Record Drawing)
AUGUST 2013

Mercury Results



Mercury Results (Continued)



SC-20 pH: 3.26 6.36 6.25 6.34

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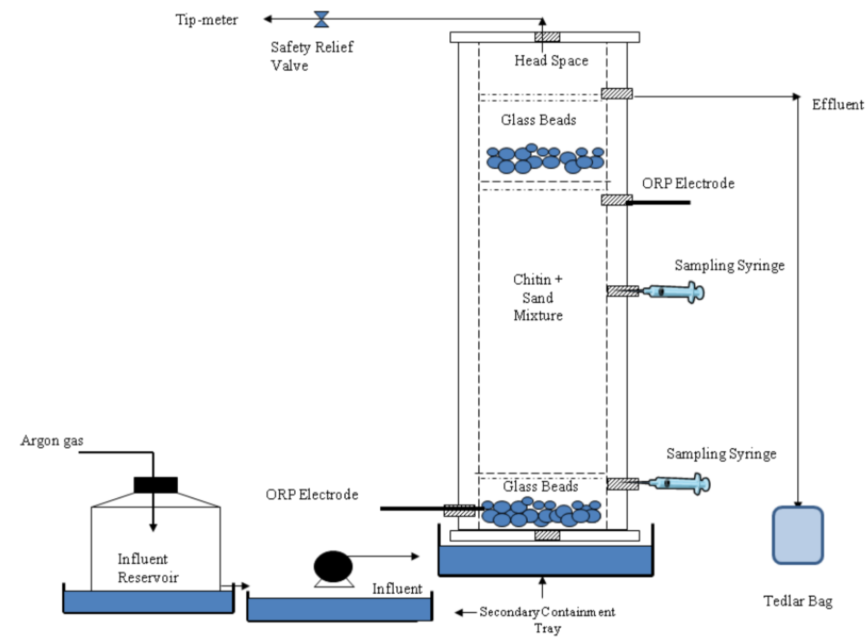
Formosa Mercury Evaluation Summary

- All SC-20 BCRs Increased THg and MeHg
  - THg Increased by 10 to 20 ng/L
  - MeHg Increased by 1 to ~3 ng/L
- THg Potentially Sourced from Media
  - Crab Hg Body Burden ~ 0.16 mg/kg
- MeHg From Release Or Generation
  - Potential Resident Source:
    - Aquatic Organisms Typically Enriched in MeHg
  - Potential MeHg Generation from Resident and Influent Hg(II)
    - Evidence of SRB Activity
      - ORP, Sulfide, Volatile Fatty Acids

