

Characterization and Remediation of Iron(III) Oxide-rich Scale in a Pipeline Carrying Acid Mine Drainage at Iron Mountain Mine, California, USA

Kate M. Campbell¹, Charles N. Alpers², D. Kirk Nordstrom³, Alex E. Blum⁴, and Amy Williams⁵

¹*U.S. Geological Survey, Boulder, Colorado, USA, kcampbell@usgs.gov*

²*U.S. Geological Survey, Sacramento, California, USA, cnalpers@usgs.gov*

³*U.S. Geological Survey, Boulder, Colorado, USA, dkn@usgs.gov*

⁴*U.S. Geological Survey, Boulder, Colorado, USA, aebalum@usgs.gov*

⁵*University of California, Davis, California, USA, amywill@ucdavis.edu*

Abstract

A 3.4 km pipeline carrying acid mine drainage to a treatment plant at the Iron Mountain Mine Superfund Site (California, USA) develops substantial scaling, resulting in occasional spillage and requiring periodic, costly clean-out. Samples of scale and water were collected from four points along the pipeline and water was collected from the mine portal influent. Mineralogy of the scale samples consisted of primarily hydrous ferric oxides including schwertmannite and goethite based on powder X-ray diffraction, wet chemical extractions, and scanning electron microscopy. Laboratory batch experiments with fresh, unfiltered water from the site showed that the scale was formed by microbial Fe(II) oxidation and precipitation of Fe(III) phases. A remediation strategy of lowering the pH of the influent water from 2.7 to 2.0-2.3 was tested using a geochemical model and laboratory batch experiments. Decreasing the pH did not substantially retard the rate of Fe(II) oxidation, but prevented precipitation of Fe(III) phases, suggesting that mixing the pipeline water with low pH water (pH ~1) from the Richmond mine portal may prevent scale formation.

Key words: Acid mine drainage, microbial iron oxidation, geochemical modeling, pipeline scaling

Introduction

Acid mine drainage (AMD) is a major environmental concern because it can degrade water quality with elevated concentrations of acidity, sulfate, iron, and other associated trace metals and metalloids. The biogeochemistry that produces AMD is complex, but can be summarized generally as the oxidation of pyrite by oxygen, facilitated by Fe(II)-oxidizing microorganisms, resulting in dissolved Fe²⁺, several potentially toxic trace metals, sulfate, and acidity (e.g., Nordstrom 2011). As the acidic water is transported away from the pyrite source, oxidation of dissolved Fe(II) to Fe(III) becomes an important process that can lead to precipitation of various Fe(III) phases. Abiotic oxidation of Fe(II) at low pH is slow, but Fe(III) can be generated rapidly by chemoautotrophic microorganisms (Nordstrom 2003 and references therein). Although precipitation of Fe(III) minerals can lead to attenuation of Fe and other elements of concern in AMD, it can also cause costly management problems when excessive precipitation interferes with treatment efforts by clogging pipelines or other treatment structures.

An example of treatment complications arising from Fe(III) precipitation occurs in a pipeline at the Iron Mountain Mine Superfund Site (California, USA), located near Redding in northern California. Mining activity at Iron Mountain began around 1879 and the site was mined intermittently through 1962. The mine produced gold, copper, zinc and pyrite. Acid waters enriched in copper had been causing fish kills since at least 1899 and several successive studies recommended remedial measures. In 1983, the site was one of the first listed on the U.S. Environmental Protection Agency's National Priority List as part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or "Superfund"). Its ranking was the third most hazardous site in the State of California (E.P.A. 2006). The ore bodies are massive sulfides, primarily pyrite (~95%) with lesser amounts of chalcopyrite, quartz, sphalerite, pyrrhotite, and galena (Kinkel et al. 1956, Nordstrom et al. 2000). Water draining the site is acidic (pH 0.5 to 3) and contains high concentrations of dissolved Fe(II) and other metals. As part of site remediation, a water treatment plant has been in operation to treat the AMD for acidity and metals; contaminated water is transported from the mine portals to the treatment

plant through underground pipelines. There are two main pipelines: one with water pumped from the “Old Mine #8” (OM8) workings (pump station PW3, typical pH 2.5 to 3) and the other draining the Richmond and Hornet portals (Richmond, typical pH 0.5 to 1). The PW3 pipeline has developed substantial scaling over its 13-year history, resulting in occasional clogging and spillage of AMD. The scaling problem requires costly clean-out which has been done approximately every 2 to 4 years. The scaling occurs over a 3.4 km length of the PW3 pipeline. The objectives of this study are: (1) to characterize the pipe scale composition along the length of the pipeline, (2) to identify the biogeochemical processes leading to its formation, and (3) to identify and bench-test possible strategies to prevent or retard scale formation in the pipeline.

