Seasonality of Progressive Iron Removal within the Initial Oxidation Cell of a Passive Treatment System

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Importance of Iron Removal

- Accessibility via chemical activity (order of operations)
- Physical and chemical complications with other treatment cells staged later in the series.
- Side benefit of sorption of other trace metals (zeta potential dependent)

Understanding the System

- Influent water quality and loading rates
 - Metals species and concentrations
 - Flow rates (hydroperiod)
- Removal efficiency (rate)
 - Overall and per surface area unit (kg/m²/year)
 - System sizing and transport state (aqueous vs. solid)

Settling and storage

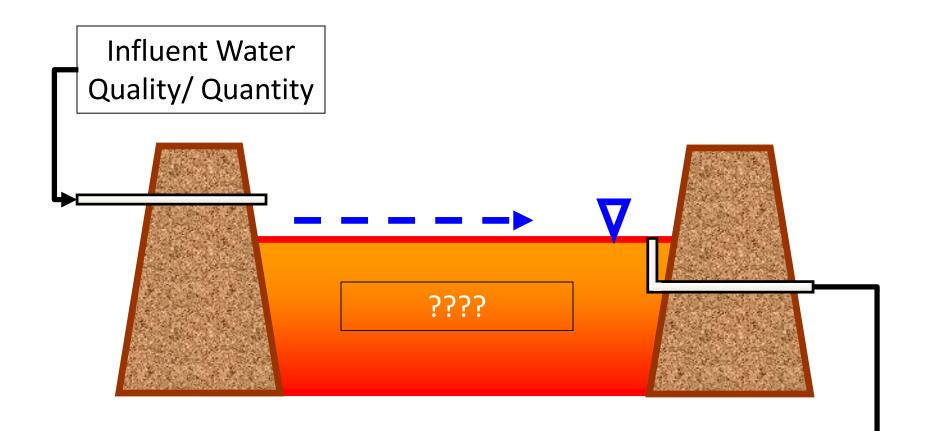
- Short term performance (seasonal)
- Long term performance (over design life)

Understanding Iron Chemistry

- Remediation of AMD impacted waters rely on a two step process for iron removal:
- Iron Oxidation Fe²⁺ oxidized to Fe³⁺
- $4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$
- Iron Hydrolysis: Iron Precipitation
- $Fe^{3+} + 3H_20 \rightarrow Fe(OH)_{3(s)} + 3H^+$



Cell Performance Monitoring



Effluent Water Quality / Quantity

Why Profile a Treatment Cell?

- Additional mechanistic information to aid in troubleshooting or design enhancement within the current or future designs.
- Detailed performance comparison to design for proof of concept or validation.

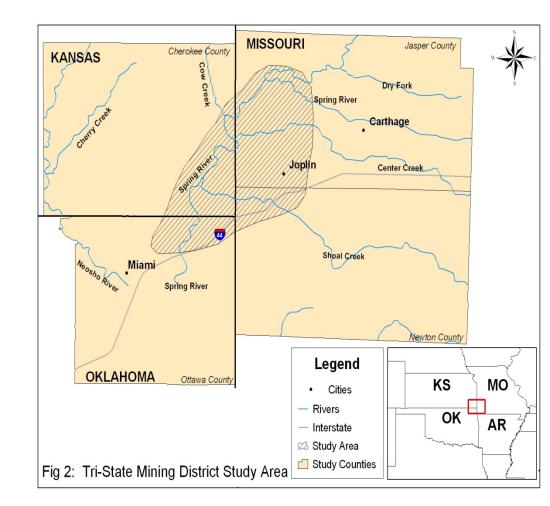
Objective and Purpose

 To investigate the performance of the preliminary oxidation cells of a passive treatment system with respect to season.

 To determine if seasonal variability in total iron removal can be mitigated through system design features (secondary oxidation cells as surface flow wetlands)

Location (Tri State Mining District)

- The Mayer Ranch Passive Treatment System (MRPTS) was designed to treat AMD that is:
 - net-alkaline
 - ferruginous
 - lead-zinc drainage
- Tar Creek Superfund Site, Commerce OK.

