UNDERSTANDING SELENIUM MOBILITY BY SORPTION AND EXTRACTION PROCESSES IN SURFACE COAL MINE SPOIL[1]

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Abstract: Surface coal mine spoil was studied to evaluate selenium (Se) mobility and solubility using batch experiments, column-leaching techniques, and sequential and individual extraction processes. Both selenite and selenate followed linear isotherm patterns at relatively lower Se treatments, whereas over a broader solution Se concentration range the sorption mechanism followed the Langmuir model. The variation in the isotherm patterns with change in Se concentrations suggested that mechanisms for selenite-selenate sorption would be a function of the concentration of solution-phase Se. Greater isotherm slope for selenite sorption suggested higher affinity of this specie for the mine spoil, while selenate was the more labile aqueous specie. In the exchangeable phase, selenite was the predominant specie. The results also indicated that adsorbed Se may be transformed into plant-available Se with time. Cationic presence enhanced selenite immobilization, with Fe being the most effective followed by Mn and Ca. The column leaching study indicated selenate had a faster mobilization rate, and there was a probable antagonistic relationship between Se species and sulfate in mine spoil solutions.

Additional Key Words: Selenite, Selenate, Adsorption, Extraction, Aqueous Phase, Exchange Phase, Batch and Column Studies.

Introduction

Selenium (Se) has been recognized as an element of environmental concern in coal mine environments (Valkovic, 1983) because of its natural occurrence and potential toxicity to wildlife and livestock (Rosenfeld and Beath, 1964). Different species of Se are: selenate (SeO_4^{-2}), selenite (SeO_3^{-2}), elemental Se (Se^0) and selenide (Se^{-2}). During surface mining activities, materials previously in reducing environments can be exposed to atmospheric conditions, thereby increasing the potential of elevated levels of oxidized Se species in surface waters and spoils (Boon, 1989). Mechanism-oriented research has been conducted for understanding the behavior of Se under different soil and aqueous environments. Selenite sorption modeling for reclaimed mine soils was discussed by Blaylock et al. (1995), and extraction studies were reported by Sharmasarkar and Vance (1995). However, no information is available on a combined approach of studying Se mobility through sorption and extraction processes in surface coal mine spoils. The objectives of this study were, therefore, to characterize and compare selenite-selenate mobility in coal mine spoil material applying different operational processes such as Se sorption, extractions, and column studies.

Materials and Methods

Soil Samples

An alkaline mine spoil having a sandy-loam texture was used for the batch and column studies. For sequential and individual extractions, 56 and 38 spoil materials from different surface coal mines of Wyoming were used. These samples were mostly alkaline, with low organic carbon contents, high sand percentages and high electrical conductivities.

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Batch Study

In 50 mL polypropylene tubes, samples were equilibrated with equimolar selenite-selenate treatments ranging from 0 to 250 mg/L (sodium salts) for 48 hr. on a reciprocating shaker (soil:solution = 1:10). The samples were centrifuged for 10 min. (2000 rpm), filtered (0.45 µm), and the selenite-selenate concentrations in filtrate solutions were analyzed by ion chromatography (IC). In our samples we did not have any peak-interference problems between sulfate and Se species. The Se treatments of 0-250 mg/L were selected to provide a broad range of Se concentrations for evaluating Se mobility behavior. A similar batch experiment was conducted with different metal (chlorides of Ca^{+2}, Mn^{+2}, Fe^{+2}) treatments (0, 0.1, 1, 10 mM/L) using a constant equimolar selenite-selenate concentration (0.1 mM/L). All the filtrates were analyzed for selenite-selenate by IC.

Column Leaching

A saturated spoil column (5.2 cm diameter, 5.5 cm length) was leached continuously with 40 mg/L of selenite-selenate (as sodium salts) at a constant hydraulic head (5.5 cm). Leachate solutions were collected with time, generally at every 5 min. for the first two and one half hours and approximately every 10 min. thereafter. The solutions were filtered (0.45 µm) and analyzed for sulfate, selenite, and selenate by IC until upper breakthrough points for both selenite and selenate were obtained.

