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Mine Soil Materials

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1995

MODELING SELENITE SORPTION IN RECLAIMED COAL MINE SOIL MATERIALS

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Selenite (SeO_3^{2-}) sorption in soils has been correlated with pH, soil mineralogy, and soil solution composition, factors that are often highly variable with respect to mine soil materials. Selenite equilibrium and adsorption batch studies were conducted with four mine soil materials to determine adsorption parameters that could be used to develop a model to predict Se retention. Initial mass, Freundlich, Langmuir, and other relationships were explored to describe adsorption and retention of Se in these soils. For equilibrium and adsorption studies, 25 ml of solution was added to 2.5 g of soil in a polyethylene centrifuge tube. Time-dependent analysis consisted of duplicate treatments of two SeO_3^{2-} levels and reaction times of 2, 6, 24, 48, 168, 336, and 504 h. Adsorption studies were arranged in a 3 × 10 × 4 factorial design (three replications, 10 SeO_3^{2-} concentrations, four soils) and equilibrated for 14 d. Selenite sorption as a function of pH in each material was also examined. Selenite sorption of 10 μg Se/g soil was not greatly affected by pH between pH 4 and 8, except in one sample where sorption decreased at pH 6. Initial mass isotherms were very similar for Se additions up to 20 mg/kg for all soils and predicted Se sorption very similar to the experimental data for these and 12 additional soils. The Freundlich and Langmuir isotherms did not effectively predict Se sorption.

Selenium (Se) is essential in the diets of animals but can be toxic at elevated levels. Soils in Wyoming tend to be high in Se and produce vegetation that exceeds recommended levels (>4

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mg/kg) (National Research Council 1983). Coal mining activities are of particular concern because mine soil and backfill materials in Wyoming contain significant concentrations of Se. These materials are brought to the surface through mining activities, where Se comes in contact with the root zone and may be available to plants. Reclaimed mine soils and backfill material present additional challenges because of their highly heterogeneous nature. They vary widely in pH and mineral content between horizons. They also contain unusually high levels of heavy metals and SO_4^{2-} compared with agricultural soils, adding to the complex equilibrium of the soil solution (Dreher and Finkelman 1992).

Selenium mobility and availability in soils is dependent on the oxidation state of Se present. Selenite (SeO_3^{2-}) is strongly adsorbed by soils and is not as available for plant uptake or leaching as selenate (SeO_4^{2-}), which is only weakly adsorbed and leaches easily (Neal et al. 1987a and b; Neal and Sposito 1989). Precipitation of Se compounds is also a factor in controlling Se solubility and availability to plants. Soluble complexes of Se and ion pair formation in solution may increase mobility of Se in the soil profile because the selenite anion will be uncharged and sorption will be limited.

Selenite adsorption is similar to that of PO_4^{3-}, occurring through ligand exchange mechanisms. Selenite adsorption occurs through the replacement of a surface hydroxyl with SeO_3^{2-} (chemisorption) (Sposito et al. 1988). Selenate is only weakly adsorbed and does not form inner-sphere complexes (Hayes et al. 1987). Both mononuclear and binuclear complexes may exist for chemisorption mechanisms of SeO_3^{2-} on oxide and mineral surfaces.

Soil pH and solution composition influence the adsorption of SeO_3^{2-} in soils (Goldberg 1985; Neal et al. 1987a). Selenite adsorption has been shown to be a function of pH, with adsorption increasing as pH decreases (Barrow and Whelan 1989). As the soil pH decreases, the affinity of the surface for anion adsorption increases to satisfy the positive charge of the surface. Thus,

we observe less mobility of Se in acidic soils than in alkaline soils.

Anion competition for adsorption sites also influences Se adsorption. Increasing PO_4^{3-} in solution decreases SeO_3^{2-} sorption (Ballistrieri and Chao 1987). The effect of SO_4^{2-} is less clear, although some reports indicate that SO_4^{2-} – SeO_3^{2-} competition exists at high SO_4^{2-} levels (150 mmol L^{-1}) (Singh et al. 1981). The effects of Ca in solution or precipitated as calcite on Se adsorption also require consideration. Neal et al. (1987b) suggested that a 100 mol m^{-3} $CaCl_2$ addition significantly increased SeO_3^{2-} sorption, which was related to the precipitation and/or increase in mineral surface charge resulting from Ca adsorption.

To predict adsorption of anions such as SeO_3^{2-}, equilibrium adsorption models are often employed. The Freundlich and Langmuir models have been adapted and adopted for use in soils to describe adsorption relationships. These models and their derivatives are based on empirical relationships determined experimentally and often rely on creative curve-fitting techniques. Thus, extrapolation to conditions outside the data set are difficult. Surprisingly, the relationships often produce predictions very close to what is observed experimentally, although the relationships are not as valid at low concentrations of sorbate (Harter 1984). The Freundlich and Langmuir models (and other adsorption models) also do not distinguish between adsorption and secondary precipitation and do not account for residual or native levels of the sorbate (Travis and Etnier 1981).