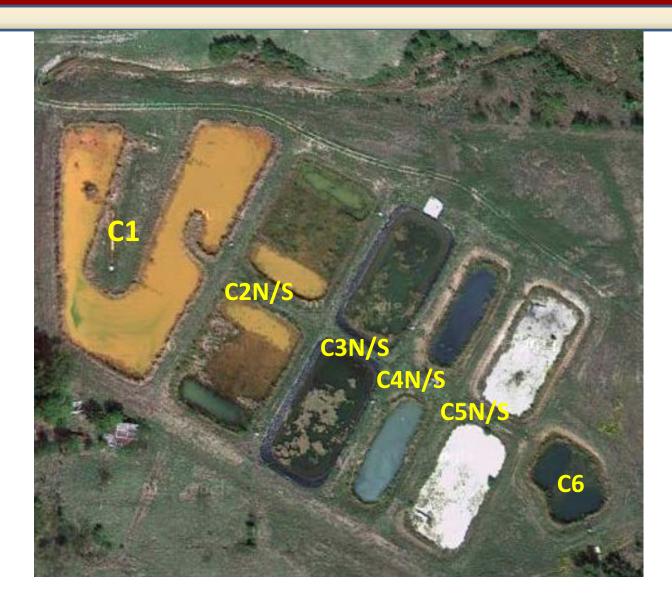


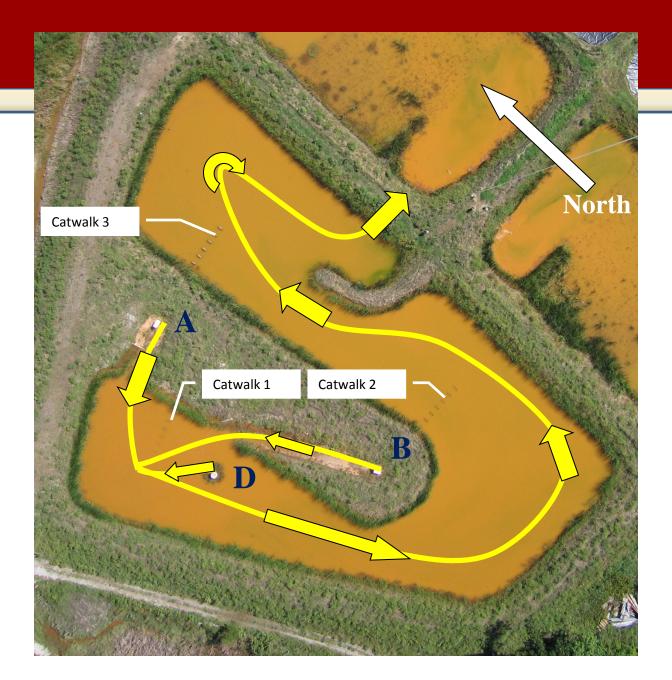
AMD and System Characteristics

- Q varies between 400-700 L\min annually
- Influent pH = 5.95 ±0.06
- Net Alkaline (Alkalinity 393 ± 13 mg\L CaCO₃)
- Mean mass loading = 106 kg Fe / Day (1st year)
- Average iron removal rate = 22 g/m²/day (1st year)

	Iron	Zinc	Lead	Cadmium
Average Influent	192±10 mg\L	11.0±0.7 mg/L	60±13 µg/L	17±4 µg/L

MRPTS Layout and Design





Sample Locations

Site #	Name	
1, 2, 3	AMD Influent	
4	Catwalk 1	
5	S2 Bottleneck	
6	S2 U-Bend	
7	Catwalk 2	
8	Catwalk 3	
9	Cell 1 Effluent	
10	C1 Out	
11	C2Nout	
12	C2Sout	



