IRONING OUT YOUR SYSTEM: REMOVAL OF FERRIHYDRITE PRECIPITATES FROM MINING INFLUENCED WATER PIPELINES[1]

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Abstract: Iron hydroxide coatings are responsible for the failure of some mining influenced water (MIW) treatment systems. Iron hydroxide coatings can reduce the effectiveness of limestone drains, clog vertical flow reactors and bioreactors, and reduce the hydraulic efficiency of pipelines and hydraulic control structures. Physical disruption of iron hydroxide coatings is not always possible. Strong acids are effective at dissolving iron hydroxide precipitates but are not safe for field application. We examined the dissolution of iron hydroxide coatings using various combinations of slightly alkaline citrate, bicarbonate and dithionite solutions in batch laboratory tests. Iron hydroxide coatings were collected from a pipeline transporting iron-containing MIW. Solutions of citrate alone and citrate plus bicarbonate were effective at partially dissolving the iron hydroxide precipitates. A solution of citrate, bicarbonate and dithionite (CBD) completely dissolved the iron hydroxide coating in laboratory tests. In November 2007, 170-L of the CBD solution was applied to a clogged field pipeline that had originally supported a flow of over 30 liters per minute (lpm) to two bioreactors in October 2006. However, the flow to both bioreactors had reduced to less than one-lpm by November 2007, which was not enough to provide at least one-lpm to each bioreactor. After the initial application, the flow increased to three-lpm. Subsequent field applications of the CBD solution in November and December 2007 increased the flow to five-lpm. This paper presents the results of the laboratory investigation and the field application of the CBD solution. The CBD solution is a safe and user-friendly method to remove iron hydroxide coatings from a broad range of MIW treatment systems and hydraulic structures.

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Introduction

Mining influenced water (MIW) is a prevalent problem in many previously mined areas, particularly in Colorado, where there are over 22,000 abandoned mines (Figueroa et al., 2007). Due to the severe environmental impacts of MIW (e.g., high levels of toxic metal species in surface and groundwater; low pH levels), remedial methods involving its collection and treatment are necessary. The National Tunnel adit at Black Hawk, CO, a once lucrative mining town, redirects approximately 95-lpm (liters per minute) of MIW into the north fork of Clear Creek. Over 100 years of regional Au and Ag mining has produced contaminated tailings and drainage tunnels, resulting in surface waters that are heavily polluted with Fe, Zn, Cu, Cd, As, and Pb (EPA, 2007). As such, the Environmental Protection Agency has deemed this area the Central City Clear Creek Superfund site. The MIW from the National Tunnel is currently undergoing experimental remediation efforts by redirecting the MIW through a pipeline to two passive biological treatment reactors. However, large quantities of suspected ferrihydrite precipitate are forming in the pipeline, hindering the MIW flow rates to the reactors. This paper discusses potential treatment strategies to remediate the iron scaling by forcing the precipitate back into solution so that the pipeline flow may be increased, and if possible, returned to its original unhindered flow rate.

The physical and chemical weathering of pyrite (i.e., iron II sulfide; FeS_2) a byproduct of mining causes MIW. Pyrite is normally a stable, insoluble mineral when it is not exposed to air in water. However, as water flows through previously mined subsurface caves, the exposed pyrite dissolves under contact with the water, and the sulfide component is converted to SO_4^{2-} through oxidation (Equation 1) (Stumm and Morgan, 1996).

$$2FeS_{2(s)} + 7O_{2(aq)} + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad \text{(Equation 1)}$$

This reaction produces proton acidity. The oxidation of ferrous (Fe^{2+}) iron to ferric (Fe^{3+}) iron then occurs, consuming part of the proton acidity (Equation 2) (Castro *et al*., 1998).

$$4Fe^{2+} + O_{2(aq)} + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad \text{(Equation 2)}$$

Following oxidation, the water contains a very low residual dissolved oxygen concentration. Additionally, Fe^{3+} ions in the water combine with OH ions to form $Fe(OH)_3$, a yellow-brown precipitate often termed "yellow-boy".