ORD Bench Top Study

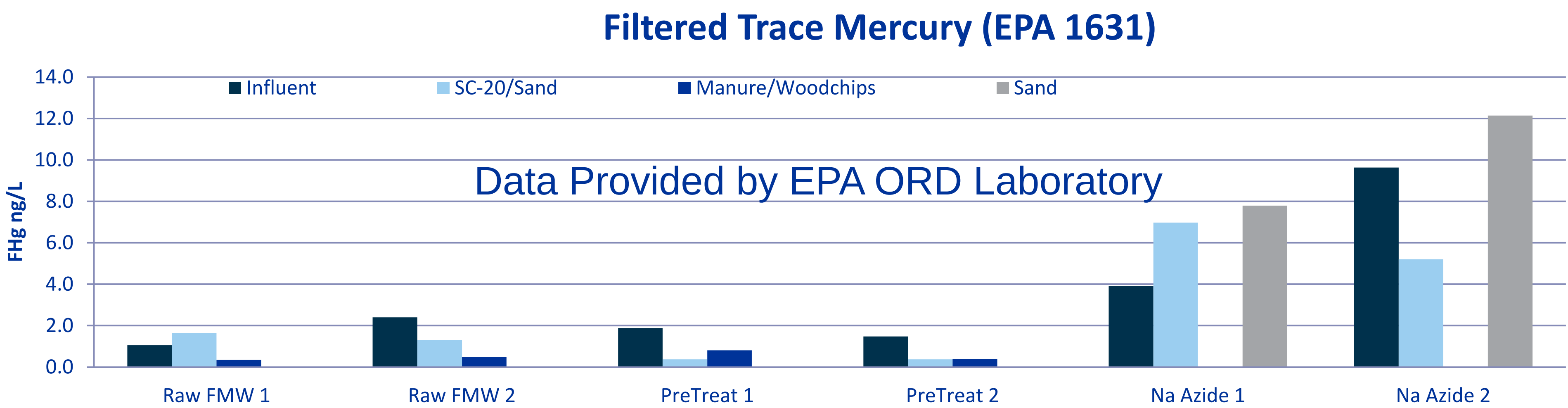


Influent and Column Specifics

24 hr Hydraulic Residence Time

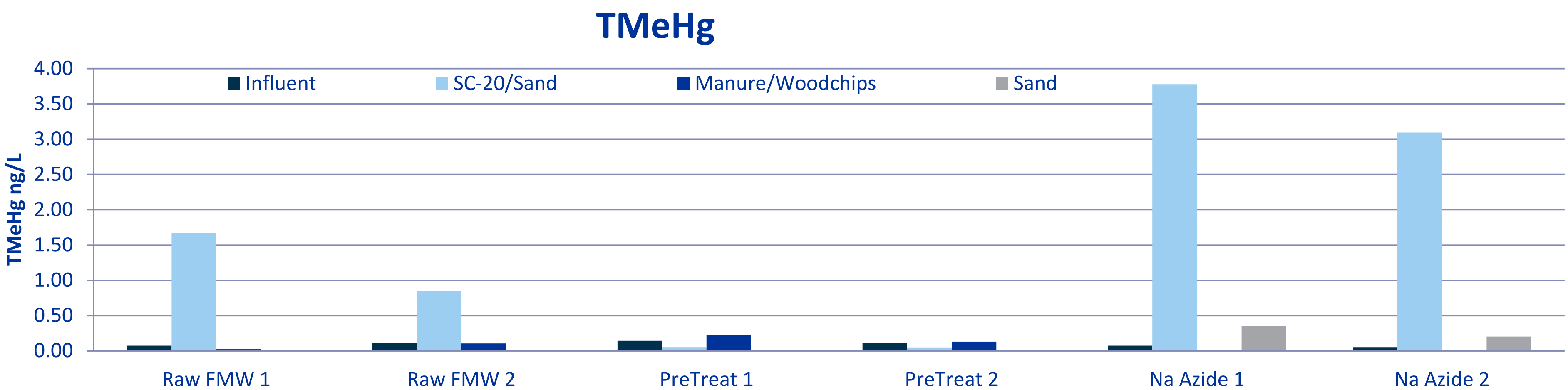
- Column 1: SC-20 (140 g) + sand (420 g) – Pretreated MIW
- Column 2: Wood Chips (253 g) + Hay (17 g) + Manure (4 g) – Pre
- Column 3: SC-20 (140 g) + Sand (420 g) – Raw MIW
- Column 4: Wood Chips (253 g) + Hay (17 g) + Manure (4 g) – Raw
- Column 5: SC-20 (140 g) + Sand (420 g) – Na Azide Raw MIW
- Column 6: Sand (420 g) – Na Azide Raw MIW

Total Filtered Mercury: 31 and 34 Weeks into Test



- Dissolved Fraction (<0.45 um) Comparable to Field Study
  - Fraction Most Available for Methylation
- Raw FMW Columns ~ GLI 1.3 ng/L
- PreTreat Columns < GLI 1.3 ng/L
- Na Azide Columns >> GLI 1.3 (With Elevated Hg Influent)

Methylmercury 31 and 34 Weeks into Test



Data Provided by EPA ORD Laboratory

Evidence of SRB Activity:

- SRB Lab Test: (+) In Raw and Pretreat Columns
- Elevated Volatile Fatty Acid In Raw and Pretreat Columns
- pH Elevated in Raw and Pretreat Columns
- ORP Depressed in Raw and Pretreat Columns

- ORD Bench Top Study

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Bench Top Study Observations

- SC-20 Pretreated: THg and MeHg Maintained Below Levels of Concern (1.3 ng/L for THg GLI & 0.06 ng/L for MeHg CWCB)
- SC-20 Effluent (Raw & Na Azide) ~75% MeHg in Dissolved Fraction
- Natural Production of MeHg Typically ~**5%** of Total
- MeHg as THg
  - Raw FMW: 0.4 to 0.5
  - Pretreat: 0.08
  - Na Azide: 0.5 to 0.6

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Key Difference Between Lab and Field Test

- Duration:
  - Field Test Sampled One Time ~2 Months Into Test
  - Lab Test Sampled Twice, at 7 and 8 Months Into Test
- Flow Consistency:
  - Field Test Flow Decreased Over Time
    - Much of Media Left Unreacted
  - Lab Test Flow Remained Consistent
- Variability of Mercury Concentrations in Influent
  - Formosa Adit Stable
    - ~ 2 ng/L
  - ORD Laboratory Influent
    - Range 1.1 to 9.6 ng/L

General Conclusions

- Effect on Total Mercury
  - Field Test: THg Increased in all SC-20 BCRs
  - Lab Test: THg Decreased in all Columns
- MeHg in SC-20 Effluent Elevated relative to Influent
  - Two Possible Explanations
    - SRB Activity Methylate Hg(II) to MeHg, or
    - Resident MeHg Released from Media
- Need for More In Depth Evaluation to Quantify and Understand Mercury Dynamics Associated with the Application of SC-20 in MIW Applications

Recommendations for Further Study

- Fully Quantify Resident Mercury Concentration and Speciation in BCR Media
  - Both SC-20 and Sand
- Evaluate Conditions that Promote Mercury Release from BCR Media
- Evaluate Conditions that Promote Methylation of Hg(II)
  - From Influent Source
  - From Resident Source

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Questions?

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