Effects of Redox Potential on the Speciation of Selenium in Ground Water and Coal-Mine Backfill Materials, Wyoming [1]

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Abstract: Determining redox potential (Eh) effects on selenium speciation is important in assessing the potential mobility of selenium in ground water and coal mine backfill. Although, general trends for redox potential conditions controlling selenium speciation have been observed, experimental data establishing specific redox potentials controlling selenium speciation is lacking. The objective of this research was to investigate the effects of redox potential on selenium speciation in ground water and coal-mine backfill material suspension. A redox controlling apparatus was designed to control redox potential of ground water and coal-mine backfill suspension. Samples of ground water and coal-mine backfill suspension were placed in a reaction chamber and were reacted to varying redox potentials. A syringe was used to obtain samples from the reaction chamber, through a sample port. Samples were analyzed for selenite and selenate with ion chromatography. The redox controlling apparatus was successful in controlling and maintaining the redox conditions of the samples. Reduction of selenate to selenite in ground-water samples was not observed in a Eh range of 444 to -280 mV. Concentrations of selenite in ground water gradually decreased at 213 mV and decreased sharply at -106 mV. Selenate concentrations in the backfill-material suspension decreased slightly at a Eh of 455 mV and by 80% at a Eh of -106 mV. Selenite in the backfill-material suspension was adsorbed to below detectable limits, possibly by iron and manganese oxides; therefore, speciation changes due to redox potential could not be determined.

Additional Key Words: Selenium speciation, selenium toxicity, selenium mobility

Introduction

Dissolved selenium (Se) concentrations ranging from 3 to 330 μg/L have been detected in shallow post-mining ground water from coal mines in the Powder River Basin, Wyoming (Martin et al., 1988; Naftz and Rice, 1989). Se can exist in different oxidation states. Some oxidation states are more mobile than others, primarily because of the adsorption processes involving iron or manganese oxides and clay minerals. For example, selenate (SeO_4^{2-}) with a +6 oxidation state is more mobile than selenite (SeO_3^{2-}), which has a +4 oxidation state (Balistrieri and Chao, 1987). Additionally, studies by Carter et al. (1969) and Page and Bingham (1986) have shown that Se toxicity in plants is related to the oxidation state of the Se present in soil. Thus, it is important to understand the effects of redox potential (Eh) on dissolved Se in ground water and coal-mine backfill materials. Such information is necessary for describing the mobility as well as the toxicity of Se in coal-mine backfill ground-water environments.

Although general trends for redox conditions controlling Se speciation have been observed, experimental evidence is lacking. Geering et al. (1968) and Elrashidi et al. (1987) developed theoretical solubility and redox criteria for Se in soil. Using data from Elrashidi et al. (1987), predictions of soluble Se speciation can be made based on Eh versus the Se mole fraction. However, because of uncertainty in the measurement of Eh and the application of Eh measurements, experimental evidence verifying redox-Se speciation predictions is lacking. Traditionally, Eh has been measured by immersing a platinum electrode in a solution in combination with a calomel or other reference electrode. The validity of measuring Eh to predict Se speciation has been questioned. Runnells and Lindberg (1990) concluded that the platinum electrode does not respond to changes in the ratio of selenate and selenite; thus, Eh measurements do not reflect Se speciation in aqueous systems. However, Runnells and Lindberg's findings do not

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mean that Se speciation cannot be affected by redox couples present in ground water or soil. Coal-mine backfill materials commonly are highly heterogeneous and contain high concentrations of soluble salts, particularly sulfate. Selenium redox transformations often are reported to occur at measured redox potentials similar to those for sulfur (Bartlett and James, 1993). Therefore, sulfate would be expected to parallel or impact the observed redox potential for the reduction of selenate to selenite and the reduction of selenite to elemental selenium or to selenide. The objective of this article is to examine the effects of Eh changes on the speciation of Se in ground water and coal-mine backfill materials.

Materials and Methods

Collection and Analysis of Ground-Water and Coal-Mine Backfill-Core Samples

Ground-water samples were collected from wells completed at reclaimed coal-mine sites in the Powder River Basin, Wyoming. Water was pumped from wells at approximately 4.5 L/min with a submersible, positive displacement pump until pH, specific conductance, and temperature stabilized (± 10%). Coal-mine backfill-core samples were collected using a rotary-driven spoon auger. Details regarding the collection of ground-water and coal-mine backfill-core samples are reported in See et al., (1995). Ground-water samples were filtered through 0.45 μm fiberglass filters, were analyzed for cations and anions, and were used for subsequent experiments. Backfill-core samples were air dried and sieved to <2 mm. The <2 mm sieved samples were used for subsequent redox potential experiments.

