ACID MINE DRAINAGE SIMULATED LEACHING BEHAVIOR OF GOETHITE AND COBALT SUBSTITUTED GOETHITE

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INTRODUCTION

The Fe-oxide goethite (α-FeOOH) is a well-known constituent of acid mine drainage (AMD), an acidic pollutant rich in trace metals such as cobalt (Hudson-Edwards, 2003; Gray and Eppinger, 2012). The mineral is also noted as a common weathering product of several other Fe minerals, such as jarosite and schwertmannite (Acero et al., 2006; Antelo et al., 2013; Welch et al., 2008). Goethite has been shown in previous studies to accommodate cobalt by replacing Fe^{3+} ions with Co^{3+} ions (Gerth, 1990; Krehula and Musić, 2008; Cornell and Giovannoli, 1989). Previous research on cobalt-substituted goethite has focused on the formation of the substituted form (Alvarez et al., 2008; Gerth, 1990; Cornell and Giovannoli, 1989), and little work has been done on the long-term stability of the impure mineral. Goethite's stability has important ramifications for AMD polluted streams, as goethite may influence long-term leaching of cobalt and other substituted trace metals into the environment.

This work aims to expand our understanding of goethite (Gt) and cobalt-substituted goethite (CoGt) stability by conducting batch leach experiments in dilute HCl (pH= 3.6) over a period of 20 days. The laboratory results were then compared to the larger context of precipitate and solution samples taken from Blackbird Creek (BBC), a remediated AMD stream that drains from the closed Blackbird Mine, which resides in the Idaho Cobalt Belt (ICB). The findings of this study have important implications for active remediation taking place at BBC and other AMD sites because it suggests that trace metals sequestered in goethite and other Fe solids may not be stable over the long term.

METHODS

To avoid compositional variability, goethite used in leach experiments was synthesized following Atkinson et al. (1967). Cobalt-substituted goethite was prepared in the same manner, except dissolved Co^{2+} was present in the original solution. The final precipitate was washed with both deionized water and 1 mM HNO_3 before being air dried at room temperature. The latter step was meant to remove residual Co sorbed to the mineral surface, leaving only structurally incorporated Co in the mineral sample. Laboratory and field solids were characterized using X-ray diffraction (XRD) and scanning electron microscopy paired with energy dispersive spectroscopy (SEM-EDS), and solutions were analyzed for pH, conductivity, and dissolved chemistry using inductively coupled plasma mass spectroscopy (ICP-MS). Additional details about the methods used in this study are described in this issue by Kimball (2016).

RESULTS

Goethite Leach Experiment

Synthesized Gt and CoGt samples were distinctly different colors (Fig. 1), and the color did not change over time. X-ray diffraction patterns for all Gt and CoGt samples matched the XRD pattern for the mineral goethite (PDF# 00-029-0713) and did not change over 20 days. SEM imagery indicated that both Gt and CoGt grains showed some signs of degradation over the course of 20 days. No discernable changes in average grain size were detected in the Gt experiment, with Gt-UL (unleached) estimated at 0.59 ± 0.15 μm (ave. $\pm$ s.d.) and Gt-20 estimated at

0.46 ± 0.08 µm. Grain sizes for CoGt were similar to those for Gt samples and also remained constant within uncertainty, with CoGt-UL at 0.40 ± 0.11 µm and CoGt-20 at 0.48 ± 0.14 µm. Unit cell axes based on Reitveld refinements of XRD patterns remained constant throughout experimentation, with Gt-UL, Gt-20, CoGt-UL, and CoGt-20 all showing a= 4.582 Å, b= 9.914 Å, c= 3.013 Å.
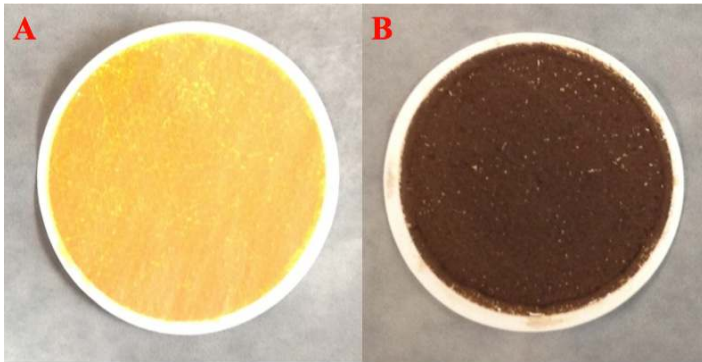