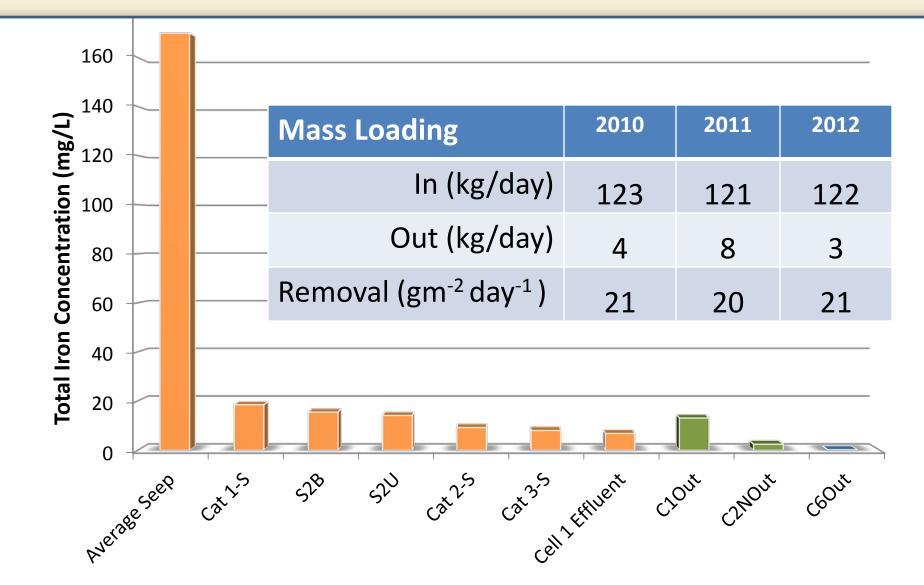
Sample Collection and Analysis

- Seasonal sampling was conducted four times a year for three years

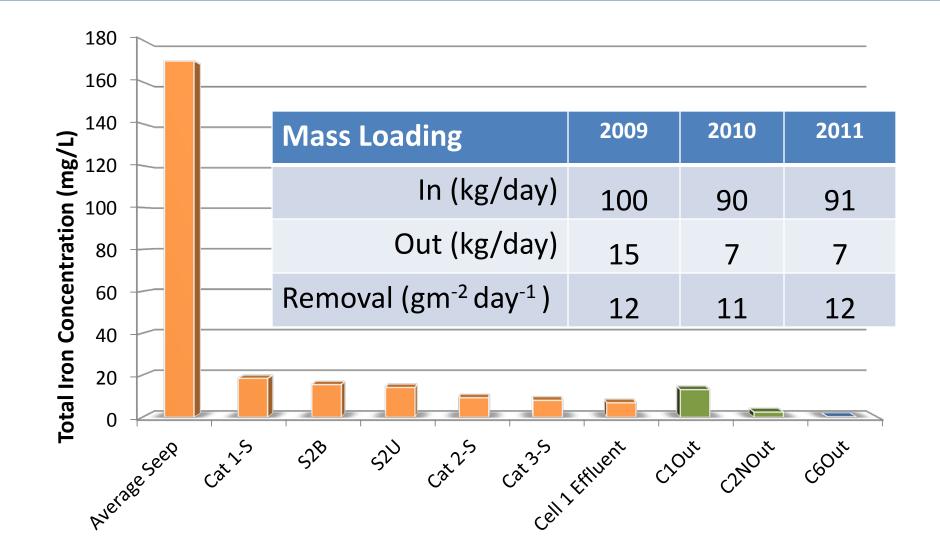
 – (Jan, Apr, July, Oct 2009-2012)
- Iron concentrations (total and dissolved) with respect to:
 - Position
 - Depth
 - Time (season)

Grab Samples	Measurements
Total Metals	SONDE: pH, DO, SC, ORP, T, R, Sal, etc.
Dissolved Metals	Turbidity
Anions	Alkalinity

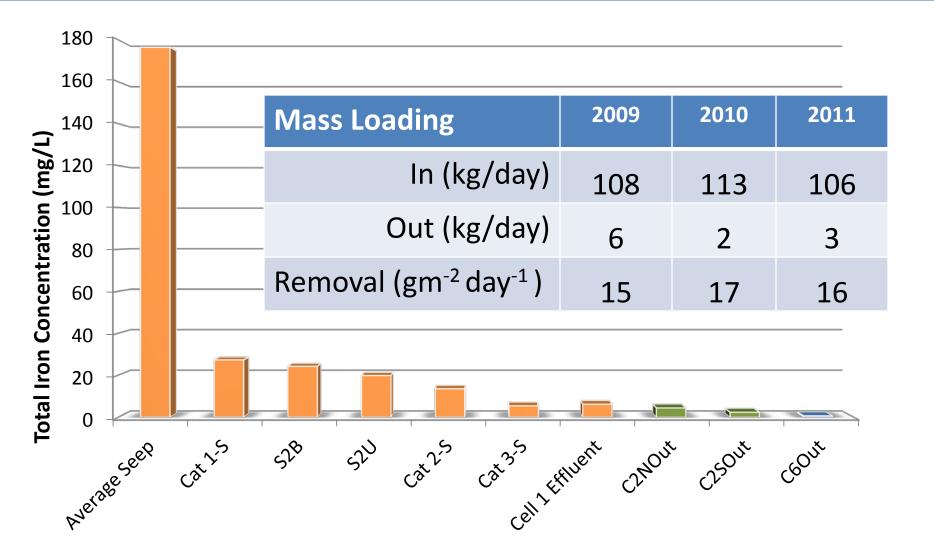
Spring (April 2010-2012): Total Iron Removal Profile (n=3 year average)



