# PROGRESSIVE IRON REMOVAL WITHIN THE INITIAL OXIDATION CELL OF A PASSIVE TREATMENT SYSTEM[1]

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**Abstract:** Iron oxidation, hydrolysis and settling are key processes promoted in passive treatment system to remove iron from influent acid mine drainage (AMD). For net alkaline mine waters, an initial oxidation cell is typically used to remove and store large amounts of precipitated iron oxyhydroxides prior to water flowing through additional wetland treatment cells. Regular monitoring of influent and effluent is suitable to determine overall decreases in iron concentrations due to treatment. However, a detailed analysis of iron removal within specific zones of the oxidation cell provides additional information about performance and functionality. The purpose of this study was to investigate progressive iron removal with increasing distance from the influent AMD discharge and depth in a U-shaped oxidation pond receiving ferruginous lead-zinc mine drainage at the Tar Creek Superfund Site. It was hypothesized that iron concentration changes would be greatest in the shallow waters nearest the mine water inflows. Three catwalk structures were used with a discrete horizontal sampler to collect samples along depth profiles at progressively greater distances through the treatment system. *In-situ* measurements included pH, temperature, specific conductance, dissolved oxygen, and oxidation-reduction potential; turbidity and total alkalinity were determined immediately upon collection. Water samples were collected for laboratory determination of total and dissolved metals (EPA methods 3050 and 6010), and sulfate (EPA method 300) concentrations. The oxidation pond had a mean iron mass loading of 106 kg/day and an average removal rate of 25 g $m^{-2}$ $day^{-1}$ based on one year of system operation. The majority of iron removal in Cell 1 occurs within the first section of the cell (82.2% total iron removal) with only an additional 5.4% removal in sections 2 and 3. Precipitated iron oxyhydroxides undergo sedimentation in all three sections of the oxidation pond rather than only in sections 1 and 2 as predicted. Finally, Changes in water quality measurements with increasing depth may have implications on long-term storage of iron precipitates within the system.

**Additional Key Words**: iron oxidation, lead-zinc mine drainage, net alkaline water

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## Introduction

Acid mine drainage (AMD) is a common environmental problem in areas around the world where mining activities have disturbed large mineral deposits. AMD is generated via natural weathering of iron-sulfide minerals and is exacerbated by the increased amounts of surface area exposed during mining operations. Water and oxygen react with iron sulfides to produce sulfuric acid and increase dissolved metal ion concentrations. In their dissolved state, metals can have devastating effects on the watershed through increased bioavailability as well as latent acidity overwhelming the buffering capacity of local streams and lakes.

Passive treatment technologies have gained increasing acceptance over the last few decades as a suitable treatment for AMD. Passive treatment systems can vary in size and composition depending on the water quality and quantity that requires treatment (Gazea et al., 1996; Johnson and Hallberg, 2005, Nairn et al., 2009). Each cell of a passive treatment system is designed to mimic aspects of natural wetlands for the removal of dissolved metal ions from the AMD as well as neutralization of latent acidity (Nyquist and Greger, 2009). Other design options focus on a blending of wastewater lagoon technologies with wetland components, such as emergent vegetation, in a structured approach to harness the processes associated with natural attenuation. For net-alkaline mine waters, a primary oxidation pond is an acceptable method to remove and store large amounts of precipitated iron oxyhydroxides prior to treatment via secondary cells such as reducing and alkalinity generating systems (RAPS) (Younger et al., 2002; Watzlaf et al., 2004; McCauley et al., 2009). The removal of dissolved iron from AMD is dependent on the both heterogeneous and homogeneous process mechanisms of oxidation and hydrolysis (Barnes et al., 2008). Iron oxidation converts dissolved iron (II) to iron (III) in the presence of dissolved oxygen (Equation 1). The newly formed iron (III) readily undergoes hydrolysis with water to form an insoluble precipitate (Equation 2). Flocculation and sedimentation of the iron oxyhydroxide occurs and the solids are retained within the system (Younger et al., 2002).

