Effects of bacterial activity on the release of trace metals from sphalerite oxidation

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Abstract

The aim of the present paper was to determine the role of Fe-oxidizing bacteria in trace metal solubilization during sphalerite oxidation. For this purpose, a trace element bearing sphalerite mineral was used in the oxidation/leaching experiments (biotic & abiotic). The experiments were conducted biologically and abiotically under aerobic conditions at pH 3. *Acidithiobacillus ferrooxidans* was used in the biological sphalerite oxidation experiments. The results showed that bacteria play the major role in the release of trace metals from sphalerite by enhancing the oxidation kinetics. These results indicate that in order to develop proper rehabilitation strategies for Acid mine drainage systems the role of bacteria should be determined.

Key words: *Acidithiobacillus ferrooxidans,* trace elements, sphalerite, acid mine drainage.

Introduction

The behavior of hazardous metal elements in acid drainage for environmental monitoring and pollution forecasting in mining districts has become a focused research area in recent years. Previous research on the transport and fate of metals in acid mine drainage showed that the metal contents in AMD are probably not controlled by a single geochemical factor but by several factors (Dai et al. 2006a; Liu et al. 2004).

Microorganisms play a predominant role in the solubilization, transport, and deposition of metals and minerals in the environment, processes that are still poorly understood ((Pronk et al. 1990; Suzuki et al. 1994; Balci et al. 2006). One of the most important bacteria in the metal sulfide oxidation is the acidophilic bacteria *A. ferrooxidans*. These bacteria are responsible for the oxidation of insoluble metal sulfides with a high acidification of sediments, controlling the transport of the metals in the environment. The trace metal contents in most natural waters are controlled by adsorption or co-precipitation processes. Co-precipitation may involve adsorption, cluster formation, homogeneous solid solution, heterogeneous solid solution, or a combination of these processes (Karthikeyan et al. 1997; Martinez and Mcbride 1998). Waters contaminated by AMD have a wide range of chemical composition and contain some elements such as Fe, Al, and Mn, which rapidly form precipitates when AMD is neutralized (Lee et al. 2002). The solubility varies for each element, causing a different efficiency of precipitation depending on pH values (Nordstrom and Alpers 1999). The precipitates formed by metal hydrolysis may include oxyhydroxides and hydroxysulfates, depending on local geochemical conditions (Bigham et al. 1996; Nordstrom and Alpers 1999). Therefore, knowledge about the release of hazardous metals from tailings, especially the key controlling factors affecting the evolution of specific metals in AMD, is important.

In order to understand and determine the cycles of trace elements in the environment, it is necessary to elucidate the role of bacteria. The aim of the present paper is to evaluate the influence of *A. ferroxidans* on the solubilization of trace metals during sphalerite oxidation under conditions which mimic the AMD environment.

Methods

Sphalerite preparation

Trace element bearing sphalerite was obtained from the United States Geological Survey (USGS), in Denver, Colorado (USGS). The trace element content of the sphalerite sample was checked by analyzing the elemental composition by ICP-MS at the United States Geological Survey (USGS), in Denver, Colorado. Prior to use, the samples were ground and sieved. A grain size of < 63 µm was used for the experiments. The surface of the sphalerite was cleaned according to the methods described by Moses et al. (1987), and subsequently sterilized (Balci et al. 2007).

Batch experiments

Leaching experiments were conducted as biological and abiotic in order to determine the part of abiotic processes in metal mobilization during sphalerite oxidation. For the biological experiments, the acidophilic Fe (II)-and sulfur-oxidizing bacteria, *Acidithiobacillus ferrooxidans* (23270); (formerly, *Thiobacillus ferrooxidans*) was obtained from the American Type Culture Collection (ATCC) and used in the biological experiments. Sterile 500 mL polycarbonate Erlenmeyer culture flasks were used for the batch experiments. For the biological and abiotic oxidation experiments, low sulfate and Fe(II) medium was used as the experimental solution (NH_4CI, 0.6 g; $MgCI_2.6H_2O$, 0.2 g ; K_2HPO_4, 0.1 g ; Wolfe's mineral solution, 5 ml) and pH was adjusted to 3 with HCl at 25 °C. The biological and abiotic-control sphalerite experiments were carried out in triplicate.

