

GEOCHEMICAL PROCESSES AND THE EFFECTS OF NATURAL ORGANIC SOLUTES ON THE SOLUBILITY OF SELENIUM IN COAL-MINE BACKFILL SAMPLES FROM THE POWDER RIVER BASIN, WYOMING

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
gram (g)	0.03527	ounce (oz)
kilogram (kg)	2.205	pound (lb)
milligram (mg)	35.27	ounce (oz)
milliliter (mL)	.03382	ounce, fluid (oz)
micrometer (micron) (μm)	.00003937	inch (in.)
millimeter (mm)	.03937	inch (in.)
meter (m)	3.281	foot (ft)
microgram (μg)	35270	ounce (oz)
liter (L)	33.82	ounce, fluid (oz)
kilometer (km)	.6214	mile

Temperature can be converted to degrees Fahrenheit (°F) or degrees Celsius (°C) by the following equations:

$$^{\circ}\text{F} = 9/5 (^{\circ}\text{C}) + 32.$$

$$^{\circ}\text{C} = 5/9 (^{\circ}\text{F} - 32).$$

Sea level: In this report “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviations used in this report:

AAS-HG	atomic absorption spectrophotometry with hydride generation
AES	atomic emission spectrophotometry
DOC	dissolved organic carbon
dS/m	decisiemens per meter
Eh	electrode potential
g	gram
GAGMO	Gillette Area Groundwater Monitoring Organization
IAP	ion activity product
IC	ion chromatography
ICP-OES	inductively coupled plasma-optical emission spectrophotometry
Kd	distribution coefficient
kg	kilogram
K _{sp}	solubility product
L	liter
m	meter
mg	milligram
μg	microgram
μm	micrometer (micron)
μS/cm	microsiemens per centimeter
mL	milliliter
mm	millimeter
mM	milliMolar
mV	millivolt
RBSP	reserve backfill selenium pool
redox	oxidation-reduction
rpm	revolutions per minute
SI	saturation index
XRD	x-ray diffraction
yr	year

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ABSTRACT

This report describes geochemical processes affecting the solubility of selenium and the effects natural organic solutes have on the solubility of selenium in surface coal-mine backfill aquifers. Three field sites selected for this study were located in reclaimed areas at two large surface coal mines in the Powder River Basin, Wyoming. These sites were selected on the basis of the known presence of selenium in ground water. Two backfill cores were collected from within an approximately 5-meter radius of each existing well site. X-ray diffraction analyses indicated that all samples contained quartz, kaolinite, potassium feldspar, illite, and muscovite. Backfill-core samples differed in elemental concentration, but were generally dominated by aluminum (14,400 to 49,000 milligrams per kilogram (mg/kg)), iron (3,330 to 23,200 mg/kg), and potassium (7,950 to 18,000 mg/kg). Backfill-core sample saturated-paste extract selenium concentrations ranged from 1 to 156 micrograms per kilogram. Analytical results from the saturated-paste extracts indicated that the backfill-core samples were heterogeneous. No correlation was apparent between measured factors and depth, or selenium. Sequential partial dissolution techniques were used to partition selenium into six operationally defined phases. The organic phase accounted for less than 5 to 58 percent of the total selenium in backfill-core samples.

Water samples collected from each well were analyzed for concentrations of cations and anions. Selenium concentrations ranged from 3 to 125 micrograms per liter. Hydrogeologic moni-

toring is conducted on a regular basis at both mines. A general decline in selenium concentrations and concurrent increase in water levels has been observed at all sites. Dissolved organic carbon in all ground-water samples was dominated by hydrophobic and hydrophilic acids (38 to 84 percent). Hydrophobic and hydrophilic acids in the ground-water samples were isolated and concentrated for use in sorption/desorption studies to determine the effect of the acids on selenium sorption.

Three selenite sorption/desorption experiments were conducted using background solutions of distilled-deionized water, 0.1 molar calcium chloride, and isolated hydrophobic and hydrophilic acids. Selenite sorption was larger when 0.1 molar calcium chloride was used as a background solution as compared to distilled-deionized water. Selenite sorption generally was smaller in the presence of hydrophobic and hydrophilic acids, and smaller in the presence of hydrophilic acids than in the presence of hydrophobic acids.

Precipitation/dissolution studies were conducted to predict the solid phases controlling dissolved selenium concentrations and to evaluate the effect of dissolved organic carbon on selenium solubility in backfill-core samples. A geochemical speciation model was used to calculate ion activities. Dissolved organic carbon had little effect on selenium speciation. Chemical speciation results suggested that backfill-core sample precipitation/dissolution extracts were dominated by magnesium selenate ion pairs (55 to 90 percent of total selenium concentration). The presence of ion pairs may represent a potential for selenium mobility in backfill aquifers.

An oxidation-reduction (redox) controlling apparatus was constructed to control Eh and pH in water and backfill-core sample suspensions. The redox controlling apparatus successfully controlled redox of the samples. The response of selenite and selenate in water samples to the imposed redox conditions of the redox controlling apparatus differed from thermodynamic predictions. Selenite reduction in water samples occurred at a larger redox than thermodynamic predictions. Reduction of selenate in water samples did not occur at any of the redox levels tested.

INTRODUCTION

Although selenium is not known to be an essential element for plants, it is necessary for animals (Oldfield, 1987, p. 202) and humans (National Research Council, 1989). However, excessive selenium can be potentially toxic to plants, animals, and humans. Because of the potential toxicity of selenium and extensive seleniferous geologic formations in Wyoming and other areas in the Western United States, selenium has become a major environmental concern. Concentrations of selenium, ranging from 3.4 µg/L (Martin and others, 1988, p. 41) to 330 µg/L (Naftz and Rice, 1989, p. 572), have been detected in shallow post-mining ground water from selected coal mines (fig. 1) in the southern Powder River structural basin of northeastern Wyoming.

Concerns about selenium prompted the Governor of Wyoming to establish a task force to evaluate selenium conditions in the State. The task force recommended that research be conducted to better understand selenium solubility, availability, and mobility in water, soil, and vegetation in relation to the health and welfare of humans, livestock, and wildlife (Governor's Task Force on Selenium, 1989, p. 18). Evidence has been published that indicates the chemistry of selenium in coal overburden materials can be affected by mining and reclamation operations (Dreher and Finkelman, 1992).

During surface coal mining, rock material overlying the coal is redistributed from the original stratigraphic position. Exposure of previously buried material to surface oxidizing conditions decreases the stability of selenium-containing sulfides and organic matter. The oxidation of such compounds can transform reduced and less mobile selenium species (Se^{2-}

and Se^0) into oxidized selenium species (Se^{6+} and Se^{4+}), which are more soluble in alkaline and oxidizing ground water (Naftz and Rice, 1989, p. 574).

Currently the Wyoming Class III ground-water standard for total selenium (suitable for livestock) is 50 µg/L (Wyoming Department of Environmental Quality, 1993, p. 9). However, the ground-water contribution to surface-water flow may provide a mechanism to transport selenium from ground-water to surface-water resources. Surface-water selenium concentrations ranging from 2 to 13 µg/L have been reported to cause reproductive problems in aquatic birds (Skorupa and Ohlendorf, 1991, p. 363).

The U.S. Geological Survey in cooperation with the Wyoming Water Resources Center and the Department of Plant, Soil, and Insect Sciences at the University of Wyoming studied geochemical processes and the effects of natural organic solutes on the solubility of selenium in coal-mine backfill samples from the Powder River Basin, Wyoming. This study was conducted to obtain a better understanding of the geochemical processes that affect the solubility of selenium in post-mining coal-mine backfill. A better knowledge of geochemical processes affecting selenium would be useful to the mining industry and State agencies for developing effective reclamation techniques. The mobility of selenium from coal-mine backfill to ground water is controlled by a number of geochemical processes including the formation of inorganic and organic complexes, sorption/desorption, and precipitation/dissolution reactions.

Purpose and Scope

This report describes geochemical processes affecting the solubility of selenium and the effects that natural organic solutes have on the solubility of selenium in surface coal-mine backfill aquifers. Natural organic solutes represent all natural organic matter in solution. Specific objectives of this study, which was conducted during 1991-94, included:

1. To characterize the chemical and physical properties of surface coal-mine backfill and associated ground water at three sites having large selenium concentrations in ground water;
2. To determine the role that natural organic solutes have on selenium sorption/desorption and precipitation/dissolution processes; and

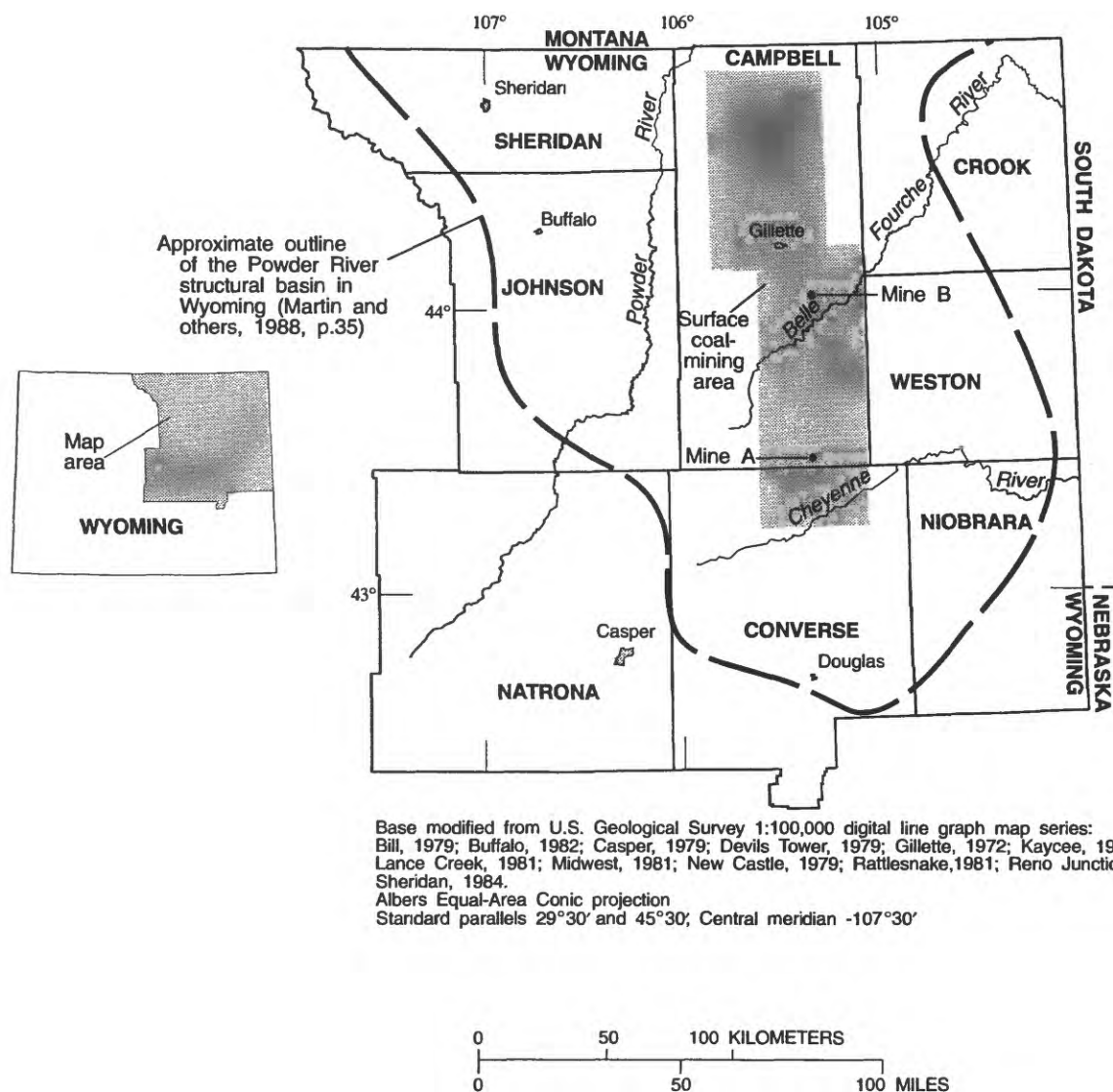


Figure 1. Location of surface coal-mining area, coal-mine sampling sites, and the Powder River structural basin, Wyoming.

3. To quantify the effects of oxidation-reduction (redox) conditions on the speciation and solubility of selenium in a redox controlling apparatus.

The scope of the work included collection of backfill and ground-water samples, characterization of samples, and laboratory experiments to determine the role of natural organic solutes on the solubility of selenium in backfill samples. This investigation was completed during 1991 through 1994 using samples collected from the Powder River Basin, Wyoming.

Acknowledgments

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Previous Studies

Lindner-Lunsford and Wilson (1992) reviewed and summarized 76 reports published during 1950-91 that described the quantity or quality of shallow ground water in the Powder River structural basin of north-eastern Wyoming. From these studies, it was evident that reliable information about hydrologic and geochemical processes that occur within the Powder River Basin was lacking. Thus, both hydrologic and geochemical processes were identified as deficiencies in the accumulated knowledge of the shallow ground-water systems of the Powder River Basin (Linder-Lunsford and Wilson, 1992, p. 1).

A study by Martin and others (1988) summarized cumulative potential hydrologic impacts of surface coal mining in the eastern Powder River structural basin using data available through 1987. Martin and others (1988, p. 58) stated that "water-soluble selenium contents of overburden material do not indicate the total quantity of selenium that could be released to ground water after mining." That study indicated total selenium content in overburden material from two mines in the Powder River Basin ranged from 100 to 3,800 $\mu\text{g}/\text{kg}$. Effluent derived after about 1 pore volume of water was passed through columns packed

with backfill material had selenium concentrations generally exceeding 50 $\mu\text{g}/\text{L}$ (Martin and others, 1988, p. 58-59). Those selenium concentrations are of concern for livestock (Wyoming Department of Environmental Quality, 1993, p. 9).

Analytical results reported by Naftz and Rice (1989, p. 573) identified a statistically significant positive correlation between selenium and organic carbon. They conducted sequential extraction analyses on 11 overburden samples from 2 coal mines in the Powder River Basin and found that in 10 of these samples, the operationally defined organic phase of the overburden material contained 100 percent of the selenium (Naftz and Rice, 1989, p. 574).

Dreher and Finkelman (1992, p.155) studied selenium mobilization in a surface coal mine in the Powder River Basin. Their report examined the source of selenium, occurrences of selenium in overburden deposits and backfill water, and the fate of selenium. Results of this study indicated that the decrease in soluble selenium was due to microbially assisted reduction of selenate (SeO_4^{2-}) to selenite (SeO_3^{2-}) followed by sorption onto clay minerals in backfill materials.

None of the previous studies have examined in detail the geochemical processes controlling selenium solubility in reclaimed surface coal-mine backfill aquifers. The effect that natural organic solutes have on selenium solubility processes is important in enhancing the knowledge of selenium chemistry in coal-mine backfill environments as well as other environments, both natural and disturbed.

Selenium in soil and natural water exists in several oxidation states: selenide (Se^{2-}), elemental selenium (Se^0), selenite (Se^{4+}), and selenate (Se^{6+}). Thermodynamic calculations indicate that selenide and elemental selenium should be found in reducing environments, selenite in moderately oxidizing environments, and selenate in oxidizing environments (Elrashidi and others, 1987).

Kinetic studies involving soil indicated that selenite adsorption onto oxide surfaces occurs by ligand exchange mechanisms (Yates and Healy, 1975; Cornell and Schindler, 1980, p. 1174; Sposito, 1984, p. 138; Goldberg, 1985, p. 851; Balistrieri and Chao, 1987; Neal and others, 1987a and 1987b). Those studies also reported that the removal of selenite from solution by adsorption on metal oxides is affected by the pH of the system, by the concentration of available binding sites, and by equilibrium anion concentrations.

Little is known about the precipitation/dissolution reactions involving selenium in soil (Elrashidi and others, 1987; Masscheleyn and others, 1990; and Reddy and Gloss, 1993). This lack of knowledge is partly due to the limited thermodynamic information on selenium solution species and solid phases. Elrashidi and others (1987) developed theoretical solubility relations of selenium solid phases and reported that except for MnSeO_3 other phases such as PbSeO_3 , CaSeO_4 and BaSeO_4 are not expected to precipitate in soil. However, in reducing environments, Cu_2Se , FeSe , or PbSe may precipitate in soil. Reddy and Gloss (1993) investigated selenium solubility and availability in a seleniferous soil. They indicated that selenium in soil extracts from subsurface soil was dominated by selenite ions, and that solubility and mobility of selenium were related to redox potential, pH, and chemical speciation of selenium. Results from Masscheleyn and others (1990) indicated that redox potential and pH control the speciation and solubility of selenium in sediments. Furthermore, at low redox potential (-200 mV), selenium solubility was shown to be controlled by an iron selenide solid phase (FeSe) (Masscheleyn and others, 1990, p. 95-96).

Studies by Balistrieri and Chao (1987), Naftz and Rice (1989), Fio and Fujii (1990), and Abrams and others (1990) have shown that natural organic solutes and organic selenium compounds are important in the solubility of selenium in soil and coal-mine spoils. Particularly, results from the Naftz and Rice (1989) study 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 selenium.

Study Area

Geographic and Geologic Setting

The climate of the Powder River Basin in north-eastern Wyoming is temperate and semiarid. Average daily temperatures vary from -15°C in winter to 32°C in summer. Precipitation, which in the Powder River Basin is primarily controlled by the topography, ranges from 280 mm in the south to 460 mm in the north (Martin and others, 1988). Mean-annual pan evaporation, which ranges from 1,520 to 1,650 mm/yr, is much greater than precipitation (Martner, 1986, p. 177).

Ground-water hydrology of the Powder River Basin is described in detail in many publications including: Wyoming Water Planning Program (1972), Hodson and others (1973), and Feathers and others (1981). In a regional analysis of streamflow and water-level data, Lowry and others (1986, p. 54) state "The absence of measurable base flow in the Powder River and the presence of some base flow in the smaller streams in areas of coal-bearing formations indicate that discharge from the local ground-water systems is more important to base flow in streams than is a regional ground-water system." Ground-water recharge to the sites selected for this study is from precipitation, water pumped from the active mine pits, and underflow from adjacent areas.

Coal seams have developed in the Fort Union and Wasatch Formations. These formations of early Tertiary age consist of continental-type sediments deposited in fluvial, lacustrine, and swampy environments. These formations include lenticular strata consisting of alternating sandstone, siltstone, and claystone, with occasional coal beds (Naftz and Rice, 1989, p. 566). The Quaternary alluvium consists of unconsolidated deposits of silt, sand, and gravel (Hodson and others, 1973, sheet 3).

Site Selection

Three field sites were selected after consultation with hydrologists and other scientists from the Wyoming Department of Environmental Quality, the U.S. Geological Survey, and the mining industry in Wyoming. All available data records were researched, including: annual mining reports, Gillette Area Groundwater Monitoring Organization (GAGMO) annual reports, Wyoming Department of Environmental Quality data files, Wyoming Geological Survey data files, and the U.S. Geological Survey National Water Information System. The three field sites were identified on the basis of presence of large selenium concentrations, shallow ground-water levels, and depth of wells. Field sites were selected from active coal mines to provide the maximum amount of historical data for the study. No water samples from other wells less than 30 meters in depth and constructed in backfill material had large (greater than $100\text{ }\mu\text{g/L}$) selenium concentrations. Most other wells had selenium concentrations at or below the analytical reporting limit. Large selenium concentrations in coal-mine backfill groundwater is not a wide spread problem in the Powder River Basin based on data examined in 1991.

The three field sites selected were located in reclaimed areas at two large surface coal mines in the Powder River Basin (fig. 1). Because of previous written agreements with the participating coal mines, mines are not identified by name. For consistency, the surface coal mines are referred to by letter designation A and B in all figures, tables, and text. Two sites were investigated at mine A (A-1 and A-2) and one site was investigated at mine B (B-1).

CHEMICAL AND PHYSICAL CHARACTERISTICS

Coal-Mine Backfill Samples

Two backfill cores were collected from within an approximately 5-m radius of the existing well at each site. Core holes ranged in depth from 6.8 to 8.4 m and were at least as deep as the associated well. Drilling logs were made in the field to record sampling procedures and sample descriptions. Drilling logs and other original data generated as part of this project are available for inspection at the U.S. Geological Survey, Cheyenne, Wyoming and the Wyoming Water Resources Center, Laramie, Wyoming.

Backfill cores were collected by U.S. Geological Survey personnel using a rotary-driven, split-spoon auger. The auger head measured 218 mm in diameter and cores 83 mm in diameter were collected. The core barrel within the auger extends approximately 76 mm beyond the auger head and rests on a bearing assembly, which prevents the core-barrel sampler from rotating. The device permits collection of only slightly disturbed core samples.

Acrylic liners were used inside the core barrel to collect and store the backfill-core samples. After collection of backfill cores, void spaces in the liners were purged with pre-purified argon gas and the liners then were sealed with plastic caps and tape to prevent oxidation of the backfill-core samples during transportation and storage. Backfill cores were chilled in the field and stored under refrigeration at the University of Wyoming for subsequent laboratory experiments. A schematic diagram of the backfill-core recovery is shown in figure 2. Backfill cores were removed from the acrylic liners and partitioned into samples (fig. 2). The backfill-core samples were air dried and sieved through a 10 mesh (2 mm) sieve. A total of 157 backfill-core samples were available for analysis.

Because of the expense associated with sample analysis, a limited number of samples were selected for each of the analyses conducted for this investigation. The 70 backfill-core samples selected and the analyses conducted are shown in table 1. For each analysis and experiment, backfill-core samples from various depths were selected. This method provided samples from a wide range of oxidative conditions.

X-ray Diffraction and Chemical Analyses

X-ray diffraction (XRD) was used to determine bulk mineralogy for 18 backfill-core samples. The backfill-core samples selected for XRD analysis are shown in table 1. Bulk mineralogy was determined by XRD using the methods described in Jackson (1969) and Moore and Reynolds (1989). Bulk samples were ground to 10-20 μm in an agate mortar. A slurry then was made of each sample using acetone, was placed onto a glass slide, and was dried at room temperature. Samples then were analyzed using a Scintag x-ray diffractometer¹ at the Department of Geology, University of Wyoming.

The x-ray diffraction analyses indicated that all 18 backfill-core samples contain the common minerals: quartz, potassium feldspar, kaolinite, illite, and muscovite. Additional minerals detected in some samples included: smectite, gypsum, calcite, dolomite, carbonate-apatite, and goethite. The minerals identified and their qualitative abundance in the backfill-core samples are listed in table 2. The presence of large surface-area clay minerals (kaolinite, illite, muscovite, and smectite) indicated that the backfill-core samples had potentially large sorption capacities.

Portions of the backfill-core samples also were examined under a microscope. Although goethite, an iron oxide, was detected by XRD in only one sample, microscopic analysis revealed that a small amount of iron oxide coatings and coal particles were present in all samples. Iron oxides were estimated to occur in amounts less than 1 percent in all samples. XRD peaks of other iron oxides (such as hematite) were not detected, which suggests the iron oxides were amorphous rather than crystalline, or their concentration was below the detection limits of the XRD analysis (about 2 percent).

¹Use 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.

