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BACKFILL ENVIRONMENTS**

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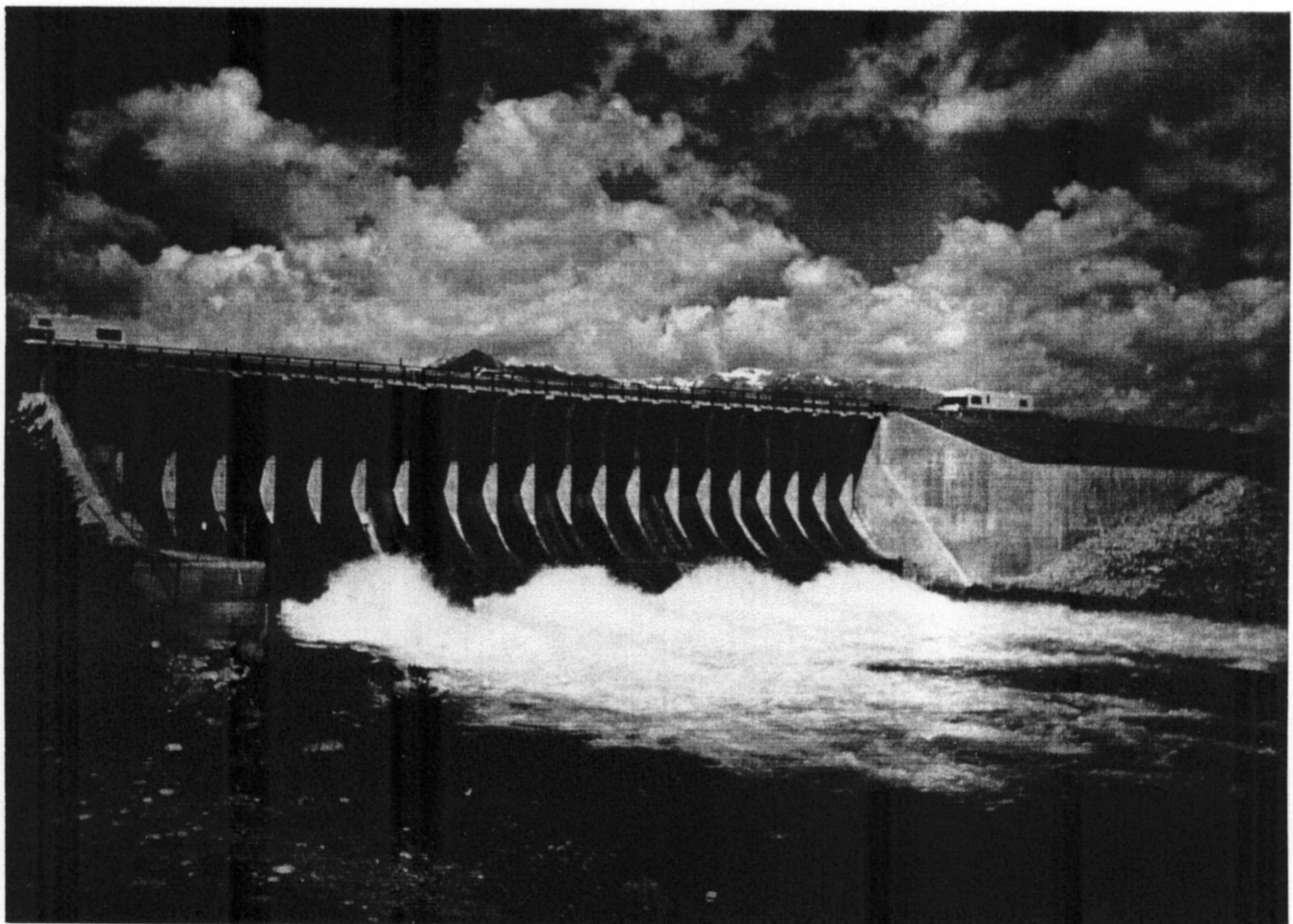
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PROCEEDINGS

**EFFECTS OF HUMAN-INDUCED CHANGES
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Geochemical Processes Affecting the Mobility of Dissolved Selenium in Surface Coal Mine Backfill Environments

