

## **The Impact of Aeration and Addition of Iron Solids on Iron and Zinc Removal at Mine Drainage Discharge near Beaver Creek**

The following document is my Honors Thesis. To graduate with Honors from the University of Oklahoma, a student must perform a research project or independent study and complete an Honors Thesis that appropriately addresses the research topic and is written in the standard of the specific field or discipline. In the Spring 2020 semester, I explored the effect of aeration and solid iron oxide addition on trace metal removal at Beaver Creek, which is an offshoot of the Tar Creek Superfund Site in northeastern Oklahoma. I presented this research at the Undergraduate Research Day at OU in Spring 2021 and am currently in the process of adapting the Thesis into a journal article and submitting it for publication.

# **The Impact of Aeration and Addition of Iron Solids on Iron and Zinc Removal at Mine Drainage Discharge near Beaver Creek**

## **Hannah Curtis**

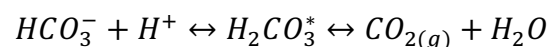
### **Abstract**

A field microcosm experiment of six triplicate treatments was performed to measure iron and zinc removal in net alkaline mine drainage contaminated with trace metals: closed, open, open + aerated, closed + Fe, open + Fe, and open + aerated + Fe. The closed microcosms had a lid and were closed to the atmosphere; the open microcosms were open to the atmosphere; the aerated microcosms were aerated with standard aquarium stones and pumps; and the Fe microcosms had 50 cm<sup>3</sup> of iron solids added. It was hypothesized that the aerated and Fe treatments would have the greatest effect on iron and zinc removal. After a 96-hour period, where water quality parameters were measured every 3 hours for the first 24 hours and every 24 hours for the final 72 hours, it was found that the microcosms with the solid Fe additions had the greatest effect on total iron and zinc removal, with final total iron concentrations reaching a low of 0.83 mg/L in the open + Fe microcosm and final total zinc concentration reaching a low of 0.12 mg/L in the open + aerated + Fe microcosm. The aerated microcosms had the greatest effect on dissolved iron and zinc removal, with final concentrations in the open + aerated + Fe microcosm at 0.14 mg/L and 0.05 mg/L, respectively.

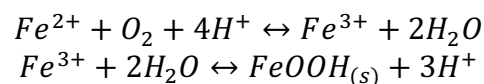
### **Introduction**

Passive treatment systems are long-term, cost-effective systems that utilize ecological engineering processes and oxidation-reduction biogeochemical mechanisms without inputting chemical reagents into the system (Hedin et al., 1994). These systems are seen as a more sustainable alternative to active and mechanical systems and typically do not require fossil fuel use. Ecologically engineered treatment systems can include installed biological and chemical processes, aeration, and processes that utilize renewable energy. Specifically, these systems have proven effective at treating mine drainage waters.

In these mine-affected waters, excess trace metals, sulfates, and CO<sub>2</sub> pose major problems. Excess CO<sub>2</sub> can be degassed from the system through aeration, which shifts the carbonate equilibria, as shown in the equation below:



This shift in carbonate equilibria increases the pH of the water which increases the rate of iron oxidation from ferrous iron to ferric iron and hydrolysis to solid Fe (III) oxide. These oxidation and hydrolysis processes are shown in the chemical equations below:



Once iron oxidizes, hydrolyzes and precipitates, it is easily removable from water through filtration.

Iron oxide solid presence has also shown positive effects on trace metal removal (Dempsey et al., 2001). The presence of iron oxide solids allows metals to sorb to this material through surface complexation of cations to the active iron oxide solid surfaces. The objective of this experiment is to evaluate the role of CO<sub>2</sub> and added iron oxide solids on iron and zinc removal through passive and active oxygenation and degassing and sorption. It is expected that aeration and solid iron oxide addition will have the greatest role in iron and zinc removal from net alkaline mine water.

## Methods

Polluted mine water was collected from a mine drainage discharge near Beaver Creek (Tar Creek Superfund Site, Ottawa County, OK) in 18 five-gallon plastic microcosms. Six treatments in triplicate were performed for these microcosms: 1) Closed, 2) Open, 3) Open + Aerated, 4) Closed + Fe, 5) Open + Fe, and 6) Open + Aerated + Fe (Figure 1).



*Figure 1: 18 Microcosms (from top to bottom: closed, open, open + aerated, closed + Fe, open + Fe, open + aerated + Fe)*

In each of the closed experiments, a plastic lid was placed on the microcosm, along with a sampling line and stoppered hole, so measurements and samples could be taken without exposing the water to open air. In each of the open experiments, the microcosms remained uncovered. In the two aerated experiments, standard aquarium aeration stones and pumps were used to aerate

the microcosms. In each of the Fe experiments, 50 cm<sup>3</sup> of iron solids (found on-site) were added to the microcosms. Temperature, pH, dissolved oxygen, oxidation-reduction potential, specific conductance, total dissolved solids, salinity, and conductivity were measured using a YSI 600QS multiparameter datasonde in situ every 3 hours for 24 hours, then every 24 hours over the next 72 hours. Alkalinity and turbidity were measured, also on-site, via titration with sulfuric acid and a Hach 2100P turbidimeter, respectively. Samples were collected in 250-mL HDPE bottles and preserved with trace metal grade HNO<sub>3</sub> to be later analyzed in the laboratories at the University of Oklahoma Center for Restoration of Ecosystems and Watersheds. Samples were collected every 3 hours for 24 hours then every 24 hours for the next 72 hours to be measured for total metal concentrations. Samples were collected every 12 hours for 24 hours then once at the end of the sampling event, using 0.45 um filters, to be measured for dissolved metals. Metals analyses were determined using a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer, for 21 analytes: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, S, Se, Si, Zn (Nairn, 2013).

## **Materials**

- 18 19-L plastic microcosms
- 6 plastic lids
- 6 sampling lines
- 6 stoppers
- 6 aquarium aeration stones
- 6 aquarium pumps
- 450 cm<sup>3</sup> iron solids
- 2 YSI 600QS multiparameter datasonde
- Hach 2100P turbidimeter
- Hach total alkalinity test kit
- 250 mL HDPE bottles
- Trace metal grade HNO<sub>3</sub>

## **Results and Discussion**

Tables 1, 2 and 3 compare the initial and final water quality values with standard deviations in each microcosm. The initial values for each water quality parameter are the same for each microcosm. The values for each water quality parameter at the end of the experiment (96 hours) are shown on the right side of the table. Overall, the total and dissolved metal concentrations generally decreased from the initial to final samples. Notably, the total and dissolved Fe concentrations decreased significantly from the initial to final readings, specifically in the microcosms where solid Fe was initially added.

