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AN ENVIRONMENTAL SERVICES FIRM

TETRA TECH

Ambatovy

Bench Scale Hexavalent Chromium Removal with a Biochemical Reactor

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Presentation Outline

- Passive Treatment Process Background
- Chemical Reactions
- Process Components
- Site Background
- Test Setup
- Results
- Conclusions/Path Forward

P.T. Metal Removal Mechanisms

Major

- Sulfide and carbonate precipitation via sulfate reducing bacteria, et al.
- Hydroxide and oxide precipitation by *thiobacillus ferro-oxidans* bacteria, et al.
- Filtering of suspended materials and precips
- Carbonate dissolution/replacement

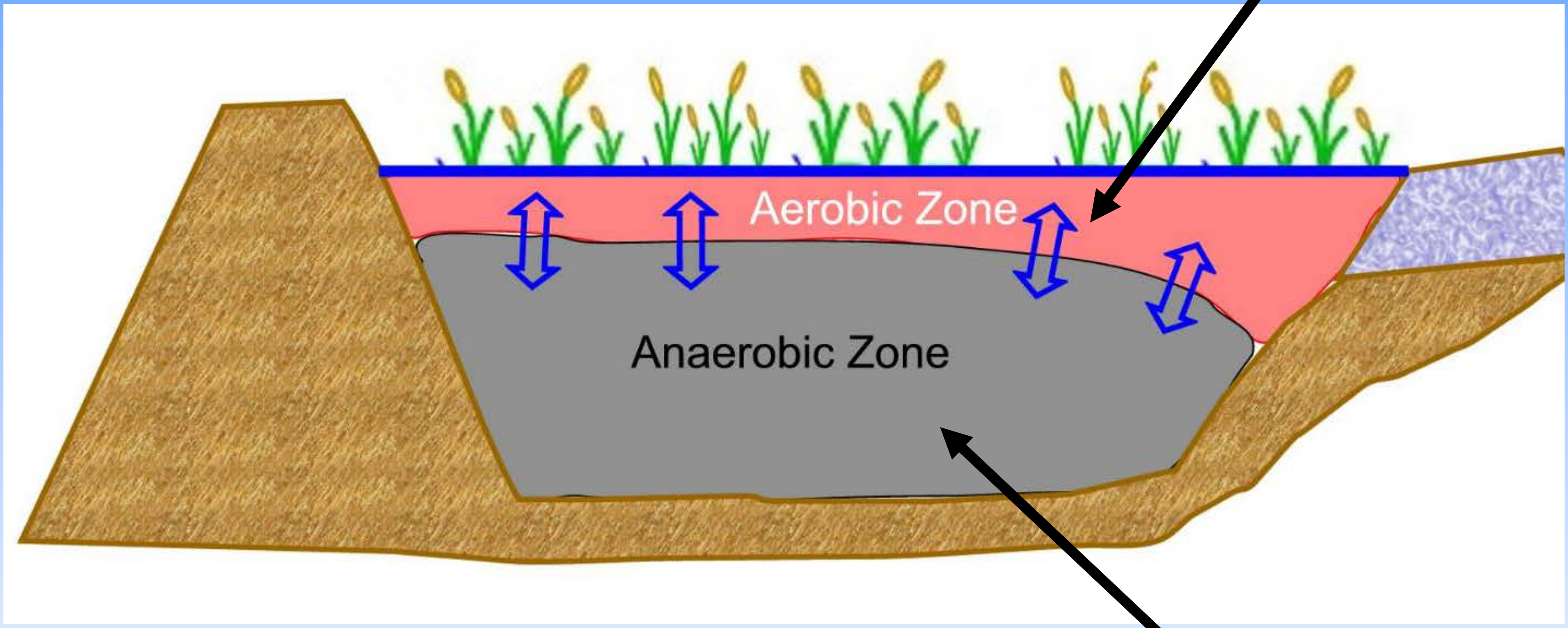
Minor

- Metal uptake into live roots, stems and leaves
- Adsorption and exchange with plant, soil and other biological materials

?

Typical Wetland Ecosystem

(oxidizing conditions)



Sulfate Reducing Bacteria (SRB's) live here (reducing conditions)

Oxidation and Reduction

Processes in Competition

Sulfate Reducing Bacteria (SRB's) live here (reducing conditions)

Thiobacillus - F. O. **live here (oxidizing conditions)**

Passive Treatment Chemistry 101

Could also be alcohol or sugar

REDUCING/ ANAEROBIC CONDITIONS

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

(Sulfate reduction and neutralization by bacteria)

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

(Sulfide precipitation)

OXIDIZING CONDITIONS

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

(Hydroxide precipitation)

ALL CONDITIONS

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

(Limestone dissolution)

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^+ + $6H_2O$ + $2SO_4^{2-}$ => $KAl_3(OH)_6(SO_4)_2$ (Alunite) + $6H^+$

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

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

What Happens to Hexavalent Chromium?