For the biological sphalerite experiments, 830 mg sphalerite and 250 ml of microbiological medium which was autoclaved at 121 °C for 20 minutes were placed into the 500 ml Erlenmeyer flasks. After autoclaving, the flasks were kept in the sterile hood under the UV for 25 minutes to decontaminate the surfaces of the flasks. Sterilized and cleaned sphalerite samples and 5 ml (~2.7×10^7 cell/ml) of the *A. Ferrooxidans* cell suspension was added to the medium. The biological experiments were incubated in the environmental room at 25 °C and were continuously shaken (150 rpm) over the entire period of the incubations. The flasks were covered with rubber stoppers fitted with inflow and outflow tubes for aeration. Sterile air filters (0.2 µm-whatman) were connected to the inflow and exit ports to prevent microbial contamination and to minimize evaporation. The flasks were continuously bubbled with compressed air (General Air Company) and several tanks were used during these experiments. During the incubations aliquots were taken periodically to monitor the concentration of trace elements, major anions, total Fe and pH. The abiotic-control sphalerite experiments were carried out under identical conditions to the biological experiments but without the culture.

Results and Discussion

The variations of pH and sulfate concentration were shown in Fig. 2. In the biological experiments, sulfate concentration increased with decreasing pH, indicating continues oxidation of sphalerite (Figs. 1,2). In contrast to the biological experiments, sulfate concentration in the abiotic experiments was significantly less and the pH rose rapidly in the first 5 days, steadily leveled off until day 22 and dropped off again to 3.6. The fluctuations seen in the pH profile from the abiotic experiments is likely related to the oxidation mechanisms. The rise in pH is likely due to formation of elemental sulfur on the surface of sphalerite which consume protons.

In general, leachate produced by biological experiments contained higher concentrations of trace metals compared with leachate produced by abiotic –control experiments, as shown for Zn, Fe, As, Cd, Co, Cu, Mn and Pb in Figs. 1, 3,4. These trace elements have a strong correlation with sulfate and zinc in the leachates, indicating that the release of these elements depends on the extent of sphalerite oxidation and dissolution. Similar results have been found for AMD in the field, especially for sulfate (Yue et al. 2004). The higher concentrations of metals measured in the biological experiments clearly reflects the bacterial influence on dissolution of sphalerite and enhanced oxidation kinetics. Compared to abiotic experiments, the concentration of Zn, As, Cd, Co, Cu, Mn and Pb increased linearly until day 40 and began to decrease in the incubated experiments. Corresponding decrease in Fe and SO_4 concentrations on day 40 indicate Fe—hydrate precipitation, most likely schwertmannite and jarosite. It is most likely that trace metals were adsorbed or/and co-precipitated by Fe(III) minerals in the incubated experiments, showing decreasing trends. This is consistent with the previous studies. Lee et al. (2002) found that 80 % of Pb in solution is removed by adsorption on and co-deposition with Fe-hydrate when the pH is less than 3.5. Furthermore, Fukushi et al. (2003) found that as soon as schwertmanite forms, the As concentration in a stream decreases nearly to the background level downstream, and the As content in the ochreous precipitates is up to several tens of mg/g. This means that arsenic is effectively removed from water by the formation of schwertmanite. In the current study, almost 80 % of the metals released from sphalerite were removed from the solution at the end of the biological experiments (Fig. 3). The highest removal was for As, Cd, Zn, Co, Mn, and Pb in decreasing order. Lee et al. (2002) suggest that Mn precipitates are the main adsorbent for Cd, and Co. Formation of Mn precipitates takes place at pH 7-8. However, under the experimental conditions of this study (pH <3), it is not likely that Mn-precipitation took place. Therefore, this is not a likely adsorption source for the metals.