Figure 1. Filtered Gt-20 (A) and CoGt-20 (B) samples. Despite nearly identical XRD patterns, mineral color was distinctly different and did not change throughout experimentation.

Dissolved concentrations of Fe and Co measured by ICP-MS were below the limit of detection (23 µg/L and 0.01 µg/L, respectively) for Gt experiments. Dissolved Fe concentrations were also below detection in the CoGt experiments, but dissolved Co concentrations increased rapidly to approximately 700 µg/L during the first day, remained at this level until day 3, then decreased to approximately 250 µg/L for the remainder of experimentation (Fig. 2).

Throughout experimentation, pH for the Gt solution remained approximately 0.5 pH units higher than the Blank (Fig. 3a). Solution pH in the CoGt experiment was also approximately constant, however, these solutions were on average much closer to neutral (pH= 6.84 ± 0.19) than average Gt leach solutions (pH=3.89 ± 0.11) (Fig. 3a). Average total dissolved solids (TDS) for Gt and CoGt solutions were also relatively constant during the experiment, remaining near 46.3 ± 4.45 mg/L and 54.2 ± 10.85 mg/L, respectively (Fig. 3b). These values were below the TDS of the Blank, which was near 70 mg/L throughout the experiment (Fig. 3b).
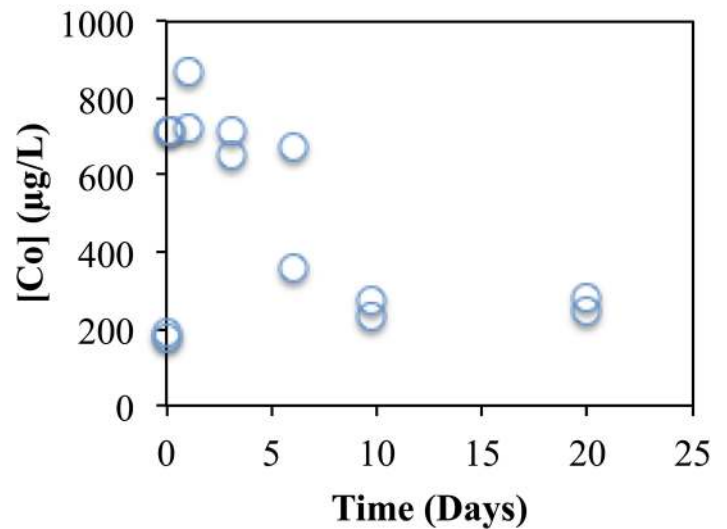