A.A. Fadlelmawla¹, K.J. Reddy², and G.F. Vance³

ABSTRACT: During surface coal mining, rock material overlying the coal is redistributed with respect to its original stratigraphic position. Oxidation of the redistributed backfill material may release dissolved selenium (Se) to groundwater in backfill systems. This study was initiated to examine the chemistry of Se in the groundwater backfill environment. Both backfill core material and groundwater samples were collected from three sites in Wyoming. Dissolved organic carbon (DOC) from groundwater samples was fractionated into six categories (hydrophobic acids, bases, and neutrals; and hydrophilic acids, bases, and neutrals). The DOC was comprised primarily of hydrophobic and hydrophilic acids which were isolated and used in competitive sorption/desorption studies with Se. Core samples were also subjected to precipitation/dissolution studies to determine potential solid phases controlling dissolved Se concentration. Results suggested that coal mine backfill material have a very high sorption capacity for Se. Hydrophilic acids reduced Se sorption by coal mine backfill materials. DOC showed very little effect on Se speciation and potential solid phases controlling dissolved Se. Water extracts from coal mine backfill materials were dominated by MgSeO_3^0 ion pair followed by CaSeO_3^0 , and SeO_3^{2-} species. Dissolved Se concentrations in coal mine backfill environments appeared to be controlled by a Cu_2Se solid phase.

KEY TERMS: Selenium; sorption/desorption; chemical modeling; precipitation/dissolution.

INTRODUCTION

Although Se is not an essential element for plants, it is necessary for animals (Oldfield, 1987). However, excessive Se can be toxic to plants, animals, and humans. In the process of surface coal mining, overburden materials are brought to the earth's surface where they are exposed to oxidizing conditions. The oxidizing conditions decrease the stability of the Se containing sulfides and organic matter, which can eventually increase dissolved Se concentrations in backfill materials. Increased dissolved Se in backfill materials can potentially enhance Se mobility into groundwater environments.

Additionally, dissolved organic carbon (DOC) has been shown to contribute to the mobility of Se in reclaimed coal mine land groundwater systems (Martin et al., 1988; Naftz and Rice, 1989). Studies also suggest Ca^{2+} enhances the adsorption of anions (Helyar et al., 1976; Neal et al., 1987b).

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At present very little is understood regarding Se sorption/desorption and precipitation/dissolution processes in coal mine backfill groundwater systems. The objectives of this study were to: 1) characterize DOC associated with coal mine spoil backfill groundwaters 2) determine the effects of the DOC compounds and Ca^{2+} have on sorption/desorption processes of Se and 3) determine the effects of the DOC compounds on precipitation/dissolution processes of Se in surface coal mine backfill environments.

MATERIALS AND METHODS

Site Selection

Field sites were selected from active coal mines in order to provide the maximum amount of historical data for this study. Three field sites were located in reclaimed areas at two large surface coal mines (Mine A and Mine B) in the Powder River Basin, Wyoming.

Collection and Analysis of Backfill Samples

Two backfill cores were obtained from within approximately 4.5 m radius of existing groundwater wells at each site. Core holes ranged from approximately 7.0 to 8.0 m deep and were at least as deep as the associated well. Backfill cores were collected using a rotary driven, split spoon auger. After the backfill cores were collected, void spaces within the liners were purged with pre-purified argon gas and the liners were then sealed with plastic caps and tape to prevent oxidation of the backfill materials.

Backfill cores were chilled in the field and were stored under refrigeration at 4°C. Backfill samples were sieved through a 10-mm sieve and the sieved samples were subjected to total elemental analysis, saturated paste extraction and analysis, and X-ray diffraction (XRD) analysis to determine major mineral composition. Eighteen core samples representing materials from above and below the water table from the three different sites were used for sorption/desorption and precipitation/dissolution studies.

Collection and Analysis of Groundwater samples

Groundwater samples were collected at each well in September, 1991, and July (Mine A) and August (Mine B), 1992. Wells were pumped at approximately $0.27 \text{ m}^3\text{h}^{-1}$ with a submersible, positive displacement pump until pH, specific conductance, and temperature were stable ($\pm 10\%$); this required pumping approximately three to five casing volumes of water from each well. After above parameter were stabilized the submersible pump was replaced with a slower, nonsubmersible positive displacement pump and filter assembly to collect groundwater samples.

Groundwater samples were filtered through $0.45 \mu\text{m}$ glass fiber filters and were collected in 4 L, high-density polyethylene bottles for DOC fractionation and isolation. DOC samples bottles were purged with argon and filled under a stream of argon gas to avoid oxidation of the samples.

