ROLE OF NATURAL ORGANIC SOLUTES ON THE SORPTION OF SELENIUM BY COAL MINE BACKFILL-CORE SAMPLES FROM THE POWDER RIVER BASIN, WYOMING[1]

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Abstract: Concentrations of dissolved selenium (Se) as large as 330 $\mu g\ L^{-1}$ have been detected in water samples from backfill aquifers in the southern Powder River Basin (PRB) of northeastern Wyoming. During surface coal mining, rock material overlying the coal is redistributed in relation to its original stratigraphic position; exposure of the previously buried material to surface oxidizing conditions decreases the stability of sulfides and organic matter containing Se, increasing Se concentrations in associated ground waters. Ground-water and backfill-core samples were collected from three sites located at two active mines in the PRB. Dissolved organic carbon (DOC) in the ground-water samples was dominated by the acid fraction (sum of hydrophobic and hydrophilic acids) at 38 to 84% of the DOC; the neutral fraction (sum of hydrophobic and hydrophilic neutrals) ranged from 10 to 55% and the base fraction (sum of hydrophobic and hydrophilic bases) was generally less than 10%. Three sorption experiments were conducted to investigate selenite sorption on backfill-core samples. Selenite concentrations in these experiments ranged from 0 to 11 mg kg^{-1} in backfill-core samples. The first experiment determined the selenite sorption capacity of the backfill-core samples with selenite in distilled-deionized water as a background solution. In the second experiment, selenite in 0.1 M $CaCl_2$ was used as a background solution. In the third experiment, hydrophobic and hydrophilic acid fractions, isolated and concentrated from ground-water samples, were added to the selenite background solutions. Results of the three experiments indicated that the backfill-core samples have a high sorption capacity for Se (generally, greater than 90% of the added Se) and can sorb as much as 99 % of Se added as selenite. Selenium sorption increased in most samples when 0.1 M $CaCl_2$ was used as a background solution compared to distilled-deionized water background solution. The increase in selenite removal might have been caused by precipitation reactions or by an increase in positively charged surfaces caused by calcium sorption, or both. A substantial decrease in selenite sorption rates occurred in the presence of individual organic-solute fractions. Hydrophilic acids caused the largest decrease in Se sorption by the backfill-core samples.

Additional Key Words: Selenium Geochemistry; Coal Mines; Sorption/Competition; Dissolved Organic Carbon; Mobility; Powder River Basin, Wyoming.

Introduction

Studies have shown that the chemistry of selenium (Se) in coal overburden materials can be affected by mining and reclamation operations (Dreher and Finkelman, 1992). Exposure of previously buried material to surface oxidizing conditions can decrease the stability of Se-containing sulfides and organic matter. The oxidation of such compounds can transform reduced and less mobile Se species such as selenide (Se^{2-}) and elemental selenium (Se^0) into oxidized Se species, selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), which are more soluble in alkaline and oxidizing ground waters (Naftz and Rice, 1989). Concentrations of Se, ranging from 3.4 $\mu g\ L^{-1}$ (Martin et al., 1988) to 330 $\mu g\ L^{-1}$ (Naftz and Rice, 1989), have been detected in shallow post-mining ground waters from coal mines in the PRB of northeastern Wyoming. Currently, the Wyoming Class I (domestic), II (agricultural), and III (livestock) ground-water standards for total Se are 10, 50 and 50 $\mu g\ L^{-1}$ (Wyoming Department of Environmental Quality, 1993). The ground-water contribution to surface water flow may provide a mechanism to transport Se from ground-water environments to surface-water resources. Surface-water Se concentrations ranging from 2 to 13 $\mu g\ L^{-1}$ have been reported to cause reproductive problems in aquatic birds (Skorupa and Ohlendorf, 1991).