Sequential and Individual Extractions

The spoil samples were sequentially extracted (soil:solution = 1:5), first with 0.25 M KCl (shaking for 30 min.) and then with 1 M KH_2PO_4 (shaking for 2 hr.). After each extraction step the samples were centrifuged for 10 min. at 2000 rpm and filtered through 0.45 µm filters. The filtrates were analyzed for total Se by atomic absorption spectrophotometry with hydride generation (AAS-HG) after a pre-treatment (30 % H_2O_2 + 12 M HCl) following the procedure of Spackman et al. (1994). The solution selenite was analyzed before pre-treatment, and selenate was calculated from the difference between pre-treated Se concentration and solution selenite. The spoil materials were also individually extracted for Se by AB-DTPA (soil:solution = 1:2, shaking for 15 min.) and 1 M KH_2PO_4 (soil:solution = 1:5, shaking for 2 hr.), and analyzed by AAS-HG.

Results and Discussions

Adsorption isotherms of both selenite and selenate at Se concentrations of 0-100 mg/L followed linear patterns (Fig. 1a). Selenite had a much greater slope than selenate (almost 10 times) suggesting a higher affinity of the former to the mine spoils. Physically this would indicate selenite as relatively immobile, and selenate as the major solution species. Similar conclusions were also drawn for different soils by other researchers (Alemi et al., 1991; Fio et al., 1991). However, besides adsorption, metal-selenite precipitation, and oxidation of selenite to selenate might have also caused depletion of the former specie from the solution phase; moreover, this would be plausible because of the alkaline pH of our spoil samples.

At the complete Se concentrations (0-250 mg/L), the isotherms followed the Langmuir model, which suggested monolayer coverage (Fig. 1b). Such a mechanism was also observed in other soil systems by Singh et al. (1981). The Langmuir equation used to describe the adsorption behavior in mine spoils was:

$$C_s = a\,C_l / (1 + b\,C_l)$$

where,

C_s = amount adsorbed (mg/kg)
C_l = equilibrium Se concentration (mg/L)
a, b = constants

The larger values for the constants of the selenite curve (a = 17.66, b = 0.03), as compared to those for selenate (a = 1.66, b = 0.01), indicated a higher adsorption potential of the former for the mine spoil materials. The variation in the isotherm patterns with change in treatment levels suggest that mechanisms for selenite-selenate sorption are a function of solution-phase Se concentration.