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (1)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \qquad (2)$$

Regular monitoring of system performance based on influent and effluent iron concentrations is suitable to determine overall decrease in iron concentrations for a specific treatment cell. However, a detailed analysis of step-wise iron removal within the oxidation pond will further the understanding of passive treatment system functionality and optimization. The Mayer Ranch Passive Treatment System at the Tar Creek Superfund Site (Commerce, OK) features a large oxidation pond (Cell 1) as the first stage in a series of parallel treatment cells. Previous work at this site determined that Cell 1 had an average iron removal rate 25 g $m^{-2}$ $day^{-1}$ over the first year of operation (Nairn et al., 2009). Additional sampling sites within Cell 1 were established in an effort to determine the progressive iron removal with increased retention time (i.e., location in the pond with respect to the influent AMD) as well as water quality changes with increased water depth. It was hypothesized that the majority of iron removal was occurring within the first section of the oxidation pond, with the lowest concentrations of iron particulates occurring in the shallow waters due to sedimentation.

## Methods

### Site Description

Sampling was conducted on Cell 1 of the Mayer Ranch Passive Treatment System at the Tar Creek Superfund Site (EPA, 2009) near Commerce, OK (Fig. 1). This passive treatment system was constructed in 2008 to treat three mine discharges impacting an unnamed tributary stream. The system was designed with an U-shaped oxidation pond (Cell 1) as the primary treatment step to supply following parallel treatment trains with water that contains significantly less dissolved iron than the system influent. Cell 1 collects the flow of three mine discharges ($Q_{total}$ = 387 L/min) and has is divided between the north and the south treatment trains at the effluent outlet (Nairn et al., 2008). Although the Mayer Ranch Passive Treatment System is designed with a series of passive treatment technologies incorporated into two parallel trains of five cells and a polishing wetland, the primary focus of this study is on the characteristics of the iron removal occurring in the initial oxidation pond (Cell 1).

### Sampling

Cell 1 was divided into three sections based on visual inspection from an aerial photo (Fig. 1). These divisions were for sampling protocol only, and did not represent any real type of boundary or separation within the cell itself. Section 1 consists of the area in which all three mine water discharges enter the system (Seeps A, B, and D), and are readily mixed prior to flowing through a narrow portion of the treatment cell (bottleneck) into Section 2. Section 2 is characterized by the large U-bend on the farthest south side of the system. Section 3 is