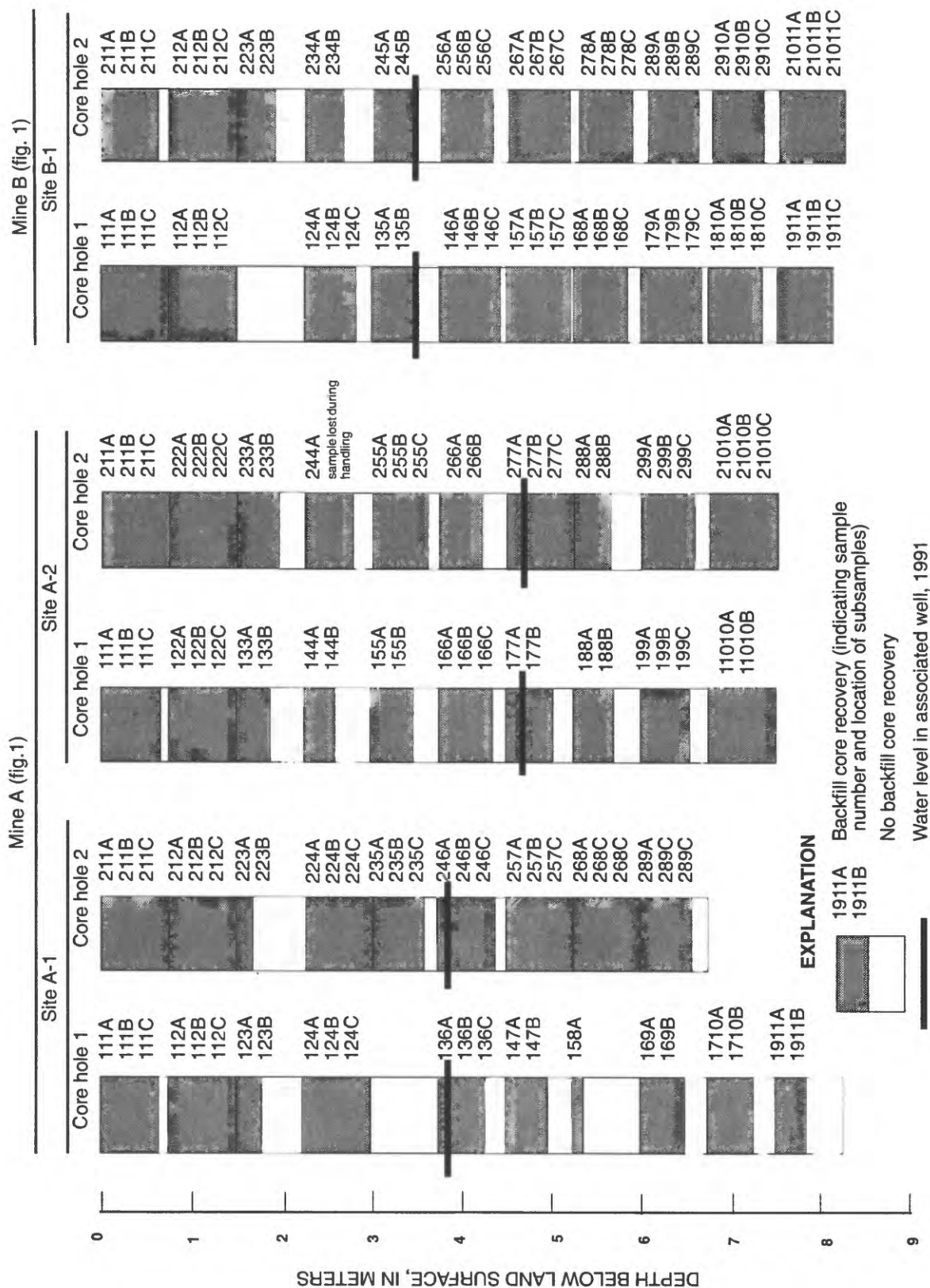


Figure 2. Schematic diagram of backfill-core recoveries, approximate depth of backfill-core samples, and depth to ground water for backfill cores collected, Powder River Basin, Wyoming.

Table 1. Backfill-core samples selected for analysis and analyses completed, Powder River Basin, Wyoming

[*, indicates type of analysis conducted on sample; --, indicates no analysis conducted on sample]

Sample code (fig. 2)			Sorption/desorption experiments							Precipitation/dissolution experiments	
Site number	Backfill- core number	X-ray diffraction (table 2)	Elemental analyses (table 3)	Saturated- paste analyses (table 4)	Sequential partial dissolution (table 5)	Distilled- deionized water (table 10)	Calcium chloride (table 10)	Hydrophobic acids added (table 11)	Hydrophilic acids added (table 11)	Preliminary (table 13)	Final (table 14)
Site A-1, Core hole 1											
A-1	1 1 2 A	--	--	*	--	--	--	--	--	--	--
A-1	1 2 3 A	--	--	*	--	--	--	--	--	--	--
A-1	1 2 4 A	--	--	*	--	--	--	--	--	--	--
A-1	1 3 6 A	*	*	*	*	--	--	--	--	--	*
A-1	1 3 6 C	*	*	*	*	*	*	*	*	--	*
A-1	1 4 7 A	*	*	*	*	*	*	*	*	--	--
A-1	1 4 7 B	--	--	*	--	--	--	--	--	--	--
A-1	1 5 8 A	--	--	*	--	--	--	--	--	--	*
A-1	1 6 9 A	--	*	*	--	--	--	--	--	--	--
A-1	1 7 10 A	--	--	*	--	--	--	--	--	--	--
A-1	1 9 11 A	--	*	*	--	--	--	--	--	--	--
Site A-1, Core hole 2											
A-1	2 1 2 A	--	--	*	--	--	--	--	--	--	--
A-1	2 2 3 A	--	--	*	--	--	--	--	--	--	--
A-1	2 2 4 A	--	--	*	--	--	--	--	--	--	--
A-1	2 3 5 A	--	--	*	--	--	--	--	--	--	--
A-1	2 4 6 A	*	*	*	*	--	--	--	--	*	*
A-1	2 4 6 C	*	*	*	*	*	*	*	*	*	*
A-1	2 5 7 A	*	*	*	*	*	*	*	*	*	*
A-1	2 5 7 C	--	--	*	--	--	--	--	--	--	--
A-1	2 6 8 A	--	*	*	--	--	--	--	--	--	--
A-1	2 8 9 A	--	--	*	--	--	--	--	--	--	--
A-1	2 8 9 C	--	*	*	--	--	--	--	--	--	--

Table 1. Backfill-core samples selected for analysis and analyses completed, Powder River Basin, Wyoming--Continued

Sample code (fig. 2)			Sorption/desorption experiments							Precipitation/dissolution experiments	
Site number	Backfill- core number	X-ray diffraction (table 2)	Elemental analyses (table 3)	Saturated- paste analyses (table 4)	Sequential partial dissolution (table 5)	Distilled- deionized water (table 10)	Calcium chloride (table 10)	Hydrophobic acids added (table 11)	Hydrophilic acids added (table 11)	Preliminary (table 13)	Final (table 14)
Site A-2, Core hole 1											
A-2	1 2 2 A	--	--	*	--	--	--	--	--	--	--
A-2	1 3 3 A	--	--	*	--	--	--	--	--	--	--
A-2	1 4 4 A	--	--	*	--	--	--	--	--	--	--
A-2	1 5 5 A	--	--	*	--	--	--	--	--	--	--
A-2	1 6 6 A	--	--	*	--	--	--	--	--	--	--
A-2	1 7 7 A	*	*	*	*	--	--	--	--	--	*
A-2	1 7 7 B	--	*	*	--	--	--	--	--	--	--
A-2	1 8 8 A	--	*	*	*	*	*	*	--	--	*
A-2	1 8 8 B	--	--	--	--	--	--	--	--	--	*
A-2	1 9 9 A	*	*	*	--	--	--	--	--	--	--
A-2	1 9 9 B	--	--	--	*	--	--	--	--	--	--
A-2	1 10 10 A	--	*	*	--	--	--	--	--	--	--
Site A-2, Core hole 2											
A-2	2 2 2 A	--	--	*	--	--	--	--	--	--	--
A-2	2 3 3 A	--	--	*	--	--	--	--	--	--	--
A-2	2 4 4 A	--	--	*	--	--	--	--	--	--	--
A-2	2 5 5 A	--	--	*	--	--	--	--	--	--	--
A-2	2 6 6 A	--	--	*	--	--	--	--	--	--	--
A-2	2 7 7 A	*	*	*	*	*	*	*	--	--	*
A-2	2 7 7 C	*	*	*	*	--	--	--	--	--	*
A-2	2 8 8 A	*	*	*	*	*	*	*	--	--	*
A-2	2 9 9 A	*	*	*	--	--	--	--	--	--	--
A-2	2 10 10 A	--	--	*	--	--	--	--	--	--	--
A-2	2 10 10 C	--	*	*	--	--	--	--	--	--	--

Table 1. Backfill-core samples selected for analysis and analyses completed, Powder River Basin, Wyoming--Continued

Sample code (fig. 2)			Sorption/desorption experiments							Precipitation/dissolution experiments	
Site number	Backfill- core number	X-ray diffraction (table 2)	Elemental analyses (table 3)	Saturated- paste analyses (table 4)	Sequential partial dissolution (table 5)	Distilled- deionized water (table 10)	Calcium chloride (table 10)	Hydrophobic acids added (table 11)	Hydrophilic acids added (table 11)	Preliminary (table 13)	Final (table 14)
Site B-1, Core hole 1											
B-1	112 A	--	--	*	--	--	--	--	--	--	--
B-1	124 A	--	--	*	--	--	--	--	--	--	--
B-1	135 A	--	--	*	--	--	--	--	--	--	--
B-1	146 A	*	*	*	*	--	--	--	--	--	--
B-1	146 C	*	*	*	*	*	*	*	*	--	*
B-1	157 A	*	*	*	--	*	*	*	*	--	*
B-1	157 C	--	--	*	--	--	--	--	--	--	--
B-1	168 A	--	--	*	--	--	--	--	--	--	--
B-1	179 A	--	*	*	--	--	--	--	--	--	--
B-1	1810 A	--	--	*	--	--	--	--	--	--	--
B-1	1911 A	--	--	*	--	--	--	--	--	--	--
B-1	1911 C	--	*	*	--	--	--	--	--	--	--
Site B-1, Core hole 2											
B-1	212 A	--	--	*	--	--	--	--	--	--	--
B-1	223 A	--	--	*	--	--	--	--	--	--	--
B-1	234 A	--	--	*	--	--	--	--	--	--	--
B-1	245 A	--	--	*	--	--	--	--	--	--	--
B-1	256 A	*	*	*	*	*	*	*	*	--	*
B-1	256 C	*	*	*	*	--	--	--	--	--	*
B-1	267 A	--	--	*	--	--	--	--	--	--	*
B-1	278 A	*	*	*	*	--	--	--	--	--	--
B-1	278 C	--	--	*	--	--	--	--	--	--	--
B-1	289 A	--	--	*	--	--	--	--	--	--	--
B-1	2910 A	--	--	*	--	--	--	--	--	--	--
B-1	2910 C	--	*	*	--	--	--	--	--	--	--
B-1	21011 A	--	*	*	--	--	--	--	--	--	--

Table 2. X-ray diffraction analyses of minerals in backfill-core samples, Powder River Basin, Wyoming

[X, indicates the qualitative amount of mineral as determined by x-ray diffraction peak height; --, indicates mineral not detected]

Sample code (fig. 2)		Backfill- core										
Site number	core number	Quartz	Potassium feldspar	Kaolinite	Illite	Muscovite	Smectite	Gypsum	Calcite	Dolomite	Carbonate- apatite	Goethite
Site A-1, Core hole 1												
A-1	136 A	X	XX	XXX	XXX	X	XX	XX	XX	XX	--	--
A-1	136 C	XX	XX	XXX	XX	X	XXX	--	X	X	--	--
A-1	147 A	XX	X	XX	X	X	X	--	XXX	--	--	--
Site A-1, Core hole 2												
A-1	246 A	XX	X	XX	X	X	--	--	X	XX	--	X
A-1	246 C	XX	X	XX	X	XX	--	X	X	--	--	--
A-1	257 A	XX	X	XXX	XXX	X	X	--	XX	--	--	--
Site A-2, Core hole 1												
A-2	177 A	XX	X	X	X	X	X	--	X	--	--	--
A-2	199 A	XXX	X	X	X	X	--	--	X	--	--	--
Site A-2, Core hole 2												
A-2	277 A	XX	XXX	X	XX	X	--	--	X	--	--	--
A-2	277 C	X	X	XX	XX	X	--	XXX	X	--	--	--
A-2	288 A	XX	X	X	X	XXX	--	--	XXX	XX	--	--
A-2	299 A	XX	XX	XXX	X	X	X	--	--	--	--	--
Site B-1, Core hole 1												
B-1	146 A	X	--	X	XXX	XX	XX	--	XX	XX	--	--
B-1	146 C	X	X	XX	XXX	X	XXX	--	XX	--	X	--
B-1	157 A	X	X	X	X	X	XX	--	XXX	--	--	--
Site B-1, Core hole 2												
B-1	256 A	X	X	XXX	XXX	X	XX	--	XX	--	--	--
B-1	256 C	X	X	XXX	XX	X	XXX	--	XXX	XXX	--	--
B-1	278 A	XX	X	XX	XXX	X	X	XXX	XX	--	--	--

Samples were tested for the presence of carbonates using 0.1 molar hydrochloric acid. All of the samples effervesced when hydrochloric acid was added. This condition is consistent with XRD results indicating the presence of calcite or dolomite or both, in all but one sample. When the hydrochloric acid was added to the samples, the iron oxide coatings became more visible as the clay particles disaggregated.

An acid digestion procedure, followed by inductively coupled plasma-optical emission spectrophotometry (ICP-OES), was used to determine concentrations of elements in 30 backfill-core samples. The backfill-core samples selected for elemental analyses are shown in table 1. Analyses were conducted at the University of Wyoming, Soil Testing Laboratory, using methods of Lim and Jackson (1982, p. 1-12). Samples were weighed (0.5 g), placed in 40-mL teflon centrifuge tubes and 10 mL of concentrated nitric acid, 10 mL of concentrated perchloric acid, and 5 mL of concentrated hydrofluoric acid were added to the samples. Samples were digested for 16 hours at 100°C. After allowing samples to cool, 10 mL of 6 molar hydrochloric acid was slowly added. The final step in the digestion was to add enough distilled-deionized water to the sample, using the rinse water from the teflon tube, for a total of 25 mL. The digested samples then were analyzed for elemental concentrations using ICP-OES.

Determination of elemental concentrations is useful in solubility studies because the concentrations help to determine which elements contribute to solubility of selenium. Backfill-core samples differed in elemental composition. Elemental concentrations in backfill-core samples are shown in table 3. The backfill-core samples were dominated by aluminum, iron, and potassium. Concentrations ranged from 14,400 to 49,000 mg/kg for aluminum, 3,330 to 23,200 mg/kg for iron, and 7,950 to 18,000 mg/kg for potassium. Total selenium concentrations ranged from 0.1 to 15.2 mg/kg.

Saturated-Paste Extracts

Saturated pastes and extracts were prepared and analyzed for 68 air dried and sieved backfill-core samples. The backfill-core samples selected for saturated-paste extraction are shown in table 1. Saturated-paste extracts were prepared according to Spackman and others (1994, p. 8-9). A 100-g backfill-

core sample was placed into a 500-mL plastic cup. Distilled-deionized water was added to the sample and mixed with a spatula until the sample had a glistening surface and slowly flowed off the spatula as it was drawn from the mixture. The samples in the cups were covered and allowed to equilibrate for 24 hours. After 24 hours, the moisture content of the pastes was determined. Before extraction, pH and electrode potential (Eh) were determined on the saturated paste. The saturated-paste extracts were analyzed for specific conductance, total selenium, dissolved organic carbon (DOC), and sulfate. The analytical results for the saturated pastes and saturated-paste extracts are shown in table 4.

Saturated-paste Eh measurements were variable but tended to be smaller with increasing depth of the backfill-core samples. Values of Eh near the ground-water table were similar to those obtained for the ground-water samples. All saturated-paste extract specific conductance values were greater than 2 dS/m, indicating a large soluble salt content in the backfill-core samples.

Saturated-paste extract selenium concentrations ranged from 1 to 156 µg/kg. Saturated-paste extract selenium concentrations were small near the surface, generally increased with depth, and decreased below the ground-water level. Saturated-paste extract selenium concentrations as a function of depth are shown in figure 3. These results may indicate ground-water dilution of selenium concentrations or possibly reduction of selenate to selenite, which is subsequently sorbed onto the backfill-core material.

The pH values for saturated pastes were variable and ranged from 3.7 to 8.1 (table 4). The larger pH values (7.2 to 8.1) were probably because of the buffering effect of carbonates, which were identified in the samples. The saturated-paste pH for backfill-core samples collected near the ground-water table were similar to those obtained from onsite measurements for ground water.

Results from the saturated pastes and saturated-paste extracts indicated that the backfill-core samples were heterogeneous. No correlation was apparent between the measured factors and collection depth of the backfill-core samples. In addition, saturated-paste extract selenium concentrations did not appear to correlate to any of the other measured factors.

Table 3. Elemental analyses of backfill-core samples, Powder River Basin, Wyoming

[--, indicates data unavailable; values represent the average of three laboratory analyses; <, less than]

Sample code (fig. 2)		Element (milligrams per kilogram)																
Site number	Backfill- core number	Calcium	Magnesium	Sodium	Potassium	Sulfur	Phosphorus	Aluminum	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Selenium	Molybdenum	Zinc
Site A-1, Core hole 1																		
A-1	136 A	2,650	2,380	1,800	9,420	2,090	334	25,130	32	1.4	31	15	12,700	67	173	15.2	6	43
A-1	136 C	2,620	3,690	4,690	9,850	1,630	341	30,510	40	1.9	38	11	12,000	58	128	1.7	2	48
A-1	147 A	4,030	3,290	1,620	9,130	1,530	387	36,300	46	1.4	41	13	14,600	60	149	3.8	2	47
A-1	169 A	1,540	2,090	1,360	9,680	2,180	497	18,500	40	2.0	47	23	11,900	67	205	2.7	6	85
A-1	1911 A	10,500	1,730	1,740	9,500	2,250	369	14,400	39	1.7	43	54	10,500	56	283	2.2	17	67
Site A-1, Core hole 2																		
A-1	246 A	1,460	2,660	1,450	9,260	1,540	320	27,800	37	6.6	41	11	13,800	89	166	2.0	3	54
A-1	246 C	1,220	2,420	1,640	9,360	1,630	444	25,300	33	9.5	370	16	20,800	58	251	.4	4	46
A-1	257 A	2,160	2,610	1,610	9,370	1,590	330	29,900	39	5.3	40	12	15,800	11	195	2.3	5	49
A-1	268 A	3,800	3,110	1,970	9,150	2,820	385	27,000	36	1.8	37	15	13,900	59	265	3.6	4	57
A-1	289 C	5,900	2,470	1,620	9,320	1,230	419	26,700	39	1.8	41	15	11,700	55	129	1.5	5	58
Site A-2, Core hole 1																		
A-2	177 A	1,850	2,310	1,300	9,190	2,120	405	29,800	33	4.1	32	11	9,830	54	126	.5	2	45
A-2	177 B	1,560	2,470	1,430	9,400	2,040	482	32,100	37	3.2	45	11	9,770	23	107	2.1	4	47
A-2	188 A	1,300	1,440	1,240	9,750	3,050	256	26,200	26	2.8	44	12	9,310	34	67	6.1	1	38
A-2	199 A	4,510	2,010	1,140	9,720	1,200	212	26,600	23	2.2	21	7	6,360	40	58	1.4	1	30
A-2	11010 A	2,540	2,200	1,700	9,590	900	328	29,900	29	3.0	42	13	17,400	67	218	.1	2	40
Site A-2, Core hole 2																		
A-2	277 A	2,920	2,800	4,250	10,240	2,520	303	29,900	33	1.7	65	11	10,300	54	139	3.4	<1	45
A-2	277 C	1,440	1,760	1,600	9,950	2,770	297	29,800	36	1.7	41	13	11,300	27	76	1.7	3	46
A-2	288 A	1,550	2,600	2,320	10,100	2,060	429	46,700	67	2.1	61	16	17,600	55	209	1.5	3	47
A-2	299 A	242	633	1,160	9,290	800	119	14,800	10	1.1	10	5	3,330	11	44	.1	3	13
A-2	21010 C	2,580	3,000	4,070	10,100	1,540	303	30,100	40	1.7	31	12	9,440	53	141	.6	1	45

Table 3. Elemental analyses of backfill-core samples, Powder River Basin, Wyoming--Continued

Sample code (fig. 2)		Element (milligrams per kilogram)																
Site number	Backfill- core number	Calcium	Magnesium	Sodium	Potassium	Sulfur	Phosphorus	Aluminum	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Selenium	Molybdenum	Zinc
Site B-1, Core hole 1																		
B-1	1 4 6 A	3,950	4,050	2,000	9,550	2,450	350	27,900	56	1.9	51	34	22,800	78	281	3.3	15	74
B-1	1 4 6 C	8,170	4,940	2,630	10,700	1,560	320	35,900	71	2.3	62	21	19,300	100	173	.3	3	71
B-1	1 5 7 A	15,290	4,040	2,340	15,700	4,990	336	29,000	43	2.0	54	24	16,800	76	184	10.5	5	67
B-1	1 7 9 A	7,410	2,420	1,850	13,000	1,080	229	18,000	13	1.4	31	20	7,260	35	120	1.8	11	35
B-1	1 9 11 C	2740	2,980	4,460	7,950	417	357	25,500	66	1.7	44	19	8,690	66	311	1.2	7	44
Site B-1, Core hole 2																		
B-1	2 5 6 A	12,540	5,400	2,030	18,000	5,630	397	49,000	96	2.0	69	22	23,200	90	188	3.5	4	--
B-1	2 5 6 C	7,280	5,800	1,690	9,510	2,300	597	38,000	84	2.3	59	22	23,000	63	260	1.4	5	82
B-1	2 7 8 A	6,000	3,930	1,690	16,700	3,080	410	32,200	59	1.8	58	27	17,200	91	244	1.3	15	79
B-1	2 9 10 C	1,070	1,960	1,200	10,600	675	178	22,900	30	1.7	43	14	7,000	95	54	2.3	8	64
B-1	2 10 11 A	3,310	3,140	1,450	15,100	1,340	212	26,200	46	1.9	50	26	18,000	73	212	2.3	19	73

Table 4. Analyses of saturated pastes and extracts from backfill-core samples, Powder River Basin, Wyoming

[mV, millivolts; dS/m, decisiemens per meter at 25 degrees Celsius; µg/kg, micrograms per kilogram; mg/L, milligrams per liter; mg/kg, milligrams per kilogram; --, indicates data unavailable]