The dissolution of iron sulfide, precipitation of $Fe(OH)_3$and the resulting low pH of the water due to proton acidity create conditions unfavorable to aquatic life and hazardous to potential downstream water sources. The north fork of Clear Creek, in Black Hawk, CO has been deemed biologically dead for these reasons. MIW generally results in the contamination of water bodies with high loads of sulfates, proton acidity, and heavy metals (Castro *et al.*, 1998).

Figure 1. MIW discharge from the National Tunnel adit into Clear Creek at Black Hawk, CO.

For abandoned mines, these problems must be mitigated, which can be costly and time-consuming with no responsible party to bear the cost. Several techniques, such as the sealing of mine shafts and re-routing of surface drainage have been used to reduce the impacts of MIW. In order to safely discharge the effluent, the drainage may be diverted and treated so that containments are safely removed and the pH neutralized to acceptable water quality standards.

A portion of the 95-lpm discharge from the National Tunnel adit in Black Hawk, CO is currently undergoing such remediation efforts by redirecting the MIW through a 244-m long PVC pipeline (3.81-cm in diameter) to two experimental biological treatment reactors. The pipeline system was originally designed to deliver a total flow of approximately 36-lpm of MIW to both bioreactors. By maintaining a fixed water elevation and controlling the diameter of the effluent valves at the bioreactors, the MIW flow into the reactors could be regulated; only approximately 1-lpm of MIW flow was allowed to enter each bioreactor. The excess 34-lpm of MIW flow effluent bypassed the reactors and discharged into Clear Creek. However, conveyance of the water over the past year has resulted in a large quantity of uncharacterized scaling within the delivery pipeline preceding the treatment systems, and total MIW flow to both reactors had slowly decreased from 36-lpm to < 1-lpm (see Fig. 2).

In the spring 2007, attempts were made to reverse the low flow by physically disrupting the lower 15-m portion of pipeline near the bioreactors and by modifying sections of the hydraulic delivery system. These actions initially increased the total MIW flow to a sufficient level to continue operation (allowing approximately 1-lpm to each reactor), but the original flow of 36-lpm was not reached. The flow proceeded to decline coincident with the onset of cold temperatures in October 2007, which led to renewed efforts for a solution. This problem is not unique to the Black Hawk remediation site; it is a common issue that affects many passive treatment systems, including limestone drains and vertical flow reactors, and often results in system failure within the first two years of initiation (Neculita et al., 2007).

Figure 2. Low flow from the effluent pipeline of the experimental bioreactor at Black Hawk, CO, on November 10, 2007. Effluent flow was originally ~36-lpm.

In pH conditions greater than approximately 3.5, Fe^{3+} reacts in water to form $Fe(OH)_3$ precipitates (Equation 3) (Neculita et al., 2007):

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3H^+ \qquad \text{(Equation 3)}$$

Over time, precipitates such as FeO and FeO(OH) may form from continual dissolution of the $Fe(OH)_{3(s)}$. Mechanical and chemical disruptions are two primary means of eradicating such precipitate scaling. Mechanical methods include snaking and high-pressure flushing of the pipelines. These techniques, while sometimes successful, are generally difficult to perform in the field. In many cases, pipelines are either too long or small in diameter (e.g., this study) for the use of commercial snaking apparatus. Also, treatment reactors may be located in remote areas, making high-pressure flushing impossible to complete without a generator.

Chemical disruption methods include the application of acids, ligands (i.e., chelators), or reducing agents directly to the problem areas. Acids are generally not a recommended course of action, as more ecological problems inevitably result. While lowering the pH of the solution in question here will encourage dissolution of the iron precipitate, the increased acidity is more debilitating to the source water than beneficial. In addition, government regulations require discharge pH to be between 6.0 and 9.0 (Colorado Department of Public Health and Environment, 2008).

Chelating treatments, such as sodium citrate, oxalate, and EDTA, are generally a more successful means of disrupting the precipitates. Chelators bind to ferrous iron that is present in solution to form more soluble complexes. However, chelating agents are unable to remove insoluble ferric iron, and do not address low pH concerns.

The third chemical disruption method involves the use of a reducing agent, such as sodium dithionite, to reduce present Fe^{3+} to the Fe^{2+} state. However, without the presence of a chelating agent, the free Fe^{2+} will bind with sulfides to precipitate additional pyrite.

