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USE OF AN INTACT CORE AND STABLE-METAL ISOTOPES TO EXAMINE LEACHING CHARACTERISTICS OF A FLUVIAL TAILINGS DEPOSIT

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ABSTRACT

The upper Arkansas River south of Leadville, Colorado, USA, contains deposits of fluvial tailings from historical mining operations in the Leadville area. These deposits are possible non-point sources of acid and metal contamination to surface- and ground-water systems. We used stable-metal isotopes to help ascertain metal retention and release mechanisms that influence metal transport from the deposits to shallow ground-water systems. To accomplish this, we excavated an intact core from a small fluvial tailings deposit and performed laboratory column experiments to examine the amount of metals leaching through the core. Deionized water was continuously applied to the top of the core, and effluent was collected from the bottom of the core for a period of about 2 months. Three saturation conditions were used, including unsaturated, partially saturated, and fully saturated. Reducing conditions developed upon partial and complete saturation of the core. During the unsaturated leaching phase, core effluents were acidic (pH 2.8-3.5) and contained elevated metal concentrations. During a portion of the unsaturated leaching phase, stable-metal isotope spikes and conservative tracers were simultaneously applied to the top of the core. The isotopes provide a means to delineate metal behavior within the core. During the unsaturated leaching phase, the isotope spikes did not exhibit breakthrough with simultaneously added conservative tracers. However, some of the stable-metal isotope spikes did break through when reducing conditions occurred in the core (during the partial- and complete-saturation conditions). In this paper, we use Cd as an example of the utility of stable-metal isotopes in geochemical studies. In the case of Cd, after the core was partially saturated, the ^{111}Cd spike was released as evidenced by a change in the Cd isotope ratios in the effluent. This release continued during the fully saturated leaching phase, however, the total Cd concentration did not increase. These results suggest that the ^{111}Cd spike was retained inside the core during the unsaturated leaching phase, and only partially released as reducing conditions developed. Results from this core-leaching experiment indicate there is a large reservoir of water-soluble material within the fluvial tailings deposit, which yields elevated metal concentrations and high acidity, and which may degrade adjacent ground- and surface-water quality. Use of stable metal isotopes in this study facilitated the determination of different metal-retention processes, metal-release processes, and metal sources in the fluvial tailings deposit in response to changing geochemical conditions.

INTRODUCTION

Tailings from historical mining operations near the Leadville, Colorado, USA, area have been washed downstream and deposited along portions of the upper reaches of the Arkansas River over the past 100+ years (URS Operating Services, 1997). These tailings are mine wastes of processed gold, silver, lead, and zinc ores from the Leadville Mining District. The resulting fluvial tailings deposits generally are found in overbank and pointbar deposits consisting of mixtures of fine-grained tailings and sediment. These deposits are possible sources of acid and metal contamination to surface and ground water. Our study site is located at one of these fluvial tailings deposits, approximately 13 km south of Leadville. The site is about 0.1 km² in size, is relatively flat, and was virtually devoid of living vegetation.

We excavated an intact 20-cm-diameter (60 cm in length) core from the bank of a distributary channel that cuts through the deposit. The deposit exhibits a high degree of vertical heterogeneity. At our study site, the top of the fluvial tailings deposit commonly consists of a fine-grained pyrite-rich layer, the middle portion is clay-rich with sand and silt lenses, and the bottom contains an organic-rich layer underlain by a sand and gravel shallow aquifer. The collection of an intact core maintained the deposit structure, and allowed for simulation of effects of fluctuating water-table levels on metal release from the deposit.

We sequentially leached the core in the laboratory under unsaturated, partially saturated, and fully saturated conditions for a period of about two months, and collected the effluent at various times. The leaching procedure is intended to simulate the impact of seasonal water infiltration through the deposit and into the shallow ground-water system. The local ground water beneath the fluvial tailings deposit exhibits lowered pH and elevated metal concentrations (Walton-Day *et al*, 2000; Smith, Walton-Day, and Ranville, 2000). Related work at this study site is reported by Walton-Day *et al* (1996, 2000), Jerz (1998), Smith *et al* (1998, 1999), and Smith, Walton-Day, and Ranville (1999, 2000).