Sample code (fig. 2)		Sample depth below land surface (meters)	Saturated paste		Saturated-paste extract			
Site number	Backfill- core number		pH (standard units)	Eh (mV)	Specific conduc- tance (dS/m)	Selenium (µg/kg)	Dissolved organic carbon (mg/L)	Sulfate (mg/kg)
Site A-1, Core hole 1								
A-1	1 1 2 A	0.9	7.4	350	6.0	4	30.3	1,270
A-1	1 2 3 A	1.7	7.1	390	3.2	8	7.8	305
A-1	1 2 4 A	2.4	5.5	590	4.5	12	4.8	397
A-1	1 3 6 A	3.3	7.2	370	5.1	22	24.3	401
A-1	1 3 6 C	4.3	7.4	340	5.9	88	15.3	420
A-1	1 4 7 A	4.8	7.5	340	5.4	15	13.5	445
A-1	1 4 7 B	5.2	7.4	360	6.0	7	22.8	468
A-1	1 5 8 A	5.7	7.2	390	5.6	9	21.3	462
A-1	1 6 9 A	6.3	7.8	350	5.1	29	--	--
A-1	1 7 10 A	7.1	8.1	310	6.1	11	--	--
A-1	1 9 11 A	7.9	7.2	310	5.5	8	25.8	603
Site A-1, Core hole 2								
A-1	2 1 2 A	.9	6.9	320	5.8	2	28.2	440
A-1	2 2 3 A	1.7	4.7	630	3.9	7	6.6	345
A-1	2 2 4 A	2.4	4.7	620	4.1	6	11.1	357
A-1	2 3 5 A	3.2	6.3	360	6.0	69	15.6	450
A-1	2 4 6 A	3.9	6.4	350	6.5	73	13.8	481
A-1	2 4 6 C	4.5	7.0	350	4.4	89	18.3	928
A-1	2 5 7 A	4.7	6.8	370	6.3	52	25.8	1,000
A-1	2 5 7 C	5.2	7.1	360	8.0	156	24.0	725
A-1	2 6 8 A	5.5	7.5	390	8.4	104	27.3	2050
A-1	2 8 9 A	6.2	7.9	360	6.2	28	24.3	418
A-1	2 8 9 C	6.7	7.3	380	4.2	12	20.4	356
Site A-2, Core hole 1								
A-2	1 2 2 A	.9	7.3	390	3.6	4	11.1	783
A-2	1 3 3 A	1.7	6.8	410	2.6	21	5.7	510
A-2	1 4 4 A	2.5	7.9	440	3.5	25	6.3	466
A-2	1 5 5 A	3.2	7.1	400	4.2	38	10.0	837
A-2	1 6 6 A	3.9	6.9	420	3.3	25	6.8	661
A-2	1 7 7 A	4.8	5.5	580	4.1	35	16.2	956
A-2	1 7 7 B	5.2	6.7	430	4.3	13	8.8	1,030
A-2	1 8 8 A	5.5	4.2	610	3.2	4	9.1	683
A-2	1 9 9 A	6.2	7.1	440	4.3	3	10.0	909
A-2	1 10 10 A	7.1	7.4	430	3.9	2	8.0	835

Table 4. Analyses of saturated pastes and extracts from backfill-core samples, Powder River Basin, Wyoming--Continued

Sample code (fig. 2)		Sample depth below land surface (meters)	Saturated paste		Saturated-paste extract			
Site number	Backfill- core number		pH (standard units)	Eh (mV)	Specific conduc- tance (dS/m)	Selenium (µg/kg)	Dissolved organic carbon (mg/L)	Sulfate (mg/kg)
Site A-2, Core hole 2								
A-2	2 2 2 A	.9	7.8	410	2.1	5	6.7	329
A-2	2 3 3 A	1.7	7.7	410	3.9	25	7.3	774
A-2	2 4 4 A	2.7	7.6	450	3.4	20	6.4	698
A-2	2 5 5 A	3.2	6.7	490	3.6	15	29.7	825
A-2	2 6 6 A	4.0	7.9	400	3.7	40	6.2	289
A-2	2 7 7 A	4.7	4.6	410	4.7	15	5.6	1,063
A-2	2 7 7 C	5.2	3.7	650	3.9	7	5.6	847
A-2	2 8 8 A	5.5	5.9	490	3.7	2	15.7	776
A-2	2 9 9 A	6.2	4.3	480	3.4	2	6.2	658
A-2	2 10 10 A	7.0	7.6	430	2.6	4	5.6	483
A-2	2 10 10 C	7.5	6.7	410	4.4	3	11.2	953
Site B-1, Core hole 1								
B-1	1 1 2 A	.9	7.5	450	3.6	1	8.1	887
B-1	1 2 4 A	1.8	6.9	330	3.2	78	36.1	874
B-1	1 3 5 A	3.2	6.6	340	3.5	140	28.7	783
B-1	1 4 6 A	3.9	7.3	330	3.3	92	39.9	1,070
B-1	1 4 6 C	4.5	7.5	310	3.7	93	35.0	1,040
B-1	1 5 7 A	4.7	7.4	310	3.5	36	45.2	648
B-1	1 5 7 C	5.2	7.0	390	3.3	22	45.2	712
B-1	1 6 8 A	5.5	6.9	400	3.2	9	33.6	754
B-1	1 7 9 A	6.2	7.0	390	2.6	6	30.5	643
B-1	1 8 10 A	7.0	7.4	220	2.8	10	23.5	335
B-1	1 9 11 A	7.7	6.8	400	2.9	2	13.7	696
B-1	1 9 11 C	8.3	7.1	430	2.3	8	14.0	509
Site B-1, Core hole 2								
B-1	2 1 2 A	.9	7.6	370	2.9	3	29.3	1,060
B-1	2 2 3 A	1.7	7.4	400	3.5	43	30.4	603
B-1	2 3 4 A	2.5	6.9	430	3.8	75	32.4	877
B-1	2 4 5 A	3.2	6.7	450	3.7	99	25.5	635
B-1	2 5 6 A	3.9	7.0	450	3.4	62	61.1	998
B-1	2 5 6 C	4.5	7.1	430	3.7	52	39.3	744
B-1	2 6 7 A	4.7	7.2	440	3.5	40	41.1	1,050
B-1	2 7 8 A	5.5	6.8	430	3.3	3	43.5	1,225
B-1	2 7 8 C	6.0	7.3	410	3.4	15	19.0	753
B-1	2 8 9 A	6.2	6.5	450	3.0	110	9.7	381
B-1	2 9 10 A	7.0	7.2	410	2.8	3	18.2	607
B-1	2 9 10 C	7.5	7.7	390	2.6	2	9.3	178
B-1	2 10 11 A	7.7	7.3	400	2.7	5	21.0	848

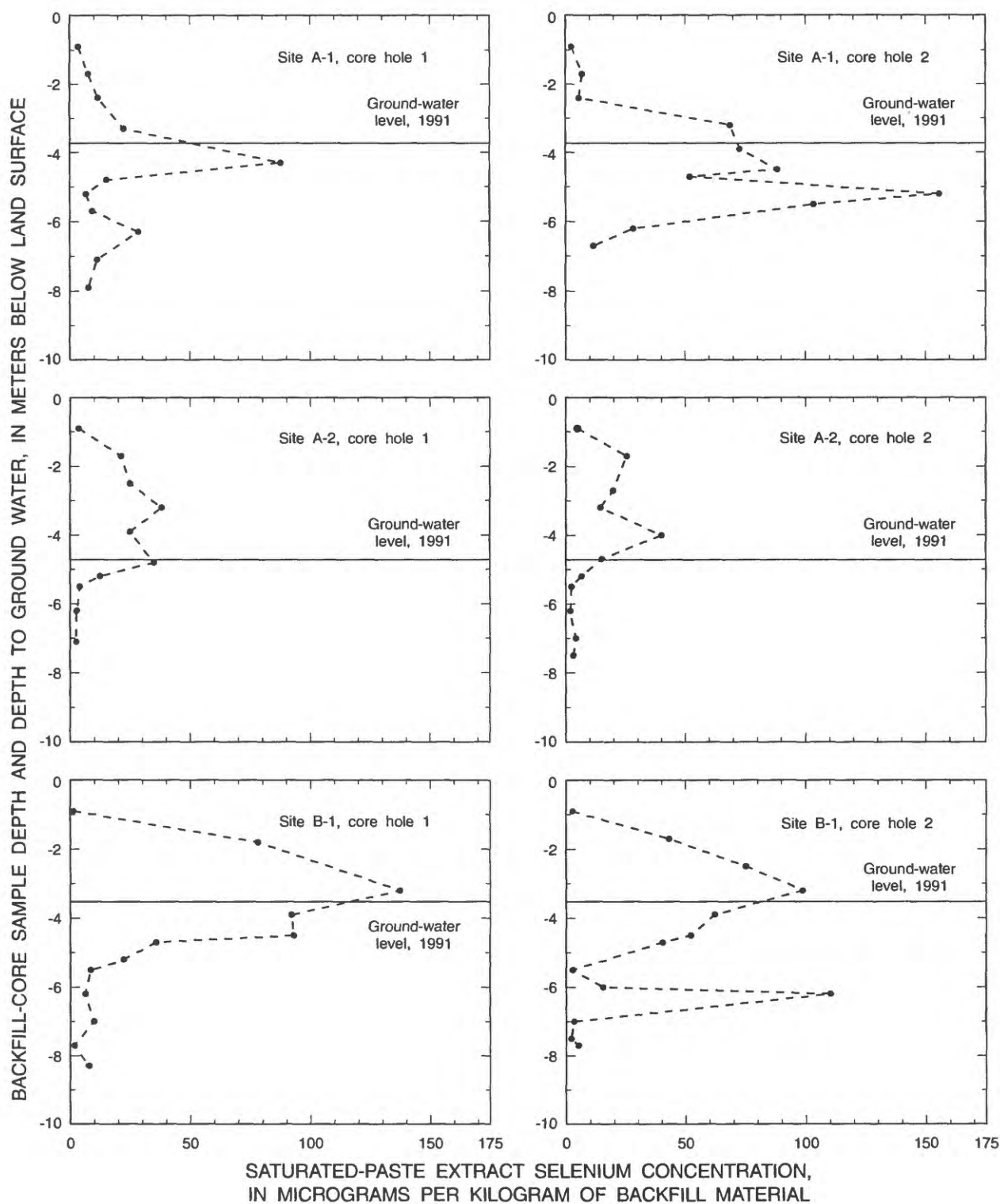


Figure 3. Saturated-paste extract selenium concentrations as a function of depth for backfill-core samples from the Powder River Basin, Wyoming.

Fractionation of Selenium by Sequential Partial Dissolution

Sequential partial dissolution techniques developed by Chao and Sanzolone (1989) were modified and used on 17 backfill-core samples to partition selenium into operationally defined fractions. The backfill-core samples selected for sequential partial dissolution are shown in table 1. The sequential partial dissolution analyses were conducted by the U.S. Geological Survey, Branch of Geochemistry, in Lakewood, Colorado. The procedure, which extracts selenium into six fractions, is as follows:

Fraction 1: Potassium dihydrogen phosphate (0.1 molar KH_2PO_4 , adjusted to a pH 8 with KOH). This fraction would correspond to the water soluble and specifically sorbed selenium. Fraction 1 would consist of selenate and selenite on exchange sites replaceable with phosphates, and would be readily available for leaching or plant uptake.

Fraction 2: Sodium acetate (1 molar $NaC_2H_3O_2$, adjusted to pH 5 with acetic acid). Fraction 2 relates to the carbonates and is potentially available through acidification of the material.

Fraction 3: Sodium hypochlorite (single treatment of 5 percent NaOCl by weight to volume, adjusted to a pH of 9.5). Fraction 3 is related to organic matter and is potentially available through microbial decomposition.

Fraction 4: Hydroxyl amine hydrochloride (0.25 molar $NH_2OH \cdot HCl$). Fraction 4 relates to manganese oxides and amorphous iron oxides and is potentially available through reduction reactions.

Fraction 5: Hydrochloric acid (4 molar HCl). Fraction 5 relates to crystalline iron oxides and acid-volatile sulfides and would be conditionally available through strong acid decomposition.

Fraction 6: Hydrofluoric, nitric, and perchloric acid ($HF + HNO_3 + HClO_4$) total digestion of the residue. Fraction 6 relates to primary crystalline sulfides, occluded and imbedded in siliceous materials, silicates, and refractory accessory minerals and would be unavailable and resistant to most weathering.

After extraction and chemical treatment, selenium was determined by using atomic absorption spectrophotometry with hydride generation (AAS-HG) (Welsch and others, 1990). Selenium concentrations in each of six fractions and total selenium concentrations of each sample are shown in table 5.

Naftz and Rice (1989, p. 570) found that the organic phase contained 100 percent of the total selenium in 10 of 11 undisturbed, overburden-rock samples collected from two coal mines in the Powder River Basin, Wyoming. The organic phase (fraction 3) accounted for less than 5 to 58 percent of the total selenium by summation in backfill-core samples analyzed for this study (table 5). This difference may be a result of dissolution and redistribution of selenium from the organic phase to other fractions in the backfill material during the mixing and disturbance associated with the mining process and subsequent reclamation.

Ground-Water Samples

Ground-water samples were collected from each well in September 1991 (mines A and B), July 1992 (mine A), and August 1992 (mine B). Water was pumped from wells at about 4.5 liters per minute with a submersible, positive displacement pump until pH, specific conductance, and temperature were stable (± 10 percent); 3 to 5 casing volumes of water were pumped from each well. Because of difficulty in filtering samples onsite in 1991, a second set of ground-water samples was collected at each site during 1992. Prior to collecting ground-water samples in 1992, and after pH, specific conductance, and temperature stabilized, the submersible pump was replaced with a slower, nonsubmersible, positive-displacement pump.

Ground-water samples were filtered onsite through 0.45- μ m glass-fiber filters. The ground-water samples were collected in 250 mL, high-density polyethylene bottles for major and trace ion analyses, and in 4L, high-density polyethylene bottles for DOC fractionation and isolation. Samples for cation analyses were acidified with nitric acid to pH 2. In 1991, the sample bottles for DOC analysis were purged with argon and filled under a stream of argon gas to avoid oxidation of the samples. In 1991 and 1992, all ground-water samples were chilled onsite with ice and subsequently stored under refrigeration (3°C) at the University of Wyoming until analyses were completed.

Chemical Analyses

Specific conductance was measured onsite, using a Lab Line Instruments Lectro Mho Meter. The pH and Eh were measured onsite, using an Orion Research Model 407A Ionalyzer. The pH was measured using

Table 5. Selenium concentrations in various fractions of backfill-core samples extracted by sequential partial dissolution (Chao and Sanzolone, 1989), Powder River Basin, Wyoming

[Concentrations in micrograms per kilogram ($\mu\text{g/kg}$); *, sample fraction was not analyzed due to a reaction of the dissolved organic material (The summation for sample B-1 278A does not include the selenium associated with the organic matter); <, less than]

Sample code (fig. 2)		Selenium concentrations, in mg/kg						Total selenium	
		Fraction 1, Potassium dihydrogen phosphate (0.1 molar)	Fraction 2, Sodium acetate (1 molar)	Fraction 3, Sodium hypo- chlorite (5 percent adjusted to pH 9.5)	Fraction 4, Hydroxyl- amine hydro- chloride (0.25 molar)	Fraction 5, Hydro- chloric acid (4 molar)	Fraction 6, Hydro- fluoric, nitric, and perchloric acid	By sum- mation ¹	By analysis
Site A-1, Core hole 1									
A-1	1 3 6 A	38	<20	190	<20	80	65	373	300
A-1	1 3 6 C	160	20	90	20	90	100	480	500
A-1	1 4 7 A	50	<20	280	20	130	100	580	500
Site A-1, Core hole 2									
A-1	2 4 6 A	130	<20	90	<20	120	110	450	400
A-1	2 4 6 C	90	<20	330	<20	150	100	670	400
A-1	2 5 7 A	120	<20	70	20	130	130	470	500
Site A-2, Core hole 1									
A-2	1 7 7 A	110	20	130	40	40	120	460	500
A-2	1 8 8 A	50	<20	50	<20	70	100	270	300
A-2	1 9 9 B	<20	<20	200	<20	70	70	340	300
Site A-2, Core hole 2									
A-2	2 7 7 A	30	<20	90	20	70	120	330	300
A-2	2 7 7 C	40	20	70	30	90	170	420	600
A-2	2 8 8 A	<20	<20	<20	<20	60	50	110	300
Site B-1, Core hole 1									
B-1	1 4 6 A	120	30	70	<20	190	460	870	1,000
B-1	1 4 6 C	110	20	<20	<20	110	160	400	500
Site B-1, Core hole 2									
B-1	2 5 6 A	120	30	80	<20	140	420	790	1,000
B-1	2 5 6 C	130	40	100	20	310	360	960	1,100
B-1	2 7 8 A	60	30	*	<20	100	510	700*	1,100

¹Values less than 20 were assumed to be zero for summation.

an Orion combination electrode. The Eh was measured using an Orion platinum electrode with an Ag/AgCl₂ reference electrode. Dissolved oxygen was measured onsite using a YSI Incorporated Model 57 dissolved-oxygen meter. Onsite measurements were made in a sealed, flow-through chamber, which minimized sample contact with the atmosphere.

Concentrations of cations (aluminum, arsenic, cadmium, calcium, chromium, copper, iron, lead, manganese, magnesium, molybdenum, silicon, and zinc) were measured using ICP-OES. Sodium and potassium were measured using atomic emission spectrophotometry (AES). Unacidified filtrates were analyzed for DOC, sulfate, chloride, fluoride, nitrate, and selenium. DOC was measured using a Shimadzu TOC-5000 carbon analyzer. Total selenium was measured using AAS-HG. Concentrations of sulfate, chloride, fluoride, and nitrate were measured using a Dionex Ion Chromatography system. Field and laboratory analyses of ground-water samples are presented in tables 6 and 7.

Selenium speciation was not determined for the ground-water samples collected as part of this study. Analyses of ground-water samples by Naftz and Rice (1989, p. 573) from wells at mine B had 99 percent of the selenium present in the selenate form and a negligible amount (less than 1 percent) as selenite.

The pH of the ground-water samples ranged from 5.5 to 7.3 (table 6). Selenium concentrations ranged from 3 (well A-2) to 125 µg/L (well A-1). DOC concentrations ranged from 11 (well A-2) to 88 mg/L (well A-1). Specific conductance in ground-water samples ranged from 3,650 (well B-1) to 10,000 µS/cm (well A-1). Ground-water samples were dominated by sulfate concentrations that ranged from 2,960 to 11,300 mg/L (table 7). Concentrations of fluoride, arsenic, chromium, lead, and zinc were below the detection limit of the analytical methods used.

Hydrogeologic monitoring is conducted on a regular basis at both mines participating in this study. Data are published annually by GAGMO. Dissolved selenium concentrations (fig. 4) and water level data (fig. 5) published by GAGMO indicate recent trends for water in the wells used in this study. A general decline in dissolved selenium concentrations is apparent in figure 4. An increase in ground-water levels, as backfill materials have resaturated, is shown in figure 5. The increasing water levels are a result of the resaturation of the backfill materials. The sources of water for resaturation are precipitation, water pumped from the active mine pits, and underflow from adjacent

areas. As the ground-water rises in the coal-mine backfill, the ground water dissolves soluble materials including selenium species.

Dissolved Organic Carbon

Both natural organic solutes and DOC are terms used throughout this report; therefore, each term needs to be clearly defined. Natural organic solutes represent all the natural organic matter in solution. The term 'natural' is used to differentiate between organic solutes originating from the dissolution of the organic fraction of the soil (living organisms, dead plants, and animal residues) and from organic solutes originating from anthropogenic sources such as municipal, industrial, or agricultural wastes. DOC may consist of both natural and anthropogenic sources of organic compounds that pass through a 0.45 µm filter (Drever, 1988). Thus, DOC is an operationally defined material that is quantified after separation of larger organic solutes (for example, particulate carbon). In this study the DOC (natural organic solutes) is assumed to be from natural sources, predominately from the dissolution of coal. DOC is usually measured by oxidizing the DOC to carbon dioxide and measuring the carbon dioxide produced using a carbon analyzer equipped with an infrared spectrophotometer detector.

Most ground water has DOC concentrations below 2 mg/L (Leenheer and Huffman, 1979; Thurman, 1985, p. 14). However, DOC concentrations in ground water associated with organic-rich environments can be extremely large; for example, ground water receiving recharge from marshes and swamps can contain as much as 10 mg/L DOC, oil-field brines can contain as much as 1,000 mg/L DOC, and trona water can contain as much as 40,000 mg/L DOC. Generally, DOC in ground water associated with coal beds ranges from 5 to 10 mg/L (Thurman, 1985, p. 14).

The following sections describe two different experiments. The experiments are (1) fractionation of the DOC from the ground-water samples and (2) isolation of the DOC from the ground-water samples. The fractionation experiment characterized the DOC in ground-water samples by determining the percent DOC in six different fractions. The isolation experiments were conducted to separate certain DOC fractions in volumes large enough to be used for further studies. The isolation experiment required the use of larger volumes of water samples (10 to 20 L) and resins (adjusted according to the volume of solution processed) as compared to the fractionation experiment.

Table 6. *Water-quality properties, total selenium, and dissolved organic carbon in ground-water samples collected in 1991 and 1992, Powder River Basin, Wyoming*

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25° degrees Celsius; mV, millivolts; °C, degrees Celsius; mg/L, milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; <, less than]

Site number	Sampling date	Water level below land surface (meters)	Specific conductance ($\mu\text{S}/\text{cm}$)	pH (standard units)	Electrode potential (Eh) (mV)	Temperature (°C)	Dissolved oxygen (mg/L)	Dissolved selenium (mg/L)	Dissolved organic carbon (mg/L)
A-1	9-17-91	3.73	10,000	7.1	350	11.0	<1	125	88
	7-07-92	3.63	10,000	7.3	370	11.0	<1	121	84
A-2	9-17-91	4.72	5,000	5.5	450	10.5	<1	3	11
	7-07-92	4.55	4,200	5.6	450	11.0	<1	13	14
B-1	9-19-91	3.53	3,650	6.3	400	10.0	<1	88	87
	8-19-92	3.46	3,800	6.4	370	14.0	<1	88	79

Table 7. *Major inorganic constituents and trace elements in ground-water samples collected in 1992, Powder River Basin, Wyoming*

[Analytical results in milligrams per liter (mg/L); <, less than; --, indicates data are unavailable]

Constituents	Concentration, in mg/L, at site number and sampling date		
	A-1 7-07-92	A-2 7-07-92	B-1 8-19-92
Inorganic constituents			
Calcium	427	470	545
Magnesium	2,080	693	391
Sodium	1,180	339	347
Potassium	38	18	33
Sulfate	11,300	4,980	2,960
Chloride	340	46	65
Fluoride	<5.0	<5.0	<5.0
Silicon	7.17	5.95	6.86
Nitrate, as nitrogen	68	41	51
Trace elements			
Aluminum	.03	--	.01
Arsenic	<.005	<.005	<.005
Cadmium	<.001	.028	<.001
Chromium	<.002	<.002	<.002
Copper	.017	.012	.009
Iron	.001	.007	.006
Lead	<.005	<.005	<.005
Manganese	.03	.01	.16
Molybdenum	.005	.006	.006
Zinc	<.001	<.001	<.001

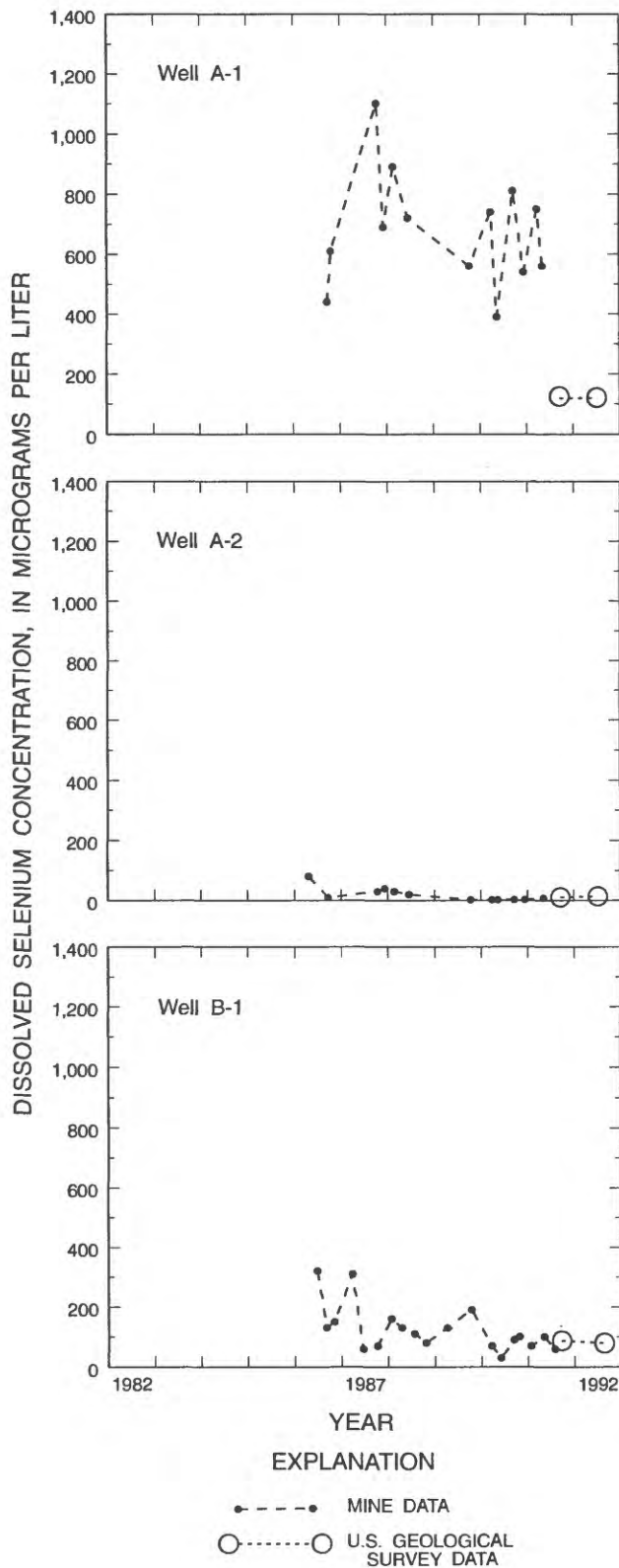


Figure 4. Dissolved selenium concentrations in ground-water samples from the Powder River Basin, Wyoming (mine data from Hydro-Engineering, 1991 and 1992).