A potential treatment for dissociating the resultant $Fe(OH)_3$ scaling involves a combination of the above chemical practices. Mehra and Jackson (1955) were highly successful in removing iron oxide precipitates from soil and clay samples in the laboratory by first reducing Fe^{3+} iron to Fe^{2+} iron through the addition of a strong reducing agent (sodium dithionite) and then forming soluble complexes with a chelating agent (sodium citrate); sodium bicarbonate was added as a buffer to increase the pH of the system to neutral conditions. This method (CBD; citrate-bicarbonate-dithionite) could be an ideal solution to the pipeline issues addressed here, as the additives are environmentally friendly and cost effective.

Methods

Visual MINTEQ, an equilibrium model to determine chemical speciation, was used to verify that a ligand dissolution treatment (sodium citrate) was slightly more successful at complexing iron from goethite than strictly an acid treatment (HCl) under acidic conditions (pH = 4.5). Based upon these results, small batch laboratory experiments were performed following the methods outlined in Table 1 to determine the feasibility of applying the CBD solution to MIW slurry that was collected from the National Tunnel adit. Once an effective method was determined, field experiments were performed on-site at Black Hawk, CO.

Table 1. Methods for Solution Analysis

Analyte or Analyte group	Measurement Method	Equipment	Reporting Units	Practical Limit
Cu, Fe , Zinc	EPA 6010B ICP-AES	Perkin Elmer Model 3000	mg/L	0.01 mg/L (lower limit) and ± 0.01 mg/L
pH	EPA 150.1	pH/mV meter with pH probe	s.u. units	± 0.1 s.u. units
Specific Conductivity	EPA 120.1	Conductivity/ temperature meter with probe	microsiemen	± 1 μS
Temperature	--	Conductivity/ temperature meter with probe	Celsius	± 0.1 ◦C

Laboratory experiments

The laboratory experiments were modified after Mehra and Jackson (1958). Solutions were prepared using reagent grade chemicals and distilled water, and the MIW slurry was collected from PVC pipeline from an adjacent bioreactor system at Black Hawk experiencing the same iron precipitation issues. Once the slurry settled, the supernatant was decanted. In order to demonstrate that pipetting the concentrated slurry solution yielded good replication, 5-ml was pipetted onto each of five aluminum pans, subsequently dried overnight in a ~103° C oven, and then reweighed. On average, five-ml of the slurry contained 0.0284-g of iron precipitate, with a relative standard deviation of 1.72%.

Table 2 outlines the experimental procedure; all trials were performed in duplicate.

Table 2. Small Batch Laboratory Matrix

ID	Slurry (ml)	0.3 M Na-Citrate (ml)	1.0 M Na-Bicarbonate (ml)	Na-Dithionite (g)
Control-1	25	0	0	0
Control-2	25	0	0	0
1-3	25	20	0	0
2-3	25	0	2.5	0
2-5	25	0	0	0.5
1-5	25	20	2.5	0
2-7	25	0	2.5	0.5
1-7	25	20	2.5	0.5

The solutions detailed in Table 2 were pipetted or weighed (in the Na-dithionite case) into a 50-ml plastic conical tube. All tubes (16 total) were placed on a rotary shaker table overnight at ~150 rpm's at room temperature. The solutions were removed from the shaker table and allowed to settle the next day.

Field methods

Based on laboratory findings (see Results section below), the CBD method (i.e., ID 1-7) was determined the most beneficial. To treat the 244-m PVC pipeline, ten 19-L batches of the CBD solution were applied during each flushing event. Table 3 indicates the laboratory-to-field concentration conversions.

Due to the large-scale nature of the field experiments, citric acid replaced sodium citrate (in the same molarity) and commercial food-grade Na-bicarbonate (i.e., Arm & Hammer) replaced reagent grade Na-bicarbonate for increased cost-effectiveness. However, in order to replicate similar pH results in the field as in the bench-top experiments (i.e., pH = ~8.3), the Na-bicarbonate buffer concentration was increased to 0.253 M, based on laboratory experiments.