**Table 1. Initial and final physical parameter data for microcosm experiment. Water quality parameters include temperature (T), specific conductance (SC), conductivity (Cond.), resistivity (Res.), total dissolved solids (TDS), salinity (Sal.), Dissolved oxygen (DO), pH, oxidation-reduction potential (ORP), total alkalinity (Alk.) and turbidity (Turb.)**

	Initial (0 hours)	Final (96 hours)					
	All Microcosms	Closed	Open	Open + Aerated	Closed + Fe	Open + Fe	Open + Aerated + Fe
<b>T (°C)</b>	14.39±0.12	-0.06±0.13	0.28±0.23	-0.08±0.01	0.33±0.19	0.65±0.12	0.23±0.03
<b>SC (mS/cm)</b>	0.693±0.003	0.697±0.009	0.693±0.012	0.696±0.003	0.717±0.011	0.723±0.004	0.709±0.006
<b>Cond. (uS/cm)</b>	553±3	363±3	366±5	362±2	380±6	387±1	374±3
<b>Res. (Ohm-cm)</b>	1807.83±10.74	2751.65±21.04	2735.16±32.55	2756.46±9.28	2635.70±38.66	2584.14±5.10	2676.08±17.80
<b>TDS (g/L)</b>	0.451±0.002	0.453±0.006	0.450±0.008	0.453±0.002	0.466±0.008	0.470±0.003	0.461±0.004
<b>Sal. (ppt)</b>	0.34±0	0.33±0.01	0.33±0.01	0.33±0	0.35±0.01	0.35±0	0.34±0
<b>DO (%)</b>	37.57±4.60	47.83±1.56	53.30±1.61	94.60±0.75	62.73±6.16	64.37±1.36	99.87±0.57
<b>DO (mg/L)</b>	3.83±0.46	6.99±0.25	7.71±0.19	13.83±0.11	9.06±0.86	9.21±0.20	14.48±0.07
<b>pH</b>	6.53±0.13	7.53±0.05	7.48±0.01	8.26±0.16	6.73±0.02	6.87±0.02	7.97±0.01
<b>ORP (mV)</b>	38.8±5.72	27.07±1.25	27.37±0.15	24.17±0.65	21.00±5.56	29.30±3.29	35.80±3.70
<b>Alk. (mg/L CaCO<sub>3</sub>)</b>	221±6	183±8	188±10	191±8	146±2	148±1	130±1
<b>Turb. (NTU)</b>	7.89±1.38	11.47±1.39	16.63±2.02	33.97±2.47	17.40±2.95	15.20±2.26	23.27±9.64

**Table 2. Initial and final total metals data for microcosm experiment. <PQL refers to concentrations below the practical quantitation limit.**

	Initial (0 hours)		Final (96 hours)				
	All Microcosms	Closed	Open	Open + Aerated	Closed + Fe	Open + Fe	Open + Aerated + Fe
<b>Ag</b>	0.0053±0.0006	0.0042±0.0011	0.0052±0.0007	0.0052±0.0008	0.0042±0.0001	0.0049±0.0004	0.0048±0.0005
<b>Al</b>	0.068±0.002	0.146±0.027	0.106±0.007	0.109±0.019	0.093±0.002	0.092±0.003	0.102±0.007
<b>Ba</b>	0.018±0	0.014±0	0.015±0	0.015±0	0.0029±0	0.0032±0.0004	<PQL -
<b>Ca</b>	146.16±1.11	144.85±0.92	146.89±0.39	148.20±0.45	149.72±1.40	152.66±1.67	146.18±3.39
<b>Cd</b>	0.0014±0	<PQL	0.0010±0	0.0011±0.0001	<PQL	<PQL	<PQL
<b>Co</b>	0.0054±0	0.0032±0.0002	0.0032±0.0001	0.0023±0.0004	0.0034±0	0.0035±0.0001	0.0017±0
<b>Cu</b>	0.0056±0.0017	0.0023±0.0004	0.0023±0.0003	0.0043±0.0011	0.0026±0.0015	0.0041±0.0022	0.0058±0.0034
<b>Fe</b>	6.180±0.058	1.080±0.043	1.471±0.330	3.391±0.512	1.424±0.255	0.830±0.200	2.878±1.318
<b>K</b>	1.825±0.023	2.522±0.079	2.454±0.028	2.845±0.439	2.927±0.095	2.893±0.056	3.097±0.172
<b>Li</b>	0.013±0	0.013±0	0.013±0	0.013±0	0.015±0	0.015±0	0.016±0
<b>Mg</b>	6.819±0.030	6.795±0.037	6.844±0.025	6.910±0.048	8.546±0.205	8.589±0.175	9.175±0.275
<b>Mn</b>	0.160±0	0.165±0.001	0.168±0.002	0.167±0.005	0.168±0.002	0.171±0.004	0.085±0.005
<b>Na</b>	10.532±0.053	10.689±0.111	10.783±0.031	11.050±0.186	11.871±0.227	11.959±0.194	12.322±0.379
<b>Ni</b>	0.035±0	0.020±0	0.021±0.001	0.019±0.001	0.043±0.003	0.040±0.001	0.025±0.004
<b>S</b>	58.822±0.260	58.274±0.287	59.499±0.218	59.946±0.691	70.059±1.301	71.261±1.597	79.681±2.724
<b>Si</b>	5.289±0.011	5.059±0.039	5.206±0.022	5.238±0.075	5.027±0.054	5.051±0.097	3.844±0.146
<b>Zn</b>	1.340±0.014	1.103±0.008	1.108±0.010	0.838±0.079	0.625±0.044	0.657±0.024	0.123±0.026

**Table 3. Initial and final dissolved (<0.45  $\mu$ m) metals data for microcosm experiment. <PQL refers to concentrations below the practical quantitation limit.**