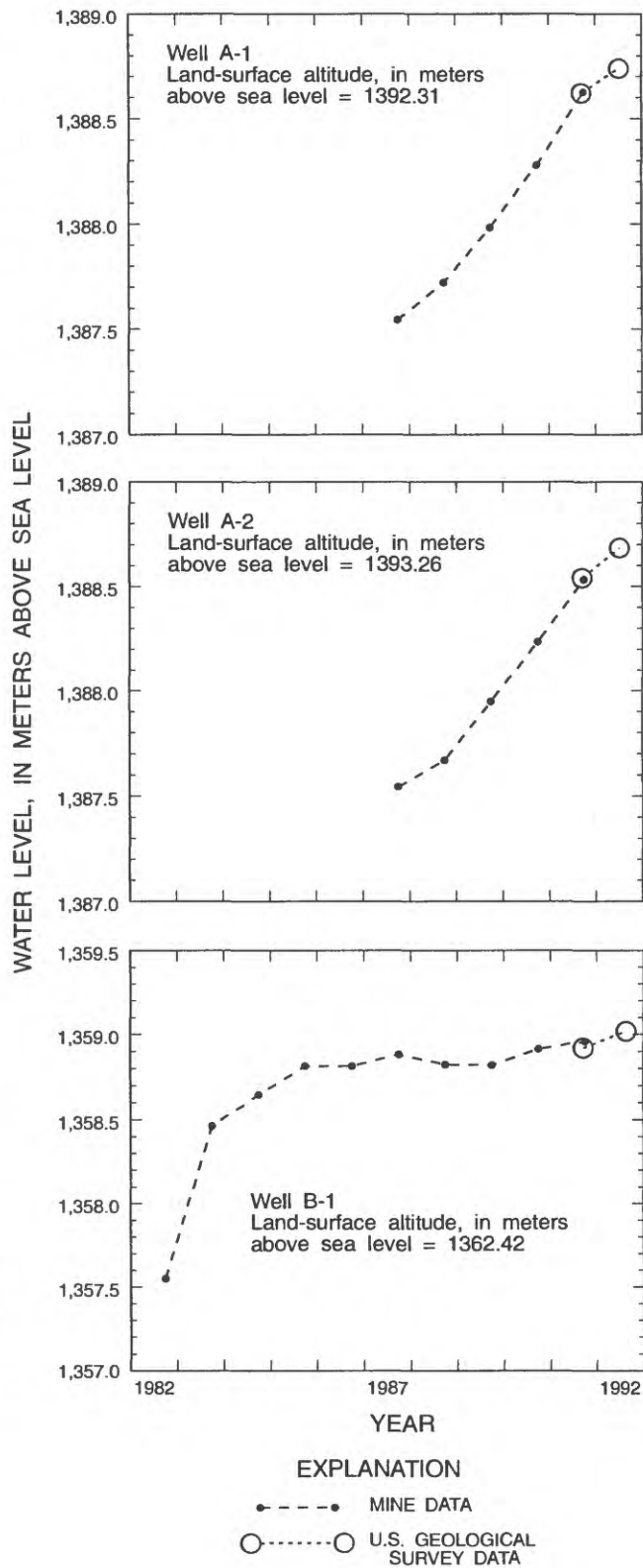


Figure 5. Water levels in wells in the Powder River Basin, Wyoming (mine data from Hydro-Engineering, 1991 and 1992).

Fractionation

DOC in ground-water samples was fractionated using the method developed by 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). Hydrophobic bases were determined only in the initial phases of this study and were subsequently discontinued because of the small amounts present in the ground-water samples. The percent DOC in the different fractions was determined, and the dominant fractions identified so that these fractions could be isolated and used in sorption/desorption experiments involving selenium. The DOC fractionation analytical scheme is shown in figure 6.

The results of the DOC fractionation analysis (table 8) indicate DOC in the ground-water samples was dominated by combined hydrophobic and hydrophilic acids: 74 to 84 percent for well A-1, 38 to 69 percent for well A-2, and 68 to 83 percent for well B-1. The combined hydrophobic and hydrophilic neutrals in ground-water samples ranged from 16 to 23 percent for well A-1, 21 to 55 percent for well A-2, and 10 to 25 percent for well B-1. Hydrophobic and hydrophilic bases in ground-water samples were generally less than 10 percent.

Isolation

Hydrophobic and hydrophilic acids in ground-water samples were isolated and concentrated following the methods described in Vance and David (1991) and Malcolm and MacCarthy (1992). Ground-water samples from wells A-1 and B-1 were used in the isolation procedure; ground-water samples from well A-2 were not used for isolation because of their small (11 and 14 mg/L) DOC concentrations. The isolated fractions were used later in the sorption/desorption studies to determine their effect on selenium sorption. The DOC isolation analytical scheme is shown in figure 7.

The DOC isolation method separates DOC into hydrophobic and hydrophilic acids. The isolation method is based on the sorption affinity of hydrophobic solutes to XAD-8 resin (macroporous methylmethacrylate copolymer), and the sorption affinity of hydrophilic acids to XAD-4 resin (Malcolm and MacCarthy, 1992). Hydrophobic acids are desorbed from XAD-8 and hydrophilic acids are desorbed from XAD-4 resins, using 0.1 Normal sodium hydroxide.

Characterization of the isolated fractions

For the DOC isolation study, 16 L of ground water from well A-1 (88 mg/L DOC) and 18 L from well B-1 (87 mg/L 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 DOC) and 0.8 L of hydrophilic acid (145 mg/L DOC) were isolated. For ground water from well B-1, 3.1 L of hydrophobic acid (300 mg/L DOC) and 0.8 L of hydrophilic acid (130 mg/L DOC) were isolated. The DOC and percentage DOC in hydrophobic and hydrophilic isolated fractions are shown in table 9.

Selenium also was analyzed in the isolated fractions. The selenium concentrations in well A-1 hydrophobic acid isolated fractions contained 10.5 µg/L selenium and the hydrophilic acid fraction contained 110 µg/L selenium. Well B-1 hydrophobic and hydrophilic acid solutions had smaller selenium concentration than well A-1. The selenium concentrations in well B-1 isolated fractions were 4.5 µg/L for the hydrophobic acid solutions and 24.2 µg/L for the hydrophilic acid solutions.

The isolation experimental results indicates larger percentages of hydrophobic acids and smaller percentages of hydrophilic acids were determined as compared to the fractionation experiment. Results of the two experiments indicated there are differences between the DOC fractionation and isolation methods. The differences between the two experiments may be because of the different volumes of resins used in the two experiments, or the difference in flow rates. Also, XAD-4 resin was used in the isolation procedure to retain the hydrophilic acids, whereas anion exchange resin was used in the fractionation procedure.

EFFECTS OF NATURAL ORGANIC SOLUTES ON SORPTION/DESORPTION OF SELENIUM

Sorption is one of the major processes controlling the solubility of selenium in subsurface environments. Sorption of selenium is the result of two mechanisms: electrostatic attraction (selenate) and ligand exchange (selenite) (Yates and Healy, 1975; Stumm and others, 1980). Selenium sorption is affected by pH, redox, and ion competition (Merrill and others, 1986; Balistrieri and Chao, 1987; Bar-Yosef and Meek, 1987; and Neal and others, 1987a and 1987b).

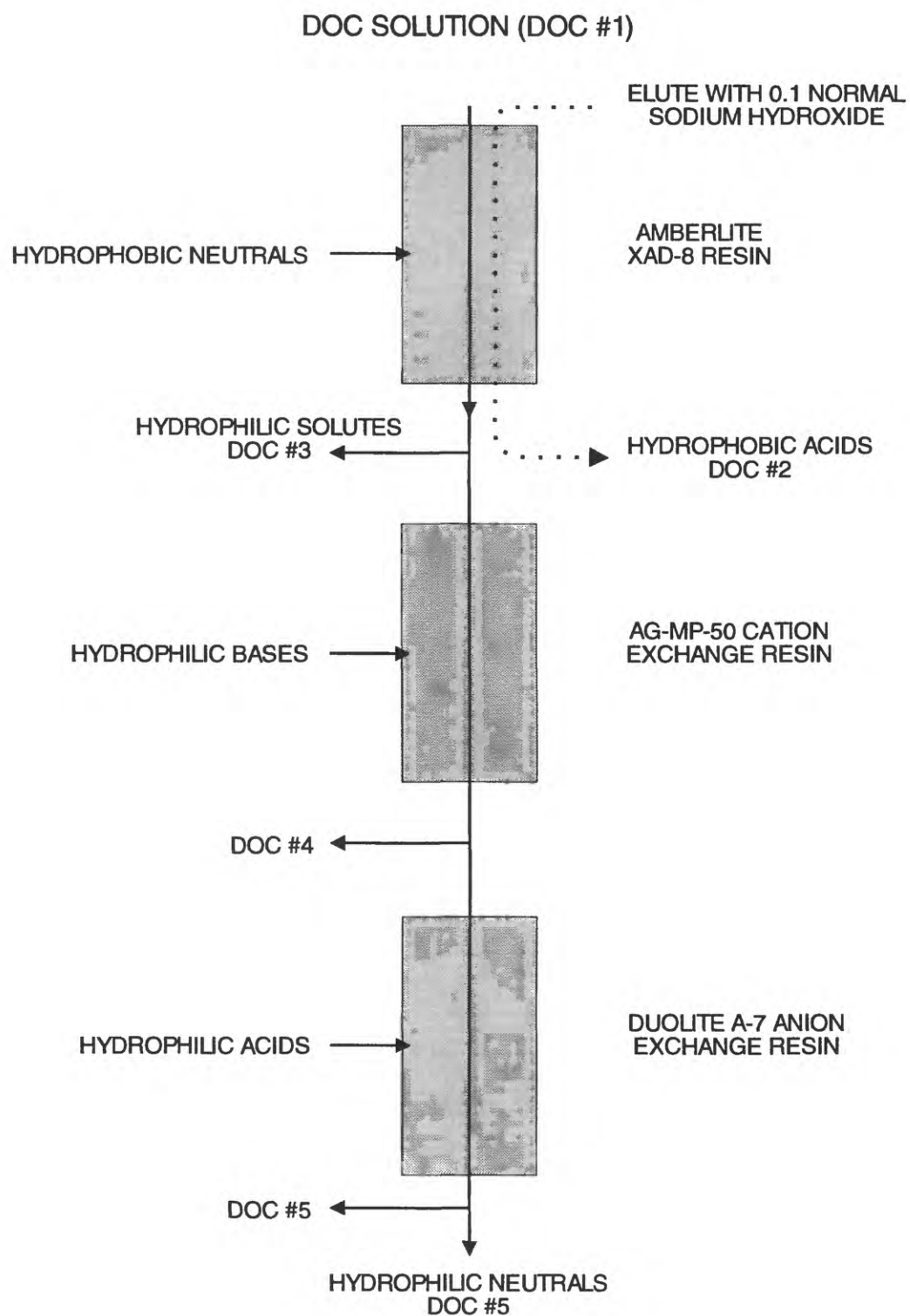


Figure 6. Dissolved organic carbon (DOC) fractionation analytical scheme.

Table 8. Analytical results of dissolved organic carbon (DOC) fractionation of ground-water samples, Powder River Basin, Wyoming

[<, indicates less than; DOC, dissolved organic carbon]

Well number	Sampling date	Hydrophobic solutes (percent of DOC) ¹				Hydrophilic solutes (percent of DOC) ¹			
		Total	Bases	Acids	Neutrals	Total	Bases	Acids	Neutrals
A-1	9-17-91	59	2	42	15	42	2	32	8
A-1	7-07-92	57	<1	42	15	43	0	42	1
A-2	9-17-91	49	<1	43	6	51	10	26	15
A-2	7-07-92	42	<1	22	20	58	7	16	35
B-1	9-18-91	70	<1	53	17	30	6	15	8
B-1	8-19-92	63	<1	53	10	38	8	30	0

¹Value may not sum to totals due to rounding

Three sorption/desorption experiments were conducted to determine the role that natural organic solutes (hydrophobic and hydrophilic acids) have on selenium sorption/desorption processes. Backfill-core samples were selected from various collection depths from each of the three field sites to investigate selenite sorption reactions. The backfill-core samples selected for sorption/desorption experiments are identified in table 1. The experiments determined the sorption capacity of the backfill-core samples when the background solution composition was distilled-deionized water, 0.1 molar calcium chloride, or distilled-deionized water with isolated hydrophobic and hydrophilic acids that were added to the background solutions. The hydrophobic and hydrophilic acids used in these experiments were isolated from the ground water using the procedure described in the chemical and physical characteristics section in this report.

Materials and Methods

The sorption batch experiments were conducted according to the following procedure: 2 g backfill-core samples were placed in polyethylene centrifuge tubes and mixed with 20 mL of solution containing a known selenium concentration. Concentrations of selenite in the added solutions ranged from 0 to 1,000 µg/L; selenite solutions were prepared using Na₂SeO₃. Samples were capped and placed on a mechanical shaker for 24 hours. A reaction time of 24 hours was chosen on

the basis of kinetic experiments by Balistrieri and Chao (1987, p. 1146), which indicated that sorption reactions involving selenite occurred rapidly. After 24 hours, samples were centrifuged for 15 minutes at 2,000 rpm, and an aliquot of approximately 17 mL of supernatant was filtered through 0.7-µm Whatman glass-microfiber filters (pre-rinsed with distilled-deionized water). Total selenium in sorption/desorption solutions was determined using AAS-HG according to Spackman and others (1994). After filtering, backfill-core samples were extracted with 1 molar potassium phosphate monobasic and the extracted selenium was measured to determine the amount of total selenium desorbed.

Three selenite-sorption experiments were conducted: (1) 10 core samples with background solution composition of distilled-deionized water, (2) 10 core samples with background solution composition of 0.1 molar calcium chloride, and (3) core samples with a background solution of distilled-deionized water with isolated fractions of hydrophobic acids (10 samples) and hydrophilic acids (7 samples). In experiment 3, isolated hydrophobic or hydrophilic acids were added to the background solution. For well A-1, concentrations of the isolated DOC in the sorption experiments were 157 mg/L for hydrophobic acids and 107 mg/L for hydrophilic acids. The DOC of ground water from well A-2 was not isolated because of the small DOC concentration in this water. Concentrations of the isolated DOC from well B-1 were 110 mg/L for hydrophobic acids and 88 mg/L for hydrophilic acids. The

DOC ISOLATION SCHEME

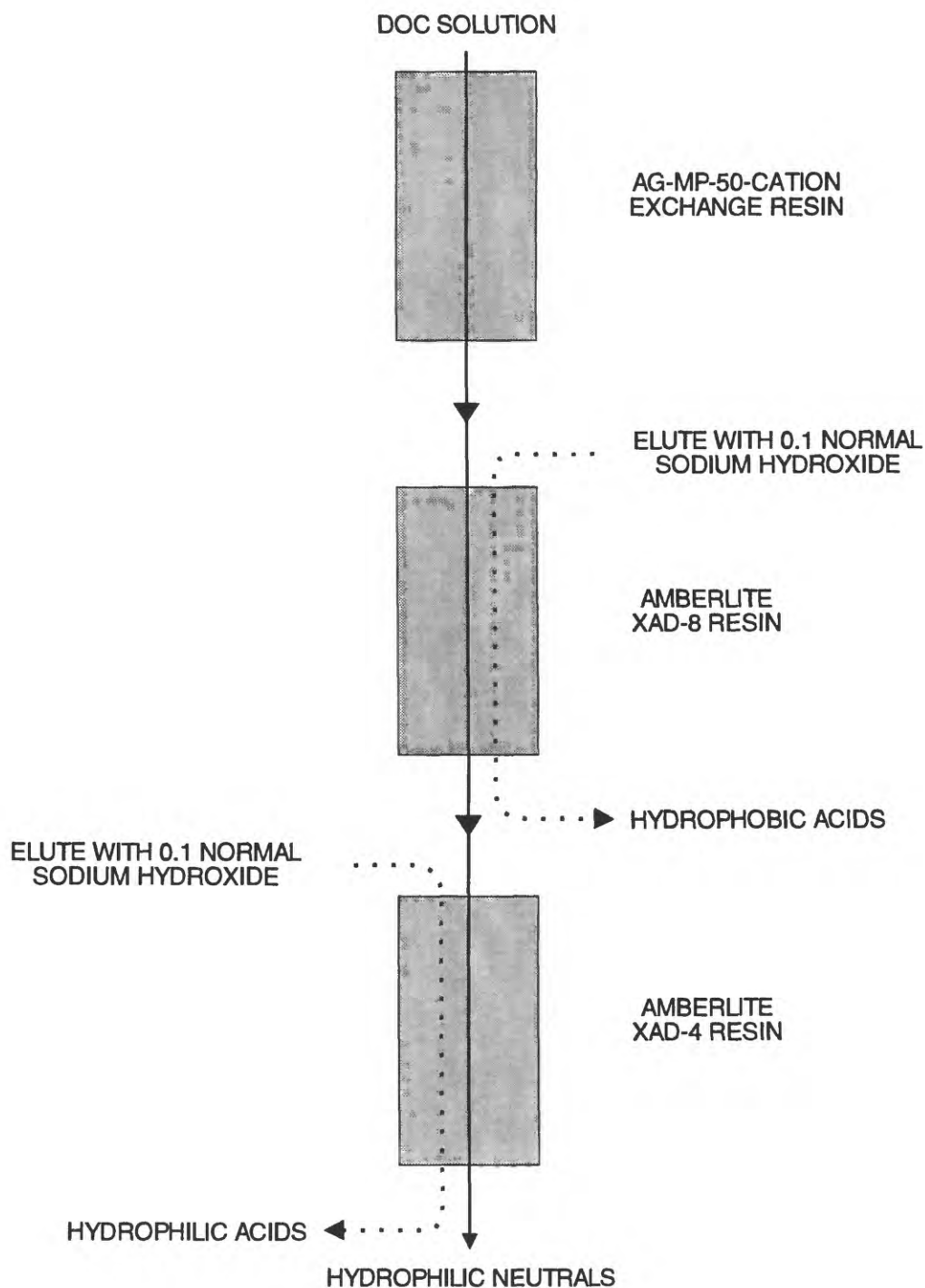


Figure 7. Dissolved organic carbon (DOC) isolation analytical scheme.

Table 9. Percent concentration and volume of concentrates of hydrophobic and hydrophilic solutes after organic carbon isolation of ground-water samples, Powder River Basin, Wyoming

[Percent, indicates percent of total dissolved organic carbon]

Constituent	Well number	
	A-1	B-1
Sampling date	07-07-92	08-19-92
Volume of sample isolated (liters)	16	18
Hydrophobic		
Volume of concentrate (liters)	3.3	3.1
Dissolved organic carbon (milligrams per liter)	280	300
Total solutes (percent) ¹	78	77
Acids (percent)	65	62
Neutrals (percent)	13	15
Hydrophilic		
Volume of concentrate (liters)	.8	.8
Dissolved organic carbon (milligrams per liter)	145	130
Total solutes (percent) ¹	22	23
Acids (percent)	11	10
Neutrals and bases (percent)	7	9
Lost in isolation of hydrophilic solutes (percent)	3	4

¹Values may not sum to totals due to rounding.

isolated DOC fractions from each of the ground-water samples were added to corresponding backfill-core samples collected at the site near each well, except for the backfill-core samples corresponding to site A-2, where hydrophobic acids from well A-1 were used. Insufficient isolated hydrophilic acids were available for use with backfill-core samples from site A-2.

Results and Discussion

Results from sorption/desorption studies were evaluated on the basis of both (1) the direct comparison of the selenium sorbed and desorbed as a function of the amount of selenite added, that is, percent removed or released, and (2) the evaluation of equilibrium data using several sorption isotherms (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 are capable of providing additional information on the sorption process.

Parameters such as empirical constants, binding affinities, sorption maxima, indigenous soil pools, and distribution coefficients may be determined by the different sorption isotherms. However, depending on the data, some sorption isotherm approaches fail to provide results due primarily to indigenous concentrations of solutes present in the backfill material.

Results obtained by the direct comparison method for experiment 1 (distilled-deionized water background solution) are shown in table 10. Selenite sorption on A-1 backfill-core samples ranged from 65 to 92 percent, on A-2 core samples ranged from 92 to 98 percent, and on B-1 core samples ranged from 56 to 97 percent. Sorption of selenite increased with decreasing pH, as was expected, because of the increase of positively charged sorption sites; similar results were obtained by Balistrieri and Chao (1987), Bar-Yosef and Meek (1987); and Neal and others (1987a). Figure 8 represents concentrations of the selenite sorbed on the backfill-core samples as a function of the equilibrium selenite concentration. As the slope of the lines shown in figure 8 decreases, selenite sorption decreases.