Methods

The PW3 pipeline was sampled for water and scale along a 2.1 km reach from service saddles that allowed direct access to the interior of the pipe. Water samples were collected under a low flow condition (approximately 380 L/min), although there are substantial variations in flow depending on season and weather conditions. The pipe was not completely filled with AMD at the time of sampling. Scale samples were collected by physically removing the scale with a clean chisel, then placing a representative sample (~0.5 kg) into an acid-washed glass jar and storing on ice until refrigerated in the laboratory. Four scale samples were collected: (1) SS12, an upper service saddle 180 m from the start of the pipe; (2) SS10, 646 m downstream of SS12; (3) SS8, 665 m downstream of SS10; and (4) SS6, 588 m downstream of SS8. In the laboratory, a subsample of each scale sample was homogenized and either air dried or gently washed with deionized water and methanol before air drying. Once dry, the sample was gently ground with an agate mortar and pestle. Samples for microscopy were dissected into 1 cm³ subsamples and mounted on aluminum specimen mounts as wet samples or air-dried before analysis.

Water samples were pumped from the pipe using a peristaltic pump and filtered (0.45 μm) into pre-washed sample bottles. Separate water splits were collected and preserved for analyses: 125 mL acidified to 1% HCl for Fe(II)/Fe(III) determination, 125 mL acidified to 1% HNO₃ for cation analysis, and 125 mL filtered, unacidified water for anion analysis. All samples were stored on ice and shipped to the laboratory for analysis. Iron redox species were determined using the FerroZine colorimetric method (Stookey 1970), in which Fe(II) and total Fe (Fe(T)) were measured and Fe(III) was calculated by difference. Cations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Perkin-Elmer 7300DV. Anions were measured by ion chromatography on a Dionex LC20 with an AS18 column. Additional water samples were collected from a valve at the OM8 mine portal (PW3) and at the Richmond portal grit chamber (Richmond). A large volume (~20 L), unfiltered water sample was collected from PW3 for Fe oxidation experiments (below). Under some conditions, water from a more dilute source, the Slickrock Creek Retention Reservoir (SCRR) mixes with PW3 water in the pipeline. However, for the purpose of this study, PW3 water was the only influent to the pipeline.

Mineralogy of the scale was determined by X-ray diffraction (XRD), a series of wet chemical extractions, and scanning electron microscopy (SEM). Chemical extractions were performed on 2 g aliquots of the water/methanol-rinsed scale samples. Each extraction was performed three times on the same scale aliquot at a solid to solution ratio of 50 g/L; the mass of each element extracted was summed over the three extractions and normalized to the starting mass of scale. The four extraction conditions were (1) deionized water, (2) 0.5M ammonium oxalate, (3) 0.5M HCl, and (4) 0.5M HCl with 0.5M hydroxylammonium hydrochloride. Pure phases of goethite and schwertmannite were synthesized according to Schwertmann and Cornell (1991) and extracted for comparison. XRD was performed on air-dried and ground scale samples mounted on a silicon wafer and analyzed on a Siemens D500 spectrometer with a Cu K-alpha radiation source. SEM was performed using a Hitachi TM3000 tabletop SEM for wet samples or a Philips XL30S field emission gun SEM with an energy-dispersive x-ray spectroscope (EDAX) Phoenix amplifier EDS system with a SUTW Si (Li) detector for dried samples. Carbon and nitrogen composition was determined on washed, air-dried scale samples on an Exeter CE-440 elemental analyzer. Biomass content was determined with a phosphate buffer (1X PBS) extraction with acridine orange cell straining to estimate solid-phase associated cell numbers.