Dissolved Organic Carbon Fractionation and Isolation

All groundwater samples were analyzed by the DOC fractionation technique. Percentages of the different fractions were determined, and the dominant fractions (hydrophobic and hydrophilic acids) were isolated and used in competitive Se sorption/desorption studies. The method used for this study was initially developed by Leenheer and Huffman (1979) and modified by Vance and David (1991). The method separates DOC into six fractions; however, for this study, only five fractions were separated (hydrophobic acids and neutrals, and hydrophilic acids, neutrals, and bases) and the hydrophobic bases were neglected due to the small amounts present in the groundwater samples.

Sorption/Desorption Experiments with DOC Fractions

Two grams of each core sample were placed in a centrifuge tube and mixed with 20 ml of solution of known Se concentration. Concentrations of Se in the added solutions ranged from 0 to 1000 ppb. Selenium solutions were prepared using analytical grade Na_2SeO_3 . Samples were shaken for 24 hours on a mechanical shaker. Reaction time was chosen according to Balistrieri and Chao (1987). After 24 hours, samples were centrifuged for 15 minutes at 2000 rpm and supernatant solutions were filtered through a 0.7 micron Whatman glass microfiber filters.

The sorption/desorption study included three sets of experiments to determine the Se sorption capacity of the core samples and to evaluate the effect of the addition of CaCl_2 and DOC on the sorption capacity of these samples. The DOC fractions used in these experiments were isolated from the collected groundwater using the procedure described earlier. The first set of experiments determined the sorption capacity of the core samples when the background solution composition was distilled water. In the second set of experiments, 0.1M CaCl_2 was added to the background solution. Finally, the third set of experiments included DOC.

For the third set of experiments, both hydrophobic acid (HPO-A) and hydrophilic acid (HPI-A) were added separately to the Se sorption solution. Concentrations of the added DOC from Mine A were 157 and 107 ppm for hydrophobic and hydrophilic acids, respectively. For Mine B concentrations of the added DOC were 110 and 88 ppm for hydrophobic and hydrophilic acids respectively. The isolated DOC fractions from each of the groundwater samples were added to the respective core samples collected near the groundwater sampling site.

Precipitation/Dissolution Experiments

Preliminary precipitation/dissolution experiments were conducted on two core samples representing the two mine sites, to determine when steady state conditions were attained for core samples. Twenty five grams of each sample, in duplicates, were reacted with 75 ml of distilled-deionized water on a mechanical shaker at 200 rpm at $25 \pm 2^\circ\text{C}$.

After reacting for 1, 3, 7, 14, 21, and 28 days, sample suspensions were filtered under argon atmosphere using 0.45 μ Millipore filter. Clear extracts were divided into two subsamples. One was acidified to pH between 2-4 with HNO_3 and the other one left unacidified. Acidified samples were analyzed for Ca, Mg, Na, K, Fe, and Mn. Unacidified samples were analyzed for pH, Eh, total Se, SO_4^{2-} , and Cl^- . Data from these analysis were plotted as time versus concentration of different elements to determine steady state conditions. These results suggested that concentration of most of the elements, including Se, did not change between 21 and 28 days thus indicating that these reaction periods can be used to obtain uniform results. Similar experiments were repeated for the eighteen core samples using a 28 day reaction period.

Analytical Procedures

Total elemental concentrations were determined following the procedure of Lim and Jackson (1982). Saturated paste extracts were prepared according to Standard Operating Procedures for sampling and analysis of overburden/spoil and soil (Wyoming Department of Environmental Quality, 1992). The XRD analysis was performed using methods described in Jackson (1969) and Moore and Reynolds (1989).

The pH was measured using an Orion combination electrode. The Eh was measured using an Orion platinum (Pt) electrode with Ag/AgCl₂ reference electrode. Total inorganic carbon was measured using a Shmadzu Carbon Analyzer. Total Se was measured using Atomic Absorption Spectrophotometry with Hydride Generator (AAS-HG). Concentrations of SO₄²⁻, Cl⁻, F⁻, and NO₃⁻ were measured using a Dionex Ion Chromatography (IC) system. Other cations and anions in the acidified samples were measured using inductively coupled plasma optical emission spectrophotometry (ICP-OES). Concentrations of Na and K were measured using Atomic Emission Spectrophotometry (AES).