Table 10. Selenite sorption on backfill-core samples in distilled-deionized water and in 0.1 molar calcium chloride background solutions, Powder River Basin, Wyoming

[mg/kg, milligrams per kilogram; Recovered, indicates total selenium extracted with 0.1 molar potassium phosphate; negative sorption values indicate desorption; --, indicates no data; Sorption (percent) = (added - equilibrium) X 100/added]

Sample code (fig. 2)			Selenium							
			Experiment 1--distilled-deionized water				Experiment 2--0.1 molar calcium chloride solution			
Site number	Backfill-core number		Added (mg/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)	Added (mg/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)
Site A-1, Core hole 1										
A-1	136 C		0	0.05	--	0.02	0.01	<0.01	100	0.03
A-1	136 C		.52	.05	90	.31	.61	.22	64	.38
A-1	136 C		1.10	.13	89	.75	1.19	.24	80	.55
A-1	136 C		2.96	.37	88	1.46	3.03	.41	86	1.28
A-1	136 C		4.67	.71	85	3.26	4.72	.58	88	2.45
A-1	136 C		10.72	1.30	88	5.91	9.04	.91	90	3.89
A-1	147 A		0	.15	--	.02	.01	.15	-2,960	.08
A-1	147 A		.52	.18	65	.39	.61	.04	94	.35
A-1	147 A		1.10	.24	78	.81	1.19	.09	93	.55
A-1	147 A		2.96	.43	86	1.78	3.03	.14	95	1.34
A-1	147 A		4.67	.88	81	3.56	4.72	.53	89	2.41
A-1	147 A		10.72	1.47	86	6.09	9.04	.62	93	3.56
Site A-1, Core hole 2										
A-1	246 C		0	.14	--	.01	.02	.01	78	.05
A-1	246 C		.52	.17	67	.35	.56	.01	99	.56
A-1	246 C		1.10	.31	72	.72	.99	.01	99	.47
A-1	246 C		3.00	.53	82	1.69	2.76	.03	99	1.21
A-1	246 C		4.67	.88	81	3.22	5.90	.15	97	2.65
A-1	246 C		10.72	1.52	86	6.14	11.15	.12	99	5.95
A-1	257 A		0	.14	--	.03	.02	<.01	10	.01
A-1	257 A		.52	.15	70	.36	.56	.01	99	.26
A-1	257 A		1.10	.21	81	.70	.99	.02	98	.46
A-1	257 A		2.96	.25	92	1.60	2.76	.06	98	1.29
A-1	257 A		4.67	.48	90	3.02	5.90	.16	97	2.71
A-1	257 A		10.72	1.00	91	5.6	11.15	.26	98	5.54
Site A-2, Core hole 1										
A-2	188 A		0	.02	--	.07	.02	.01	49	.08
A-2	188 A		.52	.03	95	.24	.56	.03	95	.30
A-2	188 A		1.10	.04	97	.54	.99	.04	96	.58
A-2	188 A		3.00	.05	98	1.41	2.76	.04	98	1.40
A-2	188 A		4.67	.08	98	3.20	5.90	.08	99	2.44
A-2	188 A		10.72	.18	98	6.84	11.15	.31	97	5.54

Table 10. Selenite sorption on backfill-core samples in distilled-deionized water and in 0.1 molar calcium chloride background solutions, Powder River Basin, Wyoming--Continued

Sample code (fig. 2)			Selenium							
Site number	Backfill-core number	Experiment 1—distilled-deionized water				Experiment 2—0.1 molar calcium chloride solution				
		Added (mg/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)	Added (mg/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)	
Site A-2, Core hole 2										
A-2	277 A	0	.03	--	.11	.02	.02	13	.11	
A-2	277 A	.52	.04	93	.44	.51	.03	94	.43	
A-2	277 A	1.10	.07	94	.59	1.10	.05	96	.66	
A-2	277 A	2.96	.24	92	1.59	2.95	.06	98	1.61	
A-2	277 A	4.67	.39	92	2.96	4.67	.09	98	3.17	
A-2	277 A	10.72	.80	93	5.67	1.69	.22	99	6.71	
A-2	288 A	0	.02	--	.11	.02	.02	13	.07	
A-2	288 A	.52	.03	94	.43	.51	.03	95	.24	
A-2	288 A	1.10	.05	96	.67	1.10	.04	97	.54	
A-2	288 A	2.96	.07	98	1.62	2.95	.04	98	1.41	
A-2	288 A	4.67	.09	98	3.17	4.67	.08	98	3.20	
A-2	288 A	10.72	.22	98	6.71	1.69	.18	98	6.84	
Site B-1, Core hole 1										
B-1	146 C	.03	.12	-297	.08	.03	.03	0	.12	
B-1	146 C	.47	.21	56	.25	.47	.07	84	.44	
B-1	146 C	.99	.28	72	.55	.99	.15	85	.67	
B-1	146 C	2.76	.58	79	1.41	2.76	.33	88	1.61	
B-1	146 C	4.82	1.06	78	3.21	4.82	.45	10	3.18	
B-1	146 C	10.98	1.58	86	6.90	1.98	.92	92	6.78	
B-1	157 A	.03	.10	-237	.12	.03	.03	0	.08	
B-1	157 A	.47	.11	76	.45	.47	.05	90	.25	
B-1	157 A	.99	.18	82	.59	.99	.12	88	.55	
B-1	157 A	2.76	.30	89	1.59	2.76	.36	88	1.41	
B-1	157 A	4.82	.37	92	2.97	4.82	.54	89	3.21	
B-1	157 A	10.98	.52	95	5.74	10.98	.99	91	6.90	
Site B-1, Core hole 2										
B-1	256 A	.03	.12	-283	.12	.03	.03	0	.12	
B-1	256 A	.47	.12	74	.44	.47	.07	84	.44	
B-1	256 A	.99	.15	85	.58	.99	.12	85	.67	
B-1	256 A	2.76	.20	93	1.61	2.76	.18	88	1.61	
B-1	256 A	4.82	.24	95	3.18	4.82	.21	91	3.18	
B-1	256 A	10.98	.34	97	5.62	10.98	.32	92	6.78	

¹Sorption values were calculated on non-rounded values of added and equilibrium selenium concentrations.

EXPERIMENT 1
DISTILLED-DEIONIZED WATER
BACKGROUND SOLUTION

EXPERIMENT 2
0.1 MOLAR CALCIUM CHLORIDE
BACKGROUND SOLUTION

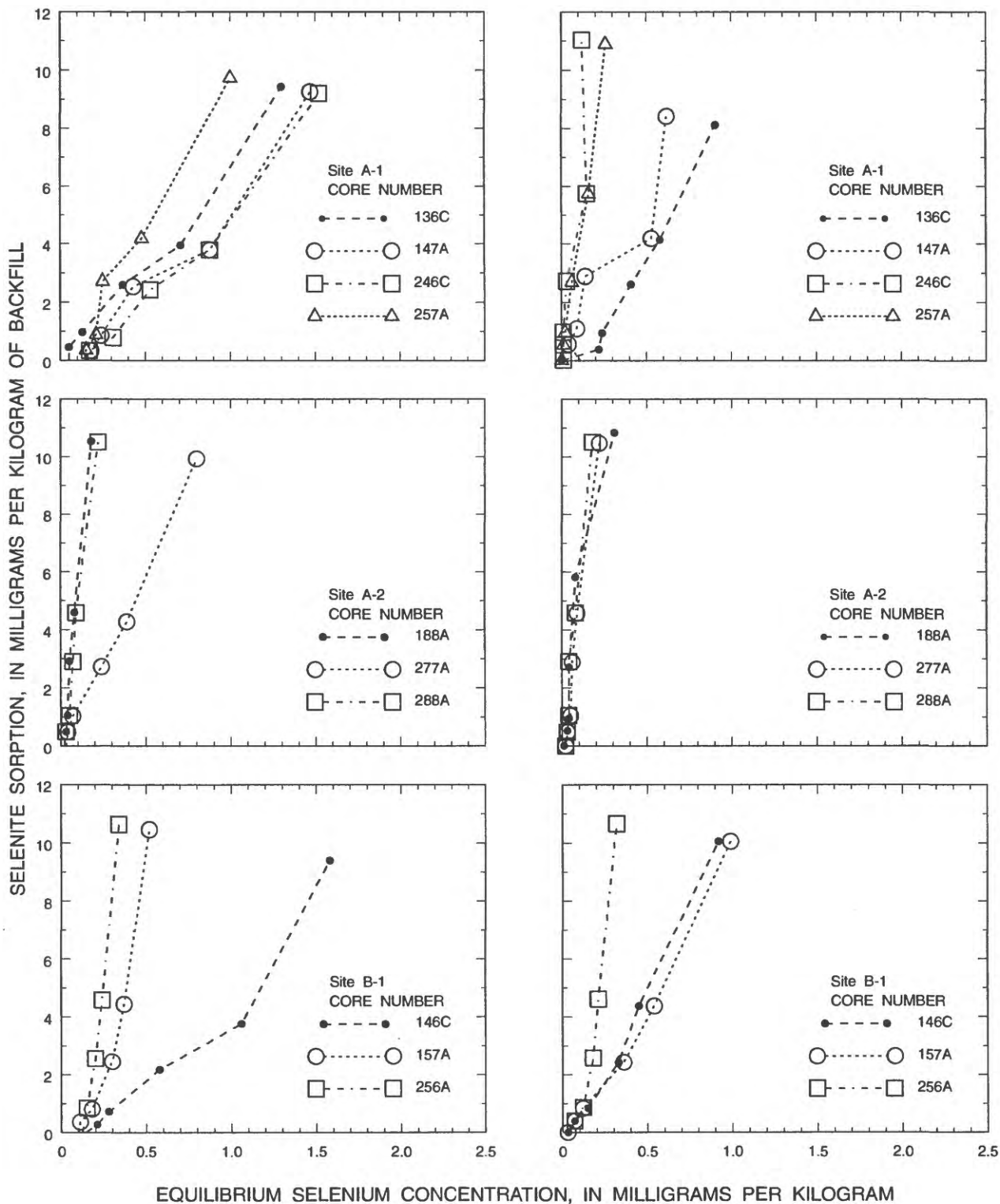


Figure 8. Selenite sorption as a function of equilibrium selenium concentrations of backfill-core sample solutions with distilled-deionized water and 0.1 molar calcium chloride background solutions.

Selenite sorption increased with increasing concentration of added selenite in all samples. The A-2 samples had the largest selenite sorption capacities, whereas the B-1 core samples had the smallest sorption capacities, which may be a function of the B-1 core samples having the largest and A-2 samples having the smallest DOC concentration in the associated ground water and saturated-paste extracts. This condition indicates an inverse relation between DOC concentration and sorption capacity for selenium.

The phosphate extraction recovered about 50 percent of the added selenium. The difference between the sorbed and recovered selenium may be caused by precipitation of selenium, or formation of strong ligand exchange reactions involving selenium.

Results obtained by the direct comparison method for experiment 2 (0.1 molar calcium chloride background solution) are presented in table 10. Selenium sorption ranged from 10 to 99 percent for A-1 samples; 13 to 99 percent for A-2 samples; and 0 to 92 percent for B-1 samples. The trends of increasing sorption with decreasing pH and the increasing sorption with the increase of the added selenium also were observed in this study.

The results of experiments 1 and 2 indicate an increase in sorption when 0.1 molar calcium chloride was the background solution. Results from experiment 1 and 2 are shown in figure 8. 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 and others, 1987b).

Results of selenite sorption in experiment 3 (hydrophobic and hydrophilic acids added to background solutions) are presented in table 11. Observed sorption capacities, when hydrophobic acids were added to the background solution, ranged from 5 to 94 percent for A-1 samples, 73 to 96 percent for A-2 samples, and 55 to 92 percent for B-1 samples. In solutions using hydrophilic acids, sorption ranged from 20 to 88 percent for A-1 samples and 3 to 89 percent for B-1 samples. Hydrophilic acids were not used in studies involving A-2 backfill-core samples because of the small volume of the isolated hydrophilic acid material.

Sorption generally was smaller in the presence of DOC, which indicates a positive interference caused by DOC in the selenite sorption process (figures 8 and 9, tables 10 and 11). This interference could be due to the formation of complexes with selenium that do not sorb

as strongly as selenite or selenate, or to competitive sorption processes involving selenium and DOC. Selenite sorption capacities decreased with the addition of hydrophobic acid (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. Selenite sorption capacity decreased for both A-1 and B-1 backfill-core samples with the addition of the hydrophilic acid. Selenite sorption decreased more with the addition of hydrophilic acid than with the addition of hydrophobic acid. The apparent effect of DOC on selenite sorption was generally greater at small, as compared to large concentrations of added selenite. A comparison of selenite sorption in the presence of hydrophobic and hydrophilic acids is shown in figure 9.

The Freundlich and Langmuir (Bohn and others, 1985, p. 201) sorption isotherms were unsatisfactory for describing the relations between equilibrium selenium concentrations and selenite sorption. A similar finding was reported by Blaylock and others (1995) who found that the initial mass isotherm could be used to develop predictive equations for describing selenite sorption on backfill materials. Results for initial mass isotherm parameters and distribution coefficients for the experiments involving the backfill materials and different background solutions are listed in table 12.

The slope (m) and intercept (b) values determined in the initial mass isotherm are important parameters for describing 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 selenium released when the initial solution contains no selenium, that is, negative intercept values indicate desorption of selenium. From slope and intercept values a reserve backfill selenium pool (RBSP) can be calculated as:

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

The RBSP is the amount of selenium present in the backfill that can be readily exchanged with substances in solution under the conditions of the experiment. Distribution coefficients (K_d), which describe the affinity of selenium for the backfill, also can be calculated from initial mass isotherm results (Nodvin and others, 1986; Vance and David, 1992).

Table 11. Selenite sorption on backfill-core samples in the presence of hydrophobic and hydrophilic acids, Powder River Basin, Wyoming

[mg/kg, milligrams per kilogram; g/kg, grams per kilogram; Recovered, indicates total selenium extracted with 0.1 molar potassium phosphate; --, no data; negative sorption values indicate desorption; Sorption (percent) = (added - equilibrium) X 100/added]

Experiment 3													
Sample code (fig. 2)		Hydrophobic acids added					Hydrophilic acids added						
		Selenite			Dissolved organic carbon		Selenite			Dissolved organic carbon			
Site number	Backfill-core number	Added (mg/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)	Added (g/kg)	Equilibrium (g/kg)	Added (mg/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)	Added (g/kg)	Equilibrium (g/kg)
Site A-1, Core hole 1													
A-1	136C	0.10	0.12	-17	--	1.1	1.0	1.20	0.45	63	--	1.6	1.5
A-1	136C	.59	.14	76	.37	1.1	.9	1.56	.97	38	.23	1.6	1.5
A-1	136C	1.05	.16	85	--	1.1	.9	2.09	.99	53	--	1.6	1.4
A-1	136C	1.98	.21	89	1.12	1.1	.8	4.84	1.12	77	1.15	1.6	1.4
A-1	136C	4.13	.30	93	--	1.1	1.0	9.67	1.21	88	--	1.6	1.4
A-1	136C	8.34	.48	94	5.08	1.1	.9	--	--	--	--	--	--
A-1	147A	.10	.14	-37	--	1.1	.9	1.20	.90	25	--	1.6	1.4
A-1	147A	.59	.19	68	.19	1.1	.8	1.56	1.33	15	.36	1.6	1.5
A-1	147A	1.05	.21	80	--	1.1	.7	2.09	1.00	52	--	1.6	1.5
A-1	147A	1.98	.26	87	1.03	1.1	.9	4.84	1.09	78	1.30	1.6	1.4
A-1	147A	4.13	.35	92	--	1.1	.9	9.67	1.57	84	--	1.6	1.4
A-1	147A	8.34	.49	94	5.08	1.1	.9	--	--	--	--	--	--
Site A-1, Core hole 2													
A-1	246C	.10	.13	-32	--	1.1	.7	1.20	.94	22	--	1.6	1.5
A-1	246C	.59	.17	71	.36	1.1	.8	1.56	1.65	-5	.42	1.6	1.4
A-1	246C	1.05	.24	78	--	1.1	1.0	2.09	.95	55	--	1.6	1.4
A-1	246C	1.98	.33	83	1.19	1.1	.9	4.84	1.10	77	1.26	1.6	1.4
A-1	246C	4.13	.39	91	--	1.1	1.0	9.67	1.35	86	--	1.6	1.4
A-1	246C	8.34	.85	90	4.98	1.1	.9	--	--	--	--	--	--
A-1	257A	.10	.10	5	--	1.1	1.0	1.20	.96	20	--	1.6	1.4
A-1	257A	.59	.10	83	.31	1.1	1.0	1.56	.99	37	.42	1.6	1.5
A-1	257A	1.05	.13	88	--	1.1	1.0	2.09	1.04	50	--	1.6	1.5
A-1	257A	1.98	.18	91	1.16	1.1	1.0	4.84	1.15	76	--	1.6	1.4
A-1	257A	4.13	.41	90	--	1.1	.9	9.67	1.34	86	--	1.6	1.4
A-1	257A	8.34	.77	91	5.18	1.1	.9	--	--	--	--	--	--
Site A-2, Core hole 1													
A-2	188A	.07	.08	-19	--	1.1	.8	--	--	--	--	--	--
A-2	188A	.62	.15	76	.39	1.1	.9	--	--	--	--	--	--
A-2	188A	1.10	.12	89	--	1.1	.9	--	--	--	--	--	--
A-2	188A	2.19	.20	91	1.13	1.1	.9	--	--	--	--	--	--
A-2	188A	4.28	.31	93	--	1.1	.9	--	--	--	--	--	--
A-2	188A	8.62	.73	92	5.97	1.1	.8	--	--	--	--	--	--

Table 11. Selenite sorption on backfill-core samples in the presence of hydrophobic and hydrophilic acids, Powder River Basin, Wyoming--Continued

Experiment 3													
Sample code (fig. 2)		Hydrophobic acids added					Hydrophilic acids added						
		Selenite			Dissolved organic carbon		Selenite			Dissolved organic carbon		Added	
Site number	Backfill- core number	Added (mg/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)	Added (g/kg)	Equilibrium (mg/kg)	Sorption ¹ (percent)	Recovered (mg/kg)	Added (mg/kg)	Equilibrium (mg/kg)	Added (g/kg)	Equilibrium (g/kg)
Site A-2, Core hole 2													
A-2	2 7 7 A	.07	.09	-30	--	1.1	.8	--	--	--	--	--	--
A-2	2 7 7 A	.62	.13	79	.44	1.1	.8	--	--	--	--	--	--
A-2	2 7 7 A	1.10	.23	79	--	1.1	.8	--	--	--	--	--	--
A-2	2 7 7 A	2.19	.60	73	1.22	1.1	.8	--	--	--	--	--	--
A-2	2 7 7 A	4.28	.20	95	--	1.1	.8	--	--	--	--	--	--
A-2	2 7 7 A	8.62	.40	95	6.00	1.1	.9	--	--	--	--	--	--
A-2	2 8 8 A	.07	.14	-97	--	1.1	.9	--	--	--	--	--	--
A-2	2 8 8 A	.62	.09	85	.26	1.1	.5	--	--	--	--	--	--
A-2	2 8 8 A	1.10	.12	89	--	1.1	.9	--	--	--	--	--	--
A-2	2 8 8 A	2.19	.15	93	1.12	1.1	.8	--	--	--	--	--	--
A-2	2 8 8 A	4.28	.16	96	--	1.1	.9	--	--	--	--	--	--
A-2	2 8 8 A	8.62	.31	96	5.93	1.1	.9	--	--	--	--	--	--
Site B-1, Core hole 1													
B-1	1 4 6 C	.02	.19	-675	--	.9	.8	-126	--	.31	.70	1.1	1.0
B-1	1 4 6 C	.44	.20	55	.18	.9	.8	-1	.01	.40	.40	1.1	1.1
B-1	1 4 6 C	.78	.33	58	--	.9	.7	16	--	.55	.46	1.1	1.0
B-1	1 4 6 C	1.80	.48	73	.47	.9	.7	48	.22	1.68	.87	1.1	1.0
B-1	1 4 6 C	4.01	.65	84	--	.9	.8	55	--	3.42	1.55	1.1	1.0
B-1	1 4 6 C	7.87	1.51	81	3.04	.9	.9	69	1.36	7.05	2.16	1.1	1.1
B-1	1 5 7 A	.02	.18	-646	--	.9	.9	-38	--	.31	.42	1.1	1.0
B-1	1 5 7 A	.44	.16	65	.25	.9	.9	-20	.13	.40	.48	1.1	1.0
B-1	1 5 7 A	.78	.22	72	--	.9	.7	35	--	.55	.36	1.1	1.0
B-1	1 5 7 A	1.80	.41	77	.45	.9	.9	58	.45	1.68	.71	1.1	1.0
B-1	1 5 7 A	4.01	.55	86	--	.9	.9	68	--	3.42	1.08	1.1	.9
B-1	1 5 7 A	7.87	.76	90	3.35	.9	.8	78	.99	7.05	1.58	1.1	.9
Site B-1, Core hole 2													
B-1	2 5 6 A	.02	.13	-454	--	.9	.9	3	--	.31	.30	1.1	1.0
B-1	2 5 6 A	.45	.16	65	.20	.9	.9	7	.03	.40	.37	1.1	1.1
B-1	2 5 6 A	.78	.16	80	--	.9	.8	21	--	.55	.43	1.1	1.0
B-1	2 5 6 A	1.80	.25	86	.43	.9	.9	73	.35	1.68	.45	1.1	1.1
B-1	2 5 6 A	4.01	.33	92	--	.9	1.0	80	--	3.42	.68	1.1	1.0
B-1	2 5 6 A	7.87	.63	92	3.25	.9	.9	89	1.92	7.05	.75	1.1	1.1

¹Sorption values were calculated on non-rounded values of added and equilibrium selenium concentrations.