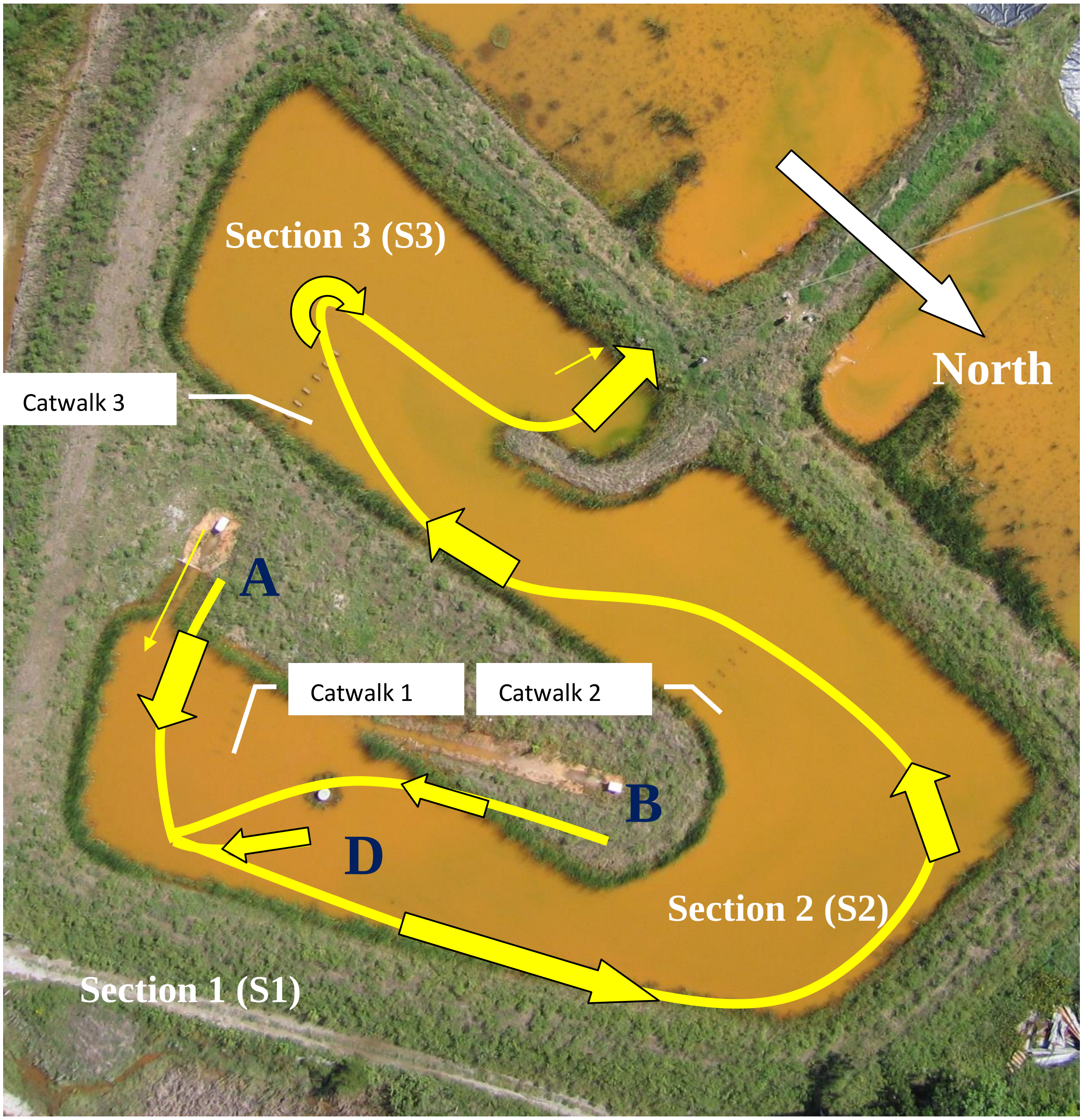

Figure 1: Mayer Ranch Passive Treatment System (MRPTS) sampling section designation based on cell design morphology. Section determined based on points within the system where the design width of the cell narrows (bottleneck). The sampling catwalk locations are labeled, Seeps A, B, and D are indicated in blue, and the direction of flow is outlined in yellow.

designated as the final section of Cell 1 treatment that includes the effluent discharge to the parallel system treatment trains. Each section includes a catwalk sampling structure (indicated in Fig. 1) that allows one to collect samples without extraneous disturbance to the water column or sediment deposits. Measurements and samples reported were collected July 2009 at increasing depths (surface, 0.5, 0.9, and 1.4 meters) from the end of each catwalk structure and the influent and effluent water quality was also determined.

Grab samples for total and dissolved metals were collected at 9 different sampling points indicated in Fig. 2. The mine seep samples (A,B,D) were collected directly from each outflow structure prior to contact with cement spillways leading into Cell 1. Anion samples were collected directly from the outflow structures for each mine seep (A, B, D) as well as for the Cell 1 effluent discharge for the system. Vertical water column samples were collected using a discrete horizontal sampler common in limnilogical studies to capture samples with increasing depth in the water column. Samples were collected starting from the surface, working towards increasingly deeper samples in order to prevent any unnecessary disturbance to the water column. Samples were collected at the surface, 0.5, 0.9, and 1.4 meter depths. *In-situ* measurements included pH, temperature ($^{o}$C), specific conductance (mS/cm), dissolved oxygen (%Sat), and oxidation-reduction potential (mV).

| Site # | Name |
|---|---|
| 1 | Seep A Discharge |
| 2 | Seep B Discharge |
| 3 | Seep D Discharge |
| 4 | Catwalk 1 |
| 5 | S2 Bottleneck |
| 6 | S2 U-Bend |
| 7 | Catwalk 2 |
| 8 | Catwalk 3 |
| 9 | Cell 1 Effluent |

Figure 2: Sample sites for the MRPTS cell 1 iron removal characterization. Sites 1, 2, and 3 are each influent AMD sources. Sites 4, 7, 8 are catwalk structures used for depth sampling. Sites 5, 6, and 9 were collected from shore with the assistance of a sampling pole.