	Initial (0 hours)			Final (96 hours)			
	All Microcosms	Closed	Open	Open + Aerated	Closed + Fe	Open + Fe	Open + Aerated + Fe
<b>Ag</b>	0.0035 $\pm$ 0.0002	0.0051 $\pm$ 0.0008	0.0048 $\pm$ 0.0010	0.0043 $\pm$ 0.0006	0.0045 $\pm$ 0.0008	0.0049 $\pm$ 0	0.0043 $\pm$ 0.0013
<b>Al</b>	0.068 $\pm$ 0.003	0.169 $\pm$ 0.013	0.156 $\pm$ 0.006	0.123 $\pm$ 0.005	0.115 $\pm$ 0.004	0.109 $\pm$ 0.006	0.107 $\pm$ 0.007
<b>Ba</b>	0.017 $\pm$ 0	0.015 $\pm$ 0	0.015 $\pm$ 0	0.014 $\pm$ 0	0.003 $\pm$ 0.001	0.003 $\pm$ 0	<PQL
<b>Ca</b>	144.09 $\pm$ 1.08	149.45 $\pm$ 3.15	151.05 $\pm$ 1.84	149.37 $\pm$ 2.70	149.07 $\pm$ 2.35	151.23 $\pm$ 1.93	145.78 $\pm$ 2.93
<b>Cd</b>	0.0013 $\pm$ 0	<PQL	<PQL	<PQL	<PQL	<PQL	<PQL
<b>Co</b>	0.0035 $\pm$ 0.0011	0.0038 $\pm$ 0.0001	0.0037 $\pm$ 0.0001	0.0035 $\pm$ 0.0003	0.0045 $\pm$ 0.0001	0.0048 $\pm$ 0.0003	0.0025 $\pm$ 0.0003
<b>Cu</b>	0.0055 $\pm$ 0.0019	0.0037 $\pm$ 0.0001	0.0047 $\pm$ 0.0004	0.0042 $\pm$ 0.0009	0.0041 $\pm$ 0.0008	0.0037 $\pm$ 0.0004	0.0039 $\pm$ 0.0007
<b>Fe</b>	5.531 $\pm$ 0.141	0.408 $\pm$ 0.022	0.163 $\pm$ 0.057	0.085 $\pm$ 0.018	0.025 $\pm$ 0.018	0.027 $\pm$ 0.009	0.140 $\pm$ 0.204
<b>K</b>	1.981 $\pm$ 0.054	2.580 $\pm$ 0.125	2.551 $\pm$ 0.038	2.878 $\pm$ 0.494	2.909 $\pm$ 0.102	2.945 $\pm$ 0.024	3.118 $\pm$ 0.153
<b>Li</b>	0.014 $\pm$ 0	0.013 $\pm$ 0	0.014 $\pm$ 0	0.013 $\pm$ 0	0.015 $\pm$ 0	0.016 $\pm$ 0	0.016 $\pm$ 0
<b>Mg</b>	6.869 $\pm$ 0.019	6.961 $\pm$ 0.075	7.063 $\pm$ 0.059	6.966 $\pm$ 0.144	8.491 $\pm$ 0.225	8.738 $\pm$ 0.036	9.300 $\pm$ 0.326
<b>Mn</b>	0.161 $\pm$ 0	0.179 $\pm$ 0.005	0.181 $\pm$ 0.007	0.162 $\pm$ 0.004	0.164 $\pm$ 0.004	0.171 $\pm$ 0.001	0.081 $\pm$ 0.003
<b>Na</b>	10.660 $\pm$ 0.014	10.993 $\pm$ 0.253	11.237 $\pm$ 0.123	11.154 $\pm$ 0.404	11.756 $\pm$ 0.204	12.170 $\pm$ 0.089	12.406 $\pm$ 0.359
<b>Ni</b>	0.037 $\pm$ 0	0.021 $\pm$ 0	0.021 $\pm$ 0.002	0.019 $\pm$ 0	0.043 $\pm$ 0.003	0.040 $\pm$ 0.001	0.025 $\pm$ 0.003
<b>S</b>	59.394 $\pm$ 0.089	60.377 $\pm$ 1.205	61.889 $\pm$ 0.853	60.805 $\pm$ 1.594	69.182 $\pm$ 1.440	70.525 $\pm$ 0.219	80.790 $\pm$ 3.253
<b>Si</b>	5.439 $\pm$ 0.170	5.246 $\pm$ 0.113	5.364 $\pm$ 0.038	5.055 $\pm$ 0.127	4.930 $\pm$ 0.017	5.103 $\pm$ 0.067	3.783 $\pm$ 0.070
<b>Zn</b>	1.308 $\pm$ 0.012	1.137 $\pm$ 0.024	1.115 $\pm$ 0.005	0.369 $\pm$ 0.010	0.611 $\pm$ 0.044	0.653 $\pm$ 0.032	0.054 $\pm$ 0.006

When plotting the results from this experiment, the measurements from the triplicates for each microcosm were averaged, and the error bars show the standard deviations in the three values for each treatment/time data point. The tables of p-values from the t-tests for determining the statistical significance in the difference of regression slopes for each metal parameter are located in Appendix A.

Initially, the pH increased then leveled off for the Closed, Open, Open + Aerated, and Open + Aerated + Fe experiments and remained relatively constant for the Closed + Fe and Open + Fe experiments (Figure 2). The initial pH was higher in the aerated experiments due to the degassing of CO<sub>2</sub>. Later, the pH leveled off as the pH increase competed against the pH decrease from the proton release caused by the hydrolysis of iron. The pH remained relatively constant for the Fe experiments because the increase in pH, as seen in the other experiments, was offset by a decrease in pH caused by the complexation of metal cations to the active iron oxide solid surfaces.

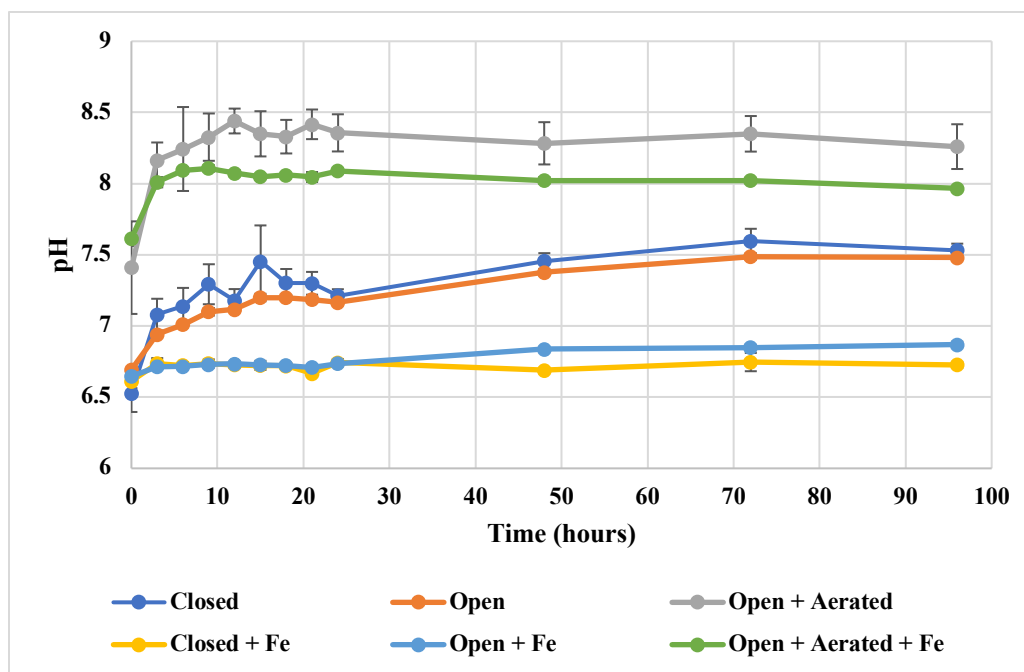


Figure 2: pH vs Time in Six Microcosms

The dissolved oxygen (DO) increased for all microcosms over the sampling period (Figure 3). The DO was initially higher in the aerated microcosms since oxygen was being pumped into the system. The DO increased faster in the Closed + Fe and Open + Fe microcosms than in the Closed and Open microcosms. Although the increase in DO in the non-aerated microcosms was unexpected, it could have been caused by decreasing temperature over the experiment, since colder water can hold more oxygen. Over the experiment, the temperature decreased from about 14.5°C to around 0°C. The plot of DO Saturation vs Time is shown in Figure 4. The DO Saturation accounts for temperature differences and shows the DO leveling out over time instead of increasing in all microcosms.



