Passive Treatment of Mn: Results from our Experimental



Pilot System

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Manganese (Mn) in Mine Drainage

Contaminant Concentrations



Removal

- Active
 - pH >10
 - Lime, sodium hydroxide
 - Oxidant
 - Potassium permanganate, ozone
- Passive
 - Wetlands (incomplete)
 - Aggregate beds (complete)

Why are we talking about Mn?

- Current PADEP Mn effluent limit
 2 to 5 mg/L
- Proposed PADEP Human Health criterion
 - 0.3 mg/L
- International mining limits
 - 0.3 0.5 mg/L



Reaction to Proposed 0.3 mg/L Limit

Industry response:

- Cost concerns
 - \$137 to \$143 million capital costs
 - \$33 to \$46 million per year in annual costs
- Passive treatment least costly treatment for low flows 50 g m)
- Passive treatme only applicable to low flows
 - Assumed retration me of 48 hours in aggregate ds



Goal: Passive Treatment is an Excellent Tool to Remove Mn to Proposed Mn Limits

- What kind of passive systems remove Mn
- How is Mn removed in passive systems
- Mn removal in installed full scale systems
- Our experimental setup
- Our experimental results
- Where this technology is applicable





Mn removal in existing full scale passive systems



Mn removal mechanisms



O.- (superovide)

• Biotic

- Fungi produce superoxide which catalyzes dissolved Mn oxidation and precipitation as MnO₂
- Bacteria oxidize Mn for energy

• Abiotic

- Dissolved Mn precipitate to form a MnO₂ crust on aggregate
- Mn oxides adsorb and oxidize dissolved Mn and grow



Passive Mn removal interpreted as a mix of biotic and abiotic processes

Mn removal at installed full scale systems – Pennsylvania

Site

Mnⁱⁿ Mn^{eff}

	mg/L	mg/L
K&J	27.8	0.4
Swisstock 1	16.4	4.4
Swisstock 2	8.5	5.6
PBS	28.1	1.1
Laurel Run	116	0.1
Stroud	8	1.2
Glenwhite	5.7	0.4
MB 1	20	6.7
MB 2	20	6.0
Ace	34.7	8.6
Glady Fork	9.4	1.7
De Sale 3	55.5	30.9
De Sale 2	31.2	17.1
Fairview	150	70
Derry Ridge	19.4	1.3
PBS	18.4	0.3
West Box	11.9	2.8
Scootac	23.5	1.6
Greene	30.8	1.1
Median	20	1.7

New types of passive systems needed to remove Mn to <0.3 mg/L.

Data from Rose et al, 2023, Luan et al 2012, and Hedin et al 2022

It can be done! Hedin Environmental International Work

- Mn removal systems installed in Laos (Lao PDR), Vietnam, Brazil, and Madagascar.
- In: 840 gpm (3,175 lpm), 2 10 mg/L Mn in
- Out: <0.3 mg/L Mn in 97% of measurements over 9 years



Experimental Locations

- Hollywood active treatment system
 - Aeration, hydrated lime, polymer, clarifier
 - Untreated = 3.3 pH, 36 mg/L Fe, 19 mg/L Al, 1.3 mg/L Mn
 - Treated = 7.3 pH, 1.4 mg/L Fe, **0.6 mg/L Mn**
- Brandy Camp active treatment system

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- Hydrogen peroxide, lime, polymer, settling ponds, wetlands
- Untreated = 4.6 pH, 6.3 mg/L Fe, 8 mg/L Al, 10 mg/L Mn
- Treated = 7.1 pH, 1.7 mg/L Fe, **5.8 mg/L Mn**



Hollywood experimental unit

- 30 yd³ steel roll off container
- 36 tons of AASHTO #3
 - 3.8 cm diameter
- "Ripened" stone from Mn removal bed
- Water from clarifier

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Brandy Camp experimental unit

- 10 yd³ steel roll off container
- 12 tons of AASHTO #8
 - 0.7 cm diameter
- "Fresh" stone from quarry
- Water from wetland





Hollywood unit (ripened AASHTO 3)



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Hollywood unit (ripened AASHTO 3)



Hollywood unit (ripened AASHTO 3)



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Brandy Camp unit (fresh AASHTO 8)



Brandy Camp unit (fresh AASHTO 8)



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Brandy Camp unit (fresh AASHTO 8)



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Results



Parameter	units	PTSs
Retention Time	hour	37
Mn ⁱⁿ	mg/L	20.0
Mn ^{eff}	mg/L	1.7
Mn ^{eff} < 0.3 mg/L	%	na