Figure 2. Dissolved Co (µg/L) over time during leaching of CoGt. Dissolved Fe was below detection (23 µg/L) during leaching of both Gt and CoGt, and thus is not shown.
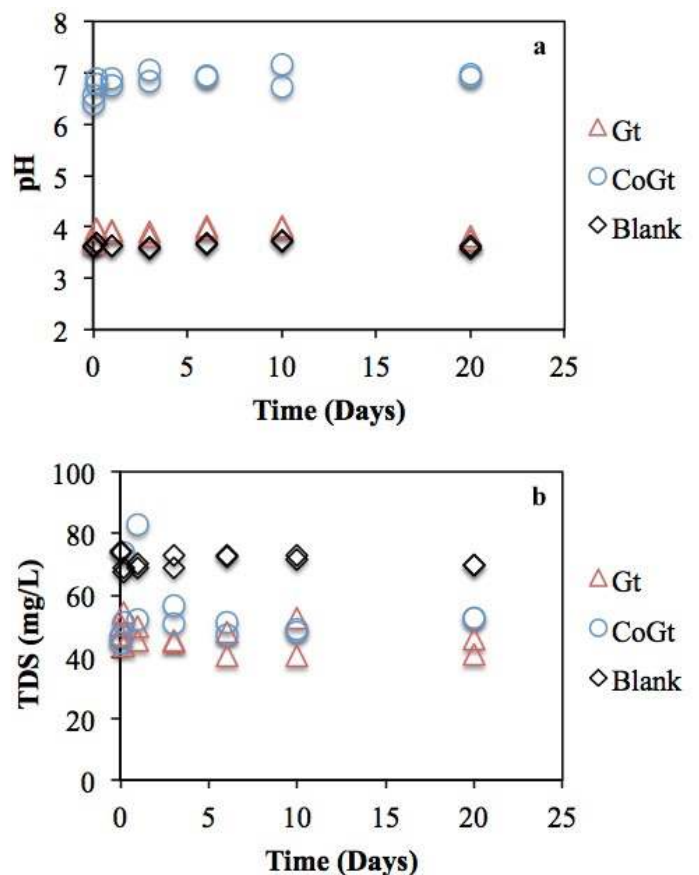

Figure 3. Time versus pH (a) and total dissolved solids (TDS) (b) for batch leach experiments with Gt, CoGt, and Blanks. TDS was calculated using measured conductivity (µS/cm) and the constant 0.67.

Blackbird Creek Precipitates

Despite the obvious presence of Fe in the stream precipitates suggested by color (Fig. 4), XRD patterns obtained from all field precipitates indicated the presence of quartz only. When viewed with SEM-EDS, BBC precipitates contained the following elements: Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, and O. The average atomic percent ratio of Fe:O decreased from 0.5 upstream to 0.2 downstream within BBC, and was lowest (0.08) in Panther Creek. Average atomic percent ratios of Si:O, on the other hand, increased from upstream (0.2) to downstream (0.3) in BBC, and were highest in Panther Creek (0.4).


Figure 4. Photo of BBC precipitates near 15BBC06. Precipitates were collected from the top 2 cm from areas with undisturbed sedimentation. Photo taken by Shanti Penprase.

DISCUSSION

Goethite Leach Experiment

Results from these leach experiments can be interpreted in the context of expected goethite stability at the given experimental pH (~ 3.6). Goethite is known to dissolve as follows (Bigham et al., 1996):

$$FeOOH + 3H^+ \longleftrightarrow Fe^{3+} + 2H_2O$$
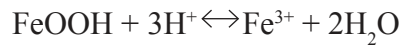
where dissolved Fe^{3+} and water are the products of FeOOH in an acidic solution. Figure 5 depicts solubility lines for this dissolution reaction at various pH levels compiled from previous sources of thermodynamic data for goethite (Nordstrom et al., 1990; Bigham et al., 1996; Parkhurst and Appelo, 1999). Values below these solubility lines represent conditions where the mineral is known to be unstable, favoring the forward direction of the above reaction. Conversely, conditions above these lines do not favor the forward reaction. Our experimental pH and log $[Fe^{3+}]$ detection limit (3.6 and -6.38, respectively) are indicated by the dashed black lines. These lines meet above the solubility lines, suggesting that the above forward reaction should not be favored under the laboratory conditions.
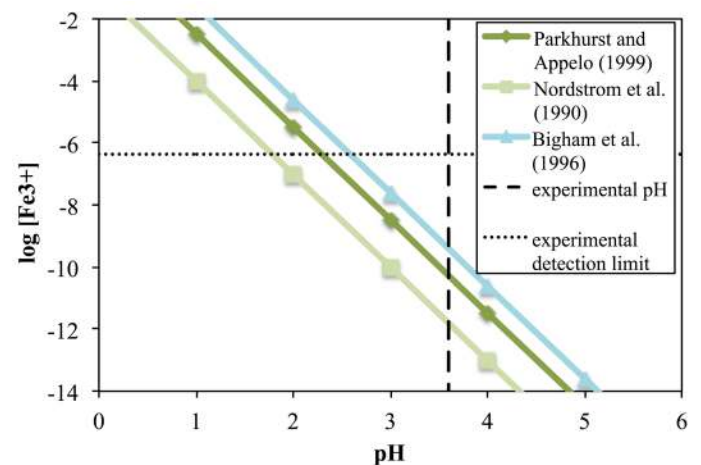