### Sample Analysis

The dissolved metal samples were filtered using a hand-pump apparatus through 0.45-um filter cartridges for each sample. Turbidity (NTU) was determined on-site using a Hach 2100P Portable Turbidimeter and a series of three measurements were averaged to produce the reported value. Total alkalinity (mg/L $CaCO_3$) was determined in the field immediately following sample collection via use of a Hach digital titrator with 1.6-N $H_2SO_4$ acid titrant and Bromocresol green / methyl red indicator (APHA 2320). All metals samples were acidified with concentrated trace-metal grade nitric acid and then kept on ice for transport back to the Center for Restoration of Ecosystems and Watersheds (CREW) laboratory for analysis. The anion samples were also stored at 4 $^{o}$C for transport back to the laboratory. Anion samples were promptly filtered and run in serial dilution on the Metrohm 761 Compact Ion Chromatograph (EPA 300) to determine total sulfate concentration (mg/L). The metal samples underwent aqueous digestion using the Mars microwave digestion system in accordance with the standard operating procedure (EPA methods 3050). The digested samples were analyzed with a Varian Inductively Coupled Plasma Optical Emission Spectrometer ICP-OES (EPA 6010) for total and dissolved metals concentrations. Appropriate QAQC procedures were observed during sample preparation as well as sample analysis.

## Results and Discussion

### Influent Discharge

There are three point source acid mine drainage discharges that supply the Mayer Ranch Passive Treatment System (MRPTS). The water quality of these seeps was determined to be net-alkaline ferruginous lead-zinc mine drainage of the composition listed in Table 1.

The three seeps are essentially identical in chemistry within the expected analytical error and have a cumulative flow of 387 L/min. The initial alkalinity of the mine drainage is elevated due to the dissolution of dolomite limestone in the site host rock increasing the concentration of $HCO_3^-$ in the influent AMD. The dramatic decrease in alkalinity observed in the Cell 1 effluent sample results from the neutralization of the latent acidity that is released as iron is oxidized and hydrolyzed (equations 1 and 2). Small decreases in lead and zinc concentrations in Cell 1 effluent are likely due to sorption onto the iron solids that are retained in the system, and not a result of direct precipitation of either of these metals in the form of a hydroxide (Cornell and

Schwertmann, 2003; Cravotta, 2008). Sulfate concentrations did not demonstrate any significant change between Cell 1 influent and effluent concentrations, which is expected based on the oxidizing function of this component of the treatment system.

Table 1: Water Quality of AMD Influent and Effluent for Cell 1- July 2009

| | pH | Alkalinity (mg/L $CaCO_3$) | SC (mS/cm) | $\%DO_{sat}$ | Temp ($^oC$) | Iron (mg/L) | Lead (mg/L) | Zinc (mg/L) | Sulfate (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| Seep B Q=238 L/min | 5.97 | 387 | 3.014 | 4.1 | 17.9 | 173.15 | 0.062 | 8.55 | 2205 |
| Seep A Q=114 L/min | 6.05 | 385 | 2.993 | 5.9 | 17.9 | 181.27 | 0.062 | 8.83 | 2178 |
| Seep D Q=35 L/min | 6.01 | 378 | 3.042 | 3.6 | 18.1 | 186.04 | 0.068 | 9.69 | 2215 |
| Cell One Effluent | 6.06 | 193 | 2.853 | 69.5 | 26.2 | 23.06 | 0.025 | 6.53 | 2229 |

## Iron Removal With Respect to Retention Time

A comparison of total and dissolved metals concentrations with respect to increasing retention time is illustrated in Fig. 3.

The greatest decrease in the iron concentrations took place in the first section of the passive treatment cell design (S1). The influent AMD had an average total iron concentration of 185.50 mg/L Fe (n = 3) which decreased to 52.35 mg/L total Fe when sampled at the first catwalk structure (sampling site 4). The total iron concentration continued to decease to 30.48 mg/L total Fe by the fifth sampling point in the bottleneck region located between Sections 1 and 2. The total iron concentration deceased in Section 1 by 82.2% from the initial influent concentration. Water flowing through Section 2 demonstrated an overall decrease in the total iron concentration of 80.0%, and the water in Section 3 showed an overall removal of total iron with respect to the initial concentration of 87.6%. A slight increase in the total iron and dissolved iron concentrations was observed in Section 2 of the passive treatment system.