Table 3. Laboratory-to-Field Equivalent Conversions

Chemical	Lab. Conc.	Vol. Added	Final Vol.	Field Conc.
Na-Citrate	0.3 M	0.0200 L	0.0475 L	0.126 M
Na-Bicarbonate	1.0 M	0.0025 L	0.0475 L	0.253 M
Na-Dithionite	0.5 g	0.0475 L	1.0 L	10.53 g/L

The field equivalent concentrations of the chemicals detailed in Table 3 were weighed and bagged in the laboratory in batches of ten. At the field site (on a bridge above the adit), approximately 19-L of MIW from the adit (used in place of distilled water) was added to a 60-L plastic utility container, which was fitted with a control valve and tubing. The chemicals were slowly added to the container one at a time, stirred, and covered. A 90º piece of PVC pipe was attached to the existing PVC pipeline at the adit discharge site to cease MIW flow to the bioreactors. The tubing leading from the utility container was then inserted into the elbow (see Fig. 3) to allow the CBD solution to enter the affected pipeline.

A. B.

Figure 3. A. National Tunnel adit discharging into Clear Creek at Black Hawk, CO. The pipeline studied here leads to the left and redirects MIW to a bioreactor 244-m downstream. B. Arial view of CBD solution application from the bridge.

The experimental bioreactors were shut off prior to each flushing event (i.e., MIW was not allowed to enter), and the pipeline was drained of MIW. Once the MIW flow was ceased, the drain to Clear Creek was also closed to create a “closed system” environment for the CBD solution to react with the precipitate; flushing was then initiated.

The valve on the container was opened, and the CBD solution was allowed to enter the 244-m pipeline. Once the first ~19-L of solution was added (over an approximately 15-min. period), the next batch was prepared and applied in the same manner as previously described; this process was repeated an additional eight times. Following the final CBD application, the effluent drain to the north fork of Clear Creek was reopened, but flow remained diverted from the reactors until it was ensured that the entire volume of CBD solution had exited the pipeline into Clear Creek.

This flushing procedure was performed three times in 2007: twice in November (10th and 18th) and once in December (20th). During the second flushing event, the MIW was heated prior to the addition of the chemicals, by using the base of a propane-fueled deep-fry turkey oven (see Fig. 4). This was done in an attempt to mimic the method by Mehra and Jackson (1958), which involved heating the Na-citrate and Na-bicarbonate solution to 80°C prior to the addition of dithionite. At the field, the MIW was heated for approximately 15-min. due to time constraints; the final temperature was unknown but the water was warm to the touch. After heating, the chemicals were added and the solution was applied to the pipeline in the same manner as previously detailed.

Figure 4. On-site heating of MIW prior to CBD addition on November 18, 2007.

On December 20, 2007, the CBD solution was added in the same manner as the first two flushings, however the pipeline outlet drain remained open, due to freezing concerns. Samples of the CBD solution were collected from the outlet drain twice on this date for future ICP analysis: approximately one hour and three hours after the initial application.

Effluent flow rates were recorded within 24 hours following each CBD flushing event.

Results

Laboratory results

Figure 5 illustrates the visual effect of each chemical component on the MIW slurry; pH measurements were also recorded (Table 4).

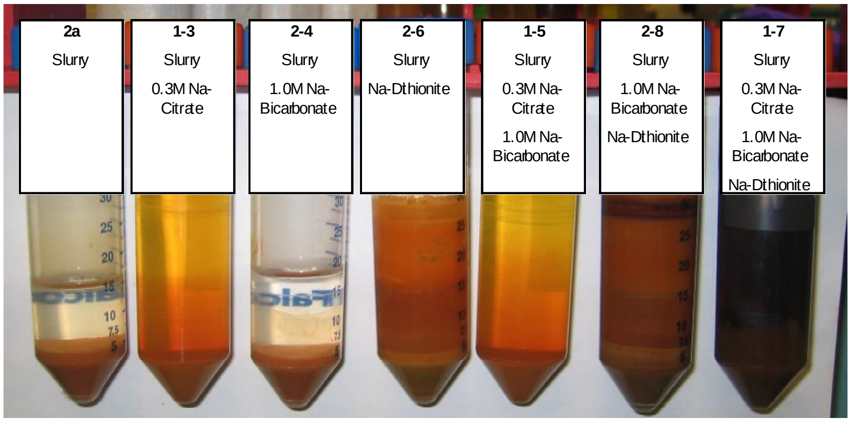

Figure 5. Selected samples from the CBD laboratory experiments; photograph was taken following sampling. See Table 2 for detailed additive volumes.