Figure 5. Plot of log $[Fe^{3+}]$ against pH for a system containing goethite and its dissolved components. Goethite solubility lines follow the equation: log$[Fe^{3+}]$ = apH + b, where a and b equal -3 and 1.4 (Bigham et al., 1996; logK = 1.4), -3 and 0.5 (Parkhurst and Appelo, 1999; logK = 0.5), and -3 and -1 (Nordstrom et al., 1990; logK = -1), respectively. Dashed lines correspond to the values for the beginning pH and the detection limit for dissolved Fe by ICP-MS (3.6 and -6.38, respectively).

Even though detectable Fe was not released from Gt or CoGt in these leach experiments, Co was released from CoGt. Release of Co under conditions where goethite is stable was unexpected. The greater pH increase in CoGt solutions compared to Gt solutions and preferential solubilization of Co from CoGt samples suggest that CoGt is less stable than Gt. The reason for this preferential Co release is unclear, and future experiments should focus on this observation. Given that environmental samples of goethite are expected to contain trace metals, the release of Co by CoGt in this laboratory experiment suggests that trace metals coprecipitated with goethite may not be stable in the long-term.

Blackbird Creek Precipitates

Field precipitates did not show any minerals beyond quartz based on XRD. With SEM-EDS, however, Fe was determined to be a major component of the BBC precipitates. Given that we sampled the most recently precipitated solids in the upper 2 cm of the streambed, the solids may have been amorphous hydrous ferric oxide or semi-crystalline ferrhydrite (Dzombak and Morel, 1990; Bigham and Nordstrom, 2000). Alternatively, the prevalence of quartz in the solid samples could have been so high that it overshadowed more minor sediment components, including any Fe minerals. Other researchers have found that the presence of highly crystalline primary minerals impede the ability to detect secondary Fe minerals using XRD (Schroth and Parnell, 2005; and references therein).

Due to the artificially high pH of the stream (pH=7.4±0.5), the presence of amorphous Fe would be expected. Marescotti et al. (2012) describe how higher pH quickens precipitation of Fe solids, and these solids are more likely to be amorphous. Amorphous and semi-crystalline materials, such as schwertmannite and ferrihydrite, have been observed to age into goethite (Acero et al., 2006; Antelo et al., 2013; Welch et al., 2008; Schwertmann and Fitzpatrick, 2000). Although goethite was not observed in BBC precipitates, these precipitates could age into goethite over time. The results of the laboratory experiment are applicable as goethite may eventually form in this stream, or could be present in sediment layers below the top 2 cm sampled.

CONCLUSION

Based on leach experiments, both Gt and CoGt samples were stable with respect to Fe under the experimental conditions. This is indicated by below detection dissolved [Fe], and constant XRD patterns and grain size measurements. Despite goethite stability, CoGt samples released Co and the pH of leach solutions increased significantly relative to the Blank. This observation suggests that goethite containing cobalt, and/or other trace metals, may not be as stable as pure goethite, and that trace metals might not be as permanently bound to mineral hosts in the long-term as previously thought.

Field results suggest that BBC precipitates consisted of amorphous Fe solids and quartz. Since amorphous Fe solids could age into goethite over time, laboratory results suggest that incorporated trace metals may destabilize goethite in the long-term. As a result, trace metals like Co might reenter the aqueous phase and possibly increase the risk of aquatic toxicity. Although active remediation is effective in raising pH values and precipitating dissolved Fe and trace metals, it does not address possible long-term instability of the precipitates.

ACKNOWLEDGEMENTS

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