Chemical adsorption models to predict adsorption of oxyanions in soils, such as the constant capacitance model, have also been developed. The constant capacitance model uses estimates of the surface potential and surface charge to derive surface complexation constants. The constant capacitance model is useful in predicting SeO_3^{2-} adsorption as a function of soil pH (Goldberg 1985; Sposito et al. 1988); however, many of these studies were conducted at Se concentrations much higher than occur naturally. Goldberg (1985) reported very good predictions of SeO_3^{2-} adsorption on goethite as a function of pH compared with experimental data in a pure system; although in a PO_4^{3-}–SeO_3^{2-} mixed system the qualitative agreement was good (the shape of the predicted and experimental adsorption curves were similar) the

quantitative results were much less satisfactory. In Goldberg's (1985) study, adsorbed SeO_3^{2-} concentrations ranged between 20 and 220 mmol/ kg. At these concentrations, a 1% error in prediction would result in a 15 to 150-mg Se/kg difference in the amount of Se adsorbed. Sposito et al. (1988) also reported that the qualitative agreement between the model prediction and experimental data was excellent at initial SeO_3^{2-} concentrations of 8 mmol m^{-3} but that the quantitative agreement was only approximate.

Current Wyoming Department of Environmental Quality (WDEQ) guidelines (1984) require backfill placed in the rooting zone of reclaimed mines to contain less than 0.1 mg/kg AB-DTPA or hot water extractable Se. At these low levels, the need for a quantitative prediction of sorbed Se for reclaimed mine soils is apparent. This study was conducted to ascertain the controlling factors of Se adsorption in reclaimed mine soils in Wyoming and to develop model parameters for predicting Se mobility through the soil profile.

MATERIALS AND METHODS

Selenium adsorption and equilibrium studies were conducted using four abandoned coal mine soil materials from the Powder River Basin area in Wyoming. The soil materials were analyzed for mineralogical content by X-ray diffraction and the surface area by the Brunauer-Emmett-Teller method (BET) at the University of Wyoming Geology Department, DCB extractable Fe (Holmgren 1967), and anion and cation exchange capacity (Wada and Okamura 1980). Some soil chemical and physical properties are listed in Table 1.

Samples were air-dried, ground, and sieved to 10 mesh prior to analysis. For equilibrium and adsorption studies, 25 ml solution was added to 2.5 g soil in a polyethylene centrifuge tube. Time-dependent analysis consisted of duplicate treatments of two SeO_3^{2-} levels (0 and 500 mg Se/L) and reaction times of 2, 6, 24, 48, 168, 336, and 504 h. Adsorption studies were arranged in a 3 × 10 × 4 factorial design (three replications, 10 SeO_3^{2-} concentrations, four soils) and equilibrated for 14 d. The soil suspensions were equilibrated on a reciprocating shaker controlled by a timer to shake at 110 cycles/min for 30 min every 4 h. After equilibration, samples were centrifuged at 2500 × g for 15 min at 25 °C

TABLE 1

Characteristics of soil materials used for Se adsorption/equilibrium studies

Soil Material	pH	pe	DOC mg/kg	AEC[a] cmol kg^{-1}	CEC[a] cmol kg^{-1}	Texture	Surface Area m^2/g[b]	%Fe$_o$[c]	%Fe$_d$[d]
277	4.3	6.9	5.6	4.2	6.8				
						loam	9.1	0.03	0.16
177	6.5	9.9	8.8	4.3	17.8				
						loam	14.6	0.19	1.19
147	7.5	5.8	22.8	2.4	11.9				
						loam	13.8	0.04	1.70
199	8.1	7.4	10	3.1	12.3				
						sandy clay loam	14.5	0.02	1.91

[a] Wada and Okamura (1980).

[b] BET-N$_2$ method.

[c] Extractable by ammonium oxalate (Chao and Zhou 1983).

[d] Extractable by dithionite-citrate buffer (Holmgren 1967).

and the supernatant solution retained for analysis. Soil solutions were analyzed for pH, pe, and for F^-, Cl^-, NO_3^-, Br^-, SO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, and SeO_4^{2-} (Dionex 2000i ion chromatograph with AI-450 software). Total Se and SeO_3^{2-} were determined by atomic absorption spectroscopy with hydride generation using a Perkin-Elmer model 303 atomic absorption spectrometer equipped with a Varian VGA-10 hydride generator (Blaylock and James 1993). Equilibrium solutions were also analyzed by ICP for total concentrations of As, Al, Ca, Cd, Cr, Cu, B, Fe, K, Mg, Mn, Na, Ni, Pb, Si, and Zn. An additional study to examine the effects of pH on SeO_3^{2-} adsorption was also conducted. A pH range between 4 and 9 was created with each soil by adjusting a 1:10 soil:solution suspension (2.5 g soil) with HCl or NaOH. The suspensions were equilibrated for 48 h and then amended with 10 mg/kg Se as SeO_3^{2-} and equilibrated for an additional 48 h on a reciprocating shaker (110 cycles/min). The samples were centrifuged and analyzed for soluble Se as described above.