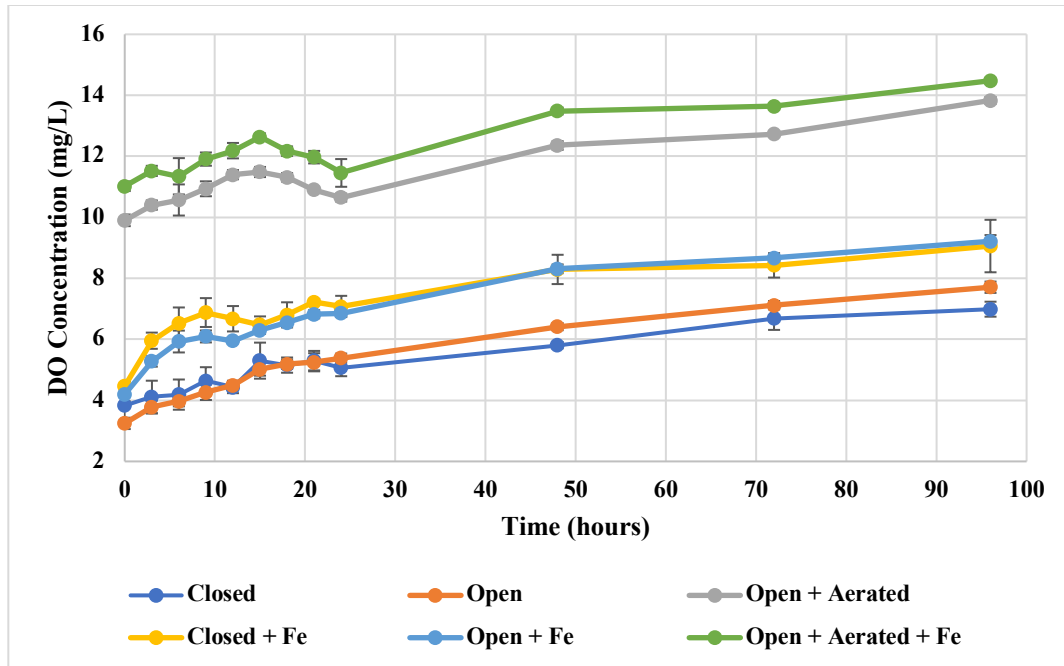


Figure 3: Dissolved Oxygen Concentration vs Time in Six Microcosms

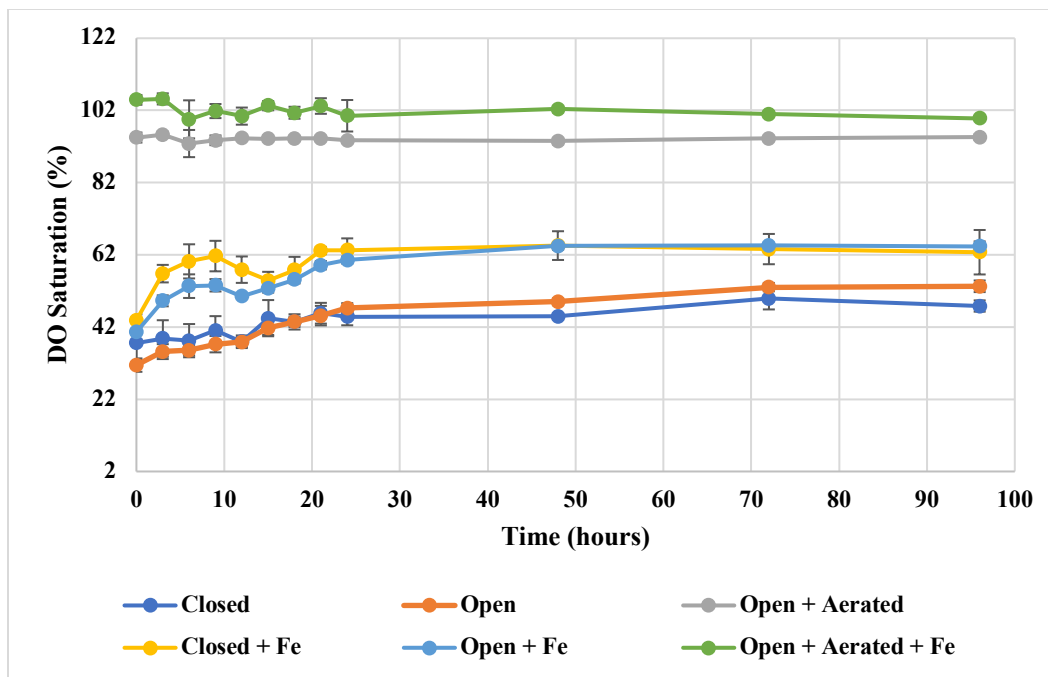


Figure 4: Dissolved Oxygen Saturation vs Time in Six Microcosms

For all six microcosms, alkalinity generally decreased over time (Figure 5). The decrease in alkalinity is most noticeable in the microcosms where solid Fe was added. These microcosms also produced the greatest decrease in iron and zinc, which could contribute to the decrease in alkalinity as iron and zinc bond with oxygen and hydroxide in the water, affecting the carbonate equilibria.

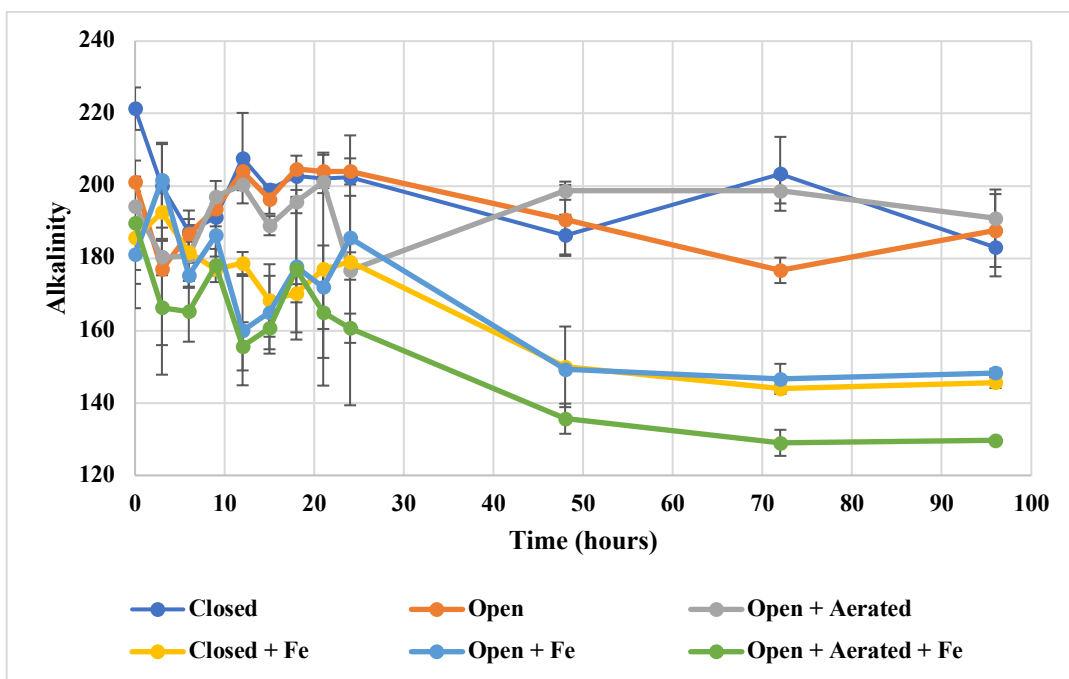


Figure 5: Alkalinity vs Time in Six Microcosms

The turbidity generally decreased for all six microcosms (Figure 6). For the microcosms where Fe solids were added, the initial turbidity was greater due to the presence of these solids and decreased as the Fe settled to the bottom of the microcosms. In the Closed and Open microcosms, the turbidity gradually increased over the first two days then decreased over the next two days. The increase in turbidity was likely caused by the precipitation of Fe.