During a portion of the leaching process, ¹¹¹Cd and several conservative tracers were added to the leaching solution to determine if interactions between the leached metals and the solid matrix were occurring within the core. The objective of this study was to use intact material and

stable-metal isotopes to determine different metal sources, and metal-attenuation and metal-release processes in our fluvial tailings deposit in response to changing geochemical conditions.

METHODS

Core Collection and Design

A 20-cm-diameter by 60-cm-length core was excavated intact from the bank of a distributary channel that cuts through the fluvial tailings deposit. A clear polymethylmethacrylate tube was placed on top of the bank. The fluvial tailings around the tube were slowly excavated and the tube pushed down to encase the remaining material. This process was repeated until the shallow aquifer sand and gravel was reached (approximately 60 cm of overlying material). The bottom of the tube was fitted with a polyvinylchloride (PVC) cap and the joint sealed with silicone cement. The cap contained sampling ports designed to separately sample water draining along the interface between the cored material and the inner edge of the tube (side-wall flow, edge port), and from water draining through the center part of the core (center port). Use of the two ports allowed segregation of water that had full contact with the cored material from water that drained down the interface between the cored material and the core tube.

Core Leaching Procedure

Three saturation conditions were used for the core leaching experiments, beginning with unsaturated, followed by partially saturated, and ending with fully saturated. Effluent was collected from both the center and edge ports at the bottom of the core (only data for the center port are reported in this paper). Effluent was collected at varying times, and sample volume, pH, and specific conductance were measured over the 57-day period of the leaching experiment. Subsamples of effluent were collected for chemical analyses. Results presented in this paper are for unfiltered samples. Filtered samples ($<0.45\ \mu\text{m}$) were also collected, but little difference was noted between filtered and unfiltered geochemical results.

In the unsaturated-flow core-leaching phase, deionized water was dripped on the top of the core at a rate of 2 mL/min using a peristaltic pump. The deionized water was allowed to freely

drain by gravity through the core, resulting in unsaturated flow conditions. The initial drip consisted of deionized water and continued for 265 hours (about 11 days). A mixed isotope spike solution was then introduced, which consisted of ^{111}Cd , ^{65}Cu , ^{54}Fe , ^{207}Pb , and ^{68}Zn spikes, with Na and ClO_4 added as conservative tracers. Due to space limitations in this paper, only the ^{111}Cd data are used to provide an example of the utility of the isotopic spike procedure. The mixed isotope solution was continuously dripped on the top of the core from 265 hours until 373 hours into the experiment. At 373 hours, deionized water was again continuously dripped on the top of the core. After 490 hours into the experiment, the drip rate was changed from 2 mL/min to 1 mL/min to determine if the flow rate was an important factor. At 565 hours, partial saturation conditions were introduced by allowing water in the core to back up from the bottom to about 15 cm from the top of the core (the water level was just below the pyritic zone). This partially saturated condition was intended to simulate rising of the underlying shallow ground water table into the fluvial tailings deposit. Partial saturation was accomplished by raising the height of the outlet tube at the bottom of the core. Complete saturation of the core was initiated at 1,152 hours into the experiment. The complete saturation phase was maintained for about 9 days with continual dripping at a rate of 1 mL/min. The core was drained at 1,369 hours into the experiment.

During the partial and complete saturation phases, determination of ferrous iron and sulfate were determined using Hach kits, and dissolved oxygen and sulfide were determined using Chemetrics kits. Acidified (pH <2; nitric acid) subsamples of unfiltered effluent were analyzed for metals by inductively coupled argon plasma-mass spectrometry (ICP-MS).