RESULTS AND DISCUSSION

Time-dependent analysis

Soluble selenite decreased up to 48 h, after which no significant decrease was observed and equilibrium was assumed (Fig. 1). Soluble Fe, Si, and As were the only other elements in which an increase or decrease in concentration was detected after 14 days. Soluble Fe levels exhibited a 4- to 5-fold increase in all soils between 168 and 504 h, while As increased from <0.04 to

above 1 mg/L in materials 147, 177, and 199. Sample 277 increased in soluble Si from 1.2 mg/L at 2 h to 8.8 mg/L at 504 h. Inorganic carbon increased approximately two-fold in samples 147, 177, and 199 over the duration of the experiment, pH showed no change with time in any of the soil materials.

Adsorption studies

Soil materials used in this study exhibited a very high SeO_3^{2-} sorption capacity, with >95% of the added SeO_3^{2-} (to 20 mg/kg) being adsorbed. Above 20 mg added Se/kg, the sorption decreased (Fig. 2). Plots of Freundlich isotherms were linear ($r^2 > 0.99$) in the range of equilibrium concentrations up to 0.1 mg/L. Langmuir adsorption plots were not linear and did not adequately describe the adsorption in any concentration range ($r^2 < 0.80$).
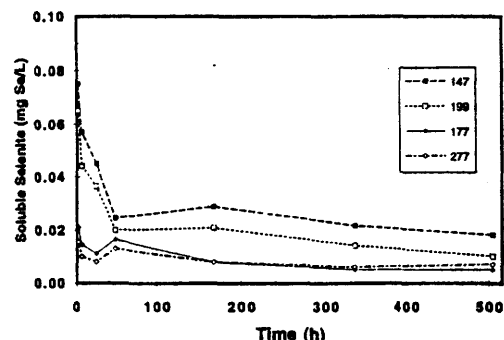
An attempt was made to predict Se adsorption

FIG. 1. Soluble SeO_3^{2-} in equilibrium with reclaimed mine soil materials as a function of time.
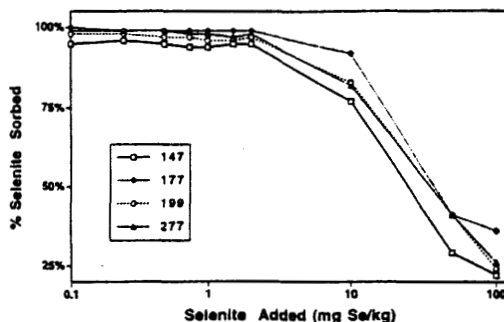
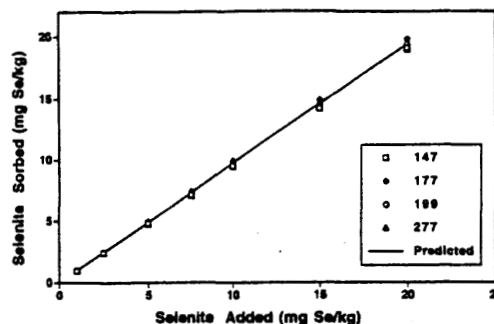FIG. 2. Percent of added SeO_3^{2-} sorbed by reclaimed mine soil materials.

FIG. 3. Initial mass prediction ($y = 0.97\chi + 0.015$) of sorbed SeO_3^{2-} and experimental sorption as a function of SeO_3^{2-} added to the soil suspension.

in the soil materials using an adsorption isotherm from one soil and from the averaged data of all the samples. Application of the initial mass isotherm (added Se vs. adsorbed Se) proposed by Nodvin et al. (1986) to describe anion and dissolved organic carbon (DOC) sorption proved successful. The initial mass isotherm was very similar and linear for all samples up to 20 mg added Se/kg. Thus, these values were averaged and an equation fit to the resulting data (Fig. 3). Above 20 mg/kg, the response became nonlinear and less reliable. A similar attempt was made with the Freundlich isotherm without success. Plotting the equilibrium concentration versus the adsorbed Se demonstrates that the equilibrium concentration is not a reliable predictor of Se adsorption in these materials (Fig. 4).