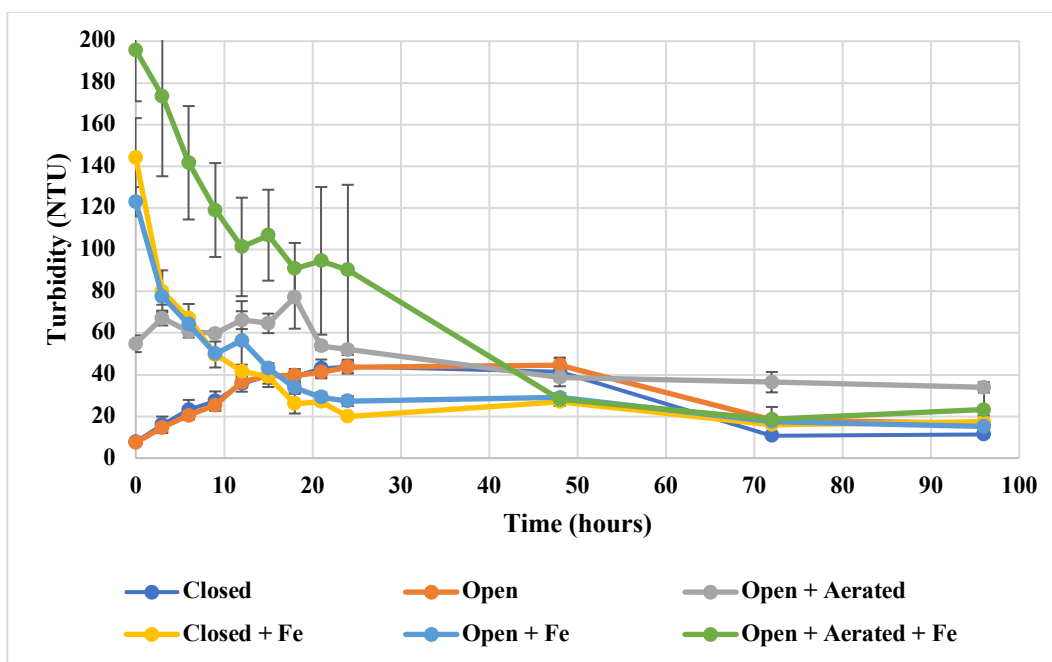


Figure 6: Turbidity vs Time in Six Microcosms

The total iron decreased to below 5 mg/L for all six microcosms (Figure 7). In the microcosms where Fe solids were added, the initial total iron concentrations are greater since iron was added to these microcosms. Performing t-tests on the slopes of the regression lines showed that there are significant differences in the slope of the Open + Fe regression line with the slopes of the Closed, Open, and Open + Aerated regression lines ( $\alpha = 0.05$ ). Similarly, there are significant differences in the slope of the Open + Aerated + Fe regression lines with the slopes of the Closed, Open, and Open + Aerated regression lines. Additionally, there is a significant difference between the slopes of the Closed + Fe and Open + Aerated lines. Performing a Permutational Multivariate Analysis of Variance (MANOVA) test showed that there is a significant difference in the difference in means between the groups where solid Fe was added and the groups where no solid Fe was added ( $\alpha = 0.05$ ). The p-value for this test was  $1.0E-4$ . This indicates that the microcosms where solid Fe was added produced significantly different results than the microcosms where no solid Fe was added, showing that adding solid Fe effectively removes total iron from net alkaline mine waters.

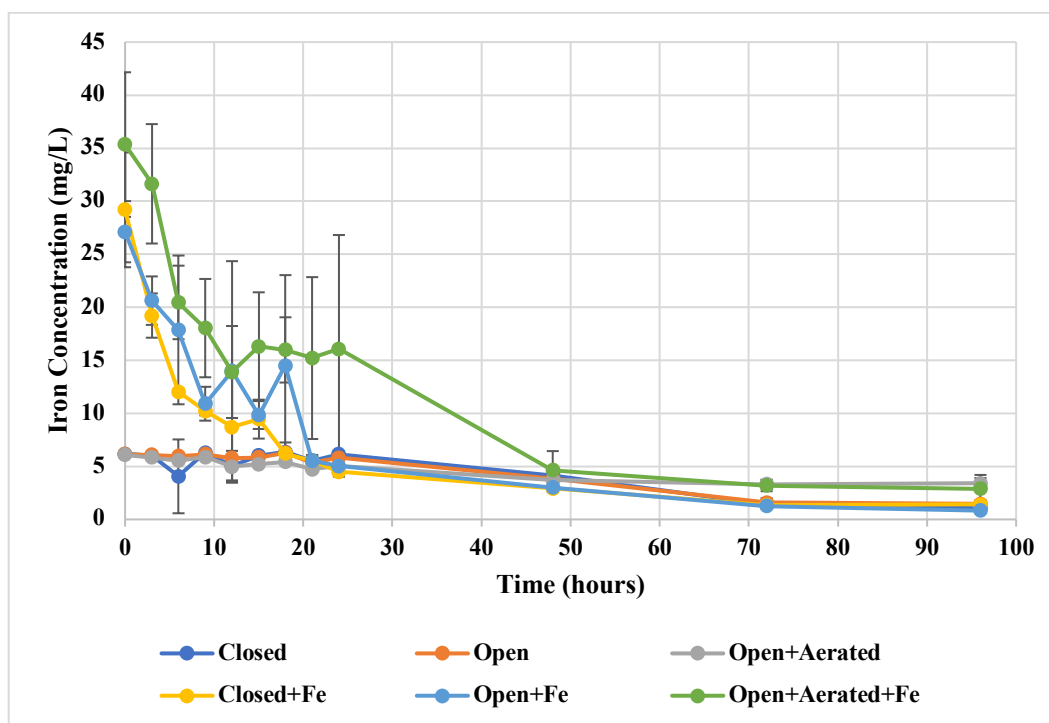


Figure 7: Total Iron vs Time for Six Microcosms

The dissolved iron decreased over time in all six microcosms (Figure 8). In the aerated microcosms, the dissolved iron was initially low and remained low throughout. The aeration in these microcosms caused the iron oxidation process to speed up, causing soluble ferrous iron to quickly change to insoluble ferric iron. Performing t-tests on the slopes of each of these regression lines showed that there is a significant difference between the slope of the Open + Aerated line and the Closed, Open, and Closed + Fe lines ( $\alpha = 0.05$ ). Similarly, there is a significant difference between the slope of the Open + Aerated + Fe line and the Closed, Open, and Closed + Fe lines. Performing a Permutational Multivariate Analysis of Variance (MANOVA) test showed that there is a significant difference in the difference in means between

the groups that were aerated and the groups that were not aerated ( $\alpha = 0.05$ ). The p-value for this test was 2.6E-3. This indicates that simple aeration can be an effective method for removing dissolved iron from an aquatic system, compared to the control and solid Fe microcosms.