Preparation and Determination of Cadmium Isotope Spike

Stable-metal isotopes were purchased from the Oak Ridge National Laboratory, with ^{111}Cd in the oxide form. The pH of the stable-metal isotope spike solutions was within a pH unit of the effluent pH values. The ^{111}Cd concentration in the spike solution was 270 $\mu\text{g/L}$. This isotope has a fairly low natural abundance (12.8%); hence it can be discriminated when mixed with metals leached from the core. The use of an enriched stable-isotope spike significantly shifts the isotope ratio away from the natural abundance, thus allowing the isotope spike to be identified in the core effluent. Isotope concentrations in the effluent were determined by ICP-MS. To

discern different behavior of the isotope spike in the system, the isotope spike value was ratioed to another isotope not used in the spike. If there is no difference in the behavior of the spiked isotope, then the value of this measured isotope ratio, relative to natural abundance, should be 1.

RESULTS AND DISCUSSION

The effluent pH and conductivity are shown in Figure 1. The pH decreased from about 3.5 to 2.8 over the first 250 hours of the experiment. The rapid decrease in pH is most likely due to the dissolution of acid-generating soluble salts present in the top portion of the core. After the rapid decrease, the pH then slowly rose over the remainder of the experiment to about 3.3. These results demonstrate that these deposits can continue to generate acidity over long periods of time. The conductivity reaches a maximum of around 3500 $\mu\text{S}/\text{cm}$ about 150 hours before the lowest pH is recorded. After 900 hours of leaching, the conductivity reaches a near-constant value of about 700 $\mu\text{S}/\text{cm}$. This high conductivity, present even after over 100 liters of water (approximately 17 pore volumes) had been passed through the core, further demonstrates the long-term release of soluble constituents from the core, and likely from the fluvial tailings deposit. Given an average annual precipitation at the site of about 40 cm/year, this represents the amount of precipitation over a period of 7-8 years.

The concentration profiles for most metals (data not shown) generally followed the pattern of the conductivity, although they exhibited slightly different patterns of release during the first 100 hours (Smith *et al*, 1999). The Cd profile is shown in Figure 2. After peaking at about 4 mg/L, the total Cd concentration decreased to about 300 $\mu\text{g}/\text{L}$ at the end of the unsaturated experiment (565 hours). After partially saturating the core, the total Cd concentration rapidly drops to below 100 $\mu\text{g}/\text{L}$, and then more slowly continues to decline to about 30 $\mu\text{g}/\text{L}$. This occurs simultaneously with the disappearance of dissolved oxygen and the appearance of ferrous iron in the effluent. The acceleration in the decrease of Cd concentration in the effluent under reducing conditions suggests a redox-sensitive mechanism is operating, such as metal-sulfide precipitation. However, dissolved sulfide was not detected in the effluent.

Also shown in Figure 2 is the measured $^{111}\text{Cd}/^{114}\text{Cd}$ normalized to the natural $^{111}\text{Cd}/^{114}\text{Cd}$ abundances. During the unsaturated portion of the experiment the ratio is near one, even after breakthrough of conservative tracers (at about 350 hours, data not shown) that were

simultaneously added with the isotope spike. This result indicates that all of the added ^{111}Cd spike was retained in the core. Retention of Cd is further supported by the fact that the effluent total Cd did not increase during the addition of the isotopes. The ratio of Cd isotopes increases to approximately two at the onset of partially saturated conditions (565 hours). This occurrence coincides with the onset of reducing conditions and the release of ferrous iron, possibly suggesting that reductive dissolution of iron oxides releases Cd that was retained during the unsaturated portion of the experiment. However, it is unexpected that Cd would be significantly sorbed at these low pHs, and suggests other additional mechanisms may be occurring. The isotope ratio increases to about three at the onset of fully saturated conditions (1,152 hours). The lack of increase in total Cd indicates that only a very small amount of the added ^{111}Cd is released under reducing conditions.

The sensitivity of the isotope method demonstrates that processes involving metal attenuation and release can be examined, even when the total metal concentrations of the introduced metals are relatively constant. In order to mitigate the impacts of fluvial tailings deposits on adjacent water bodies, it is necessary to understand processes that control metal attenuation and release within the deposits. These processes are generally very complex and encompass changing geochemical conditions and a variety of mechanisms. The combination of use of intact material from the field site and stable-metal isotopes facilitated determination of different metal sources, and different metal-attenuation and metal-release processes within the fluvial tailings deposit in response to changing geochemical conditions.