Results

Ripened AASHTO 3

Parameter	units	PTSs	Hollywood
Retention Time	hour	37	3.0 (30)
Mn ⁱⁿ	mg/L	20.0	0.6 (40)
Mn ^{eff}	mg/L	1.7	0.3 (40)
Mn ^{eff} < 0.3 mg/L	%	na	63%





Fresh AASHTO 8

Results

Ripened AASHTO 3

Parameter	units	PTSs	Hollywood	Brandy Camp
				(all)
Retention Time	hour	37	3.0 (30)	2.2 (40)
Mn ⁱⁿ	mg/L	20.0	0.6 (40)	5.8 (56)
Mn ^{eff}	mg/L	1.7	0.3 (40)	0.5 (233)
Mn ^{eff} < 0.3 mg/L	%	na	63%	68%





Results



Fresh **AASHTO** 8

Fresh ΔΔSHTO 8

Parameter	units	PTSs	Hollywood	Brandy Camp	Brandy Camp
				(all)	(Aug-Oct)
Retention Time	hour	37	3.0 (30)	2.2 (40)	2.1 (8)
Mn ⁱⁿ	mg/L	20.0	0.6 (40)	5.8 (56)	5.7 (14)
Mn ^{eff}	mg/L	1.7	0.3 (40)	0.5 (233)	0.1 (65)
Mn ^{eff} < 0.3 mg/L	%	na	63%	68%	94%

Suspect different Mn removal processes in Hollywood vs Brandy Camp Come talk to us during the conference to nerd out (exhibitor table)



Brandy Camp Performance

- Mn removal in Brandy Camp pilot system was faster and more complete than in full scale passive systems and the Hollywood pilot system
- Kinetics
 - Faster Mn removal kinetics with more surface area (aka smaller stone)
 - Documented by Stumm and Morgan (1981)
- Nutrients?
 - Wetland before Mn bed (aka pyrolusite bed) is beneficial
 - Vail and Riley



Passive Mn removal as an "add on"

• Aggregate beds as a final polishing step to remove Mn

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- Not a new idea, but an optimized idea
- Brandy Camp example
 - 6 mg/L to 0.25 mg/L
 - 900 gpm

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Site		k1	hr	Material
		hr⁻¹		tons
Traditional (kinetics)	AASHTO 3 or 5	-0.035	90	81,096
Traditional (retention time)	AASHTO 3 or 5		48	43,200

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Site		k1	hr	Material
		hr⁻¹		tons
Traditional		0.025	00	01 OOC
(kinetics)		-0.035	90	81,096
Traditional			10	12 200
(retention time)			48	43,200
Brandy Camp				
(kinetics)	AASHTO 8	-0.756	4	3,783
Brandy Camp				
(retention time)			3	2,700



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Brandy Camp				
(retention time)			3	2,700
Rapid sand filter	Sand	-17.187	0.2	166



Operation and Maintenance (O&M)

- Traditional Mn bed O&M = stone cleaning ~ every five years
- Optimized Mn bed O&M = stone stirring ~ every 3 months?
 - Brandy camp box required minor O&M to break up Fe on top of stone but no stirring or cleaning of stone over 12 months
- Rapid sand filter = backflushing ~ weekly
 - When hydraulic conductivity falls below critical threshold



Summary

- Lower Mn effluent regulations are
- Conventional passive treatment sy to <0.3 mg/L
- Our pilot scale units show that pas fast Mn removal (<<< 48 hours) to

Future

- Optimized passive Mn removal should be considered a tool in the toolbox of Mn compliance
- We can bring our pilot scale system to you for testing





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- Exhibitor booth

Questions?







Limestone thin section

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Kinetics

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- Faster Mn removal kinetics with more surface area (aka smaller stone)
 - Documented by Stumm and Morgan (1981)
- Wetland before Mn bed (aka pyrolusite bed) is beneficial
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Outline

- Mn is common constituent of polluted mine drainage
- Mn removal methods
 - Active and passive
- Why are we talking about Mn?
 - PADEP's proposed Mn instream limits
 - International Mn limits
 - Mining industry concerns on Mn removal. Cost effective removal is challenging. Passive Mn removal not considered realistic for large flows.
- Passive Mn removal
 - Mn removal in DLBs
 - Mn removal in Mn beds
 - Mechanism of Mn removal. Important variables to Mn removal.
- Documented Mn removal in full scale passive systems
 - In and out chemistry
 - Kinetics of Mn removal
- Pilot scale systems setup
 - Hollywood setup
 - Brandy Camp setup
- Pilot scale systems results
 - Hollywood results. Removal mechanism. Kinetics.
 - Brandy Camp results. Removal mechanism. Kinetics.
- Conclusions

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- Passive Mn removal can be optimized
- Passive Mn removal can be added onto existing systems