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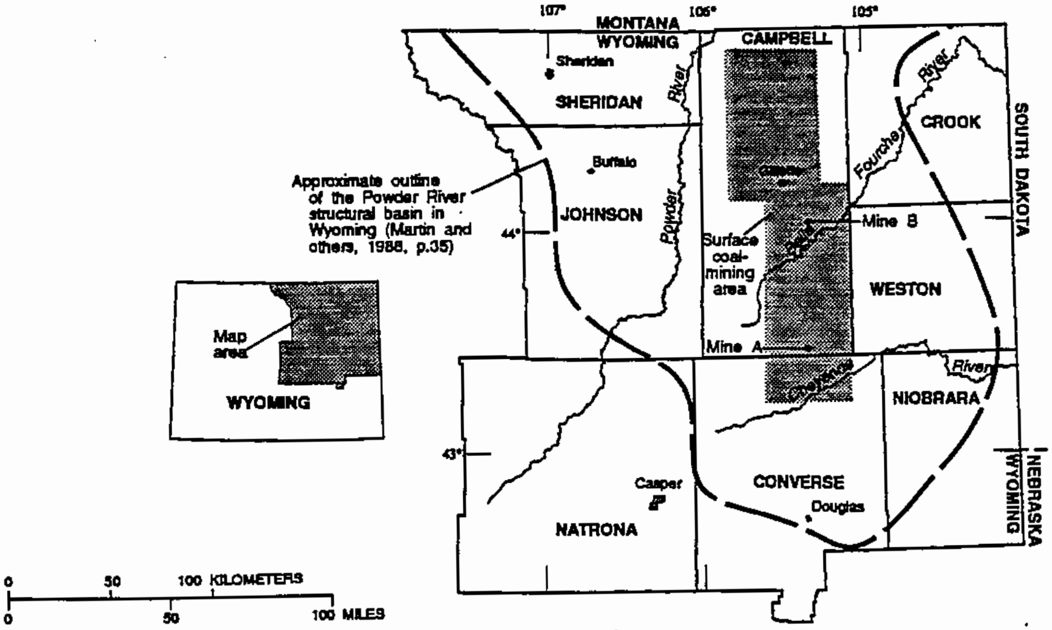
Dreher and Finkelman (1992), in a study of Se mobilization at a surface coal mine in the PRB, suggested that the source of Se, the occurrences of Se in overburden deposits and backfill water, and the fate of Se were important in understanding Se chemistry in coal-mine environments. The results of their study indicated that decreasing concentrations of soluble Se were due, in part, to microbially assisted reduction of selenate to selenite, that was followed by sorption of selenite onto clay minerals in the coal-mine backfill materials. Thus, sorption is expected to be one of the major processes controlling the solubility of Se in subsurface environments. Sorption of Se is the result of the two mechanisms, electrostatic attraction and ligand exchange (Yates and Healy, 1975), and is affected by pH, redox condition, and competition of other ions (Balistrieri and Chao, 1987; Bar-Yosef and Meek, 1987; Neal et al., 1987a,b). In addition, kinetic studies involving soils have suggested that selenite sorption onto oxide surfaces occurs by a ligand exchange mechanism (Yates and Healy, 1975; Cornell and Schindler, 1980; Sposito, 1984; Goldberg, 1985; Balistrieri and Chao, 1987; Neal et al., 1987a,b).

Studies by Balistrieri and Chao (1987), Naftz and Rice (1989), Fio and Fujii (1990), and Abrams et al. (1990) have shown that natural organic solutes and organic Se compounds are important in the mobility of Se in soil and coal-mine overburden. Particularly, results from Naftz and Rice (1989) indicated that natural organic solutes in coal-mine backfill ground-water systems may compete for adsorption sites on metal oxides and may contribute to the increased mobility of Se. They found a statistically significant positive correlation between Se and organic carbon. In the present study, we characterized the dissolved organic carbon (DOC) in ground waters at two Powder River Basin coal mines, and examined the role of isolated DOC fractions on Se sorption reactions using backfill-core materials collected from sites adjacent to the ground-water wells.

Materials and Methods

Three field sites were selected for this study. Sites were identified on the basis of the presence of Se and shallow ground-water levels. The three field sites selected were in reclaimed areas at two large surface coal mines in the PRB, Wyoming (Fig. 1). Of the sites selected, two had ground water with Se exceeding the 50 µg L^{-1} Wyoming Class I, II, and III ground-water standards, and the other had a detectable Se concentration. The surface coal mines are referred to as Mine A and Mine B in all figures, tables, and text; two sites were studied at Mine A (A-1 and A-2) and one site at Mine B (B-1).



Base modified from U.S. Geological Survey 1:100,000 digital line graph map series:
Bill, 1979; Buffalo, 1982; Casper, 1979; Devils Tower, 1979; Gillette, 1979; Kaycee, 1982;
Lance Creek, 1981; Midwest, 1981; New Castle, 1979; Rattlesnake,1981; Reno Junction, 1982
Sheridan, 1984.
Albers Equal-Area Conic projection
Standard parallels 29°30' and 45°30'; Central meridian -107°30'

Figure 1. Location of surface coal-mining area, coal-mine sampling sites, and the Powder River structural basin, Wyoming (See et al., 1995).

Coal-Mine Backfill Samples

Two backfill cores were collected from within a 5-m radius of the existing well at each field site. Core holes ranged in depth from 7.5 to 8.4 m and were at least as deep as the associated well. Acrylic liners were used to collect and store the backfill-core samples; void space in the liners was purged with pre-purified argon gas and the liners were sealed with plastic caps and tape to minimize oxidation of the samples during transportation and storage. Backfill cores were chilled in the field and stored under refrigeration until needed for laboratory experiments. The backfill cores were removed from the acrylic liners and partitioned into subsamples; splits of the core samples were air dried and sieved through a 10-mesh (2 mm) screen.