After the vials were allowed to settle, it was visually apparent that the addition of Na-citrate alone, and in combination with the bicarbonate buffer, encouraged only a small amount of precipitate back into solution (Fig. 5: vials 1-3 and 1-5, respectively). The vials containing Na-bicarbonate alone (Fig. 5: vial 2-4) were only successful in raising the pH, as expected (from 5.11 to 7.19). The addition of the reducing agent Na-dithionite alone, and in combination with Na-bicarbonate, encouraged a much larger amount of precipitate into solution, as is apparent by the darker color of the entire solution (Fig. 5: vials 2-6 and 2-8, respectively). However, the visible layering that occurred in these vials suggests that additional precipitates also formed, which were most likely iron sulfides. The vials containing all three additives (Fig. 5: vial 1-7) are visually the most successful method to force the iron slurry precipitate back into solution. Unlike the other trials, no solid remains at the bottom of this vial when rotated on its side.

Table 4 presents pH results, however some samples were measured two months after initialization; these later values may be assumed as the equilibrium pH of the particular system.

The supernatant of the settled solutions were also analyzed by ICP-AES. Preliminary results indicate that the CBD solution (Fig. 5: vial 1-7) achieved the highest concentration of iron in the supernatant. The citrate and bicarbonate solution trial achieved 700 to 900 mg/L of iron in the supernatant while the CBD solution achieved 3,100 to 3,300 mg/L. Based upon these results, the CBD solution proposed by Mehra and Jackson (1955) was applied to the field site at Black Hawk, CO.

Table 4. Small Batch Laboratory pH Results

ID	Slurry (ml)	0.3 M Na-Citrate (ml)	1.0 M Na-Bicarbonate (ml)	Na-Dithionite (g)	pH
Control-1a	25	0	0	0	5.40*
Control-1b	25	0	0	0	5.11*
Control-2a	25	0	0	0	5.11
Control-2b	25	0	0	0	5.11
1-3	25	20	0	0	9.60*
1-4	25	20	0	0	9.57*
2-3	25	0	2.5	0	7.19
2-4	25	0	2.5	0	7.23
2-5	25	0	0	0.5	7.07
2-6	25	0	0	0.5	6.95
1-5	25	20	2.5	0	9.28*
1-6	25	20	2.5	0	9.31*
2-7	25	0	2.5	0.5	7.58
2-8	25	0	2.5	0.5	7.60
1-7	25	20	2.5	0.5	8.40*
1-8	25	20	2.5	0.5	8.37*

** pH readings were taken approximately two months after solutions were made.*

Field results

Applying the CBD solution directly to the closed pipeline at the Black Hawk field site successfully increased the total MIW flow to the reactor; the flow increased from an initial hindered value of < 1-lpm on November 10, 2007 to 5-lpm after the third flushing event on December 20, 2007. As we were unable to heat the CBD solution in the field to 80˚C in a timely manner, the warming effort was abandoned after its trial on November 18, 2007.

While flow was increased to the treatment reactors, the pH of the resulting discharge solution into Clear Creek did not reach neutral values (see Table 5).

Table 5. Data from CBD Flushing on December 20, 2007

Solution	T (^oC)	pH	Conductivity (mS/cm)
AMD	9.0	6.1	1.6
CBD	NA	5.2	31.7
Discharge after flushing (12:00P)	4.7	5.6	8.5
Discharge after flushing (2:00P)	1.6	6.0	9.2
Discharge after flushing (2:50P)	2.0	NA	1.8

Preliminary Fe concentration data of the discharge solution from December 20, 2007 indicates Fe concentrations of 2,000 mg/L at 12:00 pm and 3,500 mg/L at 2:00 pm.