EXPERIMENT 3
HYDROPHOBIC ACIDS ADDED
TO BACKGROUND SOLUTION

EXPERIMENT 3
HYDROPHILIC ACIDS ADDED
TO BACKGROUND SOLUTION

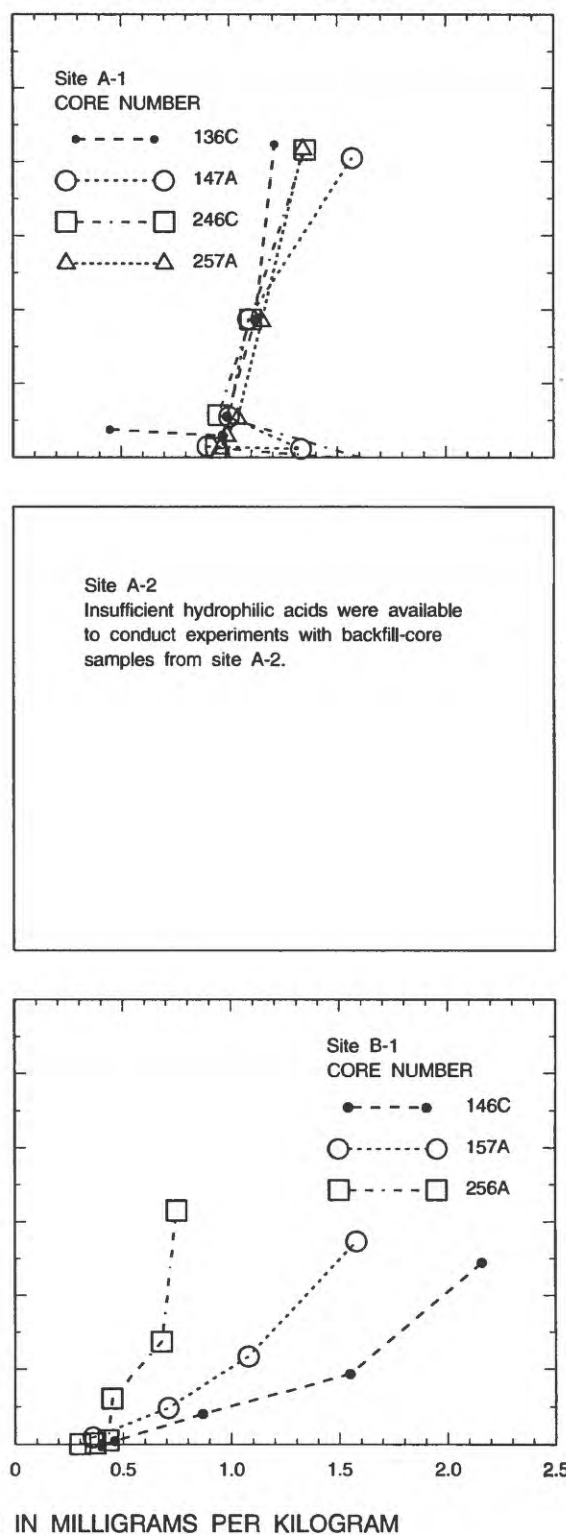
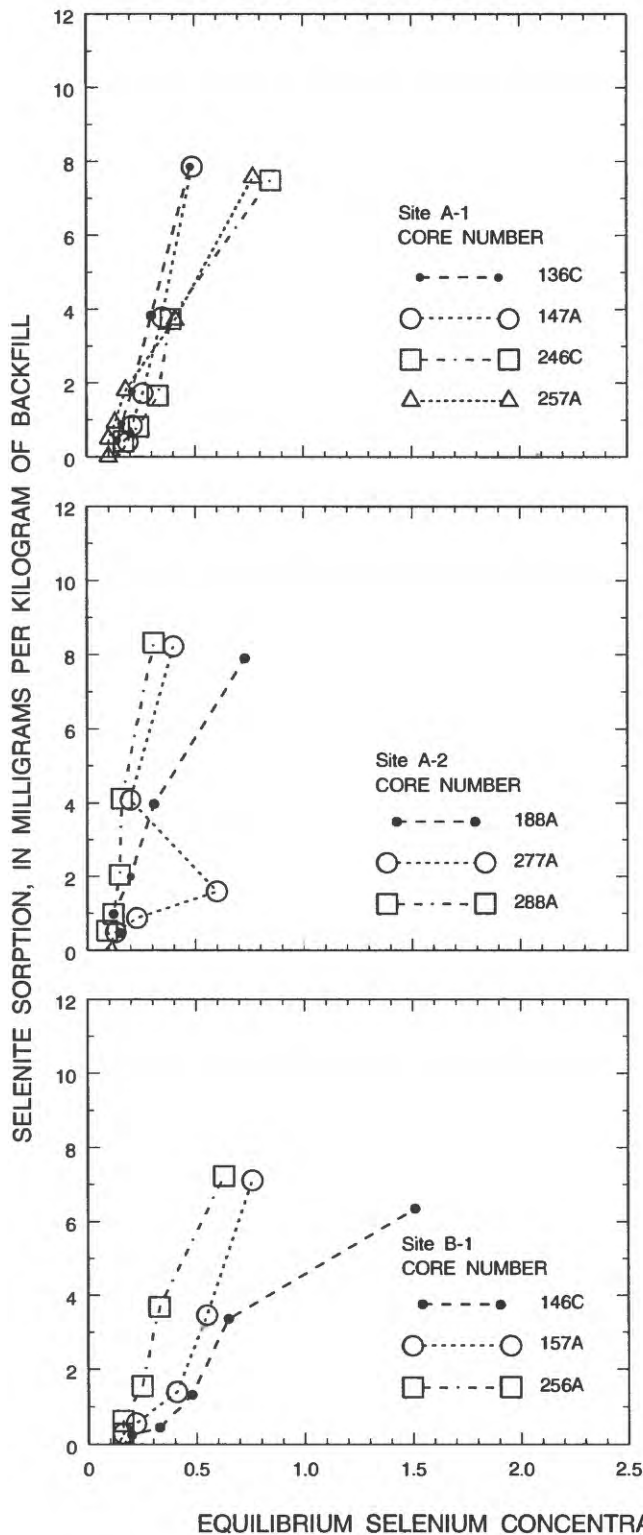


Figure 9. Selenite sorption as a function of equilibrium selenium concentrations of backfill-core sample solutions with hydrophobic and hydrophilic acids added to background solutions.

Table 12. Selenite sorption parameters and distribution coefficients determined from initial mass isotherms under different experimental conditions

[RBSP, reserve-backfill selenium pool; Kd, distribution coefficient; R², correlation coefficient]

Sample code (fig. 2)						
Site number	Backfill-core number	Slope	Intercept	RBSP	Kd	R ²
Experiment 1--Distilled-deionized water						
A-1	1 3 6 C	0.878	-0.028	0.231	143	0.9997
A-1	1 4 7 A	.871	-.130	1.01	135	.9994
A-1	2 4 6 C	.868	-.154	1.17	132	.9997
A-1	2 5 7 A	.918	-.099	1.21	224	.9998
A-2	1 8 8 A	.985	-.004	.301	1,340	.9999
A-2	2 7 7 A	.926	-.014	.191	249	.9999
A-2	2 8 8 A	.982	-.020	1.08	1,080	.9999
B-1	1 4 6 C	.864	-.184	1.36	127	.9989
B-1	1 5 7 A	.962	-.136	3.56	504	.9998
B-1	2 5 6 A	.980	-.127	6.26	966	.9999
Experiment 2--0.1 molar calcium chloride solution						
A-1	1 3 6 C	.907	-.106	1.15	196	.9996
A-1	1 4 7 A	.934	-.057	.865	283	.9989
A-1	2 4 6 C	.987	-.009	.737	1,570	.9999
A-1	2 5 7 A	.976	.001	-.055	804	.9999
A-2	1 8 8 A	.975	.004	-.143	791	.9999
A-2	2 7 7 A	.982	-.018	.988	1,090	.9999
A-2	2 8 8 A	.985	-.014	.910	1,290	.9999
B-1	1 4 6 C	.920	-.057	.710	229	.9999
B-1	1 5 7 A	.960	-.067	1.67	475	.9999
B-1	2 5 6 A	.979	-.092	4.29	912	.9999
Experiment 3--Hydrophobic acids added						
A-1	1 3 6 C	.956	-.117	2.67	437	.9999
A-1	1 4 7 A	.959	-.163	4.01	471	.9999
A-1	2 4 6 C	.917	-.127	1.52	220	.9997
A-1	2 5 7 A	.915	-.052	.607	215	.9999
A-2	1 8 8 A	.926	-.057	.766	250	.9998
A-2	2 7 7 A	.974	-.203	7.96	763	.9969
A-2	2 8 8 A	.978	-.099	4.40	873	.9999
B-1	1 4 6 C	.837	-.154	.940	102	.9988
B-1	1 5 7 A	.922	-.186	2.39	237	.9995
B-1	2 5 6 A	.938	-.122	1.95	301	.9999
Experiment 3--Hydrophilic acids added						
A-1	1 3 6 C	.942	-.725	12.6	327	.9959
A-1	1 4 7 A	.942	-.955	16.6	327	.9971
A-1	2 4 6 C	.983	-1.13	65.1	1,130	.9928
A-1	2 5 7 A	.957	-.928	21.4	442	.9999
B-1	1 4 6 C	.744	-.452	1.77	58	.9933
B-1	1 5 7 A	.822	-.374	2.10	92	.9988
B-1	2 5 6 A	.937	-.356	5.67	298	.9992

Results of the initial mass isotherm slope (0.744 to 0.987) and intercept values (-1.13 to 0.004) indicate that the backfill materials have a large retention capacity for selenite and that selenium generally is released from the backfill when background solutions containing little or no selenite are mixed with the backfill-core samples (table 12). Addition of calcium chloride to background solutions (experiment 2) increased the amount of selenite sorption, as demonstrated by generally greater slope values in the calcium chloride experiments compared to experiments containing only distilled-deionized water (experiment 1). Addition of hydrophobic acids to background solutions had only a minor effect on selenite sorption characteristics, except for the shallower backfill-core samples collected at site A-1. For these samples, sorption increased similar to the calcium chloride experiment, which may be a function of enhanced sorption due to cations associated with the hydrophobic acid solutions.

The greatest impact of 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 were determined along with small intercept values, whereas B-1 samples were found to have low slopes and intercept values. The differences between sites A-1 and B-1 indicate that hydrophilic acids may have a major role in reducing the retention of selenium by backfill materials by enhancing the desorption of indigenous selenium or by displacing selenium through competitive sorption.

Information derived from RBSP and Kd values also can be used in describing selenite sorption processes. Generally, RBSP values increased with backfill-core sample depth, indicative of greater amounts of selenium present in the backfill that could be readily exchanged by substances such as natural organic solutes. The RBSP values were generally larger in studies involving hydrophilic acids. Larger RBSP values indicate that greater amounts of selenium could be released by the addition of hydrophilic acid to backfill material. In addition, Kd values were generally greater in samples collected at greater depths from each of the backfill-core holes. A noticeable decrease in the Kd values was found in B-1 samples when comparing experimental results from studies involving distilled-deionized water or 0.1 molar calcium chloride background solutions to studies with additions of hydrophilic acid, further indicating that hydrophilic acids can affect selenite sorption.

Clay minerals have a potentially large selenium sorption capacity (Mott, 1978). Of further interest to this study was the effect clay minerals have on selenite

sorption. A simple linear regression was conducted on the selenium sorption isotherms to obtain slope values. The slope values were compared to the qualitative abundance of individual clay minerals found in the backfill-core samples. A positive correlation between the presence of clay minerals and selenite sorption was expected. However, data from this study were inconclusive. XRD analyses did not provide information to demonstrate that clay minerals had a role in selenite sorption. This could be a result of the type of XRD data collected. The method used for backfill-core sample preparation and the reporting format for the data make possible the identification of the presence of clay minerals, but not the quantity of clay minerals. Quantitative determination of small amounts of clay minerals from bulk samples using XRD analysis is difficult. X-ray intensities correlate positively with abundance of clay minerals. However, larger grains disrupt the alignment of the clay minerals and reduce the x-ray intensities. Different clay minerals tend to be affected differently, depending on their grain size. For example, smectites, often the finest grained clay minerals, seem to be affected most. A sample with poorly oriented clay particles will probably show illite and kaolinite but little smectite (J. Tribble, University of Hawaii, written commun., 1993). The correlation of selenite sorption isotherm slope values to clay mineral abundance requires accurate clay mineral data. Isolation of the clay mineral fraction and semi-quantitative XRD analysis of that fraction could provide the data necessary to better assess the role of clay minerals in selenite sorption.

EFFECT OF NATURAL ORGANIC SOLUTES ON PRECIPITATION/DISSOLUTION PROCESSES OF SELENIUM

Solubility and mobility of selenium in coal-mine backfill environments are controlled by several processes, including precipitation/dissolution reactions. In general, coal-mine backfill materials are more reactive chemically when compared to soil because backfill materials were disturbed and exposed to oxidizing environments during surface-mining processes (Neuman and others, 1987). Oxidizing conditions may favor the dissolution of more soluble selenium minerals and precipitation of less soluble selenium minerals. Naftz and Rice (1989) indicated that the oxidation of selenide containing organic matter, and the conversion of insoluble selenides to soluble selenite and selenate could increase dissolved selenium concen-

tration in ground water. Additionally, the oxidation of sulfides containing selenium could be a source for selenium in the ground water from coal-mine backfill materials. Investigations reported in the literature involving the precipitation/dissolution reactions of selenium in soil include Elrashidi and others (1987); Masscheleyn and others (1990); and Reddy and Gloss (1993). Studies by Balistreri and Chao (1987), Naftz and Rice (1989), Abrams and others (1990), and Fio and Fujii (1990) have indicated that natural organic solutes are important to the mobility of selenium in soil and coal-mine backfill materials.

The precipitation/dissolution study consisted of the following three tasks: a preliminary determination of equilibrium time, final precipitation/dissolution experiments, and geochemical modeling. The geochemical modeling analyses were performed using the results from the precipitation/dissolution experiments.

Materials and Methods

A preliminary study to determine equilibrium time was conducted on 3 backfill-core samples, and final precipitation/dissolution experiments were conducted on 17 backfill-core samples using 3 backfill-core samples from each core hole. An exception was site B-1, core hole 1, where only two backfill-core samples were used because insufficient sample was available. The backfill-core samples selected for precipitation/dissolution experiments are identified in table 1. Backfill-core samples were air-dried, ground, and sieved through 10-mm mesh screens. Twenty-five grams of each sample, in duplicates, were reacted with 75 mL of distilled-deionized water on a mechanical-reciprocal shaker (200 cycles per minute at $25 \pm 2^\circ\text{C}$).

After reacting for 1, 7, 14, 21, and 28 days, sample suspensions were filtered under argon atmosphere using 0.4- μm Millipore filters. Clear extracts were divided into two subsamples. One subsample was left unacidified and the other subsample was acidified to $\text{pH } 3 \pm 1$ with 1.0 molar nitric acid. Unacidified samples in both preliminary and final experiments were analyzed for pH, Eh, and sulfate. The pH was measured using an Orion combination electrode. The Eh was measured using an Orion platinum electrode with a Ag/AgCl_2 reference electrode. In the preliminary experiment, acidified samples were analyzed for calcium, magnesium, iron, and manganese using ICP-OES. In the final experiment, acidified samples were analyzed for calcium, magnesium, aluminum, iron,

manganese, cadmium, copper, lead, molybdenum, and boron using ICP-OES. Also in the final experiment, concentrations of sodium and potassium were measured using AES. Total selenium was measured using AAS-HG. Concentrations of sulfate, chloride, fluoride, and nitrate were measured using a Dionex 2000i Ion Chromatography (IC) system. DOC was measured using a Shimadzu TOC-5000 carbon analyzer. Carbonate was analyzed in the final experiment by titration.

Data from the preliminary experiment (table 13) were plotted to determine the equilibrium time to be used for the remaining precipitation/dissolution study. The results suggested the concentration of most of the elements were about the same after 21 and 28 days, indicating that a 28-day reaction period would give uniform results. The final precipitation/dissolution experiment was conducted for an additional 17 backfill-core samples, using a 28-day reaction period.

A geochemical speciation model, GEOCHEM (Sposito and Mattigod, 1980), was used to calculate ion activities. GEOCHEM has a large thermodynamic data base that contains equilibrium constants for several reactions. GEOCHEM uses total concentrations of elements, pH, and Eh in aqueous solutions as input. Using the thermodynamic data base, GEOCHEM speciates total concentration of an element into the possible solution species. GEOCHEM calculates the ion activities of the solution species, then, using the ion activities, computes the ion activity products (IAPs) and compares solubility products (K_{sp}) to calculate saturation indexes (SI). The SI is a measure of the equilibrium state used to determine potential solid phases controlling the concentration of the species:

$$\text{Where:} \quad \text{SI} = \log (\text{IAP}/K_{\text{sp}}) \quad (2)$$

$$\text{SI} = 0 \text{ for equilibrium}$$

$$\text{SI} < 0 \text{ for undersaturation}$$

$$\text{SI} > 0 \text{ for oversaturation}$$

Assumptions were made that an SI within ± 0.50 log unit of the solid phase value represented equilibrium, and that the solid phase was a probable control on the concentrations of ions involved. The variation within that range is accounted for by the uncertainty of IAP and K_{sp} measurements in the chemical literature (Stumm and Morgan, 1981).

Table 13. Analytical results for water extracts from preliminary precipitation/dissolution experiments using three backfill-core samples, Powder River Basin, Wyoming

[mg/L, milligrams per liter; mV, millivolts]

Sample code (fig. 2)		Reaction time (days)	pH (standard units)	Eh (mV)	Calcium (mg/L)	Magne- sium (mg/L)	Iron (mg/L)	Manga- nese (mg/L)	Selenium (mg/L)	Sulfate (mg/L)	Dissolved organic carbon (mg/L)
Site number	Backfill- core number										
Site A-1, Core hole 2											
A-1	2 4 6 A	1	7.0	232	317	225	0.045	0.030	0.173	2,756	29.76
A-1	2 4 6 A	7	8.2	247	308	410	.050	.035	.281	3,010	28.64
A-1	2 4 6 A	14	8.3	185	328	422	.150	.045	.264	2,920	32.04
A-1	2 4 6 A	21	8.5	210	348	468	.030	.040	.288	3,140	41.41
A-1	2 4 6 A	28	8.5	219	336	466	.030	.060	.291	3,007	33.19
A-1	2 4 6 C	1	7.6	260	79	200	.010	.015	.153	1,153	37.70
A-1	2 4 6 C	7	8.5	190	78	181	.015	.020	.215	1,161	37.78
A-1	2 4 6 C	14	8.5	198	190	316	.066	.030	.285	1,554	57.76
A-1	2 4 6 C	21	8.6	180	110	268	.025	.025	.289	1,510	39.64
A-1	2 4 6 C	28	8.4	188	115	280	.020	.030	.295	1,459	42.63
A-1	2 5 7 A	1	7.0	217	469	383	.040	.030	.113	2,750	31.69
A-1	2 5 7 A	7	8.3	211	323	420	.125	.040	.163	3,019	34.66
A-1	2 5 7 A	14	8.6	250	406	444	.030	.030	.155	2,780	36.21
A-1	2 5 7 A	21	8.6	208	292	386	.030	.030	.172	2,830	42.48
A-1	2 5 7 A	28	8.2	210	308	383	.030	.045	.173	2,849	40.59

GEOCHEM requires information about specific components of DOC. The determination of the concentrations of the different organic compounds is a difficult task (Drever, 1988). For this study, the total DOC was assumed equal to the sum of the humic and fulvic acids. Ten-mL samples from each of the three wells were acidified to less than pH 2. After 24 hours the acidified samples were filtered through 0.45- μ m Millipore filters, and total DOC was measured in the filtrate. Because humic acids are insoluble at pH 2 and fulvic acids are soluble at a wide pH range (Aiken and others, 1985), the total DOC measured in the filtrate was assumed to represent only fulvic acids. Total DOC in the filtrate of the acidified samples was similar to the total DOC in the original samples before acidification, suggesting that DOC in the samples was dominated by fulvic acids.

The DOC in the solution can affect the solubility of selenium by complexing with metals (such as manganese, magnesium, iron, and calcium) that usually

complex with selenium, thereby reducing their free-metal concentrations in the solution, and reducing the concentration available for selenium complexation. The effect of the DOC on selenium solubility was evaluated by: (1) speciating and calculating IAPs without considering DOC as input to the model and (2) speciating and calculating IAPs with DOC as input to the model (Mattigod and Sposito, 1979).

Results and Discussion

Analytical results obtained for 17 backfill-core samples for the precipitation/dissolution experiment are summarized in table 14. The solution pH values ranged from 3.9 to 7.9 and the Eh ranged from 222 to 282, indicating that the samples were moderately oxidized. The selenium concentration ranged from less than 2 to 200 μ g/L. The DOC concentrations ranged from 15 to 100 mg/L.

The GEOCHEM chemical speciation results calculated by the model for the 17 backfill-core samples are summarized in table 15. The DOC had a small effect on selenium speciation. Free-ion activity of all cations decreased and the activities of the anions increased with DOC addition. The decrease in cation activity could be due to the complexation of cations with DOC, which decreases the activities of the cations. At the same time, the available cations for complexing with the original anions in solution (all anions other than fulvic acid) decreased, leaving more anions as free ligands. Free activities of manganese and lead were affected more than the rest of the cations by the addition of DOC. The cation activities of Mg^{2+} and Fe^{3+} were the least affected by DOC. The DOC had a small effect on the activity of selenite, which could be because initial concentrations of selenite were small compared to the initial concentrations of its major complexing cations, calcium and magnesium. Chemical speciation of backfill-core samples collected from all core-hole depths was similar.

GEOCHEM chemical speciation also suggested that backfill-core sample precipitation/dissolution extracts were dominated by the MgSeO_3^0 ion pair (55 to 90 percent of total selenium concentration) followed by CaSeO_3^0 , and SeO_3^{2-} species. In low pH (3.9 to 6.8) extracts, the dominant selenite ion pairs were MgSeO_3^0 ion pair (55 percent of total selenium concentration), followed by HSeO_3^- (25 percent of total selenium concentration) and CaSeO_3^0 (20 percent of total selenium concentration). The presence of ion pairs in coal-mine backfill materials may represent a potential for leaching of selenium, because neutral ion pairs may not be sorbed onto oxides and clay minerals as a charged species, and therefore can be readily leached (Reddy and Gloss, 1993).

The IAPs of different selenium solid phases (for example, CuSe , MgSeO_3 , MnSeO_3 , and ZnSeO_3) in water extracts were compared with K_{sp} s to examine the possibility that one of these solid phases may be controlling the selenium concentrations in water extracts (table 16). Results indicated that IAPs of these solid phases were highly undersaturated and were not controlling solution selenium concentrations. However, in some samples selenium concentrations appeared to be controlled by CuSe . The results suggested that as depth increased, redox potential (pe + pH) decreased, and selenium concentrations probably reached saturation with respect to CuSe . It is possible that in subsurface environments, oxygen concentrations will be low and

the resulting anaerobic conditions would favor the precipitation of reduced selenium solid phases such as CuSe (Elrashidi and others, 1987; Masscheleyn and others, 1990; Reddy and Gloss, 1993).

EFFECT OF OXIDATION-REDUCTION PROCESSES ON SELENIUM SPECIATION

The redox status of the backfill determines selenium speciation in ground water, and redox is an important parameter in assessing the potential selenium hazard associated with mining activities. Although general trends for redox conditions controlling selenium speciation have been observed, experimental evidence establishing specific redox parameters controlling selenium speciation is lacking. Geering and others (1968) and Elrashidi and others (1987) developed theoretical solubility and redox criteria for selenium in soil. Using data from Elrashidi and others (1987), predictions of soluble selenium speciation can be made on the basis of pe + pH compared to the selenium mole fraction. But owing to uncertainty in the measurement of soil redox status, as well as the application of Eh measurements, experimental evidence is lacking.

Thermodynamic predictions also do not take into account the rates of transformations between various selenium valence states. The reduction of selenate to selenite and the oxidation of selenite to selenate have been reported to be very slow (Cary and Allaway, 1969). The difficulty in reducing selenate to selenite is demonstrated by the fact that most methods for selenium analysis recommend a minimum concentration of 6 molar hydrochloric acid and heating at 85 °C for 10 to 20 minutes to reduce selenate to selenite (Blaylock and James, 1993). Reduction of selenite to elemental selenium occurs almost immediately, however, with the addition of a reducing agent such as ascorbic acid (Blaylock and James, 1994). No decrease in selenate concentrations was observed with the addition of ascorbic acid.

Traditionally, soil redox status has been measured by immersing a platinum electrode in combination with a calomel or other reference electrode in a soil suspension or solution. The measured Eh or redox potential is obtained by subtracting the potential of the reference electrode. The validity of employing measured redox potentials to predict selenium speciation has been questioned. Runnells and Lindberg (1990, p. 214) concluded that the platinum electrode does not

Table 14. Analytical results for water extracts from final precipitation/

[mg/L, milligrams per;

Sample code (fig. 2)		pH (standard units)	Eh (milli- volts)	Calcium (mg/L)	Magne- sium (mg/L)	Sodium (mg/L)	Potas- sium (mg/L)	Alumi- num (mg/L)	Iron (mg/L)	Manga- nese (mg/L)
Site number	Backfill- core number									
Site A-1,										
A-1	1 3 6 A	7.2	238	487	270	47.0	19.3	0.022	0.010	0.130
A-1	1 3 6 C	7.4	243	243	281	80.9	18.5	.079	.072	.072
A-1	1 5 8 A	7.6	235	551	347	162	29.1	1.18	.824	1.24
Site A-1,										
A-1	2 4 6 A	7.1	261	254	264	93.9	13.1	.113	.026	.019
A-1	2 4 6 C	7.9	232	77	153	72.1	13.7	.015	.021	.048
A-1	2 5 7 A	7.2	222	164	215	95.9	12.6	.032	.051	.010
Site A-2,										
A-2	1 7 7 A	6.3	266	228	183	40.9	27.0	.403	1.98	10.8
A-2	1 8 8 A	6.1	264	214	147	35.0	25.3	.181	.309	8.7
A-2	1 8 8 B	6.9	245	361	282	45.0	28.2	.086	.892	1.0
Site A-2,										
A-2	2 7 7 A	5.3	266	399	232	26.5	24.7	.442	.508	14.8
A-2	2 7 7 C	3.9	277	516	271	34.8	24.4	16.0	.583	11.6
A-2	2 8 8 A	6.8	282	279	155	34.6	15.8	.103	.128	1.32
Site B-1,										
B-1	1 4 6 C	7.0	244	343	159	88.6	25.0	.099	<.001	.620
B-1	1 5 7 A	7.5	230	611	190	95.9	21.8	.039	.005	.292
Site B-1,										
B-1	2 5 6 A	7.3	238	593	205	116	25.3	.152	.082	.039
B-1	2 5 6 C	7.6	242	657	252	121	29.6	.016	<.001	.587
B-1	2 6 7 A	7.0	237	351	431	241	26.9	1.19	.679	.069

respond to changes in the ratios of selenite to selenate and thus Eh measurements do not reflect selenium speciation in natural water. This does not, however, mean that selenium does not respond to redox conditions controlled by redox couples present in the water or soil system.