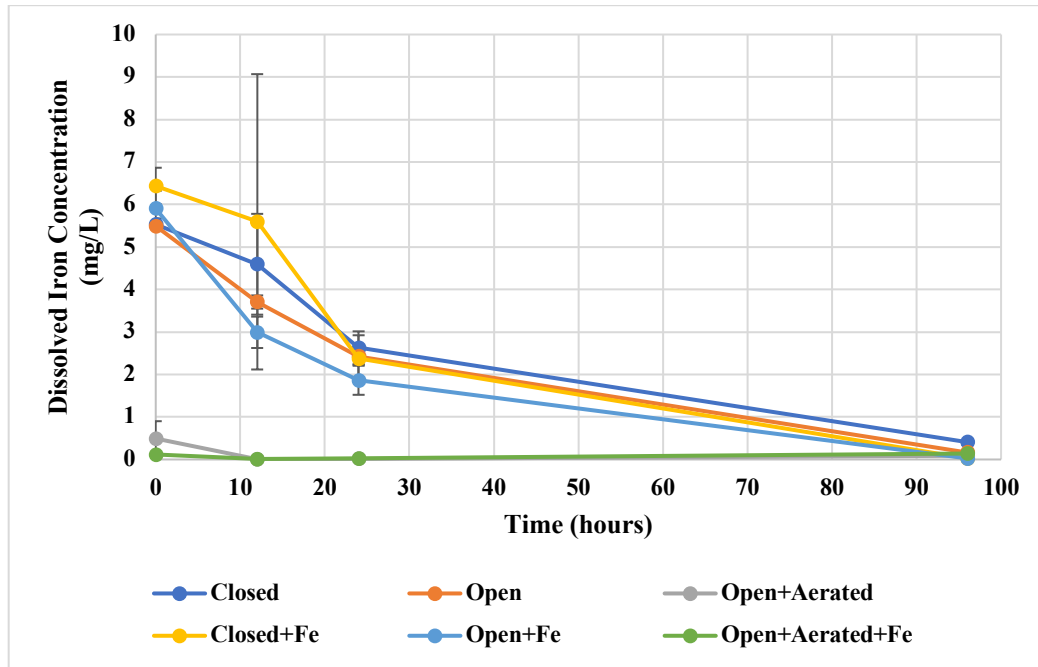


Figure 8: Dissolved Iron vs Time for Six Microcosms

The particulate iron greatly decreased over time for the microcosms with added solid Fe, slightly decreased in the Open + Aerated microcosm, and increased in the Closed and Open microcosms (Figure 9). The particulate iron was initially high in the Fe microcosms since solid Fe was initially added. Moreover, the initial particulate iron was higher in the Open + Aerated microcosm than in the Closed and Open microcosms since the aeration sped up the iron oxidation process as previously noted. The particulate iron in the Closed and Open microcosms likely increased as the iron oxidation process occurred, where soluble ferrous iron is oxidized to insoluble ferric iron. However, performing t-tests on the slopes of each of these regression lines showed that, with an  $\alpha$  value of 0.05, the null hypothesis that the regression slopes are the same cannot be rejected in any case. Performing a Permutational Multivariate analysis of variance (MANOVA) test showed that there is a significant difference in the difference in means between the groups where solid Fe was added and the groups where no solid Fe was added ( $\alpha = 0.05$ ). The p-value for this test was 1.0E-4. In this case, the addition of solid Fe could be a useful tool in removing iron from aquatic systems.

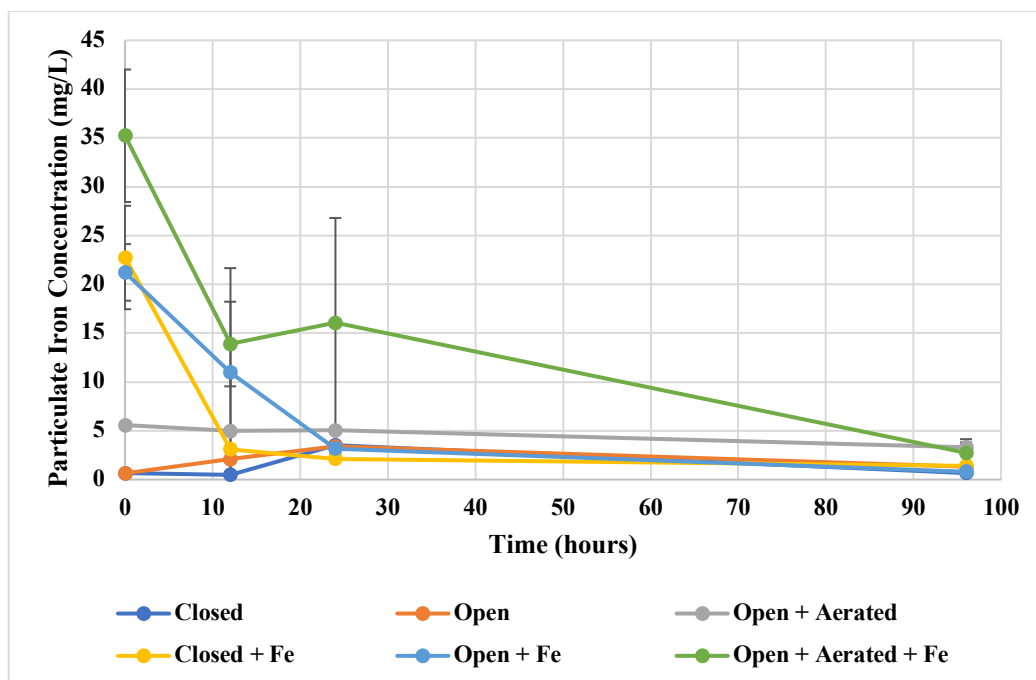


Figure 9: Particulate Iron vs Time for Six Microcosms

The total zinc concentrations decreased over time in all six microcosms (Figure 10). In the microcosms where the solid Fe was added, the final zinc concentrations were the lowest, with the lowest final concentration in the Open + Aerated + Fe microcosm. The zinc concentrations were likely lowest in the microcosms where solid Fe was added because the zinc sorbed to the solid Fe. Additionally, in the microcosms without Fe solids added, the final zinc concentration was lowest in the Open + Aerated microcosm. Performing t-tests on the slopes of each of these regression lines showed that there is a significant difference between the slope of the Open + Aerated + Fe regression line and the Closed, Open, Closed + Fe, and Open + Fe lines ( $\alpha = 0.05$ ). Additionally, this test showed there is a significant difference in the slopes of the Open + Aerated regression line and the Closed and Open regression lines. Performing a Permutational Multivariate Analysis of Variance (MANOVA) test showed that there is a significant difference in the difference in means between the groups where solid Fe was added and the groups where no solid Fe was added ( $\alpha = 0.05$ ). The p-value for this test was 1.0E-4. In this case, both adding solid Fe and aeration positively contribute to the removal of zinc from net alkaline mine waters.