Ground-Water Samples

Ground-water samples were collected from wells located at each field site; samples were taken after pH, specific conductance, and temperature of continuously pumped well water had stabilized. Ground-water samples were filtered onsite through 0.45 µm glass-fiber filters into 250-mL, high-density polyethylene (HDP) bottles for major- and trace-ion analyses, and into 4L, HDP bottles for DOC fractionation and isolation studies. Subsamples used for cation analyses were acidified with HNO_3 to ≈pH 2; subsamples for DOC analysis were purged with argon gas and filled under a stream of argon gas to minimize oxidation. All ground-water samples were chilled in the field with ice and subsequently stored under refrigeration (3°C) until time of analysis.

Onsite measurements of ground-water samples were made in a sealed, flow-through chamber that minimized sample contact with the atmosphere. Specific conductance was measured using a Lab Line Instruments Lectro Mho Meter[3]; pH (Orion combination electrode) and Eh (Orion platinum electrode with an $Ag/AgCl_2$ reference electrode) were measured using an Orion Research Model 407A Ionanalyzer; dissolved oxygen was measured using a YSI Incorporated Model 57 dissolved oxygen meter; DOC was determined using a Shimadzu TOC-5000 carbon analyzer; and total Se was determined by AAS-HG (Spackman et al., 1994).

DOC in ground-water samples was fractionated using the method of Leenheer and Huffman (1979) as modified by Vance and David (1991). The method separates DOC into six fractions (hydrophobic bases, acids, and neutrals, and hydrophilic bases, acids, and neutrals). The percent DOC in the different fractions was determined, and the dominant fractions were identified so these fractions could be isolated and used in sorption experiments involving Se.

Hydrophobic and hydrophilic acids in ground-water samples were isolated and concentrated in accordance with the methods described in Vance and David (1991) with the substitution of XAD-4 resin for the anion-exchange resin typically used in the DOC fractionation method (Malcolm and MacCarthy, 1992). Ground-water samples from wells A-1 and B-1 were used in the isolation procedure; ground-water DOC from well A-2 was not isolated because of low DOC concentrations. The isolated fractions were used later in the sorption studies to determine their effect on Se sorption.

For the DOC isolation study, 16 L of ground water from well A-1 (88 mg L^{-1} DOC) and 18 L from well B-1 (79 mg L^{-1} DOC) were used. After isolation of the hydrophobic and hydrophilic acids, the solutions were passed through a column containing cation exchange resin. For the well A-1 ground-water sample, 3.3 L of hydrophobic acid (280 mg L^{-1} DOC) and 0.8 L of hydrophilic acid (145 mg L^{-1} DOC) were isolated. For the ground- water sample from well B-1, 3.1 L of hydrophobic acid (300 mg L^{-1} DOC) and 0.8 L of hydrophilic acid (130 mg L^{-1} DOC) were isolated.

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[3] Use of brand, firm, or trade names is for identification purposes only and does not constitute endorsement by the University of Wyoming, U.S. Geological Survey, Wyoming Department of Environmental Quality or Wyoming Water Resources Center.

Selenite Sorption Studies

Selenium sorption experiments were conducted using: 2 g backfill-core samples in polyethylene centrifuge tubes and 20 mL solution containing known amounts of $NaSeO_3$ ranging from 0 to 1,000 µg L^{-1} SeO_3. Backfill-core samples were capped and placed on a reciprocating shaker for 24 hours. This reaction time was selected on the basis of studies by Balistrieri and Chao (1987) that indicated sorption reactions involving SeO_3^{2-} reached equilibrium in 24 hours. After 24 hours, backfill-core samples were centrifuged for 15 minutes at 2,000 rpm and an aliquot of approximately 17 mL of supernatant filtered through a prerinsed 0.7-µm Whatman glass-microfiber filter. After filtering, core samples were extracted with 1 M KH_2PO_4 and the extracted Se was measured to determine the amount of total Se desorbed.

Three selenite sorption experiments were conducted using background solutions of: distilled-deionized water, 0.1 M $CaCl_2$, and solutions containing isolated hydrophobic or hydrophilic acids. Concentrations of the isolated DOC from well A-1 used in the competitive sorption experiments were 157 mg L^{-1} for hydrophobic acids or 107 mg L^{-1} for hydrophilic acids; competitive sorption experiments using isolated DOC from well B-1 contained 110 mg L^{-1} hydrophobic or 88 mg L^{-1} hydrophilic acids. The isolated DOC fractions from each of the ground-water samples were added to corresponding core samples collected from the field sites near each well, except for the core samples corresponding to site A-2, where hydrophobic acids from well A-1 were used. Because of insufficient isolated hydrophilic acids, no sorption studies involving hydrophilic acid and core samples from site A-2 were conducted.