Bartlett and James (1993) described caveats with regard to using the platinum electrode to obtain meaningful redox relations. They stated that because of interferences from dissolved oxygen, irreversibility of redox couples, mixed potentials, and pH effects, the use of the platinum electrode to accurately predict the redox status of a soil may be unreliable. Sposito (1989) suggested assigning the redox status of soil corresponding to ranges controlled by oxygen, nitrogen, manganese-iron, and sulfur couples. Although not

necessarily quantitative, the ranges may be more representative of the soil redox chemistry. However, determining the redox status based on existing speciation of ions in solution also is difficult and unreliable. Many of the redox couple components are solid phases, difficult to quantify and even more difficult to assign an activity. Measuring valence states of ions in solution presents equally challenging aspects. Nevertheless, attempts to quantify and assign numerical values on the basis of measured redox potentials continue, in hopes of establishing a means to predict speciation of soluble components, often with good results.

Masscheleyn and others (1990) constructed an incubation apparatus to determine critical Eh and pH levels at which selenium transformations occur. The desired sample Eh was maintained by adding air to

Cadmi- um (mg/L)	Copper (mg/L)	Lead (mg/L)	Carbon- ate (mg/L)	Molyb- denum (mg/L)	Sele- nium (mg/L)	Boron (mg/L)	Sulfate (mg/L)	Fluo- ride (mg/L)	Chlo- ride (mg/L)	Nitrate, as nitrogen (mg/L)	Dissolved organic carbon (mg/L)
Core hole 1											
0.016	0.021	0.013	3.6	0.017	26	0.209	2,480	4.2	18	48	30
<.001	.029	.012	3.8	.027	68	.096	2,630	4.3	19	51	37
<.001	.063	.033	3.7	.101	<2	.805	3,800	4.6	14	61	18
Core hole 2											
<.001	.033	.014	4.0	.014	53	.097	2,180	3.9	30	45	25
<.001	.040	.015	3.6	.009	45	.181	1,050	1.2	19	32	31
<.001	.031	.012	4.0	.010	36	.107	1,750	3.7	26	37	15
Core hole 1											
.123	.104	.018	4.6	.005	44	.159	2,080	2.9	8.6	40	26
.141	.048	.016	4.9	.024	20	.206	1,610	1.3	6.8	36	39
.020	.023	.011	4.9	.100	11	.132	2,600	4.1	8.9	47	38
Core hole 2											
.019	.021	.013	5.7	.037	5	.135	2,450	3.2	4.8	31	19
.047	.059	.024	5.6	.018	5	.414	2,940	4.2	4.5	15	22
<.001	.032	.012	4.6	.025	13	.233	1,680	2.1	4.9	28	28
Core hole 1											
<.001	.052	.021	3.6	.024	91	.407	2,820	6.8	11	166	94
<.001	.031	.013	3.7	.024	36	.508	2,870	5.9	7.3	73	53
Core hole 2											
<.001	.044	.014	4.0	.021	39	.128	2,910	4.4	7.4	48	85
<.001	.038	.019	3.6	.020	72	.162	3,100	4.2	9.1	50	100
<.001	.069	.022	3.8	.072	200	.140	3,800	5.6	53	53	43

increase the Eh and allowing anaerobic conditions to cause a decrease in Eh. The pH was maintained by automatic additions of sodium hydroxide or hydrochloric acid. Masscheleyn and others (1990) reported oxidation of selenide to selenite at $pe + pH = 7.9$ after 2 weeks with a concurrent decrease in soluble iron and an increase in sulfate concentrations. The transformation of selenite to selenate was reported to occur after 2 days at $pe + pH = 11.0$. In another study with a similar system (Masscheleyn and others, 1991), selenite was determined to be the dominant selenium species present at Eh = 0 and 200 mV, independent of soil pH (between pH 5.0 and 7.5). Decreasing the Eh to -200 mV resulted in the disappearance of selenate and a decrease in selenite concentration.

Coal-mine backfill is heterogeneous and contains large concentrations of soluble salts, particularly sulfate. Selenium redox transformations are often reported to occur at measured redox potentials similar to those for sulfur. 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 selenide.

Although general trends for redox conditions controlling selenium speciation have been observed, experimental evidence establishing specific redox parameters controlling selenium speciation is lacking. Thus, the objective of this part of the study was to develop a redox controlling apparatus to control and

Table 15. Calculated chemical speciation of water extracts from precipitation/dissolution

[Units are in negative log, mole per liter; mV, millivolts;

Sample code (fig. 2)				Ca ²⁺		Mg ²⁺		Fe ³⁺		Mn ²⁺	
Site number	Backfill- core number	pH (standard units)	Eh (mV)	Without DOC	With DOC	Without DOC	With DOC	Without DOC	With DOC	Without DOC	With DOC
Site A-1,											
A-1	1 3 6 A	7.2	238	2.12	2.19	2.11	2.15	17.4	17.4	5.83	6.15
A-1	1 3 6 C	7.4	243	2.44	2.58	2.13	2.19	15.8	15.7	6.10	6.61
A-1	1 5 8 A	7.6	235	2.05	2.14	1.98	2.02	15.8	15.7	4.84	5.18
Site A-1,											
A-1	2 4 6 A	7.1	261	2.39	2.49	2.12	2.16	15.4	15.4	6.65	7.03
A-1	2 4 6 C	7.9	232	2.88	3.12	2.33	2.43	18.7	18.7	6.22	6.97
A-1	2 5 7 A	7.2	222	2.58	2.66	2.21	2.24	15.0	15.0	6.93	7.27
Site A-2,											
A-2	1 7 7 A	6.3	266	2.41	2.53	2.23	2.28	13.0	13.0	5.09	5.53
A-2	1 8 8 A	6.1	264	2.46	2.65	2.37	2.46	10.3	10.3	3.99	4.62
A-2	1 8 8 B	6.9	245	2.17	2.23	2.07	2.10	12.9	13.0	4.87	5.11
Site A-2,											
A-2	2 7 7 A	5.3	266	2.21	2.26	2.19	2.21	9.68	9.68	3.77	4.00
A-2	2 7 7 C	3.9	277	2.11	2.16	2.13	2.15	6.91	6.92	3.90	4.12
A-2	2 8 8 A	6.8	282	2.33	2.45	2.34	2.39	14.4	14.4	4.79	5.24
Site B-1,											
B-1	1 4 6 C	7.0	244	2.59	2.67	2.47	2.56	19.3	19.3	5.31	6.14
B-1	1 5 7 A	7.5	230	1.97	2.16	2.21	2.35	17.9	17.9	5.43	5.96
Site B-1,											
B-1	2 5 6 A	7.3	238	2.04	2.25	2.25	2.34	16.3	16.4	6.36	7.03
B-1	2 5 6 C	7.6	242	2.01	2.23	2.17	2.27	21.2	21.2	5.19	5.88
B-1	2 6 7 A	7.0	237	2.27	2.4	1.93	1.99	14.2	14.3	6.11	6.56

maintain a given redox level in soil and water samples to quantify the effects of redox conditions on the speciation and solubility of selenium.

Materials and Methods

A redox controlling apparatus was constructed to control redox potential (Eh) and pH in water and backfill-core sample suspensions. The apparatus included a sample chamber (approximately 1.5 L volume) constructed from borosilicate glass with a large opening at the top; a small opening at the bottom; and two ports on the side, one for sampling and one for the platinum electrode. The pH and reference electrodes, the exhaust vent, and the gas and circulation tubing were inserted through holes drilled in a silicone

stopper placed in the top of the apparatus (fig. 10). The pH, platinum, and reference electrodes were calibrated for accuracy using standard solutions. The sample in the redox controlling apparatus was circulated using a peristaltic pump. Gas mixtures of hydrogen (3 percent hydrogen, 5 percent carbon dioxide, and 92 percent argon) or oxygen (95 percent oxygen and 5 percent carbon dioxide) were bubbled in the apparatus to control pH (carbon dioxide) and Eh (hydrogen and oxygen) based on the setting of the control box connected to the Eh meter. Hydrogen (to reduce) and oxygen (to oxidize) gas tanks were connected to solenoid valves controlling gas flow for oxidation-reduction reactions. The purpose of the carbon dioxide in the gas mixtures was to stabilize the pH of the

DOC, dissolved organic carbon; --, indicates data unavailable]

Pb ²⁺		SeO ₃ ²⁻		H ₂ SeO ₃		CaSeO ₃		MgSeO ₃	
Without DOC	With DOC	Without DOC	With DOC	Without DOC	With DOC	Without DOC	With DOC	Without DOC	With DOC
Core hole 1									
7.66	8.02	8.91	8.88	9.31	9.27	7.61	7.65	6.81	6.81
7.7	8.26	8.44	8.39	8.79	8.73	7.48	7.55	6.36	6.36
8.27	8.62	10.1	10.1	10.81	10.76	8.93	8.89	8.06	8.06
Core hole 2									
7.57	8.00	8.59	8.56	8.77	8.73	7.55	7.60	6.48	6.47
7.71	8.38	8.59	8.51	9.46	9.37	7.87	8.01	6.52	6.52
7.65	8.04	8.74	8.72	8.84	8.82	7.81	7.86	6.64	6.64
Core hole 1									
7.43	7.96	12.1	12.1	11.95	11.91	11.0	11.1	10.1	10.1
7.47	8.22	9.39	9.33	8	7.94	8.33	8.43	7.45	7.44
7.65	7.95	9.24	9.23	9.28	9.27	8.09	8.12	7.19	7.19
Core hole 2									
7.59	7.89	9.84	9.83	8.34	8.33	8.63	8.66	7.82	7.82
7.35	7.62	6.91	6.92	8.41	8.4	10.1	10.1	9.31	9.32
7.59	8.12	9.39	9.35	9.5	9.45	8.22	8.28	7.43	7.42
Core hole 1									
--	8.48	7.87	7.93	7.94	7.92	7.25	7.32	6.70	6.70
--	8.18	8.51	8.57	9.3	9.1	7.04	7.19	6.28	6.28
7.68	8.37	8.60	8.50	9.26	9.15	7.26	7.36	6.67	6.65
Core hole 2									
7.54	8.25	8.40	8.29	8.99	8.87	7.03	7.14	6.40	6.38
7.41	7.90	7.98	7.98	8.24	8.18	7.03	7.14	5.88	6.38

samples. The redox controlling apparatus was calibrated to maintain the desired measured Eh (± 15 mV) of samples between +500 and -500 mV (table 17).

The control box recorded the readings from platinum and reference electrodes (in mV) and compared the readings with the minimum and maximum values set on the hydrogen and oxygen dials. If the sample mV reading was below the value set on the dials, the relay switched on oxygen gas to increase the mV reading to the set value. Similarly, if the sample mV reading was above the set value, the relay switched on hydrogen gas, driving down the mV reading to the set value. The redox controlling apparatus was tested and calibrated for distilled-deionized water and backfill-core samples amended with 0.5 g platinum-coated carbon black. The apparatus controlled redox

potential from +500 to -500 mV to an accuracy of ± 15 mV. This accuracy appeared to be slightly different when the apparatus was used to control highly oxidized or reduced environments. However, a plot of calibration data in table 17 is almost linear. The time required for obtaining stable mV readings (± 15 mV) ranged from 10 to 45 minutes. From +200 to -200 mV readings stabilized within 10 to 20 minutes. Longer time intervals (30-45 minutes) were required to reach a stable reading above +200 and below -200 mV.

Experiments to determine the response of selenium speciation to changes in redox status were conducted using distilled-deionized water, tap water, ground water, and backfill-core sample suspensions amended with selenite and selenate. A 1.2-L sample was used for water samples and 1 L distilled-deionized

Table 16. Potential solid phases controlling dissolved selenium

[Units are log mole per liter; K_{sp} , solubility product;

Sample code (fig. 2)		CaSeO ₃			MgSeO ₃			Fe ₂ (SeO ₃) ₃			MnSeO ₃		
Site number	Backfill- core number	K_{sp}	IAP	SI	K_{sp}	IAP	SI	K_{sp}	IAP	SI	K_{sp}	IAP	SI
Site A-1,													
A-1	1 3 6 A	-5.4	-11.8	-6.4	-5.4	-11.8	-6.4	-33	-64.3	-31.3	-7.3	-15.7	-8.4
A-1	1 3 6 C	-5.4	-11.7	-6.3	-5.4	-11.3	-5.9	-33	-59.5	-26.5	-7.3	-15.8	-8.5
A-1	1 5 8 A	-5.4	-13.1	-7.7	-5.4	-12.9	-7.5	-33	-64.8	-31.8	-7.3	-16.1	-8.8
Site A-1,													
A-1	2 4 6 A	-5.4	-11.7	-6.3	-5.4	-11.4	-6.0	-33	-59.1	-26.1	-7.3	-16.0	-8.7
A-1	2 4 6 C	-5.4	-12.1	-6.7	-5.4	-11.5	-6.1	-33	-65.1	-32.1	-7.3	-15.4	-8.1
A-1	2 5 7 A	-5.4	-12.1	-6.7	-5.4	-11.6	-6.2	-33	-58.6	-25.6	-7.3	-16.7	-9.4
Site A-2,													
A-2	1 7 7 A	-5.4	-15.2	-9.8	-5.4	-15.0	-9.6	-33	-64.7	-31.7	-7.3	-17.9	-10.6
A-2	1 8 8 A	-5.4	-12.5	-7.1	-5.4	-12.4	-7.0	-33	-51.0	-18.0	-7.3	-14.0	-6.7
A-2	1 8 8 B	-5.4	-12.2	-6.8	-5.4	-12.1	-6.7	-33	-56.7	-23.7	-7.3	-14.9	-7.6
Site A-2,													
A-2	2 7 7 A	-5.4	-12.8	-7.4	-5.4	-12.8	-7.4	-33	-51.6	-18.6	-7.3	-14.6	-7.3
A-2	2 7 7 C	-5.4	-14.3	-8.9	-5.4	-14.3	-8.9	-33	-50.9	-17.9	-7.3	-16.3	-9.0
A-2	2 8 8 A	-5.4	-14.3	-8.9	-5.4	-14.1	-8.7	-33	-59.3	-26.9	-7.3	-16.3	-9.0
Site B-1,													
B-1	1 4 6 C	-5.4	-11.4	-6.0	-5.4	-11.3	-5.9	-33	-65.1	-32.1	-7.3	-14.8	-7.5
B-1	1 5 7 A	-5.4	-11.5	-6.1	-5.4	-11.7	-6.3	-33	-64.4	-31.4	-7.3	-15.3	-8.0
Site B-1,													
B-1	2 5 6 A	-5.4	-11.4	-6.0	-5.4	-11.6	-6.2	-33	-61.2	-28.2	-7.3	-15.8	-8.5
B-1	2 5 6 C	-5.4	-11.2	-5.8	-5.4	-11.4	-6.0	-33	-70.3	-37.3	-7.3	-14.4	-7.1
B-1	2 6 7 A	-5.4	-11.2	-5.8	-5.4	-10.8	-5.4	-33	-55.8	-22.8	-7.3	-15.4	-8.1

water with the addition of 250 g backfill-core sample was used for backfill-core samples. All samples were amended with 0.5 g platinum-coated carbon black to improve the response of the electrode. Toluene was added to prevent microbial growth. Water and backfill-core samples were amended with as much as 10 mg/L selenite and 10 mg/L selenate. Preliminary experiments with standards and tap water were equilibrated at a given redox level for 6 hours. Experiments with ground-water and backfill-core samples were equilibrated for 72 hours at a given redox level. Samples were withdrawn from the apparatus with a syringe and immediately analyzed for selenate, selenite, fluoride, chloride, nitrite, nitrate, and sulfate by IC, using manual injections through a 0.2- μ m filter (Gelman Ion Chromatography Acrodisc), without exposure to the

atmosphere. Analysis was conducted with a Dionex 2000i IC equipped with a conductivity detector, AI-45 software, Dionex AG% guard column, and AS4A-SC separator column using a 1.8/1.7 mM Na₂CO₃/NaHO₃ eluent.

Results and Discussion

The redox controlling apparatus was successful in controlling the redox status of the samples at a given measured Eh value. The addition of 5-percent carbon dioxide to the gas mixture maintained a constant pH 5.0 \pm 0.1 in the water samples. The pH of the backfill-core samples also remained constant, but was affected by the original pH of the backfill-core material. The backfill-core samples were also balanced against Eh

in backfill-core samples, Powder River Basin, Wyoming

IAP, ion activity product; SI, saturation index]

ZnSeO ₃			CuSe			MnSe			Cu ₂ Se		
K _{sp}	IAP	SI	K _{sp}	IAP	SI	K _{sp}	IAP	SI	K _{sp}	IAP	SI
Core hole 1											
-7.7	-17.3	-9.6	-48.1	-44.5	3.6	-11.5	-45.6	-34.1	-60.8	-52.3	8.5
-7.7	-19.7	-12.0	-48.1	-44.3	3.8	-11.5	-46.2	-34.7	-60.8	-52.2	8.7
-7.7	-17.4	-9.7	-48.1	-47.0	1.1	-11.5	-47.9	-36.4	-60.8	-54.5	6.3
Core hole 2											
-7.7	-16.0	-8.3	-48.1	-45.5	2.6	-11.5	-48.2	-36.7	-60.8	-53.7	7.1
-7.7	-19.4	-11.7	-48.1	-48.2	-1	-11.5	-50.6	-39.1	-60.8	-56.0	4.8
-7.7	-16.6	-8.9	-48.1	-42.3	5.8	-11.5	-44.3	-32.8	-60.8	-50.2	10.6
Core hole 1											
-7.7	-19.2	-11.5	-48.1	-52.9	-4.8	-11.5	-50.9	-39.4	-60.8	-65.2	-4.4
-7.7	-15.6	-7.9	-48.1	-37.0	11.1	-11.5	-37.5	-26.0	-60.8	-45.0	15.8
-7.7	-16.5	-8.8	-48.1	-43.0	5.1	-11.5	-43.3	-31.8	-60.8	-50.9	9.9
Core hole 2											
-7.7	-16.2	-8.5	-48.1	-37.6	10.5	-11.5	-37.4	-25.9	-60.8	-46.1	14.7
-7.7	-16.8	-9.1	-48.1	-30.9	17.2	-11.5	-31.4	-19.9	-60.8	-39.1	21.7
-7.7	-16.8	-9.1	-48.1	-47.2	.9	-11.5	-48.5	-37.0	-60.8	-55.7	5.2
Core hole 1											
-7.7	-19.6	-11.9	-48.1	-42.2	5.9	-11.5	-44.0	-33.0	-60.8	-49.9	10.9
-7.7	-16.6	-8.9	-48.1	-45.2	2.9	-11.5	-46.5	-35.0	-60.8	-53.0	7.9
Core hole 2											
-7.7	-15.9	-8.2	-48.1	-45.3	2.8	-11.5	-47.7	-36.2	-60.8	-52.7	8.1
-7.7	-16.2	-8.5	-48.1	-45.3	2.9	-11.5	-46.5	-35.0	-60.8	-52.9	7.9
-7.7	-15.8	-8.1	-48.1	-42.7	5.5	-11.5	-44.8	-33.3	-60.8	-50.3	10.5

changes imposed by the addition of hydrogen and oxygen, indicated by the longer times required for the Eh to stabilize at a particular setting.

The response of selenite and selenate in water samples to the imposed redox conditions of the redox controlling apparatus differed from thermodynamic predictions of Elrashidi and others (1987). As stated previously, the rates of selenium redox transformations have been reported to be "slow." This study focused mainly on short equilibration periods; thus, the non-occurrence of some of the predicted redox transformations could be due to a lack of equilibrium conditions in the redox controlling apparatus.

Oxidation of selenite to selenate was not observed in any of the samples at pe + pH of about 18.

Reduction of selenate to selenite in the water samples also was not observed in a pe + pH range from 0 to 17. Reduction of selenite in solution in the water samples occurred much more readily than reduction of selenate. Selenite in the tap-water sample gradually decreased when pe + pH was decreased from about 18 to 12 and decreased sharply when pe + pH was decreased from 6.0 to 4.5 (fig. 11). The ground-water sample showed results similar to the tap water sample with only a slight decrease in soluble selenite until pe + pH = 6 (fig. 12). Selenate concentrations in the backfill-core sample suspension, however, decreased initially at pe + pH = 12.7 and had decreased by over 90 percent at pe + pH = 3.2 (table 18). Selenite in the soil suspension was sorbed by the soil and removed from solution; therefore, speciation changes due to redox could not be determined.

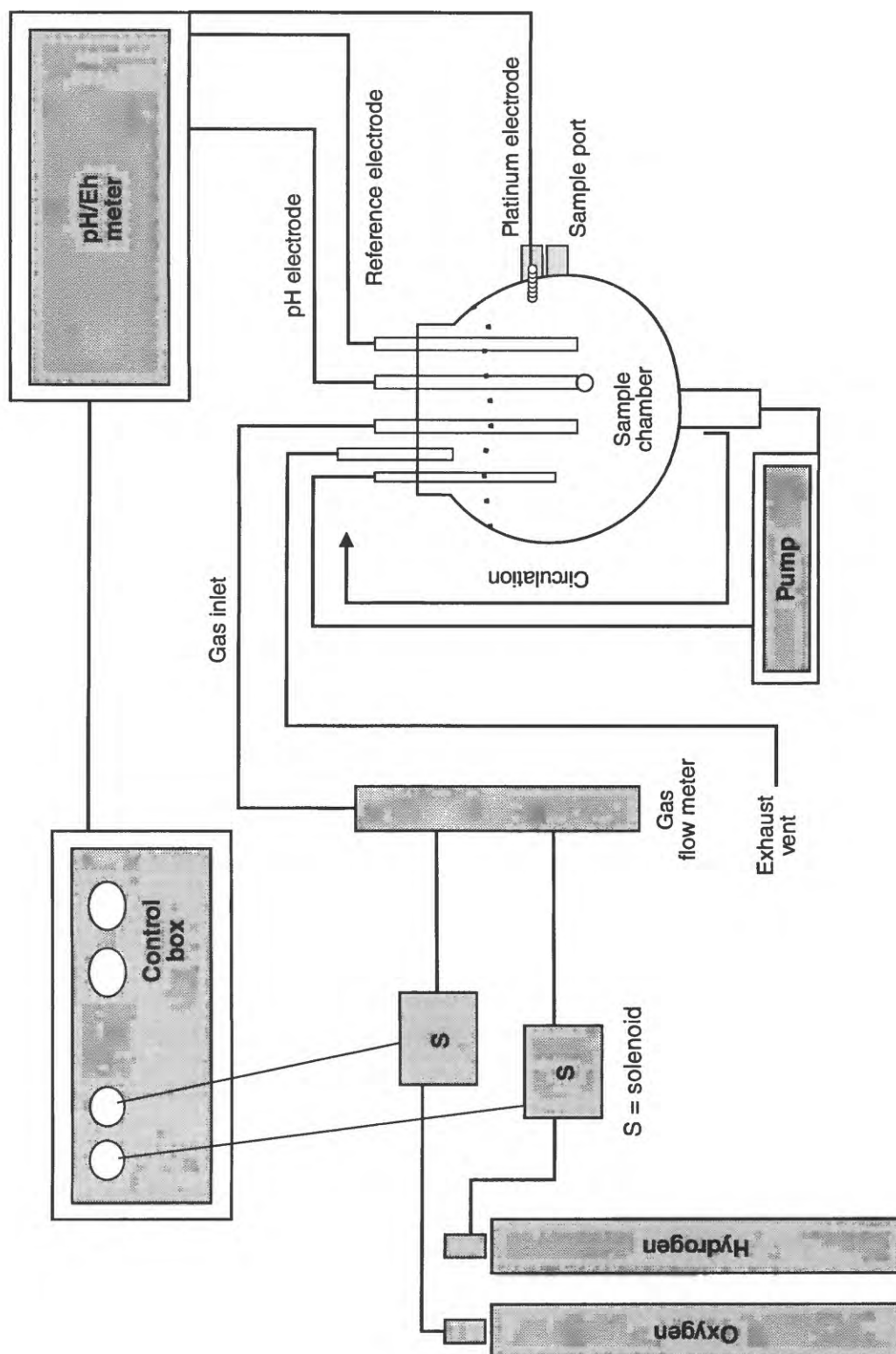


Figure 10. Schematic diagram of redox controlling apparatus.