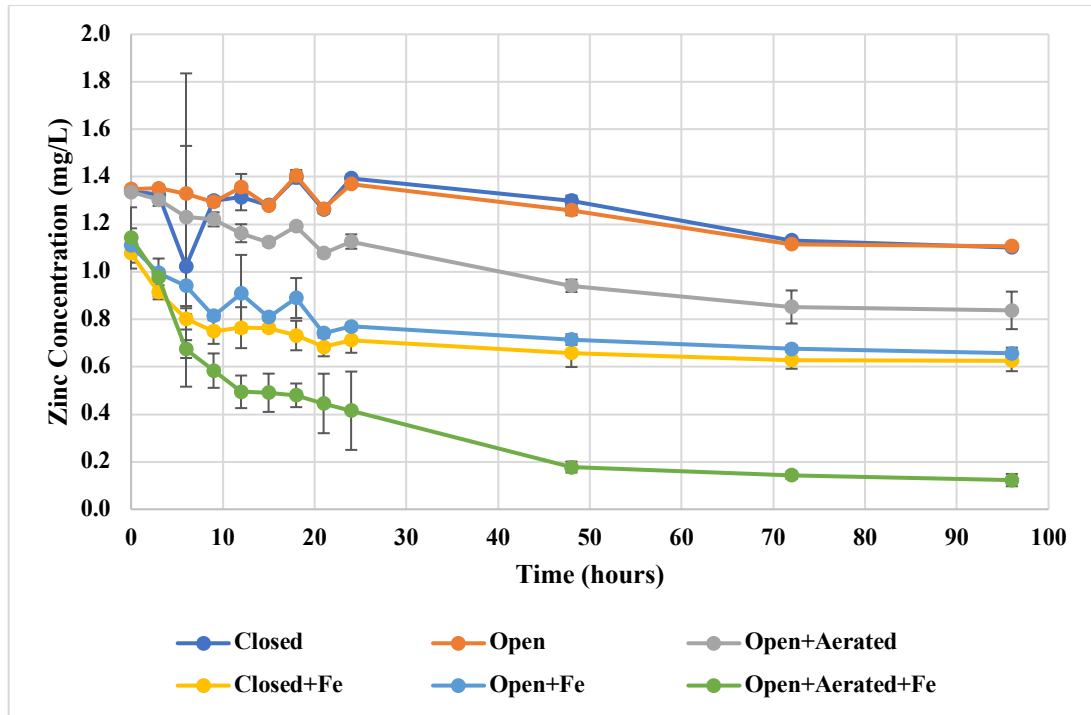
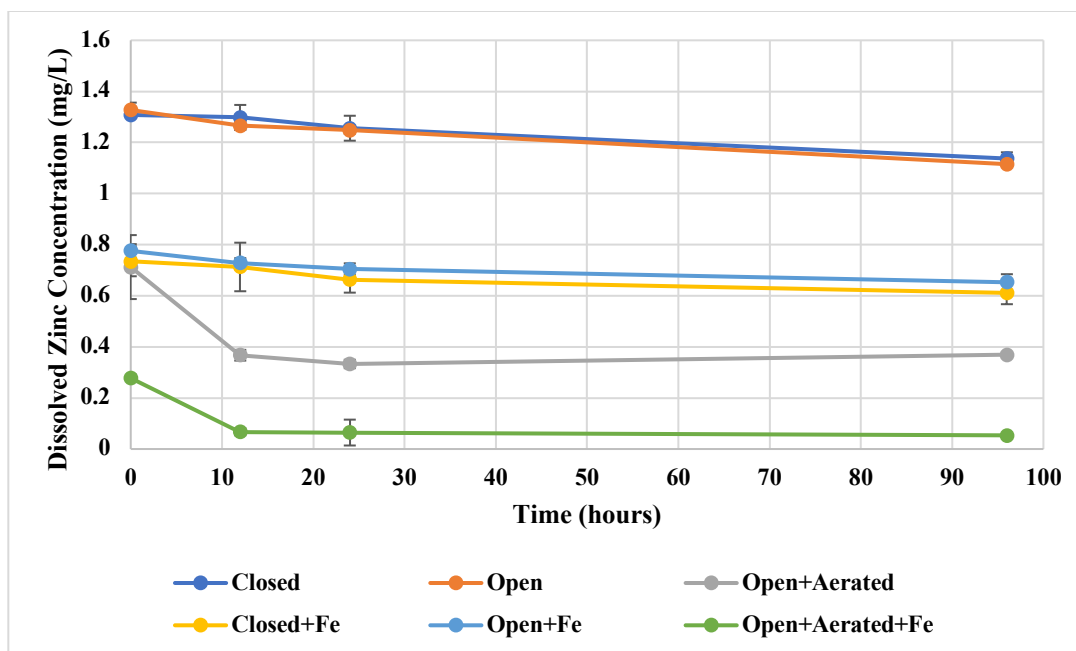


Figure 10: Total Zinc vs Time for Six Microcosms

The dissolved zinc concentrations gradually decreased over time in the Closed, Open, Closed + Fe, and Open + Fe microcosms, and decreased quickly initially in the Open + Aerated and Open + Aerated + Fe microcosms (Figure 11). However, performing t-tests on the slopes of each of these regression lines showed that, with an  $\alpha$  value of 0.05, the null hypothesis that the regression slopes are the same cannot be rejected in any case. Performing a Permutational Multivariate Analysis of Variance (MANOVA) test showed that there is a significant difference in the difference in means between the groups that were aerated and the groups that were not aerated ( $\alpha = 0.05$ ). The p-value for this test was 1.9E-3. Like with the dissolved iron, aeration can be an important tool for removing dissolved zinc from aquatic systems in the presence of iron particulates.



*Figure 11: Dissolved Zinc vs Time in Six Microcosms*

The total cadmium fluctuated over time but decreased overall for each microcosm (Figure 12). The final cadmium concentrations in all six microcosms dropped to below 0.002 mg/L. Performing t-tests on the slopes of each of these regression lines showed that there is a significant difference between the slope of the Open + Aerated regression line and the Closed + Fe, Open + Fe, and Open + Aerated + Fe lines, and there is a significant difference between the slope of the Open line and the Closed + Fe and Open + Aerated + Fe lines ( $\alpha = 0.05$ ). Performing a Permutational Multivariate Analysis of Variance (MANOVA) test showed that there is a significant difference in the difference in means between the groups where solid Fe was added and the groups where no solid Fe was added ( $\alpha = 0.05$ ). The p-value for this test was 2.0E-4. As with total iron and zinc, the microcosms where solid Fe was added had the greatest effect on total cadmium removal.