The pH was measured using an Orion[3] combination electrode. The Eh was measured with an Orion platinum (Pt) electrode with a Ag/AgCl$_2$ reference electrode. Concentrations of nitrate, sulfate, and chloride, were measured with a Dionex ion chromatograph (IC). Cations (arsenic, cadmium, calcium, chromium, lead magnesium, and zinc) in the acidified samples were measured with inductively coupled plasma optical emission spectrophotometry (ICP-OES). Concentrations of potassium and sodium were measured with Atomic Emission Spectrophotometry (AES). The concentration of Se speciation in samples was determined with an IC. The limit of quantification for selenate and selenite, using IC, was 180 μg/L, with a detection limit of 20 μg/L. Complete details regarding the procedures involved in determining Se speciation with an IC are published in Blaylock and James (1993).

Design of Redox Controlling Apparatus

Patrick et al. (1973) developed a simple system to control Eh and pH in soil suspensions. Reddy et al. (1976), Schwab and Lindsay (1983), and Boyle and Lindsay (1986) employed a Eh and pH controlling system to examine iron and manganese solubility and availability in soils. Brennen and Lindsay (1994) made an improved redox potential controlling system to determine iron solubility in soils. Recently, we developed a redox controlling apparatus similar in concept to that used by Brennen and Lindsay, with a few modifications (Reddy, 1994). Unlike previously described systems, the system described in our study does not require the addition of organic matter to provide energy for microorganisms to reduce soils. Decomposition of organic matter may release organic acids, which may complex with metals.

The design of the redox controlling apparatus (RCA) is shown in Figure 1. The RCA consists of a sample chamber containing pH, platinum (Pt), and reference electrodes connected to the pH/Eh meter. The pH/Eh meter and oxygen and hydrogen gas tanks were connected to a control box to maintain the desired redox potential (Eh) in the sample chamber. The oxygen gas tank contained 95% oxygen and 5% carbon dioxide and the hydrogen gas tank contained 3% hydrogen, 5% carbon dioxide, and 92% argon. The carbon dioxide in the gas mixture maintained a constant pH (5.0±0.1) in the samples. A peristaltic pump circulated ground water in the sample chamber. The gas outlet was connected to a fume hood.

The RCA control box was designed to read mV signals from the platinum (Pt) and reference electrodes and the signals were compared to the minimum and maximum set values on the oxygen and hydrogen dials.

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[3]Any use of trade, product, or firm name is for descriptive purposes only and does not imply endorsement by the Wyoming Water Resources Center, Rutgers University, the University of Wyoming, or the U.S. Geological Survey.

If the mV signal was less than the set range, the controller switched on a solenoid that released oxygen gas into the sample chamber to increase the mV reading to the set value. Similarly, hydrogen was switched on if the mV reading was greater than the upper limit. The relay was calibrated to operate from +1.2V to -1.2V.
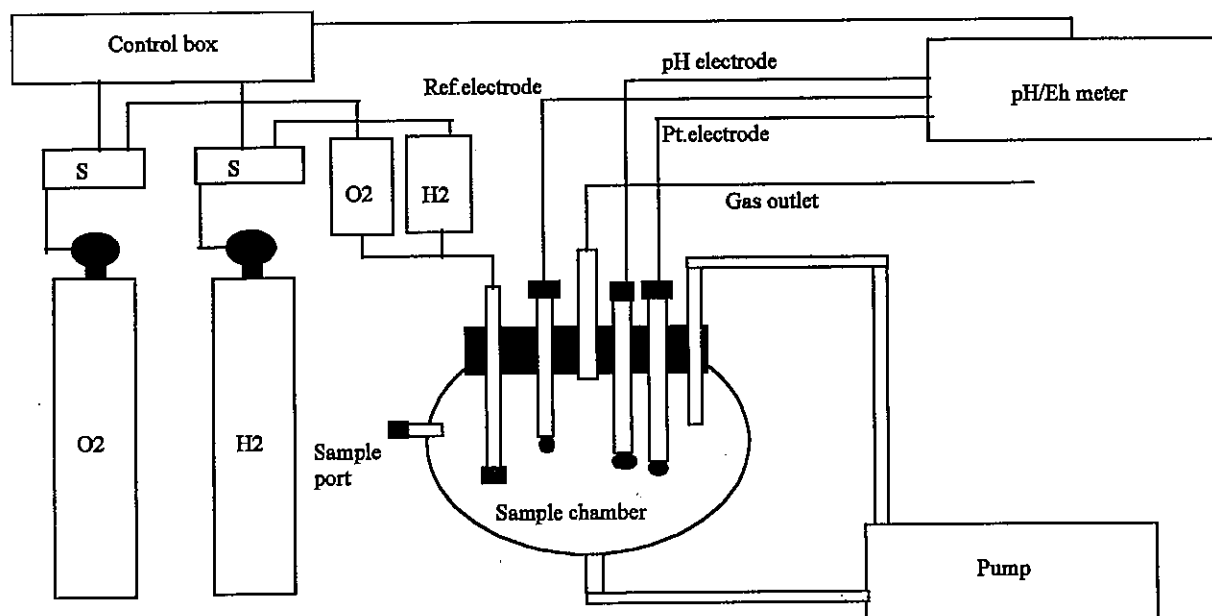