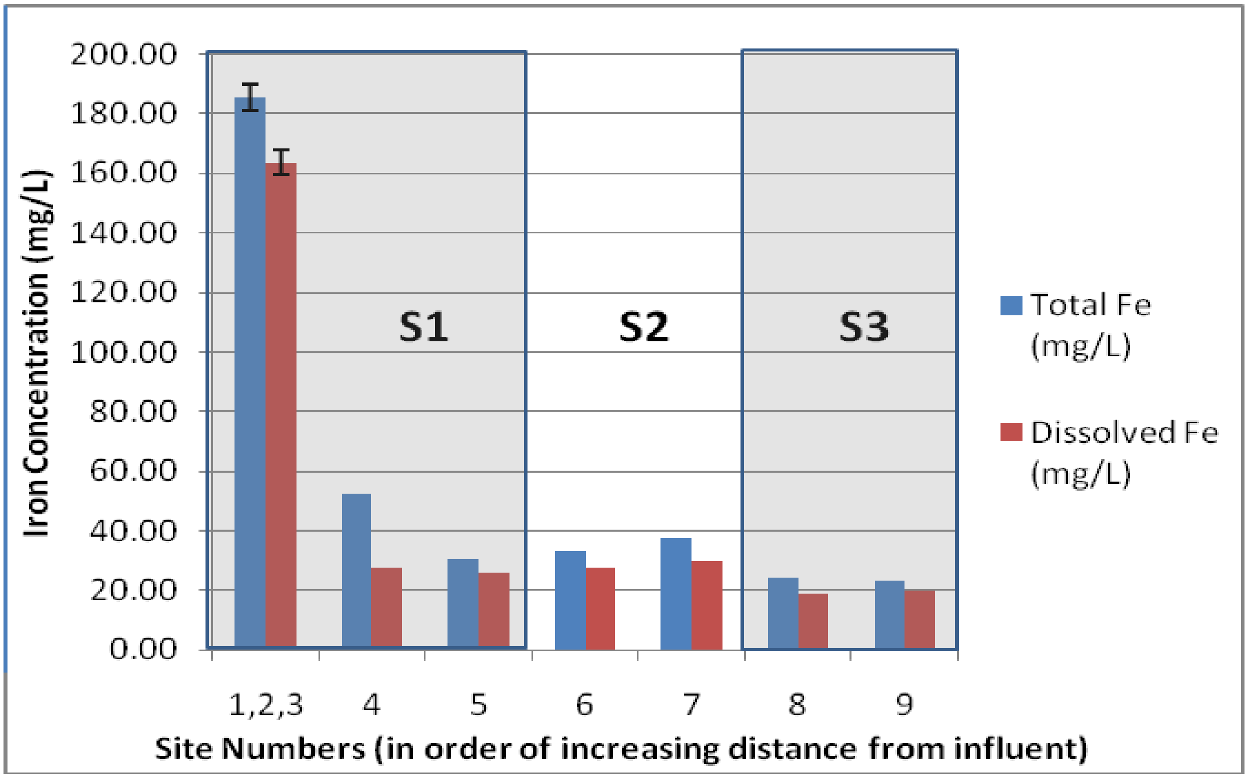

Figure 3: Total and Dissolved Iron Concentrations Sampled with increasing distance from the influent mine drainage discharges. S1, S2, and S3 refer to the sectional divisions used to distinguish one portion of the cell from another. The numeric values on the x-axis refer to the sampling sites in order of increasing relative distance from the initial AMD discharges. (1, 2, 3=average of influent iron concentrations for the three mine seeps).

## Iron Removal With Respect to Depth

The total iron concentrations in each section increased with increasing depth of the oxidation pond (Fig. 4). This is consistent with the idea that as iron particulates precipitate out of solution, they coagulate into larger particles and sediment to the bottom of the oxidation pond. The lowest total iron concentrations were observed near the surface of the water due to settling of the particulate material over time. The sample collected at 1.4 meters likely penetrated the surface of the blanket of settled iron oxyhydroxides resulting in the excessively high concentrations of total iron observed as it is approaching the 1.5 meter Cell 1 design specification for depth. This is significant as it demonstrates that the iron oxyhydroxide precipitates are being deposited in all three sections of Cell 1, rather than just in Sections 1 and 2 as previously predicted.