Results and Discussion

Ground-water Analysis

The pH of the ground-water samples ranged from 5.5 to 7.3 and specific conductance from 3,650 (well B-1) to 10,000 µS cm^{-1} (well A-1) (Table 1). Results of other parameters measured in the ground-water solutions included: Se from 3 mg L^{-1} (well A-2) to 125 mg L^{-1} (well A-1) and DOC from 11 mg L^{-1} (well A-2) to 88 mg L^{-1} (well A-1). The DOC in wells A1 and B1 was assumed to be high due to increased dissolution of coal fines in the backfill materials.

Table 1. Water-quality properties, total selenium, and dissolved organic carbon (DOC) in ground-water samples collected in 1991 and 1992, Powder River Basin, Wyoming.*

Sampling date, properties, and constituents	Well Number A-1	A-1	A-2	A-2	B-1	B-1
	Field Analysis					
Sampling Date	9-17-91	7-07-92	9-17-91	7-07-92	9-19-91	8-19-92
Water level (meters)	3.73	3.63	4.72	4.55	3.53	3.46
pH (standard units)	7.1	7.3	5.5	5.6	6.3	6.4
Specific conductance (µS cm^{-1})	10,000	10,000	5,000	4,200	3,650	3,800
Electrical potential (mV)	350	370	450	450	400	370
Temperature (°C)	11	11	10	11	10	14
Dissolved oxygen (mg L^{-1})	<1	<1	<1	<1	<1	<1
	Laboratory Analysis					
Total selenium (µg L^{-1})	125	121	3	13	88	88
DOC (mg L^{-1})	88	84	11	14	87	79

* µS cm^{-1}, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg L^{-1}, milligrams per liter; µg L^{-1}, micrograms per liter, <, less than

The results of the DOC fractionation analysis (Table 2) indicate that DOC in the ground-water samples was dominated by the acid fraction (sum of hydrophobic and hydrophilic acids) at 74 to 84% for well A-1, 38 to 69% for well A-2, and 69 to 82% for well B-1. The neutral fraction (sum of hydrophobic and hydrophilic neutrals) in ground-water samples ranged from 16 to 23% for well A-1, 21 to 55% for well A-2, and 10 to 25% for well B-1. The base fraction (sum of hydrophobic and hydrophilic bases) in ground-water samples was generally less than 10%. Comparing DOC fractionation (Table 2) and isolation (Table 3) results for ground water from sites A-1 and B-1 indicates higher hydrophobic and lower hydrophilic acid recovery in the isolation studies. The differences between DOC results in the two studies could be caused, in part, by the different volumes of resins used in the two experiments, or the difference in flow rates. In addition, XAD-4 resin was used in the isolation procedure to retain the hydrophilic acids, whereas an anion exchange resin was used in the fractionation procedure.

Table 2. Analytical results of dissolved organic carbon (DOC) fractionation of ground-water samples, Powder River Basin, Wyoming*.

Sampling date and Constituents	Well Number A-1	A-1	A-2	A-2	B-1	B-1
			Field Analysis			
Sampling Date	9-17-91	7-07-92	9-17-91	7-07-92	9-19-91	8-19-92
Hydrophobic solutes						
Total solutes (% of total DOC)	58	57	49	42	70	62
Acids (%)	42	42	43	22	53	52
Bases (%)	1	<1	<1	<1	<1	<1
Neutrals (%)	15	15	6	20	17	10
Hydrophilic solutes						
Total solutes (% of total DOC)	42	43	51	58	30	38
Acids (%)	32	42	26	16	16	30
Bases (%)	2	<1	10	7	6	8
Neutrals (%)	8	1	15	35	8	<1

* <, less than; %, percent

Selenite Sorption Studies

Results from sorption studies were evaluated (1) by comparing directly the Se sorbed and desorbed as a function of the amount of selenite added, i.e., % Se removed or released and (2) by evaluating the equilibrium data using several sorption isotherms (e.g., Freundlich, Langmuir, and initial mass isotherms). The direct comparison method of characterizing selenite sorption on backfill materials provides a general description of how selenite removal is dependent on solution selenite concentrations. Sorption isotherms, on the other hand, have been used extensively to study sorption reactions in soils, sediments, and other geological materials, and are capable of providing additional information about the sorption process. Parameters such as empirical constants, binding affinities, sorption maxima, indigenous soil pools, and distribution coefficients may be determined by using the different adsorption isotherms. However, depending on the data, some sorption isotherm approaches fail to provide useful results primarily because of indigenous concentrations of solutes present in the backfill material.