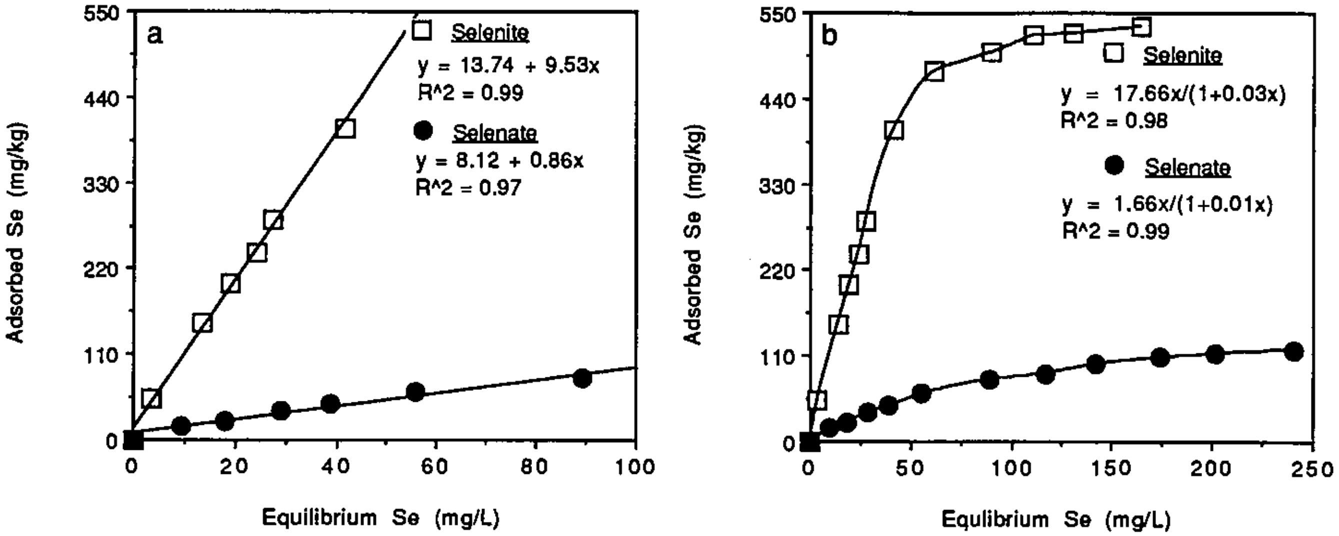

Figure 1. Different patterns of selenium adsorption in surface coal mine spoils: (a) Linear, (b) Langmuir.

Recognition of selenate as the potential solution specie was again supported by a sequential extraction study, which indicated a strong correlation between the aqueous Se phase and corresponding selenate concentration (Fig. 2a). However, in the exchange-phase, selenite was the predominant specie (Fig. 2b). The Se in exchange phase was extracted by phosphate, which would probably replace inner-sphere complexed selenite by a ligand exchange mechanism (Neal et al., 1987). Thus, this fraction would account for the adsorbed Se, and higher selenite distribution in this phase would further support the findings of our adsorption studies.

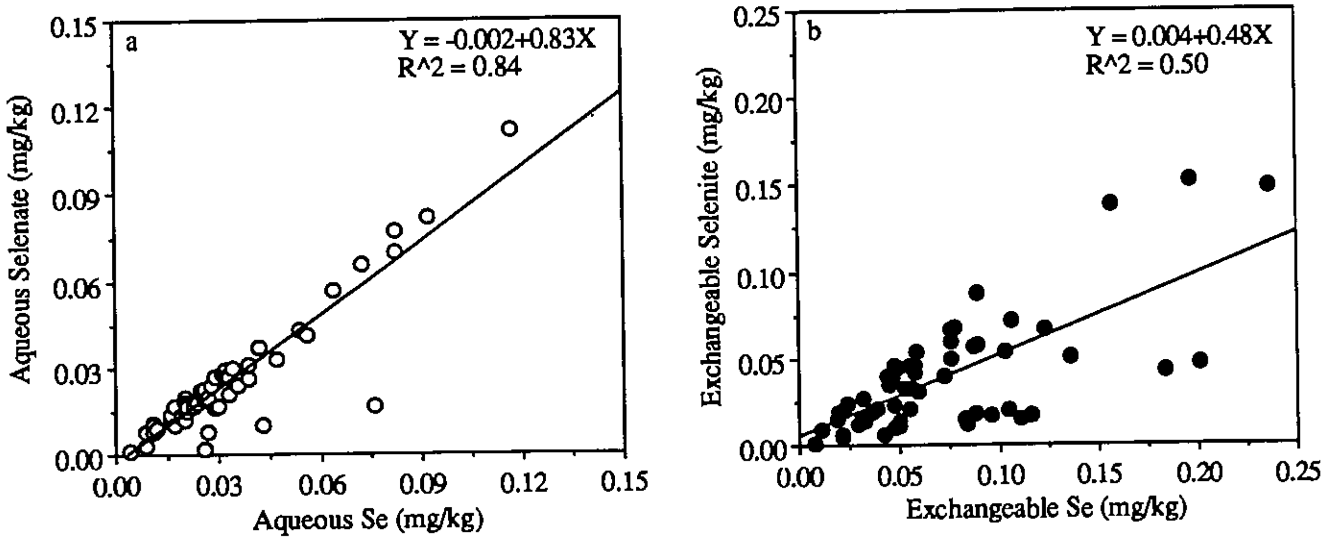

Figure 2. Selenium speciation in spoil extracts: (a) Selenate distribution in aqueous-phase, (b) Selenite distribution in exchange-phase.

With increasing exchangeable Se, there was a corresponding increase of Se in the aqueous fraction suggesting an interconversion between these two phases (Fig. 3a). The exchange-phase (phosphate extractable) Se was also found to be linearly related to AB-DTPA extractable Se, which is also indicative of plant-available Se (Soltanpour and Workman, 1980). The linear increment of AB-DTPA extractable Se with increasing phosphate extractable Se indicated that adsorbed Se would be gradually transformed into plant-available Se (Fig. 3b).