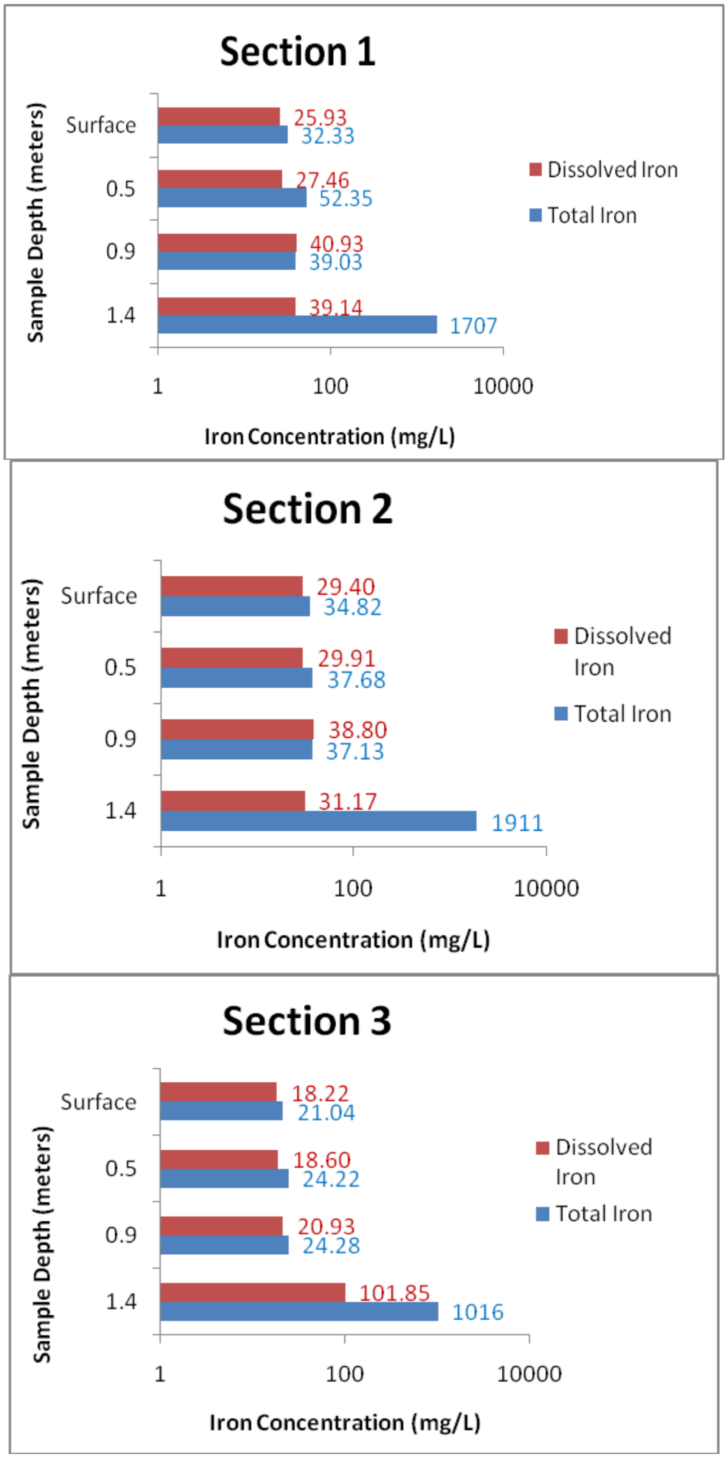

Figure 4: Total and dissolved iron concentration profiles with increasing depth for each section of Cell 1.

*In situ* water quality was also measured with increasing depth at each catwalk. Table 2 and Fig. 5 summarize the average of the three locations with increasing depth. A comparison of the average dissolved oxygen concentration and the oxidation reduction potential (ORP) with increasing sample depth is featured in Fig. 5.