Results obtained by the direct comparison method for experiment 1 (distilled-deionized water background solution) indicate that selenite sorption ranged from 65 to 92 % on A-1 backfill-core samples, 92 to 98 % on A-2 core samples, and 56 to 97 % on B-1 core samples. Sorption of selenite increased with decreasing pH, as was expected because of the increase of positively charged sites; similar results were obtained by Balistrieri and Chao (1987), Bar-Yosef and Meek (1987); and Neal et al. (1987a). Figures 2 and 3 represent concentrations of the selenite sorbed on the backfill-core samples as a function of the equilibrium selenite concentration.

Table 3. Percent concentration and volume of concentrates of hydrophobic and hydrophilic solutes after organic carbon isolation of ground-water samples, Powder River Basin, Wyoming*.

Sampling date and constituents	Well Number A-1	 B-1
Sampling Date	07-07-92	08-19-92
Volume of sample isolated (L)	16	18
Hydrophobic isolates		
Volume of concentrate (L)	3.3	3.1
Dissolved organic carbon (DOC) (mg L^{-1})	280	300
Total solutes (% of total DOC)	78	77
Acids (%)	65	62
Neutrals (%)	13	15
Hydrophilic isolates		
Volume of concentrate (L)	0.8	0.8
Dissolved organic carbon (DOC) (mg L^{-1})	145	130
Total solutes (% of total DOC)	22	23
Acids (%)	11	10
Neutrals and bases (%)	7	9
Lost in isolation of hydrophilic solutes (%)	5	4

*Values may not sum to totals due to rounding

Selenite sorption increased with increasing concentration of the added selenite in all samples. The A-2 samples had the largest selenite sorption capacities, whereas the B-1 core samples had the smallest. The differences between these samples may be due to the B-1 core samples having the largest, and A-2 samples having the smallest, DOC concentration in their associated ground water and saturated-paste extracts. In addition, the results would suggest an inverse relation between DOC concentration and sorption capacity for Se. In addition, the phosphate extraction recovered only about 50 % of the added Se. The difference between the sorbed and recovered Se may be caused by precipitation of metal-Se compounds, or by formation of strong ligand exchange reactions involving Se, or both.

Results of experiment 2 (0.1 M $CaCl_2$ background solution) indicate selenite sorption ranged from 0 to 99 % for A-1 samples, 13 to 99 % for A-2 samples, and 0 to 97 % for B-1 samples. The trends of increasing sorption with decreasing pH and the increase in sorption capacity with increasing selenite added also were observed in this study.

A comparison of experiments 1 and 2 indicates an increase in selenite sorption in most samples when 0.1 M $CaCl_2$ was added to the background solution. Results from experiments 1 and 2 are shown in Figure 2. The increased sorption of selenite in experiment 2 may have been caused by precipitation reactions or by an increase in positively charged surfaces caused by calcium sorption (Neal et al., 1987b).

Selenite sorption in experiment 3 (addition of hydrophobic or hydrophilic acids to background solutions) ranged from 5 to 94 % for A-1 samples, 73 to 96 % for A-2 samples, and 55 to 92 % for B-1 samples with hydrophobic acid (see Figure 3 for graphic representation of the results). In experiments containing hydrophilic acid, sorption ranged from 15 to 88 % for A-1 samples and 3 to 89 % for B-1 samples.

Results from the Freundlich and Langmuir adsorption isotherms were unable to describe the relations between equilibrium Se concentrations and selenite sorption. A similar finding was reported by Blaylock et al. (1995), who found the initial mass isotherm could be used to develop predictive equations for describing selenite sorption on backfill materials. Initial mass isotherm parameters and distribution coefficients for the experiments involving the backfill materials and different background solutions are listed in Table 4.

Table 4. Selenite sorption parameters and distribution coefficients determined from initial mass isotherms under different experimental conditions.