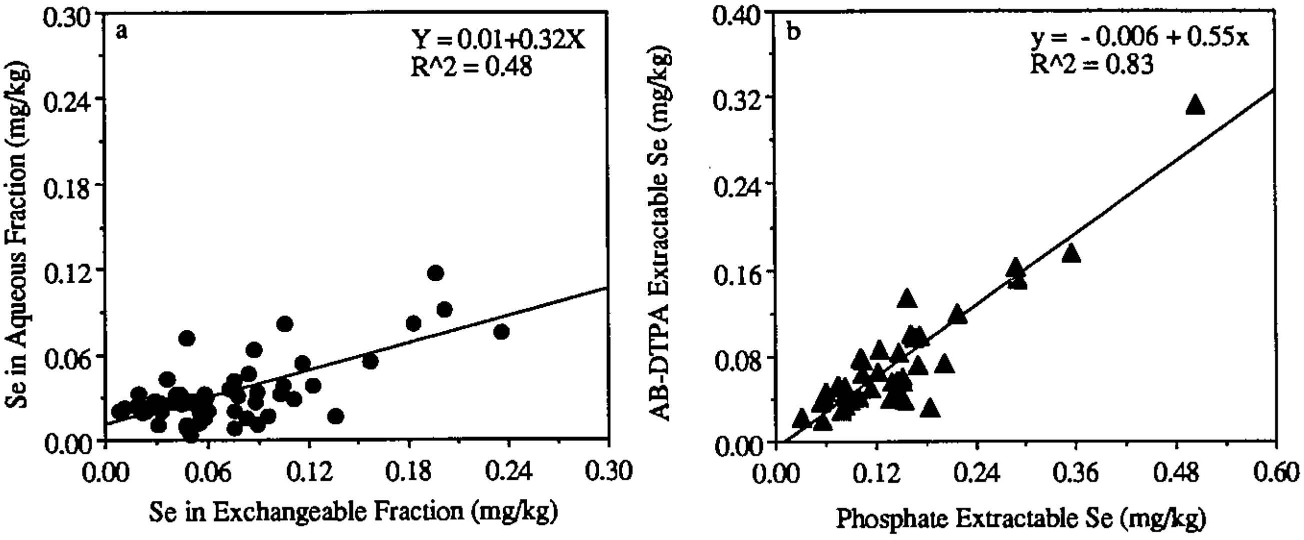

Figure 3. Relationship between various types of extractable selenium present in coal mine spoils: (a) Aqueous versus exchangeable Se, (b) AB-DTPA versus phosphate extractable Se.

Presence of Ca, Fe, and Mn in solution enhanced both selenite and selenate retention; however, metal-effect on selenite was found to be more pronounced (Fig. 4). With samples from similar mine environments as used in this study, selenite was also identified by Blaylock et al. (1995) as the adsorbed specie. The disappearance of Se from solution could have been due to precipitation with the metals. Another reason might have been lowering of the negative charge density at the sorption sites caused by presence of the metal ions, which could result in a subsequent increase in Se adsorption. Similar findings have also been explained by Neal et al. (1987). Also metal oxyhydroxide formation could have enhanced selenite adsorption. Selenium retention followed the order: Fe>Mn>Ca. This order of Se retention could be attributed to the respective electronic structure and bonding force of the bivalent cations. Moreover, presence of Fe or Mn in solution would typically simulate an acidic environment, whereas Ca will simulate an alkaline condition; thus, Fe and Mn might enhance adsorption through oxyhydroxide formation.