Figure 1 *Variations in Zinc and Fe_{tot} concentration during oxidation experiments*

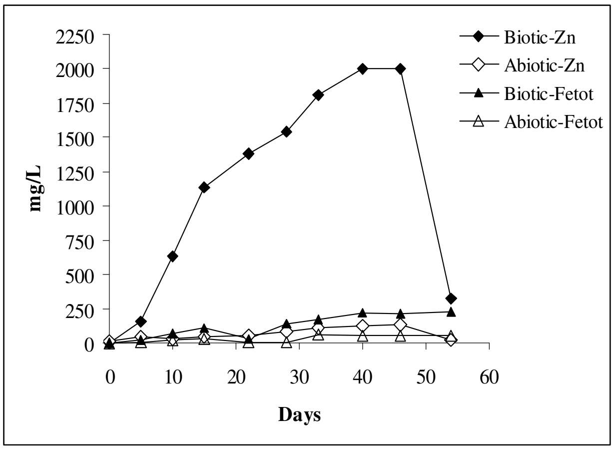


Figure 2 *Sulfate and pH profile of the oxidation experiments*

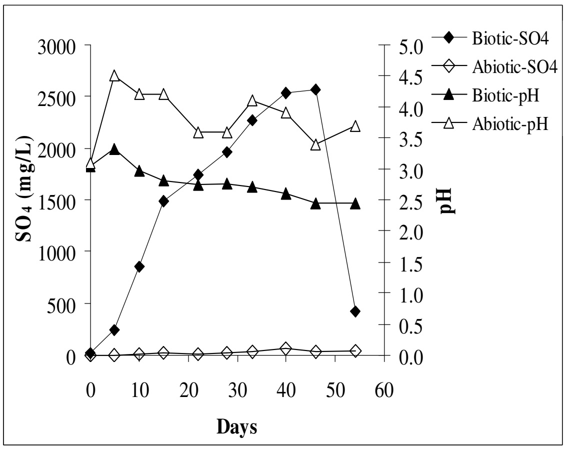


Figure 3 *Element release behavior in the biological oxidation experiments*

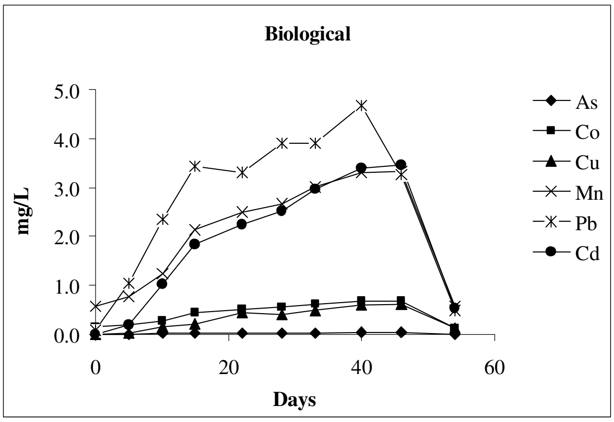
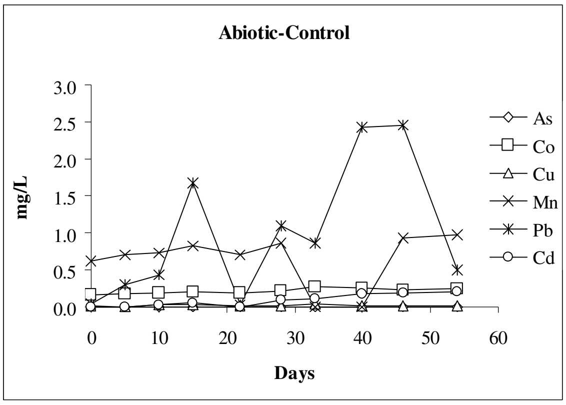


***Figure 4** Element release behavior in the abiotic-control oxidation experiments*



Conclusions

The experiments carried out in this study clearly indicated that release of trace metals from sphalerite is primarily controlled by bacterial reactions. The role of bacteria is not only oxidation of the sulfur component of sphalerite but also the oxidization of Fe(II) to Fe(III). The current experimental study also showed biological Fe-oxyhydrate formation in the incubated experiments; which can adsorb the metals. These results indicate that although bacteria can enhance the oxidation of sphalerite and release of trace metals in AMD environments, Fe-oxyhydrate minerals have final control on the distribution and migration of the metals.

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