Site number	Backfill-core number	Depth (m)	Slope (m)	Intercept (b)	Reserve backfill Se pool (RBSP)	Distribution coefficient (Kd)
Experiment 1 -- Distilled-deionized water						
A-1	136C	4.3	0.878	-0.028	0.231	143
A-1	147A	4.8	0.871	-0.130	1.01	135
A-1	246C	4.5	0.868	-0.154	1.17	132
A-1	257A	4.7	0.918	-0.099	1.21	224
A-2	188A	5.5	0.985	-0.004	0.301	1340
A-2	277A	4.7	0.926	-0.014	0.191	249
A-2	288A	5.5	0.982	-0.020	1.08	1080
B-1	146C	4.5	0.864	-0.184	1.36	127
B-1	157A	4.7	0.962	-0.136	3.56	504
B-1	256A	3.9	0.980	-0.127	6.26	966
Experiment 2 -- 0.1 M calcium chloride solution						
A-1	136C	4.3	0.907	-0.106	1.15	196
A-1	147A	4.8	0.934	-0.057	0.865	283
A-1	246C	4.5	0.987	-0.009	0.737	1,570
A-1	257A	4.7	0.976	0.001	-0.055	804
A-2	188A	5.5	0.975	0.004	-0.143	791
A-2	277A	4.7	0.982	-0.018	0.988	1,090
A-2	288A	5.5	0.985	-0.014	0.910	1,290
B-1	146C	4.5	0.920	-0.057	0.710	229
B-1	157A	4.7	0.960	-0.067	1.67	475
B-1	256A	3.9	0.979	-0.092	4.29	912
Experiment 3 -- Hydrophobic acids added						
A-1	136C	4.3	0.956	-0.117	2.67	437
A-1	146A	4.8	0.959	-0.163	4.01	471
A-1	246C	4.5	0.917	-0.127	1.52	220
A-1	257A	4.7	0.915	-0.052	0.607	215
A-2	188A	5.5	0.926	-0.057	0.766	250
A-2	277A	4.7	0.974	-0.203	7.96	763
A-2	288A	5.5	0.978	-0.099	4.40	873
B-1	146C	4.5	0.837	-0.154	0.940	102
B-1	157A	4.7	0.922	-0.186	2.39	237
B-1	256A	3.9	0.938	-0.122	1.95	301
Experiment 3 -- Hydrophilic acids added						
A-1	136C	4.3	0.942	-0.725	12.6	327
A-1	146A	4.8	0.942	-0.955	16.6	327
A-1	246C	4.5	0.983	-1.13	65.1	1,130
A-1	257A	4.7	0.957	-0.928	21.4	442
B-1	146C	4.5	0.744	-0.452	1.77	58
B-1	157A	4.7	0.822	-0.374	2.10	92
B-1	256A	3.9	0.937	-0.356	5.67	298

The slope (m) and intercept (b) values determined by the initial mass isotherm are important for characterizing selenite sorption relations. The slope defines the fraction of the selenite added that is retained by the backfill material; that is, the greater the slope the larger the sorption. The intercept indicates the amount of Se released when the initial solution contains no Se; that is, negative intercept values indicate desorption of Se. From slope and intercept values, a reserve backfill Se pool (RBSP) can be calculated as:

$$RBSP = b/(1-m)$$

The RBSP is the amount of Se present in the backfill that can be readily exchanged with substances in solution under the conditions of the experiment. The distribution coefficient (Kd), which describes the affinity of Se for the backfill, also can be calculated from initial mass isotherm results (Nodvin et al., 1986; Vance and David, 1991).

Values determined from the initial mass isotherms, i.e., slope (0.744 to 0.987) and intercept (-1.13 to 0.004) values, indicate that backfill materials have a large retention capacity for selenite and that generally Se is released from the backfill when background solutions containing little or no selenite are mixed with the backfill-core samples. Addition of $CaCl_2$ to background solutions increased sorption of selenite, as demonstrated by generally greater slope values in the $CaCl_2$ experiment compared to the experiment containing only distilled-deionized water (Table 4 and Figure 2). Addition of hydrophobic acid to background solutions had only a minor effect on selenite sorption characteristics, except for shallow core samples collected at site A-1 (Table 4 and Figure 3). For these samples, sorption increased as in the $CaCl_2$ experiment, which may be because of cations associated with the hydrophobic acid solutions.

The greatest impact on selenite sorption was noted with the hydrophilic acid additions. Because of the limited quantities of hydrophilic acids, only backfill-core samples from A-1 and B-1 were studied. For A-1 samples, large initial mass isotherm slopes ($\geq$0.942) were determined along with smaller intercept values ($\leq$-0.725), whereas B-1 samples were found to have low slopes ($\leq$0.937) and intercept values ($\leq$-0.356) (Table 4 and Figure 3). These results suggest hydrophilic acids have a major role in reducing the retention of Se by backfill materials by enhancing the desorption of indigenous Se or by displacing Se through competitive sorption.

Information derived from RBSP and Kd values also can be used in describing selenite sorption processes. The larger RBSPs with backfill-core sample depth are indicative of greater amounts of Se present in the backfill that can be exchanged readily by substances such as natural organic solutes. The RBSP values were largest in studies involving hydrophilic acid. Larger RBSP values suggest that greater amounts of Se could be released by additions of hydrophilic acid to backfill materials. In addition, Kd values generally were greater in samples collected at greater depths for each of the backfill-core holes. A noticeable decrease in the Kd values was found in B-1 samples when comparing results from studies involving distilled-deionized water or 0.1 M $CaCl_2$ background solutions to studies with additions of hydrophilic acid, further indicating that hydrophilic acid can impact selenite sorption of Se. However, dissolved selenite concentrations often comprise only a small fraction of ground-water solutions because selenite is highly adsorbed by backfill material.

