



Zinc and nickel removal in limestone based treatment of acid mine drainage: The relative role of adsorption and co-precipitation



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ABSTRACT

Mining influenced water may contain high metal and sulfate loads, and have low pH (acid mine drainage). Removal of these metals prior to environmental discharge is critical to maintain ecosystem vitality. Limestone based passive treatment systems are commonly used for pH neutralization. The same conditions that lead to pH neutralization may also remove a substantial amount of metals from solution, but the connection between treatment conditions and metal removal are not well understood. In this study, zinc and nickel removals are quantified in batch reactor simulated limestone treatment of acid mine drainage. The resulting solid phase is characterized with a sequential extraction procedure, and the removals are interpreted using surface complexation and surface precipitation models. Zinc and nickel removals are closely linked to the initial iron concentration in the mine water, but are also affected by pH, alkalinity, calcium and sulfate concentrations. The surface complexation model was based on literature descriptions of hydrous ferric oxide. In order to obtain a sufficient fit to the data, the surface site density was increased to an unrealistically high value. Uptake data was also fit to an existing surface precipitation model. The values used are similar to those found in previous studies. Both models indicate that adsorption is not the dominant removal process in the treatment system. Using adsorption only models will generally underpredict metal removals within limestone based treatment systems.

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1. Introduction

Post-mining impacts to water resources from historic mining practices continue to affect mineral rich regions worldwide. Mining influenced water (MIW), both acidic (acid mine drainage, AMD) and pH neutral, is typified by high concentrations of heavy metals and sulfate. Further, MIW production may continue post-mining due to local hydrological alterations. The continuous MIW flow can impact environmental water quality for decades. In post-mine closure scenarios, passive treatment is viewed as a much less expensive proposition than active treatment. Passive systems rely on flow gradients present at a site and typically use natural processes in an engineered system for water treatment (Cravotta, 2010). A major application of passive treatment is the use of limestone dissolution for pH control (Alcolea et al., 2012; Cravotta and Trahan, 1999; Robbins et al., 1999; Watzlaf et al., 2004; Ziemkiewicz et al., 1997). There are several designs for passive MIW treatment with limestone including: oxic limestone drains, anoxic limestone drains, open limestone channels, and limestone diversion wells (Cravotta and Trahan, 1999). Each of these has slightly different designs and design constraints.

However, all use the dissolution of limestone to neutralize pH with concomitant metals removal.

Dissolved metal fate in limestone treatment systems is known to varying degrees. Manganese is typically conserved through most limestone treatment systems, while aluminum most often precipitates as an (oxy)hydroxide species. Iron fate is dependent on oxidation state; iron(II) is conserved unless oxygen is present in the limestone treatment system, while iron(III) is typically removed from solution via precipitation. The iron based precipitate can take many forms including: ferrihydrite, goethite, schwertmannite, or jarosite (Bigam et al., 1996). The presence of each of these minerals is dependent on the rate of pH change, the retention time in the reactor, the ionic components in the MIW, and the presence of significant microbial activity (Bigam et al., 1990). The iron precipitates found in limestone treatment systems are known to be excellent sorbent materials for other metals, including nickel and zinc; it is not surprising that some of these secondary metals (e.g., zinc and nickel) will also be removed.

Secondary metal removals have been observed in the field both under conditions of natural neutralization as well as with limestone treatment. A major route of secondary metal removal is adsorption and co-precipitation with newly formed mineral particulates. In this paper we use adsorption to mean specific ion interaction and bond formation with the surface; co-precipitation can include surface precipitation, solid solution formation,

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or physical encapsulation of ions by the primary precipitate. Sorption is used as a general term when metal removal mechanisms are unknown or unspecified. Secondary metal removal when AMD is mixed with uncontaminated stream water has been shown to trend with iron removal, and has been quantitatively described using adsorption based surface complexation parameters for ferrihydrite (Tonkin et al., 2002; Lee et al., 2002). Mixing a limestone slurry into an AMD impacted stream led to pH neutralization and Zn removal consistent with sorption to ferrihydrite, however the pH was not high enough to remove Ni (Davies et al., 2011). Sorption as a removal process in passive limestone systems is often cited using solids deconstruction as experimental evidence. Total precipitate dissolution and bulk ion analysis showed an enrichment of Zn relative to Fe as a function of flow path within a reactor (Cravotta and Trahan, 1999). Sequential extractions of precipitates from limestone based treatment systems showed only small amounts of secondary metals in the ‘exchangeable’ phase, and higher proportions associated with the iron and manganese phases (Kairies et al., 2005). While more realistic, bulk solid analysis on limestone treatment precipitates complicates removal process distinction as the solid phase represents a time integrated set of processes. At the other end of the spectrum, traditional sorption and co-precipitation experiments in pure symmetrical electrolytes may not capture behaviors which occur as a function of inherent complexities associated with MIW treatment. For example, high sulfate concentrations have been shown to enhance metal sorption either through ternary surface complex formation or through direct sulfate incorporation in the mineral phase (Ali and Dzombak, 1996; Bigham et al., 1996; Walter et al., 2003; Webster et al., 1998).