Geochemical Modeling

The geochemical model GEOCHEM (Sposito and Mattigod, 1980) was used to calculate ion activities and potential solid phases controlling the dissolved Se concentrations. The DOC in the solution can affect the solubility of Se by complexing with metals (such as Mn, Mg, Fe, Ca) that usually complex with Se, reducing their free metal concentrations in the solution and concentrations available to complex Se. Two types of calculations were made with GEOCHEM to determine the effects of DOC on ion activity products (IAPs) of different Se solid phases. First, IAPs were calculated without including DOC in the input data to the model. Second, IAPs were calculated after adding DOC to the input data to the model. Fulvic acid was used to simulate DOC in GEOCHEM (Sposito et al., 1981).

RESULTS AND DISCUSSION

Data from total elemental analysis suggested that core samples were dominated by Fe, Al, Mg, Ca, S, K, and Na. The pH values for saturated pastes ranged between 3.7 and 8.1. The pH values for saturated paste extracts for samples taken near the groundwater table were very similar to those obtained from measurements of the groundwater. Redox potential (Eh) ranged between 308 and 653 mV. Values of Eh near the groundwater table were also very similar to those obtained for the groundwater samples. Total Se concentration determined from saturated paste extracts ranged between 1.3 and 155 µg/kg. Samples collected near the surface contained low concentrations of Se. Concentrations of Se were found to increase with depth and then decrease near the groundwater table.

XRD analysis indicated that all of the backfill samples contain the following common minerals: quartz, kaolinite, potassium feldspar, illite, and muscovite. Additional minerals that were detected in some samples included: smectite, gypsum, calcite, dolomite, carbonate apatite, and goethite. Calcite occurred in all but one sample with most of the calcite being magnesium calcite. Dolomite was identified in six of the samples. Samples were also visually examined under a microscope. The mineral goethite, an iron oxide, was detected by x-ray diffraction in only one sample, but a microscopic inspection indicated that a small amount of iron oxide was present in each sample.

The results of the DOC fractionation analysis indicated that the DOC in the groundwater samples was dominated by organic acids (i.e., hydrophobic and hydrophilic acids) with 74 to 84 percent for Mine A and 68 to 83 percent for Mine B, respectively. Organic neutrals ranged from 16 to 23 percent for Mine A and 10 to 25 percent for Mine B. Organic bases ranged from 0 to 4 percent for Mine A and 6 to 8 percent for Mine B.

All coal mine backfill samples had high sorption capacities for selenite (83 to 94%). Addition of the hydrophobic acid slightly decreased selenite sorption for both Mine A and Mine B. Whereas addition of hydrophilic acid greatly decreased selenite sorption for all samples (Fig. 1). The effect of DOC on the sorption was in general greater at low concentrations of the added selenite. A small increase in selenite sorption was observed in samples containing 0.1 M CaCl_2 (Fig. 1).