Environmental Implications

Sorption generally decreased in the presence of DOC, as indicated by a decrease in slope (m) or intercept (b), or both (Table 4), which indicates a positive interference in the selenite sorption process caused by DOC. This interference could be caused by the formation of neutral complexes with Se that is not sorbed as strongly as selenite, or by competitive sorption processes involving Se and DOC. Addition of hydrophobic acid decreased selenite sorption capacities (when compared to sorption with distilled- deionized water) of the A-2 and B-1 samples, whereas the sorption capacities remained almost constant for the A-1 backfill-core samples. The addition of the hydrophilic acid decreased selenite sorption capacity for both A-1 and B-1 backfill-core samples more than did the addition of hydrophobic acid. The effect of DOC on selenite sorption generally was greater at lower concentrations of added selenite. A comparison of selenite sorption in the presence of hydrophobic and hydrophilic acids would suggest that the latter is capable of enhancing the potential migration of Se in reclaimed coal mines in the PRB of Wyoming.

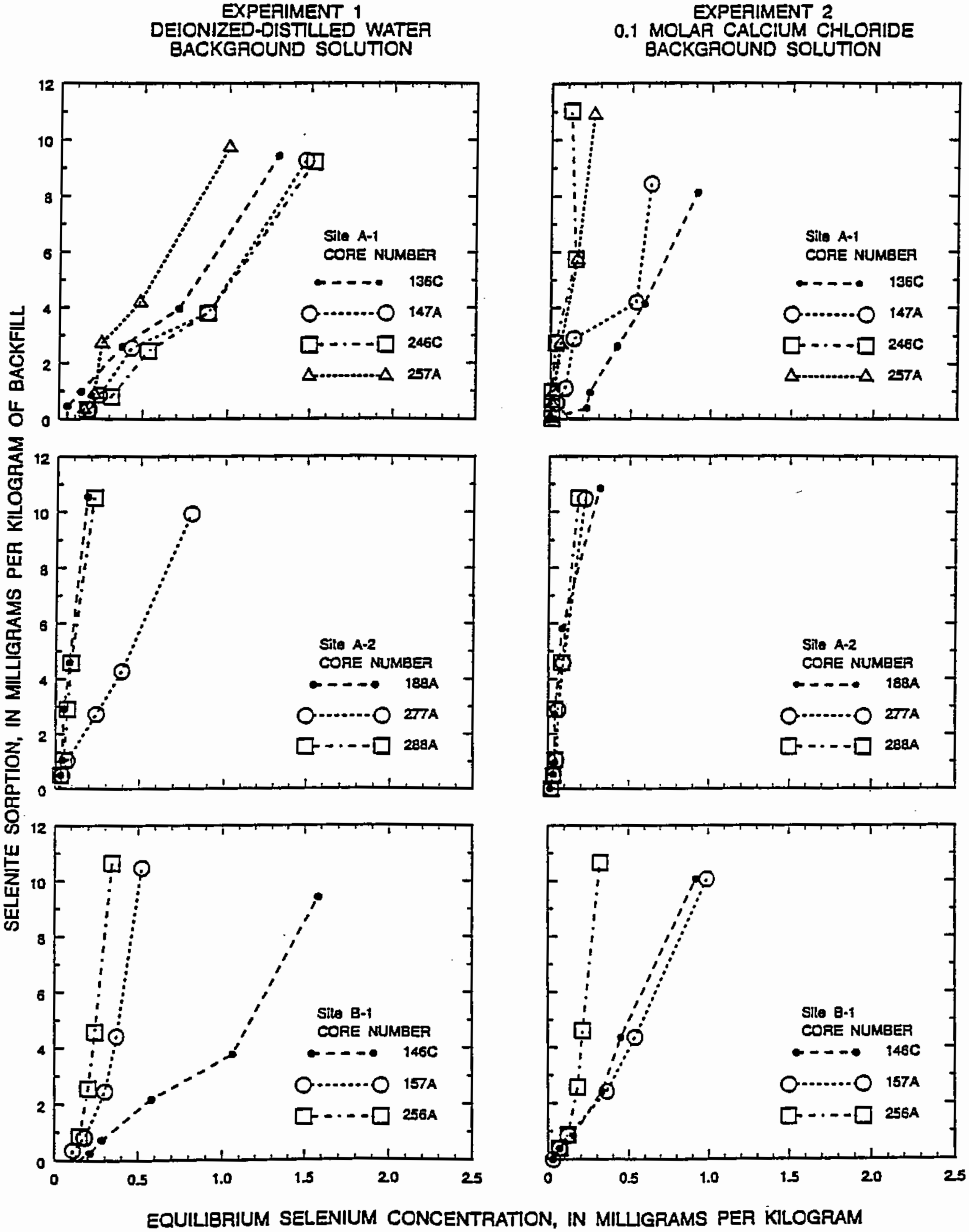
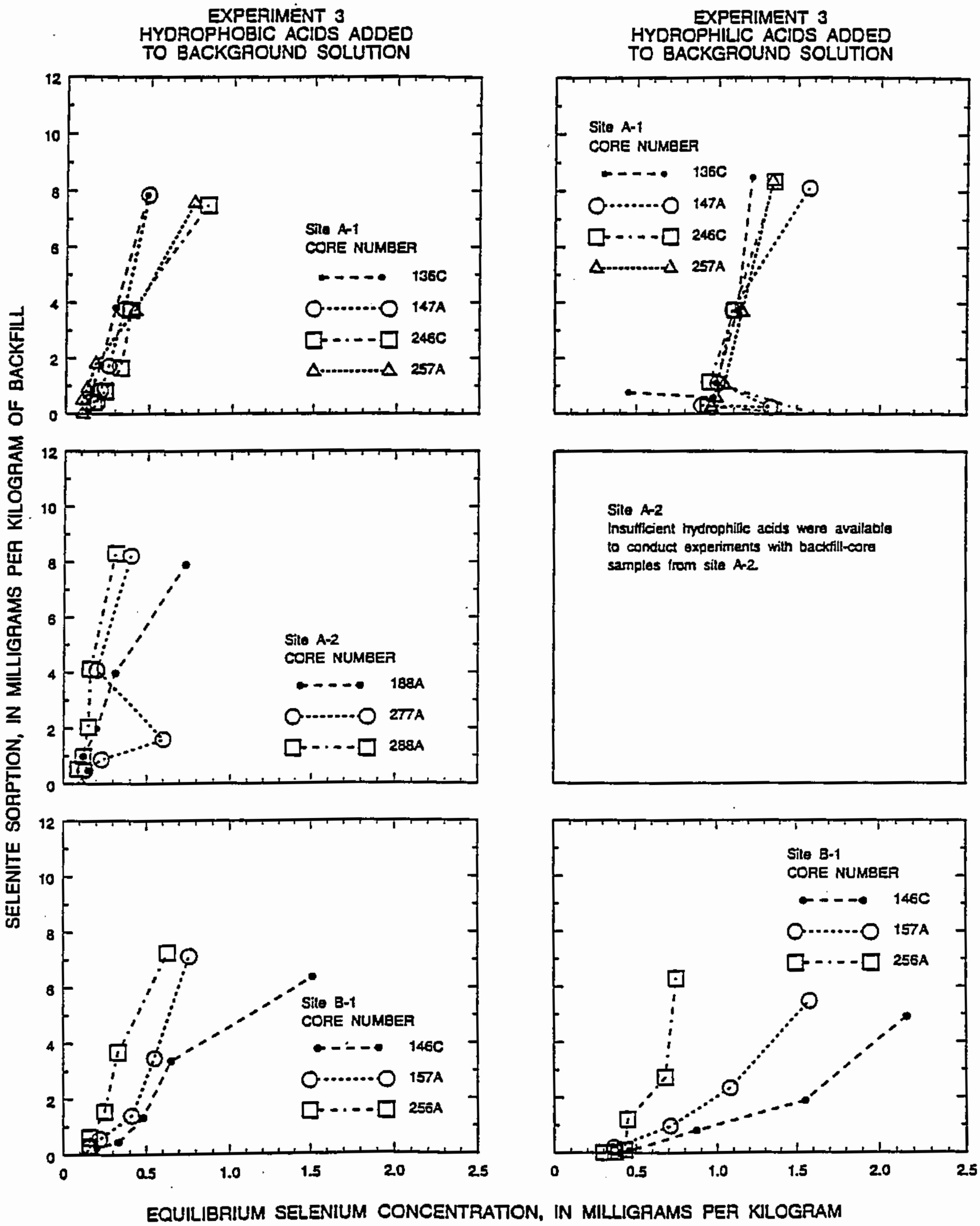


Figure 2. Selenite sorption as a function of equilibrium selenium concentrations of backfill-core sample solutions with distilled-deionized water and 0.1 M calcium chloride background solutions.


EXPERIMENT 3
HYDROPHOBIC ACIDS ADDED
TO BACKGROUND SOLUTION

EXPERIMENT 3
HYDROPHILIC ACIDS ADDED
TO BACKGROUND SOLUTION

Site A-2
Insufficient hydrophilic acids were available to conduct experiments with backfill-core samples from site A-2.

Figure 3. Selenite sorption as a function of equilibrium selenium concentrations of backfill-core sample solutions with hydrophobic and hydrophilic acids added to background solutions.

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