Previous Study: **T. Ozawa, R. Cohen, and R. Klusman, 1995**

At steady state:

Reduce Cr^{+6} to Cr^{+3}

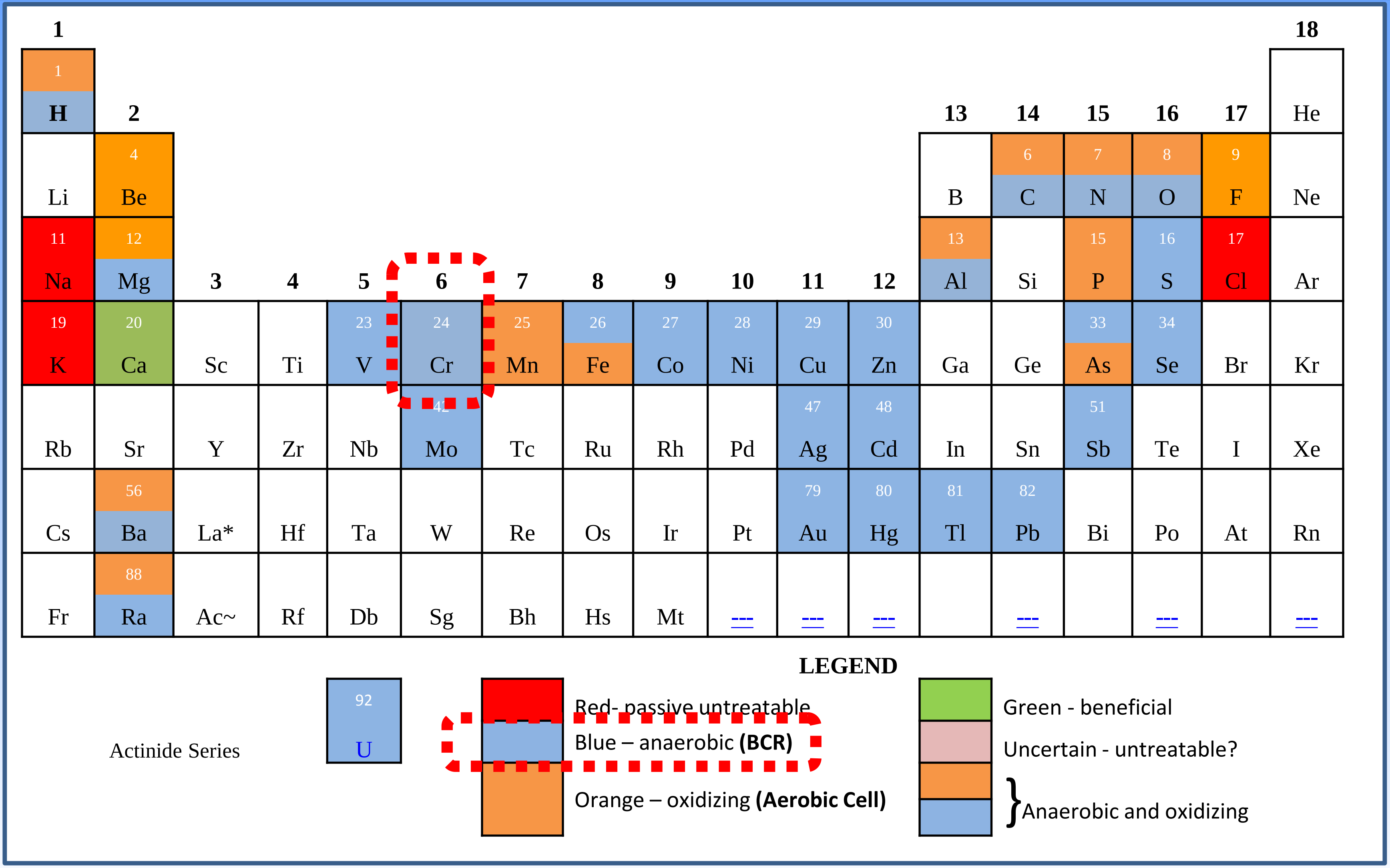
$$3S^{-2} + 8\,H^{+} + 4CrO_4^{-2} \Rightarrow 4Cr^{+3} + 4\,H_2O + 3SO_4^{-2}$$

Hydrolyze Cr^{+3} to Chromium Hydroxide

$$4Cr^{+3} + 12\,H_2O \Rightarrow 4\,Cr(OH)_3 + 12\,H^{+}$$

Chromium hydroxide is similar to aluminum hydroxide in behavior

Periodic Table of Passive Treatment (2009)