Table 2: Average Catwalk Water Quality Measurements with Increasing Depth

| Depth (meters) | Alkalinity (mg/L $CaCO_3$) | Turbidity (NTU) | Temp (°C) | Specific Cond. (mS/cm) | %DOsat | pH | ORP (mV) |
|---|---|---|---|---|---|---|---|
| Surface | 171 | 55.4 | 27.05 | 2.870 | 72.3 | 6.03 | 190.2 |
| 0.4 | 183 | 58.9 | 25.83 | 2.884 | 61.9 | 6.02 | 190.5 |
| 0.9 | 180 | 56.5 | 23.89 | 2.899 | 24.0 | 5.94 | 187.8 |
| 1.4 | 167 | >1000 | 22.59 | 3.357 | 6.3 | 6.15 | 116.2 |

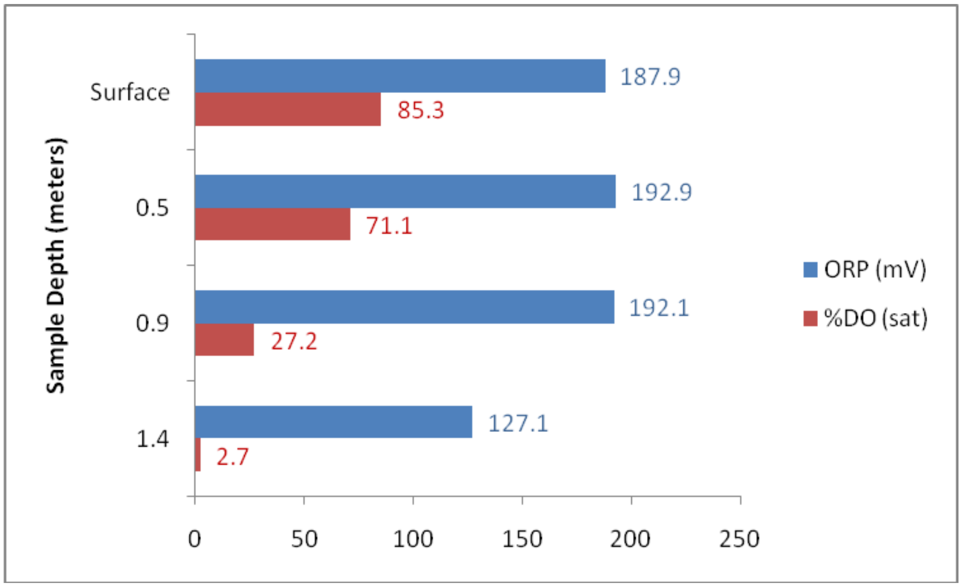

Figure 5: Average Catwalk samples (n=3) dissolved oxygen (%sat) and oxidation reduction potential (mV) measurements with increasing depth.

The dissolved oxygen decreases in a nearly linear trend with respect to increasing depth. The oxidation reduction potential decreased sharply between the 0.9 meter and the 1.4 meter depth measurements indicating reducing conditions could be present within the underlying water column and sediments accumulated at the bottom of the oxidation pond. This supports the idea that the iron oxidation is occurring most actively near the surface of the water column. However, if reducing conditions develop within the sediments, remobilization of the iron and associated trace metals could result.

## Conclusions

Iron oxidation, hydrolysis, and settling are key processes promoted in passive treatment system oxidation cells to decrease dissolved iron concentrations in influent mine drainage. Although monitoring the influent and effluent water quality of a treatment cell is sufficient to determine overall performance, it is insufficient to determine the step-wise iron removal profile. Sampling at key points throughout the U-shaped Cell 1 design determined that the majority of the iron removal achieved in the oxidation pond occurs in the first section of the pond (S1), rather than along a uniform gradient throughout all three sections (S1, S2, S3). This is consistent with the initial hypothesis regarding iron removal in Cell 1. High turbulence and degassing of dissolved carbon dioxide work synergistically to increase the dissolved oxygen content of the water as well as to increase the pH to favor oxidation and hydrolysis reactions. The loss of large quantities of iron from solution in section 1 of cell one may have implications on long-term precipitate deposition and storage within the system. Additional work is required to determine if uneven deposition of the retained iron solids will affect the performance of the system (e.g., retention time, short circuiting, and sediment mineralization) over the life of the system. Also, further work is needed to determine where reducing conditions may be present within the treatment cell and to evaluate the stability of the precipitated iron hydroxide under such conditions.

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