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Figure 1. Specific conductance and pH of core effluents over the course of the leaching experiment.

Figure 2. Log total cadmium concentrations in core effluents, and cadmium isotope ratios for ^{111}Cd spike added to the core during the leaching experiment.

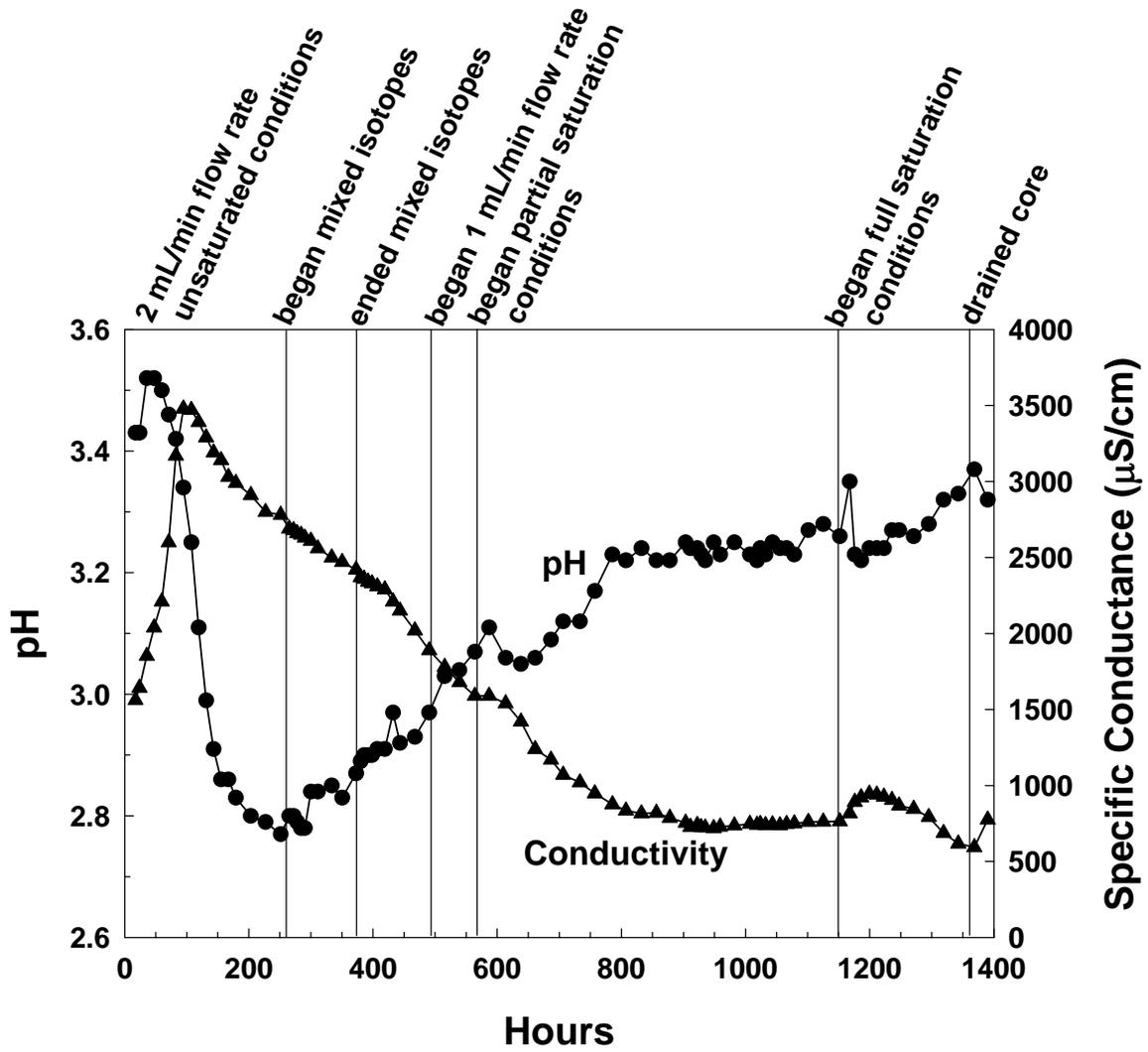


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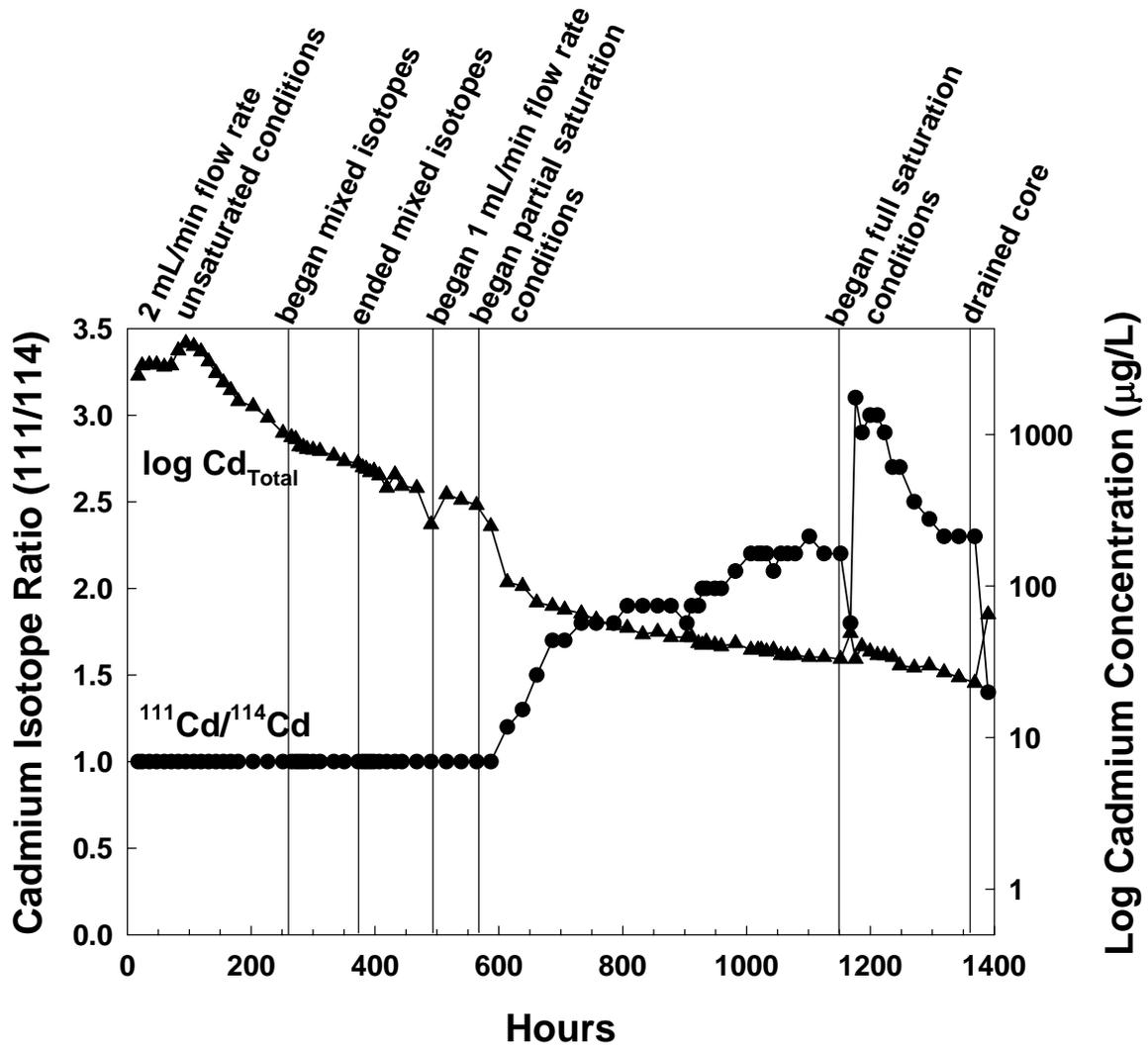


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