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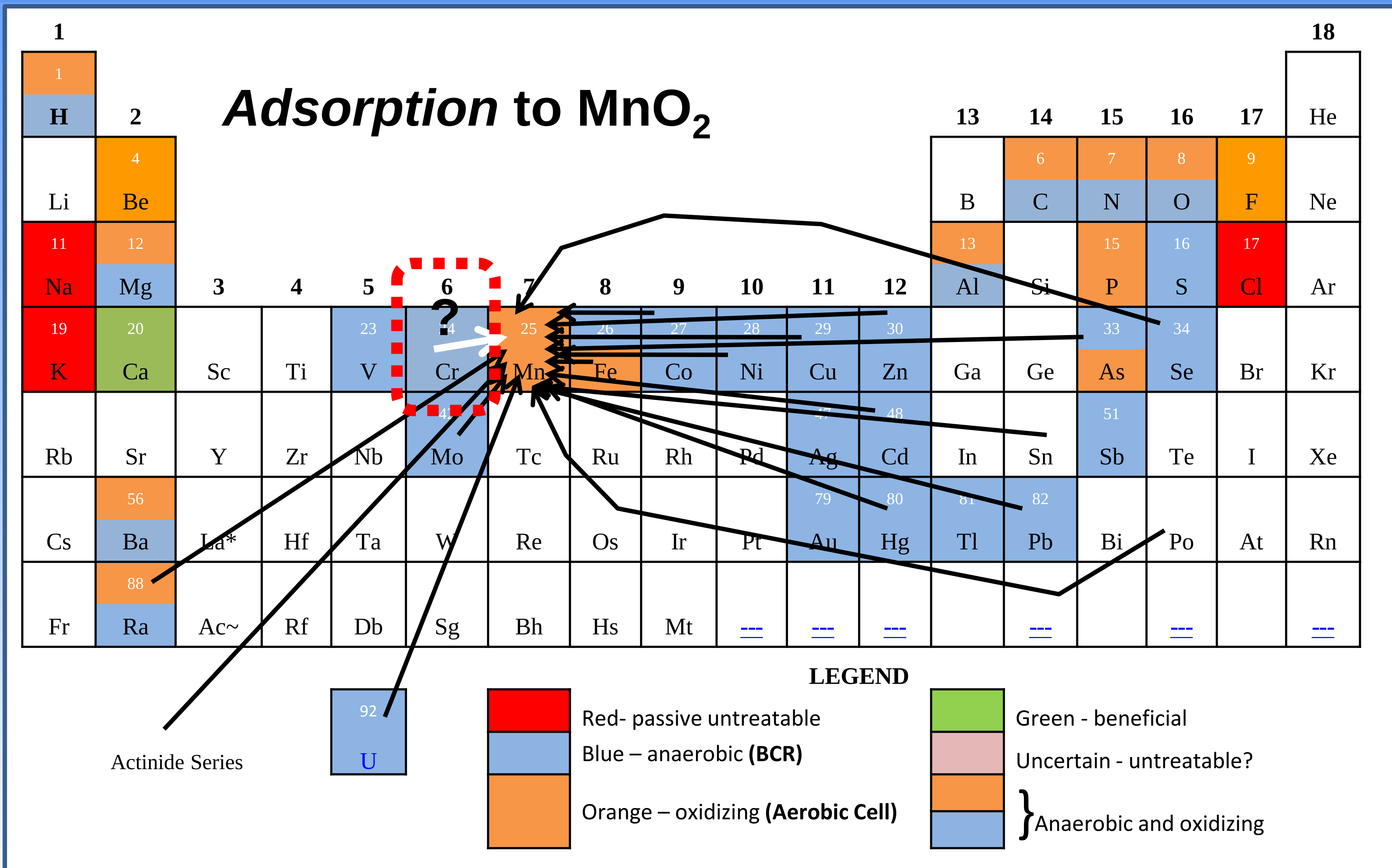
2016 Periodic Table of Passive Treatment (Revisited)



Passive Treatment System Components

Biological Components

- Anaerobic Biochemical Reactors (BCRs)
- Aerobic Cells or Rock Filters
- Successive Alkalinity Producing Systems (SAPS)

Limestone Components

- Limestone Sand
- Anoxic Limestone Drains (ALD's)
- Alkaline Ponds
- Open Limestone Channels

- Manganese Removal Beds

Settling Ponds & Flow Equalization Ponds

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

BCR Cell Construction – Substrate Placement

Aerobic Polishing Wetland Cells

Fe, As, **Biochemical Oxygen Demand (BOD),** and Mn removal

(plus adsorbed metals)

AKA Rock Filters

Passive Cell Design Parameters

NO COOKBOOK (YET)

- MIW Geochemistry (cell sequencing & cell type)
- Metal Loading = (concentration X flow rate)
- Surface Area is a function of loading
- Cell Depth can be a function of loading

PHOTOS & SITE MAP

North Dam (Source Water)

SITE PHOTOS

Passive Treatment Staged Design Phases

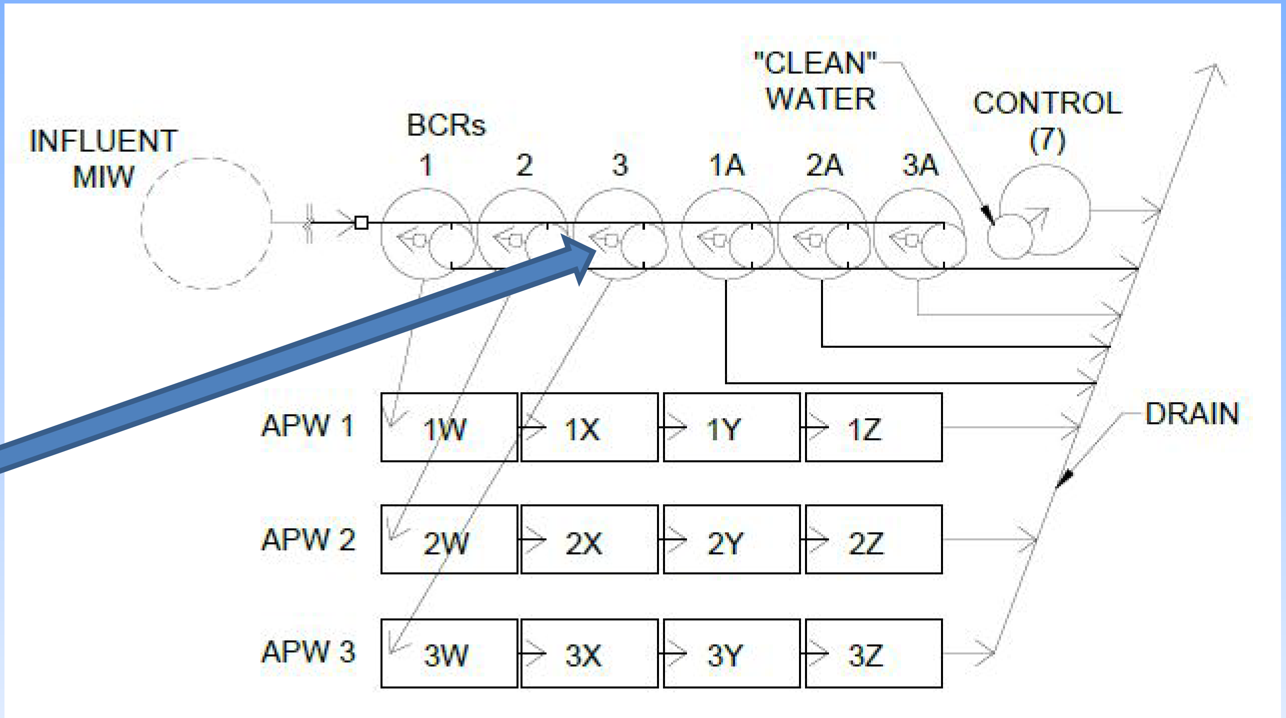
- Lab (proof of principle) tests
- Bench tests
- Pilot tests
- Limited full scale (modules)
- Full scale implementation