Figure 1. **Redox controlling apparatus used to examine the effects of redox potential (Eh) on the concentration of dissolved Se in ground water and coal-mine backfill suspension.**

Ground-Water and Coal-Mine Backfill Suspension with Redox Controlling Apparatus

A 1-L sample of ground water was amended with 0.5g of carbon black containing 10% platinum, 8.0 mg/L of selenate, and 8.0 mg/L of selenite. The coal-mine backfill suspension was amended with 0.5g of carbon black containing 10% platinum, 5.0 mg/L of selenate, and 5.0 mg/L of selenite. All samples were amended with carbon black containing platinum to improve the response of the Eh electrode. The samples were reacted from 72 to 170 hours to equilibrate the samples at a particular Eh level. Samples were withdrawn from the sample chamber through a sample port with a syringe and were analyzed immediately with an IC, using manual injection through a 0.45-μm, filter for selenate, selenite, nitrate, nitrite, chloride, and sulfate.

Results and Discussion

The pH for ground water was 6.3, and the Eh was 400 mV. The natural ground water also contained large concentrations of sulfate (2,960 mg/L) and nitrate (51 mg/L, as nitrogen). The concentrations of arsenic, cadmium, chromium, lead, and zinc were less than 0.001 mg/L. The pH for coal-mine backfill suspension was 7.6.

The RCA was successful in controlling the redox status of the ground water and coal-mine backfill suspension at a given measured Eh value. The addition of 5% CO_2 to the gas mixture maintained a constant pH 5.0±0.1 in the ground-water sample. The pH of coal-mine backfill also remained constant and was more representative of the native pH of the sample.

The coal-mine backfill suspension also resisted Eh changes caused by adding hydrogen and oxygen. This was evidenced by the longer time periods required for the Eh to stabilize at a particular setting. Oxidation of selenite to selenate was not observed in ground-water samples at an Eh of 444 mV. Reduction of selenate to selenite in the

ground-water samples also was not observed in a Eh range of 444 to -280 mV. Reduction of selenite in ground-water samples occurred much more readily (Figure 2). Selenite in the ground water began to reduce after 72 hours at an Eh of 213 mV and the concentration diminished by 99% at a redox potential of -280 mV. When the redox potential in the ground-water sample was increased to +603 mV, very little or no selenite was recovered, indicating that selenite probably was converted to hydrogen selenide gas.
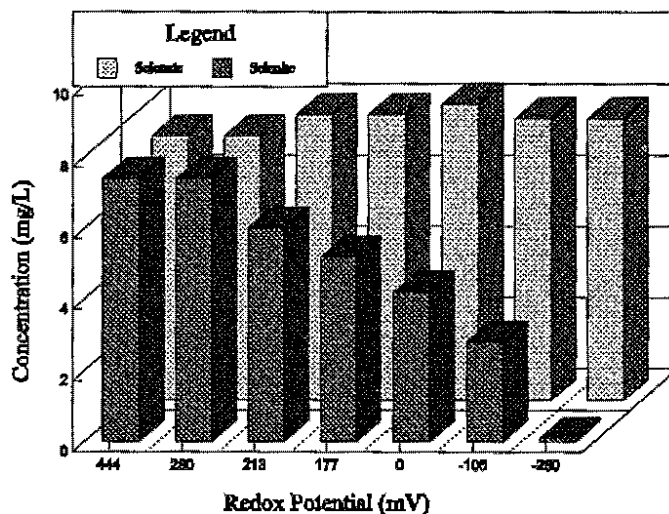

Figure 2. Effect of redox potential on the dissolved concentration of selenate and selenite in ground-water samples during a 25-day sampling period with 72-hour sampling intervals.