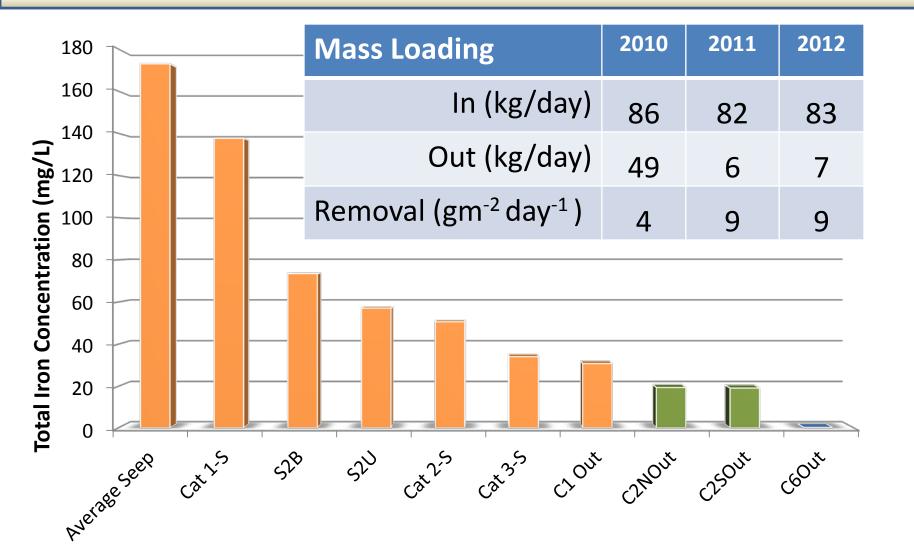
Summer (July 2009-2011) Total Iron Removal Profile (n= 3 year average)



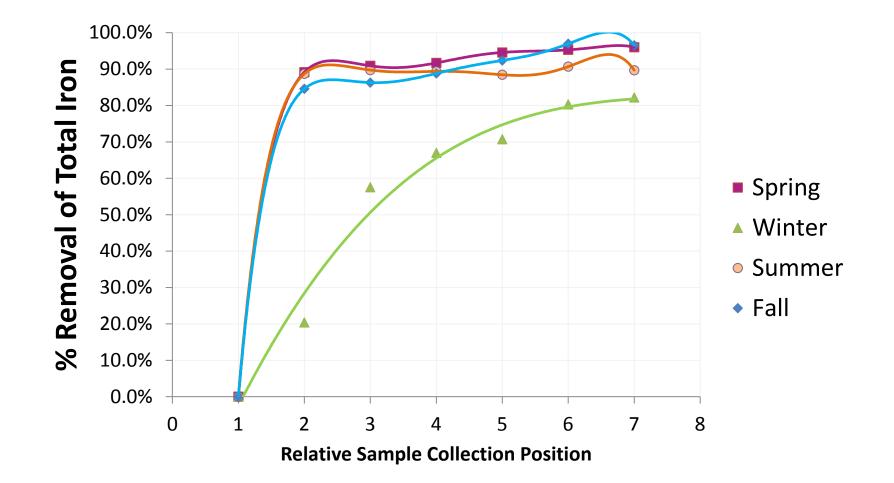
Fall (Oct 2009-2011) Total Iron Removal Profile (n= 3 year average)



Winter (Jan 2010-2012) Total Iron Removal Profile (n= 3 year average)



Total Iron Removal Comparison Cell 1 Removal Profile (n= 3 year average)



Objective: To investigate performance with respect to season and design specification

- For most of the year (spring, summer, and fall), approximately 88% of loaded iron is removed in the first section of oxidation pond, and nearly all of it (~90%) is removed before reaching cells2N&S
- However, winter conditions reduce the removal of iron in the first section of the oxidation pond to a mere 20% with only 80% total removal within Cell 1.
 - Up to 90% removal observed at C2(N&S) effluent.