Ambatovy - Passive Treatment System

Test Arrangement

Biochemical Reactor (BCR)

Test Layout Plan



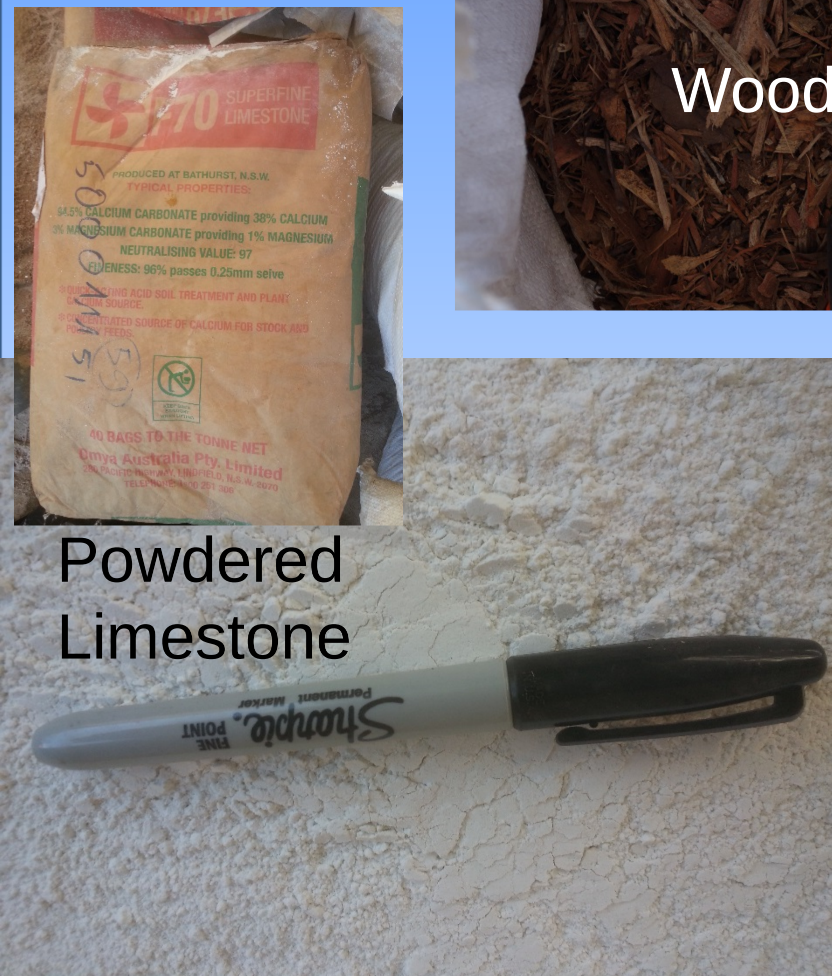
Ambatovy - Passive Treatment System

Test Arrangement

Biochemical Reactors (BCRs): 1, 2, 3, 1A, 2A, 3A, Control

Aerobic Polishing Wetlands (APWs): 1, 2, 3

BCR Substrate Materials



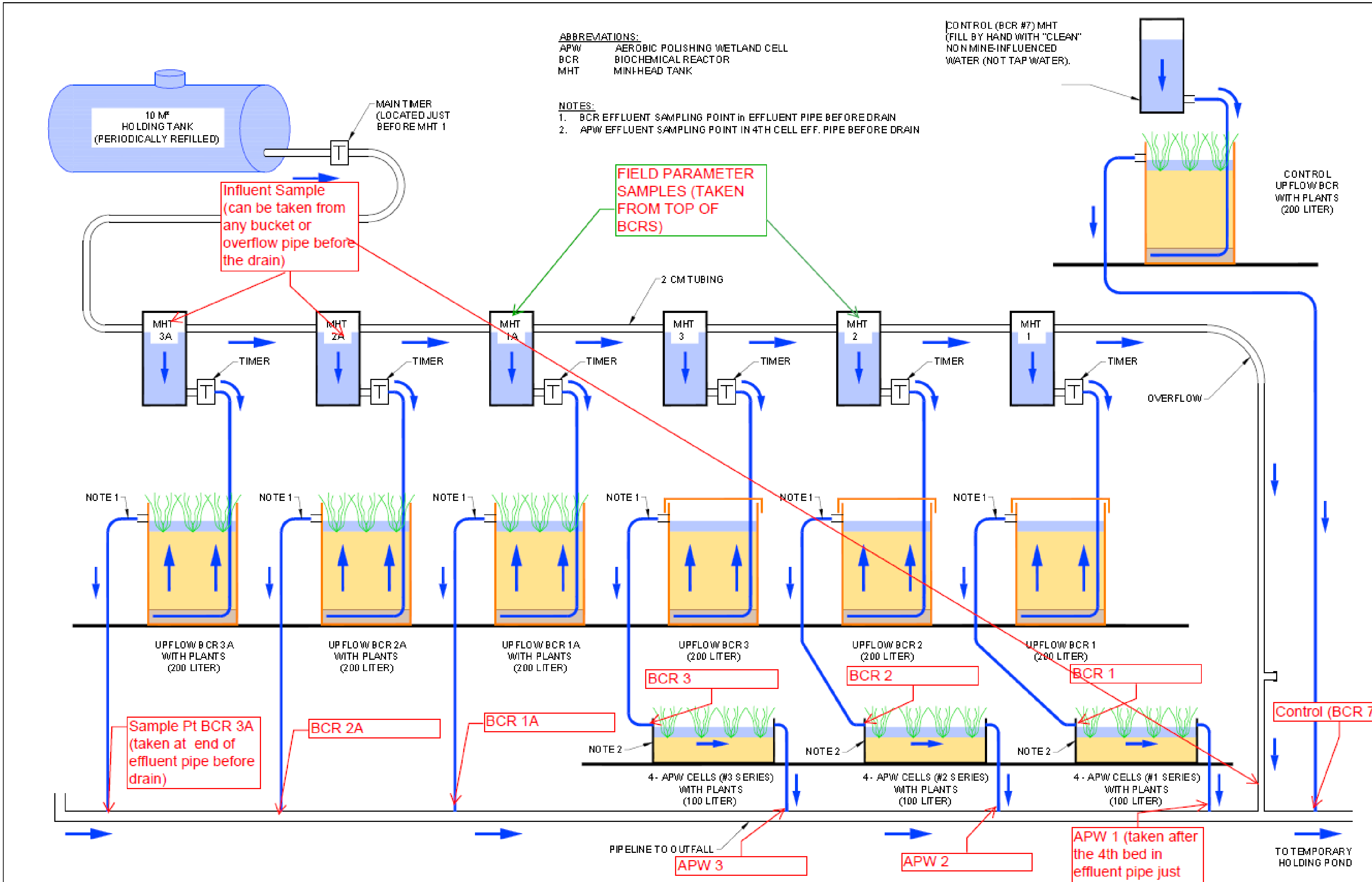
BCR Mixture Proportions

By As-Received Weight

Material	Barrel 1	Barrel 2	Barrel 3	Control
Wood Chips	80%	20%	45%	83%
Rice Straw	10%	70%	45%	8.2%
Limestone Powder	9.5%	9.5%	9.5%	8.2%
Manure	0.5%	0.5%	0.5%	0.8%
Logic	Baseline/ Wood & Control	Straw Substituted for Wood	Wood/Straw 50-50	"Control"
Voids	60%	53%	44%	45%