The selenate in coal-mine backfill suspension decreased initially by 30% after 72 hours at 455 mV and decreased by 80% after a total elapsed time of 288 hours and 72 hours at -106 mV(Table 1). This decrease in selenate concentration may be caused by both chemical and biological processes. Selenite in the coal-mine backfill suspensions was apparently adsorbed by iron and manganese oxides and clay minerals in the coal-mine backfill material; therefore, speciation changes caused by redox potential could not be determined.

Table 1. Selenate response to Eh changes in coal-mine backfill suspension.

Redox potential (mV)	Elapsed time (hours)	Selenate (mg/L)	% Se reduced
700	72	5.0	0
455	144	3.5	30
207	216	3.0	40
-106	288	1.0	80

To help substantiate measured Eh values in relation to particular redox conditions, the concentrations of other anions participating in redox transformations also were monitored. Nitrate concentrations in the ground-water sample decreased at 236 mV and were not detected after 120 hours. A concomitant increase in nitrite concentrations was observed with the decrease in nitrate. However, after another 72 hours, nitrite concentrations diminished. Sulfate concentrations remained constant and appeared unaffected by redox in this study.

The reduction of nitrate, nitrite, and selenite indicates that appropriate electron pressure for the rapid reduction of sulfate and selenate should be present in ground-water samples. Weres et al. (1990) reported that nitrate

was highly correlated with Se in ground water and that nitrate maintains the Eh above what is required for selenate reduction. When oxygen and nitrate are removed from the system, the Eh decreases and selenate is reduced. This effect, however, was not observed for ground-water samples in our study. Selenite in solution is susceptible to reducing conditions, but does not appear to be oxidizable in ground-water samples under the experimental conditions employed. These results could be caused by the lack of labile electrons to participate in the particular redox couples in the ground-water samples or could be caused by kinetic constraints. Oxidation of selenite in soil has been reported to require from 48 to 240 hours (Masscheleyn et al., 1991; Blaylock and James, 1993).

The response of the selenate and selenite conversions to the imposed redox conditions of the redox controlling apparatus on the ground-water sample did not completely follow the thermodynamic predictions of Elrashidi et al. (1987). As stated previously, the rates of Se redox transformations have been reported to be slow. Our study focused mainly on relatively short reaction periods; thus, the non-occurrence of some of the predicted redox transformations could be caused by a lack of equilibrium conditions in the redox chambers.

The reduction of selenate in coal-mine backfill suspension followed thermodynamic predictions somewhat more closely than in the ground-water sample. Reduction of selenate in the coal-mine backfill suspension occurred at redox potentials similar to those reported by Masscheleyn et al. (1991). Dreher and Finkelman (1992) and Gillette Area Ground Water Monitoring Organization (GAGMO) (Hydro-Engineering, 1991 and 1992) also have reported a general decline in dissolved Se concentrations in ground water in coal-mine backfill material from the Powder River Basin. Overall, the GAGMO results and the results obtained in our study indicate that dissolved Se in coal-mine backfill material may attenuate naturally through chemical and biological processes. However, oxidation and reduction of selenite in coal-mine backfill materials was not observed in this study, probably because of adsorption of selenite by iron or manganese oxides or clay minerals. Coal-mine backfill materials typically have high (80-90%) sorption capacities for selenite, leaving very little soluble Se to participate in the solution chemistry (Blaylock et al., 1995).

The absence of selenite oxidation to selenate in ground water has important implications. Because of the difficulty in obtaining reliable measurements of Se speciation in soil or water samples, total Se is often the only measurement determined. The speciation of Se into selenate and selenite generally is calculated on the basis of thermodynamic models. Results obtained in this study show that in ground water, selenate and sulfate will remain stable under reduced conditions when thermodynamic predictions would indicate otherwise. A comparison between ground water and coal-mine backfill materials with respect to reduction of selenate indicates the importance of chemical (iron and manganese oxides)and physical (surface area and adsorption) properties in the oxidation and reduction processes. For example, if we react ground water in the presence of backfill materials, as occurs in field conditions, selenate may be reduced to selenite and selenite may be adsorbed by the sediments in the ground water. This mechanism may explain selenate removal in coal-mine backfill materials.

Conclusions

The redox controlling apparatus was successful in controlling and maintaining desired Eh in ground-water and coal-mine backfill suspensions. Results indicate that selenate in ground water was not affected by any redox potential conditions. However, selenite was reduced 99% at a redox potential of -280 mV. Similarly, nitrate reduction to nitrite was observed in ground-water samples. An 80% reduction in selenate occurred in coal-mine backfill suspensions at a redox potential of -106 mV. Results of this study indicate the importance of both chemical and physical properties in oxidation and reduction processes of Se species in ground water in coal-mine backfill environments.

Acknowledgments

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