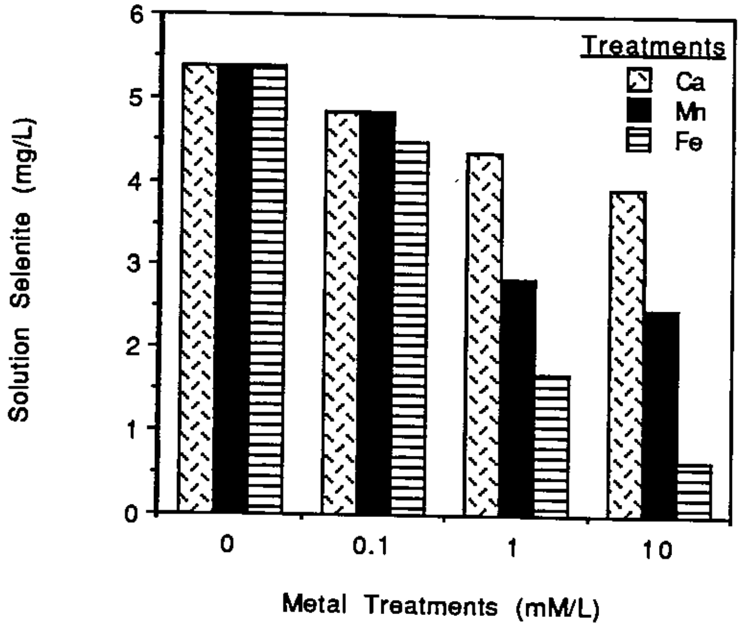

Figure 4. Cationic influence on selenite mobility in a coal mine spoil.

The column leaching study indicated that selenate had a shorter breakthrough time in comparison to selenite, which had a lower slope for the breakthrough curve (Fig. 5).. Physically this would mean there was greater mobilization of selenate through the soil column; a similar conclusion was drawn by Alemi et al. (1991). The pH of the collected leachate samples was found to vary in the range of 7-8. Slight oxidation of selenite to selenate might have also occurred during the experiment. It was also noted that solution sulfate concentrations decreased exponentially as selenate and selenite concentrations increased. This could be due to the depletion of sulfate with time; however, an antagonistic relationship between the Se species and sulfate in soil solution might be also a possibility.

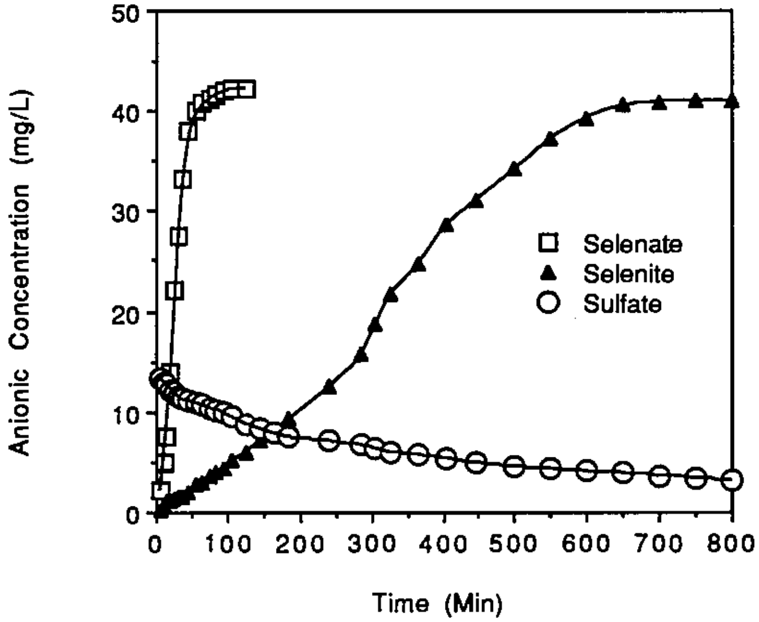

Figure 5. Time dependence of anionic mobility in a mine spoil column.

Summary and Conclusions

Sorption and extraction studies with surface coal mine spoil indicated selenite is relatively immobile as compared to selenate. Selenate, on the other hand, would be more available for plant-uptake and water contamination. The similar isotherm patterns for the species, however, suggested there was resemblance in their sorption pathways. The Langmuir pattern suggested monolayer coverage, i.e., sorption would not be an infinite process for spoil Se retention. Time is also an important factor in the mobilization process, as reflected by a distinct time lag between the transport of the two species. The findings of our study also suggested that Se mobility would be affected by other ions, such as, iron, manganese, calcium, and sulfate.

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