Barrels 1 to 3 replicated with emergent plants on the cell surfaces

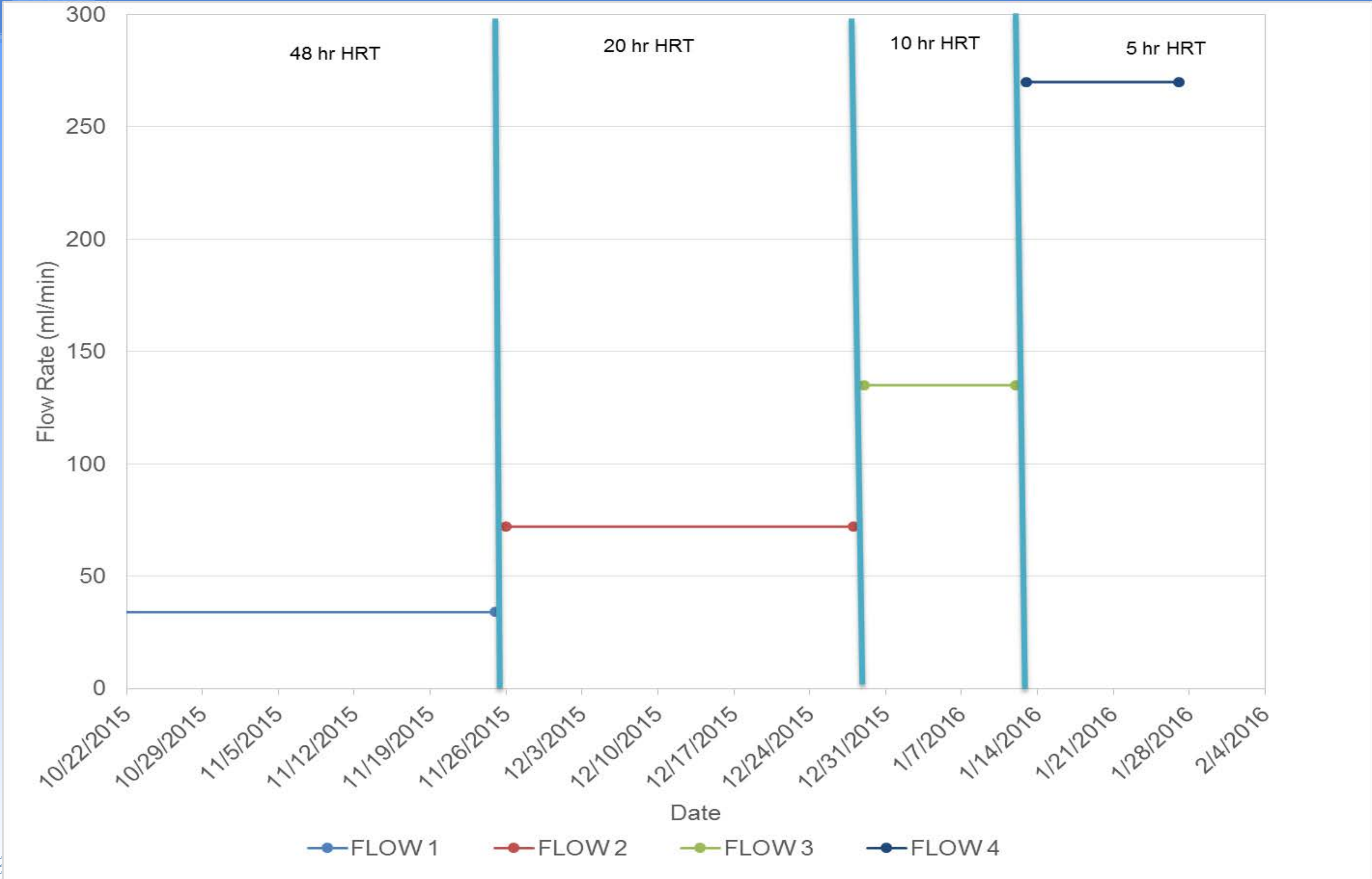
Sample Points



Test Schedule

Week	Date(s)	Event/Activity
0	October 6, 2015	Start Incubation
1	October 12, 2015	Start Flow
2 through 16	October 18, 2015 to January 28, 2016	Steady State Operation with variable flow rates; weekly sampling events
17 through 30	January to early May, 2016	Care & maintenance – low flow, **No Sampling**