Microbiological processes affecting Fe(II) oxidation and Fe(III) scale formation were investigated in laboratory batch experiments with unfiltered and filtered PW3 water. Three conditions were tested: (1) unfiltered water, (2) unfiltered water with scale, and (3) filtered water (0.1 μm) as an abiotic control. Conditions (1) and (2) were performed in triplicate, and condition (3) was performed in duplicate. A 700 mL aliquot was placed in a sterile, closed, 1L, acid-washed Teflon® bottle, bubbled with sterile air, and incubated on an orbital mixer at room temperature. Condition (2) contained 100 g of wet, homogenized composite scale from SS6 and SS10. Samples were collected periodically for analysis of Fe redox species, and pH, temperature, and E_h were routinely monitored with a pH electrode (Orion Ross), temperature probe (Orion), and platinum redox electrode (Orion), respectively.

The potential viability of mixing PW3 water with Richmond water to prevent scale formation was tested using a geochemical model and batch-scale experiments. The model used the geochemical code PHREEQC (Parkhurst and Appelo 1999) and an amended WATEQ4F database (Ball and Nordstrom 1991, with additional constants from Bigham et al. 1996 for schwertmannite and Baron and Palmer 1996 for jarosite). The precipitation of schwertmannite, goethite, jarosite, and ferrihydrite was calculated when PW3 and Richmond waters were mixed at various ratios with variable Fe(II):Fe(III) composition. The results were then used to guide bench-scale tests of mixing PW3 water with Richmond water in proportions of 99:1, 95:5, and 90:10. Filtered water was mixed at the appropriate ratio, then inoculated with a fresh culture of Iron Mountain Fe(II) oxidizing microorganisms grown in PW3 water. The effect of pre-existing scale also was tested by amending another set of bottles with composite air-dried scale (20 g/L) and mixtures of PW3 and Richmond waters at the same ratios as above. For comparison, composite scale also was mixed with 100% Richmond water (20 g/L). Each condition was performed in duplicate. Samples were collected periodically for analysis of Fe redox species and pH was routinely monitored.

Results

Selected results from water samples collected from the OM8 portal valve (PW3) and from sampling sites along the pipeline are presented in Table 1. Iron was initially present as $\geq 97\%$ Fe(II) (PW3 and SS12), but became progressively oxidized as the water flowed through the pipeline, containing 22% Fe(III) at SS6. In addition, the total amount of Fe in solution decreased along the pipeline, consistent with precipitation of hydrous Fe(III) oxides. Other elements, such as Al, K, and Zn, also showed small but measureable decreases in aqueous concentration along the pipeline. The pH increased slightly, consistent with proton consumption during Fe(II) oxidation by dissolved oxygen (Equation 1).



The travel time along this reach of the pipeline is less than one hour, and the water experiences turbulent flow along the pipeline because the water does not completely fill the pipe.

Mineralogical characterization of the scale indicated that the dominant phase is schwertmannite [ideal composition: $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$], with poorly ordered goethite (FeOOH) and trace amounts of jarosite [$\text{MFe}_3(\text{OH})_6(\text{SO}_4)_2$, where M is a cation, most commonly K^+]. The powder XRD patterns showed the broad peaks associated with schwertmannite and some peaks characteristic of goethite, and the XRD patterns were similar between all four scale samples. The amounts of Fe and S measured in the chemical extractions of the scale samples were similar to the schwertmannite reference compound, and the composition indicated a hydrated schwertmannite and/or schwertmannite with goethite, consistent with the XRD results. Mineral textures characterized in SEM are consistent with documented schwertmannite textures (Cornell and Schwertmann 2003), and observed EDS spectra indicate a S peak associated with the schwertmannite. The bulk of the pipe scale is composed of agglomerations of schwertmannite mineral spheres 1.5 to 7 μm in diameter, with a sporadic distribution of filamentous schwertmannite mineral structures (diameter $\sim 2.2 \mu\text{m}$) and bare putative microbial filaments (diameter $\sim 0.7 \mu\text{m}$).

Table 1 Selected water chemistry for samples collected from OM8 portal valve (PW3), Richmond portal, and four service saddles (SS) along the PW3 pipeline. SS12 is closest to the OM8 portal and SS6 is the farthest downstream. All values reported in mg/L except for pH, Eh (reported in V), and specific conductance (SC, reported as $\mu\text{S}/\text{cm}$). Because Fe(III) is calculated by difference between Fe(T) and Fe(II), any Fe(III) value less than 3% of Fe(T) is considered not detectable (nd).