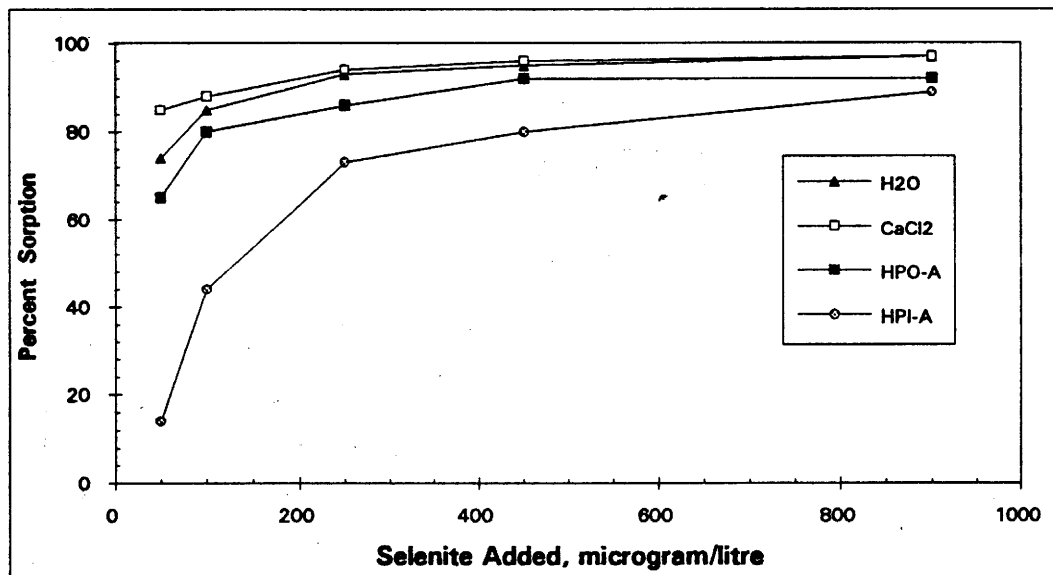


Figure 1. Sorption of selenite as a function of added selenite

The IAPs of different Se solid phases (e.g. $\text{Fe}_2(\text{SeO}_3)_3$, MnSeO_3 , PbSeO_3 , and Cu_2Se) in water extracts from the precipitation/dissolution experiments were compared with K_{sp} s to examine the possibility that one of these solid phases may be controlling the dissolved concentrations of Se. Results indicated that IAPs of these solid phases were highly undersaturated and were not controlling the Se concentrations. However, in some samples, Se concentrations appeared to be controlled by Cu_2Se (average SI of 3.3 ± 1.9). The precipitation/dissolution experiments results suggested that as depth increased, redox potential ($pe + pH$) decreased and Se concentrations probably reached saturation with respect to Cu_2Se . It is possible that in subsurface environments O_2 concentrations will be low and such an anaerobic condition would favor the precipitation of reduced Se solid phases such as Cu_2Se (Elrashidi et al., 1987; Masscheleyn et al., 1990; Reddy and Gloss, 1993).

Chemical speciation from the GEOCHEM model suggested that core sample water extracts were dominated by the MgSeO_3^0 ion pair (55 to 90% of total Se concentration) followed by CaSeO_3^0 , and SeO_3^{2-} species (Fig. 2). In extracts with low pH (between 3.7 and 6.0), MgSeO_3^0 ion pair (55% of total Se concentration) followed by HSeO_3^- (25% of total Se concentration) and CaSeO_3^0 (20% of total Se concentration) were predominant (Fig. 2). The predominance of ion pairs in coal mine backfill materials may represent a potential for leaching problems because these neutral species may not be sorbed onto oxides and clays as charged species, and therefore become mobile (Reddy and Gloss, 1993). The DOC showed very little effect on Se speciation.

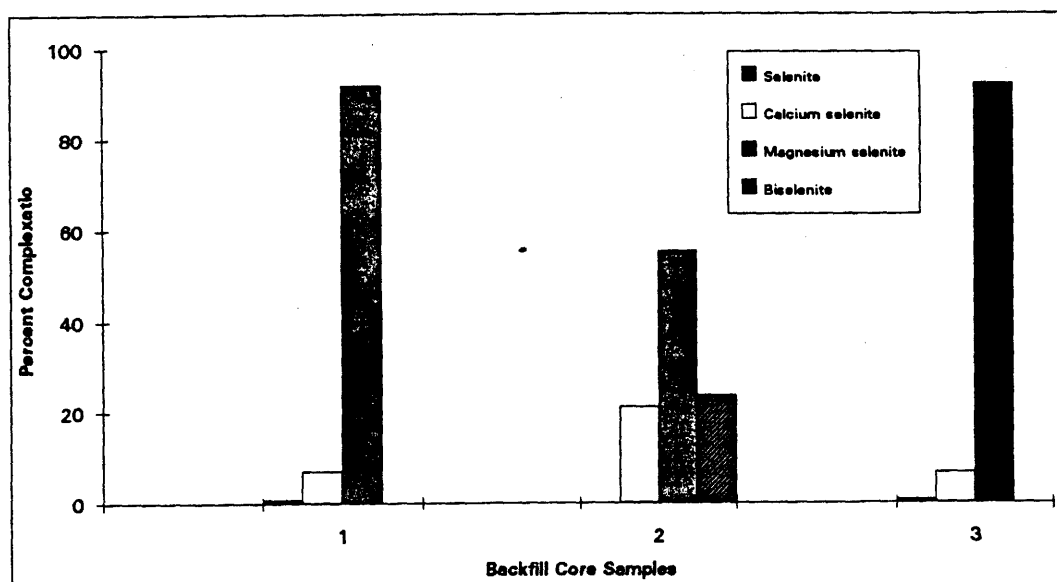


Figure 2. Chemical speciation of selenium in water extracts of core samples

CONCLUSIONS

Sorption/desorption studies suggested that coal mine backfill materials have a very high sorption capacity for Se. Hydrophilic acids reduced Se sorption by coal mine backfill materials. Precipitation/dissolution studies suggested that dissolved Se concentrations in coal mine backfill environments may be controlled by a Cu_2Se solid phase. Chemical speciation results indicated that water extracts from coal mine backfill materials were dominated by MgSeO_3^0 followed by CaSeO_3^0 , and SeO_3^{2-} species.

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