31 through 39	May, 2016 to July, 2016	Restart to test high flow with “ballasted” substrate

Flow Rate Changes



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HRT = f(Flow Rate); Upward Velocity = f(Flow Rate)

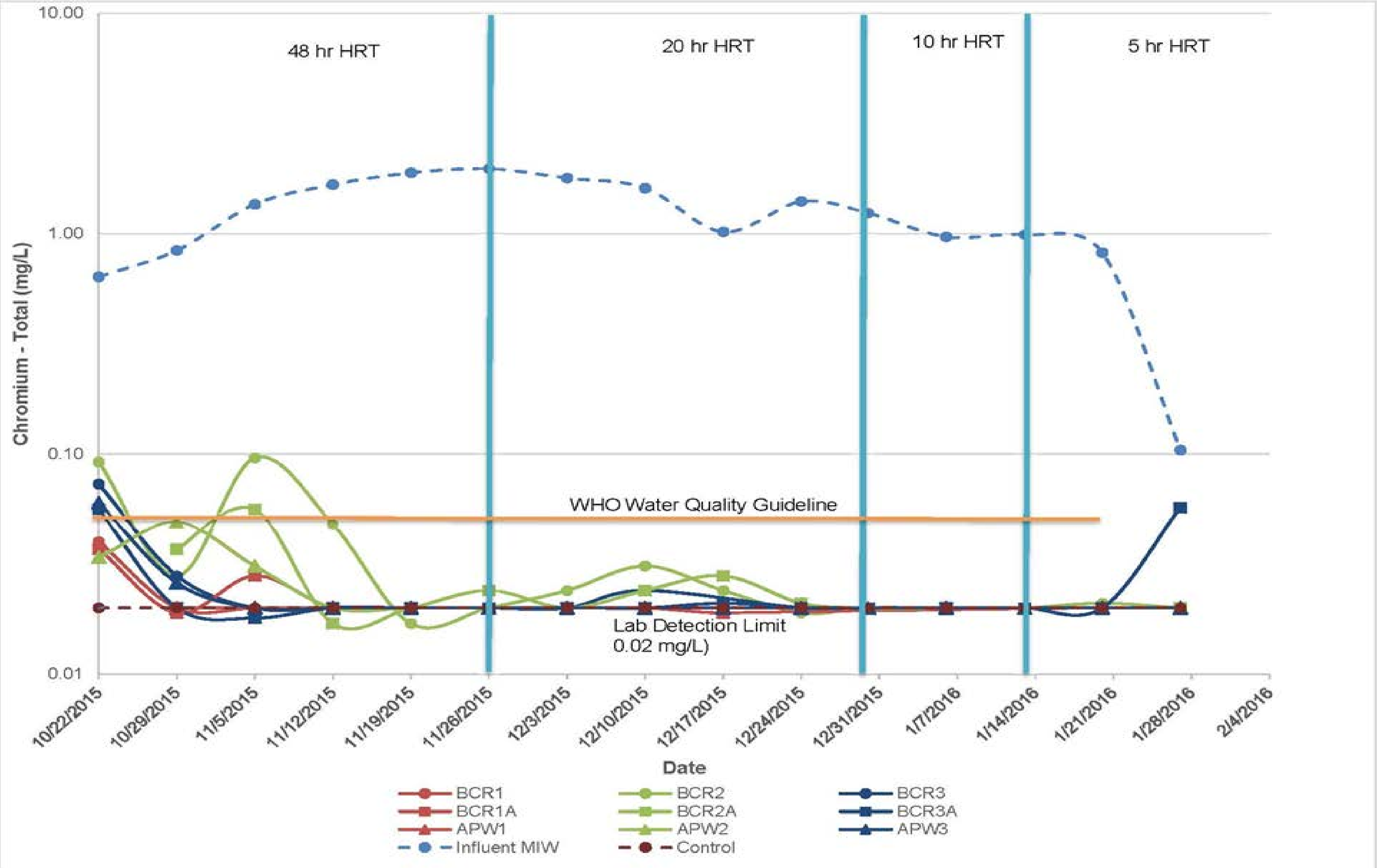
HRT (hours)	Flow Rate (mL/hour)	Upward Velocity (meters/day)
48	34	0.34
20	72	0.73
10	135	**<u>1.4</u>**
5	270	2.8

Test Data (Photos)