Purpose: To determine if seasonal variability can be mitigated through secondary oxidation wetlands

Comparison between the relative standard deviation (%) between area adjusted removal efficiencies (g m⁻²day⁻¹)

Removal Conditions	Cell 1 Only (% RSD)	Cells 1 and 2 Together (%RSD)
All Seasons	40.5%	35.6%
No Winter	28.3%	28.5%

Small improvement in variability with oxidation cell series, but not as dramatic as expected.

Extracting the winter data from the set yields less variability overall.

Future Work

- Tracer study to determine actual hydraulic retention time of Cell 1.
- Interpretation of iron concentrations from depth samples as an indicator of solids accumulation.
 - core sampling for accumulation profiling and assessment



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Questions / Comments?



Selected References

- Barnes, A., Sapsford, D.J., Dey, M., Williams, K.P. 2009. Heterogeneous Fe(II) oxidation and zeta potential. Journal of Geochemical Exploration 100: 192–198
- Cornell, R.M and U. Schwertmann. 2003. <u>The Iron Oxides: Structure, Properties, Reactions,Occurrences, and Uses.</u> WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. 2:254-296
- Cravotta, C.A., III. 2008. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA--Part 2. Geochemical controls on constituent concentrations: Applied Geochemistry, 23:203-226.
- EPA Tar Creek Fact Sheet (Region 6). Updated Spring 2009. EPA ID# OKD980629844 Site ID:0601269
- Gazea, B., K. Adam, and A. Kontopoulos. 1996. A review of passive systems for the treatment
- of acid mine drainage. *Minerals Engineering*. 9: 23-42
- •
- Johnson, D.B, and K.B. Hallberg. 2005. Acid mine drainage remediation options: a review.
- Science of the Total Environment. 338: 3-14
- McCauley, C.A., A.D. O'Sullivan, M.W. Milke, P.A. Weber, and D.A Trumm, 2009. Sulfate and
- metal removal in bioreactors treating acid mine drainage dominated with iron and aluminum. Water Research. 43: 961-970
- ٠
- Nairn, R.W., K.A. Strevett, J. LaBar, A. Sutter, J. Clifton, W. Strosnider, J. Brumley, D. Lutes, B. Santamaria, J. McAllister, A. Brewer, M. Roberts, and K. Kauk. (2008). Watershed-Scale environmental monitoring to prioritize mine drainage passive treatment implementation. Poster 2008 National Meeting of the American Society of Mining and Reclamation, Richmond, VA, New Opportunities to Apply Our Science June 14-19, 2008. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502
- •
- Nairn, T. Beisel, R. Thomas, J. LaBar, K. Strevett, D. Fuller, W. Strosnider, W. Andrews, J. Bays, and R. Knox. 2009. Challenges in Design and Construction of a Large Multi-Cell Passive Treatment System for Ferruginous Lead-Zinc Mine Waters. Center for the Restoration of Ecosystems and Watersheds (CREW) team meeting. University of Oklahoma. Department of Civil Engineering and Environmental Science.
- •
- Nyquist, J. and M. Greger, 2009. A field study of constructed wetlands for preventing and treating acid mine drainage. *Ecological Engineering*. 35:630-642
- ٠
- Watzlaf, G., K.Schroeder, R. Kleinmann, C. Kairies, and R. Nairn. 2004. The Passive Treatment of Coal Mine Drainage. National Energy Laboratory. US Department of Energy. Information Circular.
- •
- Younger, P.L., S.A.Banwart, and R.S. Hedin. 2002. Mine Water Hydrology, Pollution, Remediation. Environmental Pollution. Kluwer academic publishers 5: 65-126