Site name	pH	E _h	SC	Fe(T)	Fe(II)	Fe(III)	Sulfate	Al	Cu	K	Zn
Richmond	0.84	0.63	76200	12590	12460	130	57500	772	130	86.4	1030
PW3	2.62	0.60	7250	1460	1440	nd	6890	465	85.8	0.64	36.5
SS12	2.63	0.60	6900	1400	1400	nd	6690	452	84.6	0.55	34.3
SS10	2.71	0.62	6600	1390	1320	70	6480	420	78.3	0.53	32.6
SS8	2.73	0.62	6440	1360	1040	320	6820	453	83.7	0.52	33.8
SS6	2.74	0.62	6340	1360	1060	300	6770	453	84.7	0.52	33.3

Results of wet chemical extraction and XRD indicate very little bulk mineralogical difference between the four scale samples. The extractions show, however, that several trace elements (Al, Cu, Zn, Ca, Co, Mg, and Sr) decrease in concentration from SS12 to SS6, with preferential accumulation upstream in the pipeline, where the scale is softer and has a higher water content. Concentrations of total carbon and nitrogen in the scale also decrease along the flow path from SS12 to SS6, indicating a higher biomass content in the upstream scale. This is consistent with a phosphate buffer extraction to estimate solid-phase associated cell numbers, in which the most upstream site (SS12) had 100 times more cells than the most downstream site (SS6). Microbial community analysis of the scale samples is ongoing.

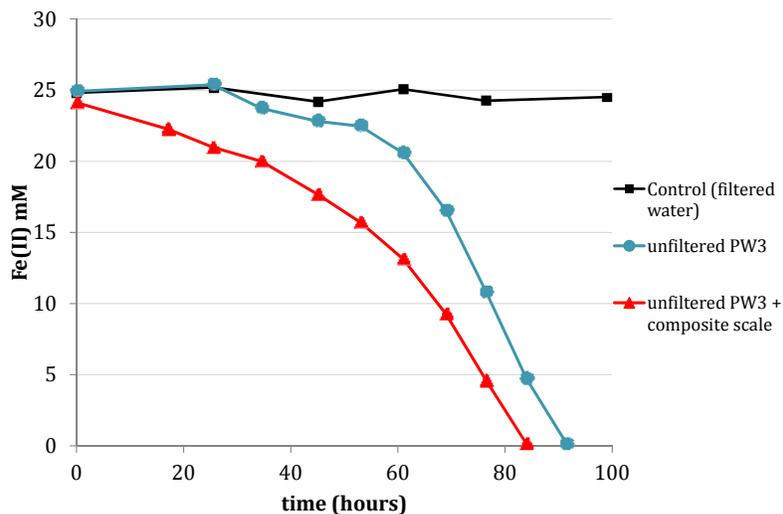


Figure 1. Ferrous iron concentrations during filtered (abiotic control) and unfiltered (biotic) Fe(II) oxidation experiments.

Results from bench Fe(II) oxidation experiments with filtered PW3 water, unfiltered PW3 water, and unfiltered PW3 water with composite scale are shown in Figure 1. Oxidation of Fe(II) occurred in the unfiltered experiments, whereas no oxidation occurred in the filtered control, indicating that the Fe(II) oxidation in the unfiltered experiments was driven by microbial processes. The shapes of the Fe(II) oxidation curves are typical of substrate consumption caused by microbial growth. The presence of scale increased the initial rate of Fe(II) oxidation, but the fastest instantaneous rate occurred without the scale. In general, the rates of Fe(II) oxidation observed in these experiments are consistent with experiments utilizing synthetic AMD media (pH 2.5) and a pure culture of *Acidithiobacillus ferrooxidans* (Campbell et al., 2012).

Microbial community analysis of the Iron Mountain batch experiments is underway. The precipitate formed during the batch experiments was primarily schwertmannite, as identified by XRD, and is similar to the pipe scale.

One of the most promising options to reduce costs associated with the pipe scale problem at Iron Mountain is to prevent scale formation by lowering the pH. The scale was composed of primarily schwertmannite and goethite, and pH is an important control in the solubility of these phases. Calculations using the PHREEQC code with the PW3 water composition showed that a relatively small decrease in pH from 2.6 to 2.3 may be enough to prevent schwertmannite from forming upon oxidation of Fe(II). A second set of calculations determined that the theoretical proportion of Richmond water (pH 0.84) needed to decrease the pH and prevent Fe(III) precipitation was about 5% Richmond water mixed with 95% PW3 water. These calculations were used to design a bench-scale experiment in which PW3 water was mixed with 1%, 5% or 10% Richmond water; each condition was performed with and without composite scale added. The water from the site had been filtered, so it was necessary to inoculate the solution with a microbial culture that had been grown in PW3 water.