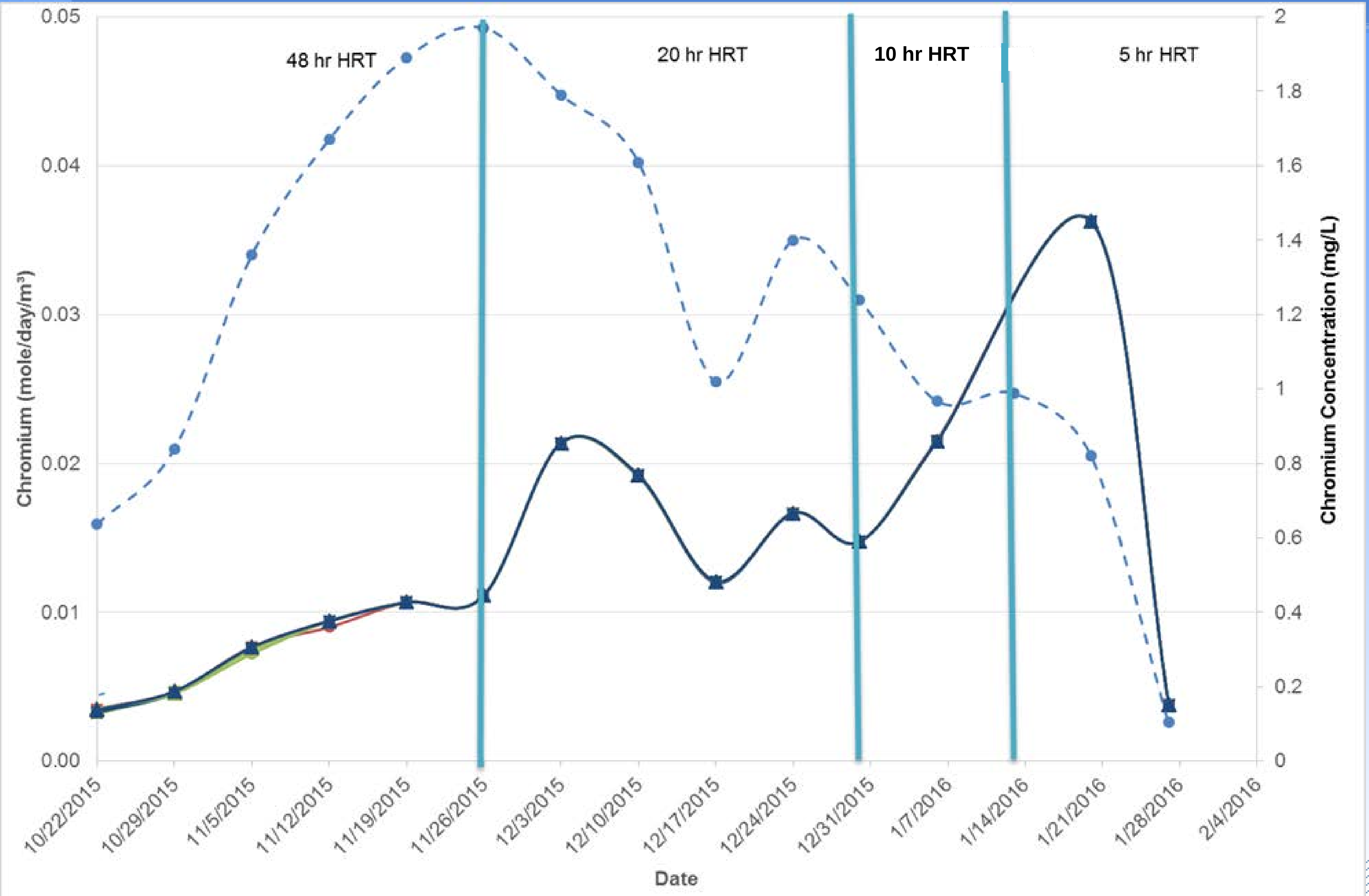
Average Metals Results (dissolved) – mg/L

Parameter	Influent MIW	DL	WHO	BCR 1	BCR 2	BCR 3	BCR 1A	BCR 2A	BCR 3A	APW 1	APW 2	APW 3
Al	0.07	0.05	-	0.08	0.07	0.07	0.08	0.09	0.07	0.10	0.08	0.09
As	0.09	0.1	0.01	***0.1***	***0.1***	***0.1***	***0.13***	***0.1***	***0.1***	***0.13***	***0.1***	***0.1***
Cd	0.03	0.03	0.003	***0.03***	***0.03***	***0.03***	***0.03***	***0.03***	***0.03***	***0.03***	***0.03***	***0.03***
Cr	1.26	0.02	0.05	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Cu	0.04	0.05	2	0.08	0.06	0.09	0.07	0.05	0.08	0.07	0.07	0.07
Fe	0.18	0.05	-	0.7	0.7	0.6	1.0	0.7	0.9	1.8	3.4	2.7
Mn	0.11	0.02	-	1.8	2.2	2.4	2.7	1.9	3.5	10.4	11.2	8.0
Pb	0.16	0.2	0.01	***0.2***	***0.2***	***0.2***	***0.2***	***0.2***	***0.2***	***0.2***	***0.2***	***0.2***
Sn	0.24	0.3	-	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Ti	0.008	0.01	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
V	0.009	0.01	-	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Zn	0.01	0.05	-	0.08	0.05	0.05	0.05	0.05	0.06	0.06	0.05	0.05

Chromium Results (total)