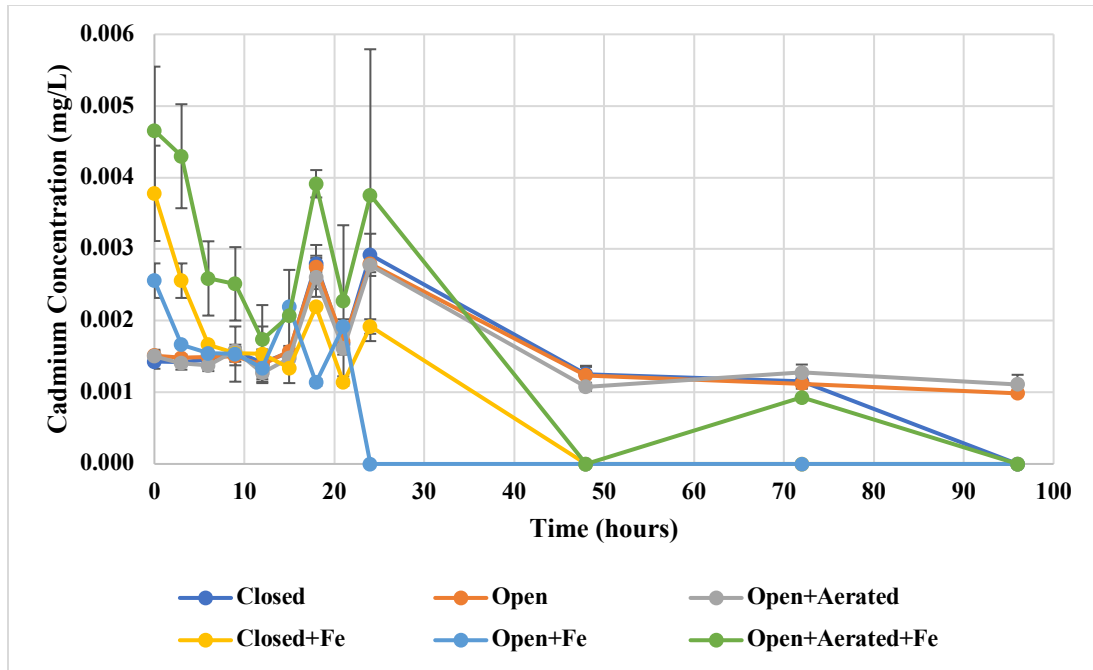


Figure 12: Total Cadmium vs Time for Six Microcosms

## Conclusions

Aeration and solid iron addition play an important role in removing trace metals from net alkaline mine water. Solid iron addition promoted total iron, zinc, and cadmium removal from net alkaline mine drainage through sorption. Simple aeration promoted dissolved iron removal by degassing  $\text{CO}_2$ . Passive treatment systems that utilize aeration and iron oxide solids could be key in the removal of iron and trace metals from net alkaline mine drainage.

Several other passive treatment systems have found aeration to be effective at removing trace metals from mine drainage by degassing  $\text{CO}_2$  and increasing pH (Nairn 2013, Kirby et al. 2009). Therefore, it was expected that aeration would be successful in other locations with trace metal concentrations. Aeration is a useful tool that can be implemented through several methods, such as diffusion systems or cascade systems (Oh et al. 2014). Both of these systems use either no energy or can be implemented with renewable energy, which creates a sustainable alternative to active treatment systems. From these results, it is evident that aeration can be an important supplement to passive treatment systems.

However, the results showing the efficacy of added solid iron on trace metal removal are more surprising. While solid iron oxides have shown initial promise for trace metal removal, this method is not as widely used as aeration in passive treatment systems (Dempsey, 2001). Nevertheless, this method can be a sustainable and inexpensive addition to passive treatment systems, especially if solid iron oxide found at passive treatment sites is utilized. Again, the addition of solid iron oxide could be a critical piece to the passive treatment puzzle.



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## Appendix A: p-values for Regression Slope Analysis

**Table A1: Total Iron p-values**

	<b>Open</b>	<b>Open + Aerated</b>	<b>Closed + Fe</b>	<b>Open + Fe</b>	<b>Open + Aerated + Fe</b>
<b>Closed</b>	0.8783	<b>0.0191</b>	0.0515	<b>0.0074</b>	<b>0.0015</b>
<b>Open</b>		<b>0.0002</b>	0.0525	<b>0.0074</b>	<b>0.0015</b>
<b>Open + Aerated</b>			<b>0.0213</b>	<b>0.0023</b>	<b>0.0005</b>
<b>Closed + Fe</b>				0.6988	0.3000
<b>Open + Fe</b>					0.4690

**Table A2: Dissolved Iron p-values**

	<b>Open</b>	<b>Open + Aerated</b>	<b>Closed + Fe</b>	<b>Open + Fe</b>	<b>Open + Aerated + Fe</b>
<b>Closed</b>	0.9531	<b>0.0210</b>	0.6079	0.9764	<b>0.0154</b>
<b>Open</b>		<b>0.0274</b>	0.5851	0.9887	<b>0.0205</b>
<b>Open + Aerated</b>			<b>0.0397</b>	0.0911	0.4798
<b>Closed + Fe</b>				0.6573	<b>0.0331</b>
<b>Open + Fe</b>					0.0760

**Table A3: Particulate Iron p-values**

	<b>Open</b>	<b>Open + Aerated</b>	<b>Closed + Fe</b>	<b>Open + Fe</b>	<b>Open + Aerated + Fe</b>
<b>Closed</b>	0.9678	0.4779	0.4107	0.1884	0.1243
<b>Open</b>		0.3625	0.4043	0.1821	0.1213
<b>Open + Aerated</b>			0.4703	0.2238	0.1418
<b>Closed + Fe</b>				0.8729	0.5551
<b>Open + Fe</b>					0.5950

**Table A4: Total Zinc p-values**

	<b>Open</b>	<b>Open + Aerated</b>	<b>Closed + Fe</b>	<b>Open + Fe</b>	<b>Open + Aerated + Fe</b>
<b>Closed</b>	0.4538	<b>0.0134</b>	0.4287	0.2148	<b>0.0087</b>
<b>Open</b>		<b>0.0040</b>	0.8097	0.3899	<b>0.0116</b>
<b>Open + Aerated</b>			0.0676	0.1570	0.1358
<b>Closed + Fe</b>				0.6399	<b>0.0239</b>
<b>Open + Fe</b>					<b>0.0401</b>

**Table A5: Dissolved Zinc p-values**

	<b>Open</b>	<b>Open + Aerated</b>	<b>Closed + Fe</b>	<b>Open + Fe</b>	<b>Open + Aerated + Fe</b>
<b>Closed</b>	0.4824	0.9522	0.1514	0.1106	0.7942
<b>Open</b>		0.9809	0.1110	0.0858	0.6892
<b>Open + Aerated</b>			0.7809	0.7529	0.8554
<b>Closed + Fe</b>				0.8285	0.9027
<b>Open + Fe</b>					0.8520

**Table A6: Total Cadmium p-values**

	<b>Open</b>	<b>Open + Aerated</b>	<b>Closed + Fe</b>	<b>Open + Fe</b>	<b>Open + Aerated + Fe</b>
<b>Closed</b>	0.5881	0.4528	0.1214	0.2854	0.0516
<b>Open</b>		0.7917	<b>0.0190</b>	<b>0.0591</b>	<b>0.0118</b>
<b>Open + Aerated</b>			<b>0.0110</b>	<b>0.0346</b>	<b>0.0078</b>
<b>Closed + Fe</b>				0.5196	0.4304
<b>Open + Fe</b>					0.1969