The soil materials varied in pH from 4.3 (277) to 8.1 (199). However, pH does not appear to be the controlling factor affecting SeO_3^{2-} adsorption in these soils. Sample 177 (pH 6.5) had the greatest sorption (lowest equilibrium concentrations of SeO_3^{2-}) and sample 147 (pH 7.5) had the least sorption. This is substantiated by the cation/anion exchange capacity data that was obtained as a function of pH (Table 1). The amount of positive and negative charge in these samples (measured as a function of NH_4^+ and Cl^- retention) was not affected by pH, and all samples showed a net positive charge between pH 4 and 8. The study using SeO_3^{2-} to determine the effect of pH on Se adsorption in these materials showed that SeO_3^{2-} sorption was relatively independent of pH between pH 4 and 8. Only one soil (277) exhibited a substantial decrease in sorption at pH 6 (Fig. 5). X-ray diffraction results indicated very little crystalline oxide material in these soils, while the DCB extraction
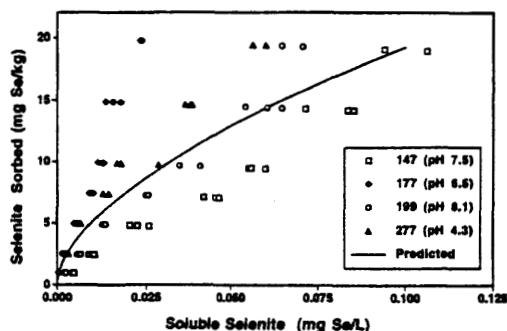

FIG. 4. Sorbed SeO_3^{2-} by reclaimed mine soil materials in relationship to equilibrium solution concentrations and sorption predicted by the Freundlich isotherm.
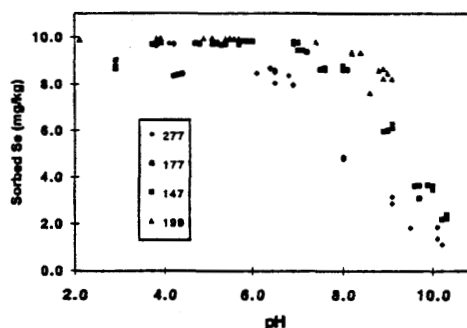

FIG. 5. Selenite sorption as a function of soil pH.

for Fe oxides indicated between 1.7 to 2.7% Fe_2O_3 for samples 147, 177, and 199, with sample 277 having only 0.2% (Table 1). Additional analysis examining Fe oxide and mineralogical content did not yield conclusive results pertain-

ing to the controlling factor of Se adsorption in these soils.

The initial mass isotherm appears to be the most promising predictor of Se adsorption. One drawback is that it uses initial concentration (a parameter difficult to obtain from a soil profile) to predict sorption or an equilibrium concentration. It is effective, however, in predicting Se removal by these materials from a contaminated water supply moving through the soil profile. To assess the predictive accuracy, adsorption data from 12 additional samples from varying depths (above and below the water table) and pH (3.7 to 7.5) were compared with the values predicted by the initial mass isotherm developed in this study. With the exception of one soil, the predicted Se adsorption values from added Se concentrations up to 1.2 $\mu g/g$ were very close to the experimental values (Fig. 6).

The lack of a clear correlation between measured soil characteristics and Se sorption illustrates the difficulty in predicting Se adsorption at sub-$\mu g/g$ concentrations. The only consistent factor appeared to be the DOC concentration. Sample 147 contained substantially greater concentrations of DOC than the other samples (Table 1) and also exhibited the least amount of Se sorption. However, relationships established by four soils are very tenuous and need to be confirmed with a greater number of samples. From the data obtained in this study it appears that SeO_3^{2-} adsorption is not controlled by one particular soil factor, but is probably an interaction of several soil characteristics. Considering the relatively small quantities of Se present in the soil solution, only a small percentage of

reactive surface sites would be necessary to adsorb soluble SeO_3^{2-}. The variability in these soil materials is probably not sufficient to influence the sorption capacity for the low concentration of a strongly adsorbed anion such as SeO_3^{2-}.

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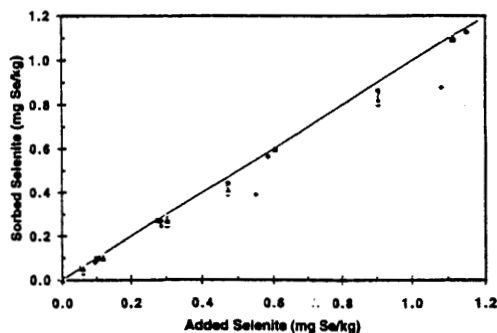
FIG. 6. Initial mass prediction of SeO_3^{2-} sorption in 12 mine soil materials in relationship to experimentally observed sorption.

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