Working between these two extremes has allowed for the observation of secondary metal removal consistent with sorption and co-precipitation processes on both iron and aluminum precipitates (Miller et al., 2011). However, only empirical data descriptions were provided which did not describe field data particularly well. The data produced was insufficient for modeling within a traditional surface complexation framework. The lack of rigorous descriptions limited the examination of different secondary metal removal routes. In this study, the aim is to provide a more controlled dataset of secondary metal behaviors in simulated limestone treatment of AMD. This dataset is focused solely on secondary metal interactions with iron precipitates and is more amenable to quantitative descriptions. Secondary metal removals are modeled with both a surface complexation and surface precipitation model describing secondary metal interactions with the precipitated iron phases. Both the surface complexation and surface precipitation models suggest that adsorption is playing a lesser role in secondary metal removal within limestone based treatment systems.

2. Methods

2.1. Batch reactors and sequential extraction

Parent solutions were made from metal-sulfate salts for Fe, Zn, and Ni dissolved in 0.02 N H₂SO₄ (pH = 2.1 ± 0.1). The Fe solution was made with ferrous sulfate, and a small amount of 30% HOOH was added to convert the iron from Fe(II) to Fe(III). It is assumed that all of the iron was oxidized by this procedure. The synthetic mine waters used in the batch reactors were a mixture of the iron solution, and either the zinc or nickel solution. The batch reactors used were 50 mL HDPE centrifuge tubes; wall sorption for the pH range considered was negligible. To these tubes, appropriate amounts of the parent solutions were added to get the desired concentrations (Table 1). When necessary, the parent solutions were

Table 1
Initial metal concentrations used in the batch reactors.

| | Iron concentrations (mg/L) | | | | |
|---------------------|----------------------------|------|------|------|------|
| | 0 | 54 | 540 | 62 | 620 |
| Zinc conc. (mg/L) | 5.3 | 5.3 | 5.3 | | |
| | 10.7 | 10.7 | 10.7 | | |
| | 16.0 | 16.0 | 16.0 | | |
| | 21.3 | 21.3 | 21.3 | | |
| | 26.7 | 26.7 | 26.7 | | |
| Nickel conc. (mg/L) | 5.8 | | | 5.8 | 5.8 |
| | 11.6 | | | 11.6 | 11.6 |
| | 17.3 | | | 17.3 | 17.3 |
| | 23.1 | | | 23.1 | 23.1 |
| | 28.9 | | | 28.9 | 28.9 |

diluted with 0.02 N H₂SO₄ to achieve a consistent 45 mL of total volume.

To simulate limestone treatment chemistry 0.1 g of CaCO₃ was added to each of the reactors. Preliminary experimentation showed that 0.1 g was sufficient to raise the pH from 2.1 to circum-neutral over 4 days of mixing time. Upon addition of the CaCO₃, carbon dioxide bubbles immediately formed. The solutions were capped, and vigorously shaken by hand to suspend the CaCO₃. The vials were then vented to the atmosphere to avoid pressure buildup in the vial. Over the 4 day mixing time, the vials were vented twice daily to both avoid overpressuring the vials, and to maintain head-space gas compositions approximating atmospheric conditions. The vials were mixed on a shaker table. For the first 24 h, they were mixed in an upright position to minimize pressure induced leakage. For the remaining time, they were mixed in a horizontal position to allow for more efficient mixing and gas exchange. Batch experiments were performed in triplicate.

At the end of the 4 day mixing period, the samples were centrifuged at 10,000g for 30 min. The supernatant liquid was removed, and pH was measured immediately with a standard pH meter and probe calibrated with pH 4, 7, and 10 buffers. The sample was split, with part of the sample being acidified for metals analysis, and alkalinity titrations being performed on the remainder. Alkalinity was determined through colorimetric titration using a Hach® digital titrator kit. The reacted solid phase was subjected to a modified version of the (Tessier et al., 1979) sequential extraction procedure. Between each extraction, the solid and liquid phases were separated by centrifugation (10,000g, 30 min) and the supernatant was removed for analysis. The easily exchangeable fraction was obtained by mixing the solid phase with a 1 M MgCl₂ solution for 1 h. The carbonate associated fraction was then created by mixing the remaining solid phase in a 1 M acetate buffer adjusted to pH 5; 10 mL of buffer were added to the solid phase and the suspension was mixed for 30 min. To the remaining solid phase, 15 mL of a 0.04 M hydroxylamine hydrochloride solution prepared in 25% (v/v) acetic acid was added. The reactors were placed in a hot water bath at 93 ± 3 °C for 2.5 h with hand agitation approximately every 30 min. The organic extraction was not completed, and the residual digestion was completed at room temperature with a 30% (v/v) HNO₃ solution. Although the residual dissolution was completed, secondary metals were never present in significant concentrations. For simplicity this is not shown on the figures in the results section. The final extraction procedure divided metal partitioning in the reactors into the following categories: solution, easily exchangeable, carbonate associated, and iron associated. For each of these phases, metal concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Total sulfur was also determined via ICP-OES, and it was assumed that all sulfur was present as sulfate.

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