Chromium (total) Volumetric Removal Rate



Preliminary BCR Design Criteria

Design Criteria	Value
Flow Rate	**50 m³/hr**
Chromium Removal Rate	1.4 g/day-m²
Hydraulic Retention Time (HRT)	17 hr
BCR Drainage Gravel	0.15 m
Substrate Thickness	**1 m**
Standing Water (above substrate) depth	0.15 m
Freeboard (top of water to cell liner crest)	0.6 m
BCR Cell total depth with drainage gravel & pipe layer, substrate, standing water (above substrate) and freeboard (standing water to crest of liner)	2 m
Total Bottom Footprint Area	1,700 m²
Resultant upward velocity (assuming 50 percent void volume)	**1.4 m/day**

Preliminary Aerobic Polishing Wetland Design Criteria

Design Criteria	**Value**
Flow Rate	**50 m^3/hr**
BOD Removal Rate	**66 g/day-m^3**
Hydraulic Retention Time (HRT)	15 hr
APW soil depth	0.3 m
APW water depth	0.15 m
Freeboard (top of water to cell liner crest)	0.6 m
APW Cell Total Depth	1 m
APW Bottom Footprint Area	2,400 m^2

Path Forward

- Hexavalent chromium can be passively treated with biochemical reactor (BCR) technology
- BCR effluent will meet permit standards but it needs to be polished for biochemical oxygen demand (BOD) in an aerobic polishing wetland
- BCR substrate longevity is on the order of a decade for short HRT values
- Scale up PTS design process is underway; design flows up to 300 m^3/hr

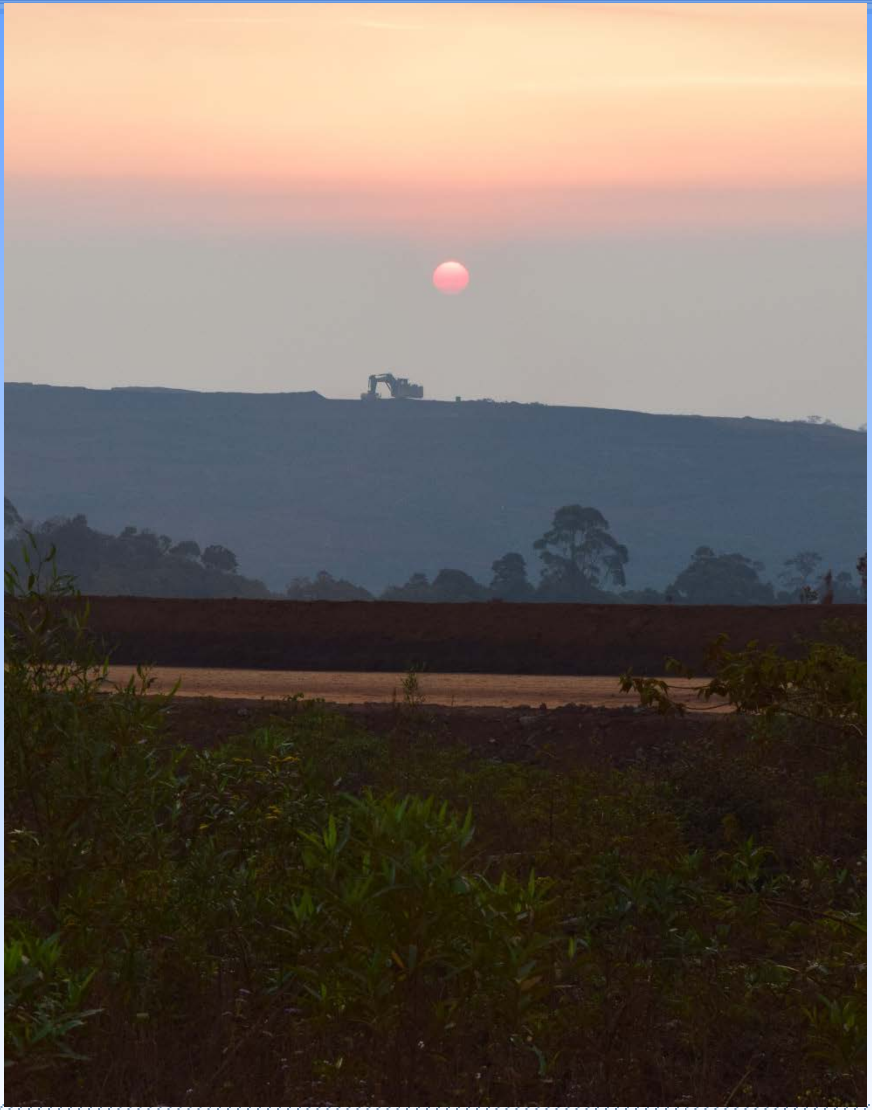
P.T. Advancements 1985 to 2016

- Established design protocol
  - Lab, bench, pilot studies
  - Physical and geochemical design parameters
  - Better understanding of microbiology
- Wide range of operating conditions
  - pH 2.5 to 8.5
  - Metals (Fe, Cu, Pb, Zn, Cd, **Cr^{+6}**, Mn, Hg, Mo, Al, Se, As, U, Co, Tl)
  - *Adsorption to MnO_2 @ neutral pH gaining ground*
  - Non-metals (CN, SO_4, NO_3, NH_3, BOD_5, P)
  - Temperatures (0 to 30 deg C)
  - Flows up to 1,200 gpm (4,540 liters per minute)

Advantages of Passive Treatment

- Low NPV cost
- No moving parts
- Simple to operate
- Resilient to quantity variations
- Wildlife habitat?
- Long term (but not walk-away) solution
- Mimics Mother Nature
- Blends into landscape
- Politically correct
- Non-hazardous residuals (typically)
- Regulatory acceptance
- Resource recovery in the future

Thank You



In Water Treatment, if you’re not part of the **solution**, you’re part of the **precipitate**.

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