Table 17. Calibration of redox controlling apparatus using distilled-deionized water

Oxygen dial setting	Control box redox setting (millivolts)	pH (standard units)	Hydrogen dial setting	Time required for stable reading (minutes)
385	+500	6.00	385	30-45
401	+400	6.00	401	30-45
417	+300	5.00	417	30-45
433	+200	5.00	433	20
450	+100	5.00	450	15
466	0	4.80	466	10-15
482	-100	4.81	482	15-20
498	-200	4.88	498	15-20
514	-300	4.92	514	30-45
530	-400	4.90	530	30-45
546	-500	4.90	546	30-45

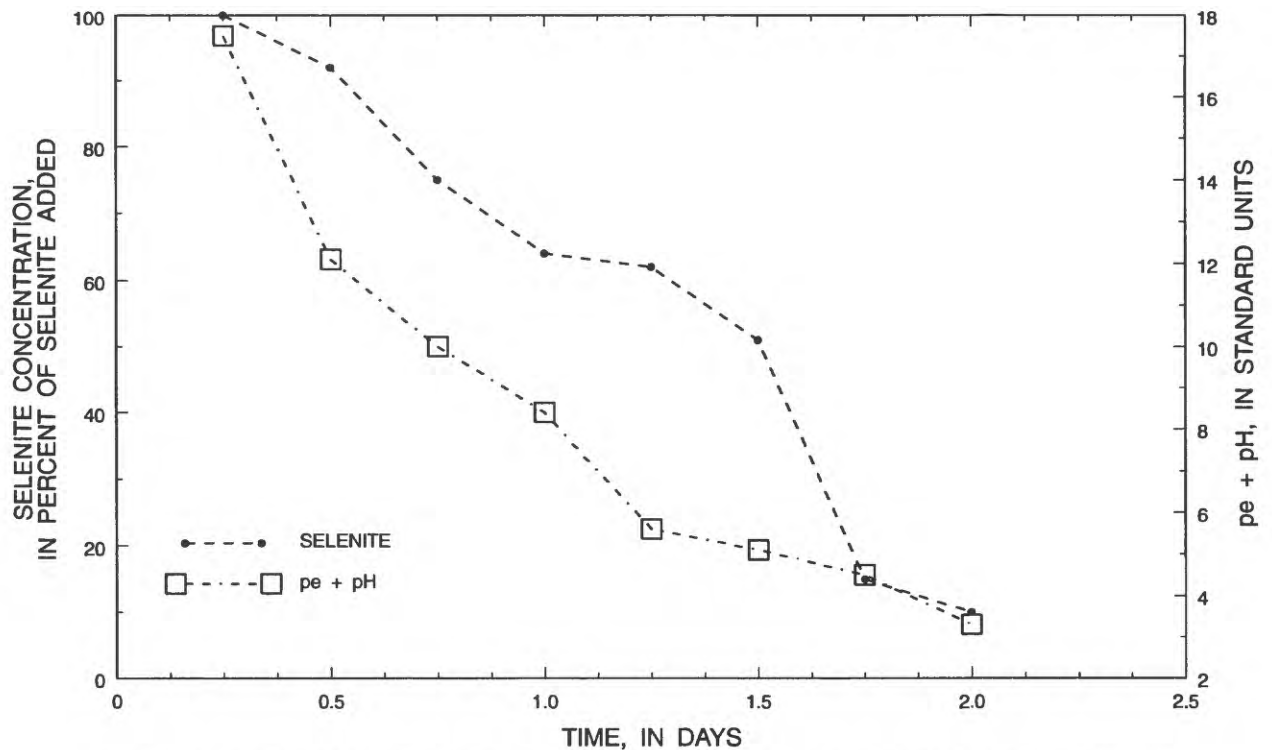


Figure 11. Selenite concentration response to pe + pH changes in a tap-water sample amended with 10 milligrams selenite per liter during a 2-day period.

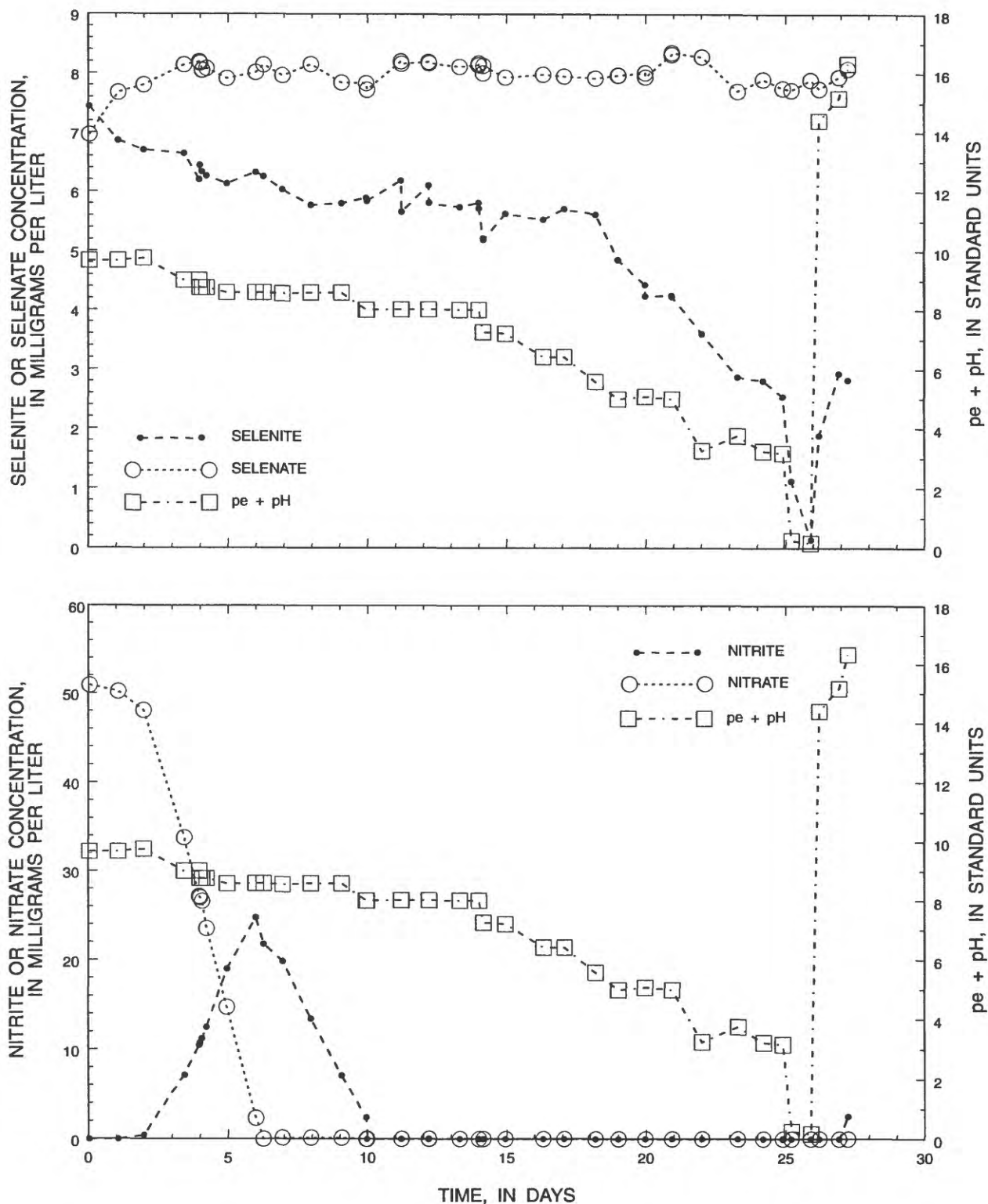


Figure 12. Selenite, selenate, nitrite, and nitrate response to pe + pH changes in a ground-water sample from well B-1 in the Powder River Basin, Wyoming, amended with 8 milligrams selenite and 8 milligrams selenate per liter, in redox controlling apparatus during a 27-day period.

Table 18. Selenite and selenate response to $pe + pH$ changes in a backfill-core sample suspension in redox controlling apparatus.

$pe + pH$	Selenite (percent)	Selenate (percent)	Selenium not recovered (percent)
17.8	0.5	50	49.5
12.7	.5	35	64.5
8.5	.4	30	69.6
3.2	.4	1.2	98.4

To help substantiate the correlation of measured Eh values to particular redox conditions, the concentrations of other anions (nitrate and nitrite) participating in redox transformations were also monitored. Nitrate concentrations in the ground-water sample decreased when $pe + pH$ was lowered to about 9 and nitrate was not detected after 6 days (fig. 12). An initial increase in nitrite concentrations with the decrease in nitrate was observed. After 10 days, however, nitrite was not detected (fig. 12). Sulfate concentrations remained constant and appeared unaffected by redox in this study.

The absence of selenate reduction to selenite and selenite oxidation to selenate has important implications for the bio-availability of selenium in backfill materials and ground water. Because of the difficulty in obtaining reliable measurements of selenium speciation in water and soil samples, total selenium is often the only measurement made. The speciation of selenium into selenate and selenite is then determined based on thermodynamic models. The results obtained in this study indicate that in ground water, selenate and sulfate will remain stable and available under reduced conditions when thermodynamic models would predict otherwise. Selenite in solution is susceptible to reducing conditions, but does not appear to be oxidizable in the water samples under the conditions used. These results could be due to the lack of labile electrons to participate in the particular redox couples in the water samples or due to kinetic constraints. Oxidation of selenite in soil has been reported from 2 to 10 days (Masscheleyn and others, 1990; Blaylock and James, 1994). However, the reduction of nitrate, nitrite, and selenite indicates that the appropriate electron pressure for the reduction of sulfate and selenate should be present. Weres and others (1990) reported that nitrate was highly correlated with selenium in ground water and that nitrate balances the Eh above what is required

for selenate reduction. When oxygen and nitrate were removed from the system, the Eh decreased and selenate was quickly removed. That effect was not observed in this study. The water sample used had only trace levels of soluble iron and manganese; therefore, an assessment of whether the redox range controlled by iron and manganese (Sposito, 1989) was achieved could not be determined in the water samples.

The reduction of selenate in the backfill-core sample followed thermodynamic predictions more closely than the water samples. The reduction of selenate in the backfill sample occurred at redox levels similar to those reported by Masscheleyn and others (1991). However, oxidation of selenite to selenate in the backfill-core samples was not observed. This is presumably due to the selenite being sorbed and not being present in solution to participate in oxidation-reduction mechanisms. Reduction of selenite in the backfill-core samples was not observed, due to sorption of the selenite. Coal-mine backfill materials typically have large sorption capacities for selenite, leaving little soluble selenite to participate in the solution chemistry (Tawfic, T.A., and others, Department of Plants, Soil, and Insect Sciences, University of Wyoming, written commun., 1994).

Selenite reduction in water samples occurred at a larger $pe + pH$ than thermodynamic predictions. Reduction of selenate did not occur in water samples or standards at any redox level tested. Selenate reduction in the backfill-core suspension occurred at a slightly lower redox than predicted. Oxidation of selenite to selenate was not detected at any of the redox conditions tested. Although some of the redox transformations occurred as expected, others did not. Because selenate was not reduced to selenite in water samples, kinetic parameters controlling the redox processes need to be identified.

SUMMARY AND CONCLUSIONS

Selenium is an essential as well as a potentially toxic element to humans and animals. Because of this potential toxicity, the extensive seleniferous geologic formations in Wyoming and other areas in the Western United States are a major environmental concern. During surface coal mining, rock material overlying coal seams is redistributed from the original stratigraphic position; exposure of previously buried material to surface oxidizing conditions can decrease the stability of selenium-containing sulfides and organic matter. The oxidation of such compounds can transform reduced and less mobile selenium species (Se^{2-} and Se^0) into oxidized selenium species (Se^{6+} and Se^{4+}), which are more soluble in alkaline and oxidizing ground water.

Sites near three wells in the Powder River Basin constructed in coal-mine backfill material having large selenium concentrations in the associated ground water were identified and investigated. Two sites were investigated at mine A (A-1 and A-2) and one site was investigated at mine B (B-1). Most other backfill wells researched in the Powder River Basin had selenium concentrations at or below the analytical reporting limit. Large selenium concentrations in coal-mine backfill ground water is not a widespread problem in the Powder River Basin.

The results of a study of the geochemical processes affecting the solubility of selenium, and the effects of natural organic solutes on the solubility of selenium in surface coal-mine backfill aquifers in the Powder River Basin are described in this report. This study had three specific objectives:

Objective 1. To characterize the chemical and physical properties of surface coal-mine backfill and associated ground water at three sites having large selenium concentrations in ground water.

Six backfill cores were collected, two from each site, from within about 5 m of each existing site well. A total of 157 backfill-core samples were separated from the six cores. For each analysis or experiment, backfill samples from varying depths were selected. XRD analysis on 18 backfill-core samples indicated that the following common minerals were present in all samples: quartz, kaolinite, potassium feldspar, illite, and muscovite; some samples contained smectite, gypsum, calcite, dolomite, carbonate-apatite, and

goethite. Large surface-area clay minerals (kaolinite, illite, muscovite, and smectite) indicated the backfill-core samples had potentially large sorption capacities.

Acid digestion of 30 backfill-core samples indicated total selenium concentrations ranged from 0.1 to 15.2 mg/kg. Saturated-paste extracts for 68 air dried and sieved backfill-core samples indicated Eh values of backfill-core samples taken near the ground-water table were similar to Eh measurements for ground water. Saturated-paste extract selenium concentrations ranged from 1 to 156 $\mu\text{g/kg}$.

Sequential partial dissolution of 17 backfill-core samples indicated less than 5 to 58 percent of the total selenium was found in the organic phase (fraction 3) in backfill-core samples analyzed for this study. Differences between this study and an earlier study which found 100 percent of the selenium in the organic phase in undisturbed overburden samples, may be due to dissolution and redistribution of selenium from the organic phase to other fractions in the backfill material during the mixing and disturbance associated with the mining process and subsequent reclamation.

As the ground-water level rises in the coal-mine backfill, the ground water dissolves soluble materials including selenium species. This produces a rise in the dissolved-selenium concentrations in the ground water. Ground-water samples collected from each well were analyzed for specific conductance, pH, Eh, dissolved oxygen, dissolved selenium, DOC, sulfate, chloride, fluoride, nitrate, and major and trace ions. The pH of the ground-water samples ranged from 5.5 to 7.3. Specific conductance for the ground-water samples ranged from 3,650 $\mu\text{S/cm}$ (well B-1) to 10,000 $\mu\text{S/cm}$ (well A-1). All ground-water samples were dominated by sulfate (2,960 to 11,300 mg/L). Selenium concentrations ranged from 3 $\mu\text{g/L}$ (well A-2) to 125 $\mu\text{g/L}$ (well A-1). DOC concentrations ranged from 11 mg/L (well A-2) to 88 mg/L (well A-1).

Fractionation of the ground-water DOC indicated that hydrophobic and hydrophilic acids dominated DOC (74 to 84 percent for well A-1, 38 to 69 percent for well A-2, and 68 to 83 percent for well B-1); hydrophobic and hydrophilic neutrals in ground-water samples ranged from 16 to 23 percent for well A-1, 21 to 55 percent for well A-2, and 10 to 25 percent for well B-1; and hydrophobic and hydrophilic bases in ground-water samples were generally less than 10 percent.

Objective 2. To determine the role that natural organic solutes have on selenium sorption/desorption and precipitation/dissolution processes.

Results from sorption/desorption studies were evaluated on the basis of both (1) the direct comparison of the selenite sorbed and desorbed as a function of the amount of selenite added, that is, percent removed or released, and (2) the evaluation of equilibrium data using several sorption isotherms. The results obtained by the direct comparison method for experiment 1 (distilled-deionized water background solution) showed selenium sorption ranged from 56 to 98 percent and was found to increase with decreasing pH; percent sorption generally increased with increasing concentration of the added selenium. Samples with the largest selenium sorption capacities also had the smallest DOC concentration in the associated ground water and saturated-paste extracts, suggesting an inverse relation between DOC concentration and selenium sorption. Sorption percentages were larger when 0.1 molar calcium chloride was used as the background solution in experiment 2. This may have been caused by an increase in positively charged surfaces induced by calcium sorption, precipitation reactions, or both.

Sorption capacities were smaller when hydrophilic acid was added as a background solute, indicating there was a positive interference caused by DOC. This interference could be due to the formation of complexes with selenium that do not sorb as strongly as selenite or selenate, or to competitive sorption processes involving selenite and DOC. Selenite sorption capacities of samples from two of the backfill cores were smaller with addition of the hydrophobic acid, whereas the sorption capacities remained almost constant for samples from the other backfill core. Selenite sorption capacity was smaller with the addition of hydrophilic acid than with did the addition of hydrophobic acid and the apparent effect of DOC on sorption was generally larger at small concentrations of added selenite.

Most backfill-core samples examined had large selenite sorption capacities (ranging from 0 to 99 percent). Sorption generally was smaller in the presence of hydrophobic and hydrophilic acids, indicating a positive interference caused by natural organic solutes in the selenite sorption process. Selenite sorption was larger in the presence of the hydrophilic acids than in the presence of hydrophobic acids. The effect of natural organic solutes on selenite sorption was generally greater at small concentrations of added selenite. These results suggest that hydrophilic acids are important in reducing the retention of selenium by backfill

materials by enhancing the desorption of indigenous selenium or by displacing selenium through competitive sorption.

A precipitation/dissolution study was conducted to predict potential solid phases controlling the dissolved selenium concentration in coal-mine backfill materials, and to evaluate the effects of DOC on selenium solubility in these environments. A geochemical speciation model, GEOCHEM, was used to calculate ion activities. The chemical speciation results indicated DOC had a small effect on selenium speciation. Free-ion activity of all cations decreased, whereas activities of anions increased with DOC addition. This could be due to the complexation of cations with DOC, which decreases the activities of the cations. At the same time, the available cations for complexing with the original anions in solution (all anions other than fulvic acid) decreased, leaving more anions as free ligands. Free activities of lead and manganese were affected more than the rest of the cations by the addition of DOC. Among the cations, activities of Mg^{2+} and Fe^{3+} were the least affected by DOC.

Chemical speciation also suggested that precipitation/dissolution extracts were dominated by the MgSeO_3^0 ion pair (55 to 90 percent of total selenium concentration) followed by CaSeO_3^0 and SeO_3^{2-} species. In low pH (3.9 to 6.8) backfill water extracts, the dominant selenite ion pairs were MgSeO_3^0 ion pair (55 percent of total selenium concentration), followed by HSeO_3^- (25 percent of total selenium concentration) and CaSeO_3^0 (20 percent of total selenium concentration). The presence of ion pairs in coal-mine backfill materials may represent a potential for leaching of selenium, because neutral ion pairs may not be sorbed onto oxides and clay minerals as a charged species, and therefore can be readily leached.

The IAPs of different selenium solid phases (for example, CuSe , MgSeO_3 , MnSeO_3 , and ZnSeO_3) in water extracts were compared with K_{sp} s to examine the possibility that one of these solid phases may be controlling the selenium concentrations in water extracts. Results indicated that IAPs of these solid phases were undersaturated and were not controlling solution selenium concentrations. However, in some backfill materials selenium concentrations appeared to be controlled by CuSe . The results suggested that as depth increased, redox potential ($\text{pe} + \text{pH}$) decreased, and selenium concentrations probably reached saturation with respect to

CuSe. It is possible that in sub-surface environments, oxygen concentrations will be low and the resulting anaerobic conditions would favor the precipitation of reduced selenium solid phases such as CuSe.

Objective 3. To quantify the effects of oxidation-reduction (redox) conditions on the speciation and solubility of selenium in a redox potential controlling apparatus.

Experiments to determine the response of selenium speciation to changes in redox status were conducted using distilled-deionized water, tap water, ground water, and backfill-core sample suspensions amended with selenite and selenate. The response of selenite and selenate to the imposed redox conditions of the redox controlling apparatus differed from thermodynamic predictions, possibly due to the slow rates of selenium redox transformations.

Oxidation of selenite to selenate was not observed at $pe + pH$ of about 18 and reduction of selenate to selenite did not occur in a $pe + pH$ range of 0 to 17. Reduction of selenite in solution in the water samples occurred more readily than reduction of selenate. Selenate concentrations in backfill-core material suspensions decreased initially at $pe + pH = 12.7$ and had decreased by over 90 percent at $pe + pH = 3.2$. Selenite in the soil suspension was sorbed by the backfill and removed from solution; therefore, speciation changes due to redox could not be determined. Nitrate concentrations in a ground-water sample decreased when $pe + pH$ was lowered to about 9 and nitrate was not detected after 6 days. An initial increase in nitrite concentrations with the decrease in nitrate was observed. After 10 days, however, nitrite was not detected.

The results obtained in this study indicate that in ground water, selenate and sulfate will remain stable and available under reduced conditions when geochemical modeling would predict otherwise. The reduction of selenate in the backfill-core material followed thermodynamic predictions more closely than water samples. The reduction of selenate in the backfill sample occurred at redox levels similar to those reported in earlier investigations. Oxidation of selenite to selenate in the backfill materials was not observed, presumably due to the selenite being sorbed and not being present in solution to participate in oxidation-reduction mechanisms. Likewise, reduction of selenite in the backfill-core samples was not observed presum-

ably due to sorption of the selenite. Coal-mine backfill materials typically have large sorption capacities for selenite, leaving very little soluble selenite to participate in the solution chemistry.

Selenite in the backfill suspension presumably was sorbed by the backfill material, and speciation changes due to redox could not be determined. Selenite reduction in water samples occurred at a larger redox than predicted. Reduction of selenate did not occur in water samples or standards at any redox level tested. Selenate in the backfill-core suspension decreased at $pe + pH = 12.7$ from 50 to 35 percent and decreased at $pe + pH = 3.2$ by more than 90 percent. Selenate reduction in the backfill-core suspension occurred at a slightly lower redox than predicted. Oxidation of selenite to selenate was not detected at any of the redox conditions tested. Although some of the redox transformations occurred as expected, selenate was not reduced to selenite in water samples. This condition illustrates the need to identify kinetic parameters controlling the redox processes.

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