Discussion

Laboratory

The ligand-buffer-reducing CBD method was the most successful trial in the laboratory. Ferrihydrite dissociates in the following manner, releasing highly insoluble ferric iron into solution (Stumm and Morgan, 1996):

$$Fe(OH)_{3(s)} + 3H^+ = Fe^{3+} + 3H_2O \qquad \text{(Equation 4)}$$

In order to promote the dissolution of the ferric iron through complexation, it must first be reduced to ferrous state. Therefore, the addition of a strong reducing agent, such as sodium dithionite ($Na_2S_2O_4$), is necessary (Drits and Manceau, 2000):

$$Na_2S_2O_4 \rightarrow 2Na^+ + S_2O_4^{2-} \qquad \text{(Equation 5)}$$

The dithionite anion continues to dissociate in water to form $SO_2\bullet^-$ radicals, which have unpaired electrons that coerce the reduction of Fe^{3+} to Fe^{2+} (Drits and Manceau, 2000). However, sulfides may form from the disproportionation of thiosulfate in pH conditions less than six (Amonette et al., 1994). Thus, a strong chelating ligand is necessary to prevent the formation of iron sulfide precipitates ($2Fe^{2+} + 2HS^- \rightarrow 2FeS_{2(s)} + 2H^+$).

By introducing the ligand sodium citrate ($Na_3C_6H_5O_7$) to the system, the now reduced Fe^{2+} iron may be complexed. The Fe^{2+} iron binds to the citrate, creating a stronger bond than with the sulfide ions.

Finally, in order to ensure the potential flushing solution does not create an even more acidic environment upon discharge, sodium bicarbonate ($NaHCO_3^-$) is added to increase the pH to more neutral levels. The recorded pH values shown in Table 4 suggest the CBD solution may be slightly alkaline (8.37 to 8.40). However, this is most likely the equilibrium pH of the solution in the laboratory after 2 months; field applications of the CBD solution will probably not reach equilibrium, as displayed in Table 5. Therefore, a higher sodium bicarbonate concentration may be required for field applications.

Field application of the CBD method involved draining and closing the MIW pipeline prior to flushing. Flushing the pipeline with the CBD solution successfully dissolved some of the iron precipitate; flow rates to the reactors exhibited improvement (from < 1-lpm to 5-lpm) after three applications. However, buffering expectations were not duplicated in the field, as the pH of the initial flushing discharge was 5.6, which was more acidic than the MIW. This was most likely caused by the use of slightly acidic MIW to create the CBD solution on-site, instead of laboratory grade distilled water (which contains less mineral acidity). The amount of iron that dissolved in the field trial (2,000 – 3,500 mg/L) was comparable to the amount dissolved in the laboratory by the CBD solution (3,100 – 3,300 mg/L), regardless of these pH differences. The ability of the CBD solution to dissolve the iron precipitate scaling in the pipeline is encouraging. Additional investigations are necessary to determine the stoichiometry of the reaction under field conditions.

Conclusions

MIW is a prevalent problem in many previously mined areas due to its potential for severe environmental impacts, threatening human health and the environment. This paper investigated several different potential treatment strategies to remediate $Fe(OH)_3$ scaling in a pipeline leading to a passive biological treatment reactor by forcing such precipitate back into solution. A solution combining an acid, buffer, and reducing agent (citric acid, sodium bicarbonate, sodium dithionite; CBD) proved most successful in laboratory experiments, and was additionally successful at increasing flow rates in the field study with certain amendments. This CBD method suggests great potential for increasing the longevity of passive MIW treatment systems. It is a relatively inexpensive, non-toxic, and user-friendly method to decrease the common ailment of iron scaling in treatment systems.

Future Work

Additional flushing events, monitoring, and sampling are necessary to determine the long-term effectiveness of the CBD applications. Additional ICP-AES analyses need to be completed to determine what metals were released through the application, and how much precipitate was removed. Also, it is necessary to determine how much additional buffering agent is required to raise the pH of the discharge solution to satisfy government regulations. Despite these needs, the CBD method is a promising solution to iron precipitation problems in MIW remediation efforts.

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