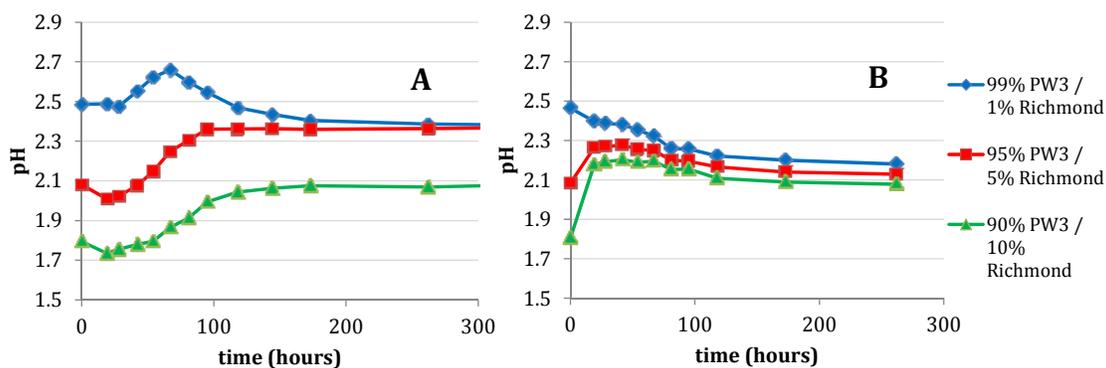


Figure 2. Changes in pH during batch experiments with 1%, 5% or 10% Richmond water (balance PW3 water) (A) without scale and (B) with scale.

In all cases, the Fe(II) was oxidized to Fe(III) within 140 hours, and oxidation was complete sooner in bottles containing scale, similar to the biotic oxidation experiment, as described above. Higher proportions of Richmond water resulted in higher initial starting concentrations of dissolved Fe(II) (data not shown) and lower initial pH (Figure 2). In bottles without added scale, the pH increased because of Fe(II) oxidation, then decreased in the 99% PW3/1% Richmond condition because of Fe(III) precipitation. No precipitation was observed in the 5% and 10% Richmond conditions, which is corroborated by the lack of a decrease in pH (Figure 2A), and is consistent with the PHREEQC calculations. In the bottles with scale, however, the scale acts as a pH buffer, causing the 1%, 5% and 10% conditions to cluster around a pH of approximately 2.2 (Figure 2B). In addition, the total amount of Fe is higher as some of the scale dissolved, then re-precipitated as Fe(II) started oxidizing after approximately 50 hours (data not shown), causing the pH to decrease slightly with time (Figure 2B). These results suggest that once scale is formed in the pipeline, it can act as a pH buffer in the system, decreasing the effectiveness of reducing pH by mixing PW3 water with Richmond water. When 100% Richmond water was mixed with scale, approximately 60% of the scale dissolved. Not surprisingly, the pipeline delivering Richmond water to the treatment plant has never had a scaling problem, consistent with the geochemical model that indicates undersaturation with respect to hydrous Fe(III) oxides at pH <1. It may also be possible to periodically flush the PW3 pipeline with Richmond water to partially dissolve the scale, but the success of that approach may depend upon the buffering capacity of the scale and the rate of dissolution.

Conclusions

Scaling in the PW3 pipeline at Iron Mountain Mine is the result of microbial Fe(II) oxidation, which causes the precipitation of primarily schwertmannite with some goethite. Dissolved

Fe(II) in the pipeline was measurably oxidized along the flow path, even though the travel time was less than 1 hour. Bulk mineralogy of the scale was similar among four scale samples taken from the pipeline, but there is a higher concentration of biomass, carbon, nitrogen, and other trace elements associated with the upstream site (SS12), with concentrations decreasing along the pipeline. Geochemical modeling and bench tests indicate that a potential management strategy for the site would be to lower the pH of the pipeline water by mixing it with Richmond water after the pipeline has been cleaned of currently existing scale, preventing schwertmannite from precipitating even when Fe(II) becomes completely oxidized. To inhibit Fe(III) precipitation on a continuous basis, Richmond water would need to be added to the PW3 pipeline at approximately 5-10% of the flow volume.

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