GEOCHEMICAL PROCESSES IN GROUND WATER RESULTING FROM SURFACE MINING OF COAL AT THE BIG SKY AND WEST DECKER MINE AREAS, SOUTHEASTERN MONTANA

by David W. Clark

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 95-4097

Prepared in cooperation with the
MONTANA DEPARTMENT OF STATE LANDS and the
BUREAU OF LAND MANAGEMENT

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

Helena, Montana
September 1995

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

Gordon P. Eaton, Director

For additional information write to:

District Chief
U.S. Geological Survey
428 Federal Building
Drawer 10076
301 South Park
Helena, MT 59626-0076

Copies of this report may be purchased from:

U.S. Geological Survey
Earth Science Information Center
Open-File Reports Section
Box 25286, Mail Stop 517
Denver Federal Center
Denver, CO 80225

CONTENTS

ILLUSTRATIONS

TABLES

TABLES --Continued

CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATED WATER-QUALITY UNITS, AND ACRONYMS

Multiply	By	To obtain
acre	4,047	square meter
foot (ft)	0.3048	meter
foot per day [($ft^3/d/ft^2$) or ft/d]	0.3048	meter per day
foot per foot (ft/ft)	1.0	meter per meter
inch (in.)	25.4	millimeter
mile	1.609	kilometer
pound	453,600,000	microgram (µg)
	453,600	milligram (mg)
	453.6	gram (g)
	0.4536	kilogram (kg)
ton (short)	907.2	kilogram

Temperature can be converted from degrees Celsius (°C) to degrees Fahrenheit (°F) by the equation:

$$°F = 9/5\ (°C) + 32$$

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum 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.

Abbreviated water-quality units used in this report:

kcal/mol	kilocalories per mole
µg/g	micrograms per gram
µg/L	micrograms per liter
µm	micrometers (micron)
µS/cm	microsiemens per centimeter at 25 degrees Celsius
meq/100g	milliequivalents per 100 grams
mg/L	milligrams per liter
mL	milliliter
M	molar
‰	per mil
pCi/L	picocuries per liter
TU	tritium units

Acronyms used in this report:

CEC	Cation exchange capacity, in milliequivalents per 100 grams
DOC	Dissolved organic carbon
EDS	Energy dispersive spectroscopy
RS	Redox state
SEM	Scanning electron microscopy
SMOW	Standard mean ocean water
TOC	Total organic carbon

The use of industry or firm names in this report is for location purposes only, and does not impute responsibility for any present effects on the natural resources.

GEOCHEMICAL PROCESSES IN GROUND WATER RESULTING FROM SURFACE MINING OF COAL AT THE BIG SKY AND WEST DECKER MINE AREAS, SOUTHEASTERN MONTANA

By David W. Clark

Abstract

A potential hydrologic effect of surface mining of coal in southeastern Montana is a change in the quality of ground water. Dissolved-solids concentrations in water in spoils aquifers generally are larger than concentrations in the coal aquifers they replaced; however, laboratory experiments have indicated that concentrations might decrease if ground water flows from a spoils aquifer to a coal aquifer. This study was conducted to determine if the decreases indicated in laboratory results occur onsite and, if so, which geochemical processes caused the decreases. The Big Sky and West Decker Mine areas were chosen for study as both contain coal of the Tongue River Member of the Paleocene Fort Union Formation, but have differences in mineralogy, ground-water quality, and flow processes.

Solid-phase core samples of spoils, unmined overburden, and coal and samples of ground water were collected from 16 observation wells at the two mine areas. Selected solid-phase samples were analyzed for elemental concentrations, exchangeable cations, and mineral constituents. Water samples were analyzed for major and trace constituents, selected isotopes, and dissolved gases.

In the Big Sky Mine area, changes in ground-water chemistry along an inferred flow path from an upgradient coal aquifer to a spoils aquifer probably were a result of dedolomitization caused by the irreversible dissolution of gypsum at or near calcite-dolomite saturation. Dissolved-solids concentrations were unchanged as water flowed from a spoils aquifer to a downgradient coal aquifer.

In the West Decker Mine area, dissolved-solids concentrations apparently decreased from about 4,100 to 2,100 milligrams per liter (mg/L) as water moved along an inferred flow path from a spoils aquifer to a downgradient coal aquifer. Apparent decreases in selected constituent concentrations included: sodium, from 1,500 mg/L to less than 900 mg/L; bicarbonate, from about 3,000 mg/L to less than 2,400 mg/L; and sulfate, from 1,100 mg/L to less than 100 mg/L. Data for solid-phase and aqueous geochemical characteristics, including types of reactive minerals, isotopic ratios, and dissolved-gas concentrations, were used to develop geochemical models to analyze changes in water chemistry. Geochemical processes postulated to result in the decrease in dissolved-solids concentrations along this inferred flow path include: bacterial reduction of sulfate utilizing the organic matter in coal as an energy source; reverse cation exchange of sodium ions for calcium or magnesium ions within the coal; and precipitation of carbonate and iron-sulfide minerals. Even though these processes are thought to be those most likely occurring, they are considered nonunique and might not be the only feasible processes. Questions about the sulfate system, the rate of sulfate reduction, the isotopic composition of the coal, the existence of secondary carbonates and amorphous iron-sulfide minerals in the coal, and other questions need to be resolved before the geochemical processes occurring in the system are fully understood.

INTRODUCTION

One of the potential hydrologic effects of surface coal mining in southeastern Montana is a change in the quality of ground water. Dissolved-solids concentrations in water in spoils aquifers are about 1,000 mg/L larger (Davis, 1984a) than in the coal aquifers they replaced. Laboratory experiments (Davis, 1984a; Davis and Dodge, 1986) have indicated that dissolved-solids concentrations might decrease by several hundred milligrams per liter when ground water flows from an aquifer in coal mine spoils (hereinafter referred to as spoils and spoils aquifer) back through a coal aquifer. Geochemical modeling of the results of those experiments indicated that several geochemical processes were occurring, including mineral dissolution and precipitation, and either exchange or adsorption reactions.

The Big Sky and West Decker Mine areas in southeastern Montana offered unique opportunities to study such geochemical processes onsite. Both mines are located in the Tongue River Member of the Paleocene Fort Union Formation, but distinct differences between the mine areas in mineralogy and ground-water flow processes have resulted in differences in water quality. The Big Sky Mine area has a local ground-water flow system, with at least some recharge by direct infiltration of precipitation on permeable overburden and spoils, and a calcium-magnesium sulfate type water. The West Decker Mine area has a more regional ground-water flow system, with little or no recharge through the mine spoils by direct infiltration of precipitation on overburden or spoils, and a sodium bicarbonate type water (Davis, 1984a). Knowledge of the geochemical processes occurring in each mine area and the relation of those processes to the flow systems and mineralogy can be of considerable value in evaluating future mining and reclamation efforts. Therefore, this project was conducted in cooperation with the Montana Department of State Lands and the Bureau of Land Management to further understand the geochemical processes controlling the quality of water in areas with surface mining of coal.

Purpose and Scope

This report describes the geochemical processes that occur in ground water as a result of surface mining of coal at the Big Sky and West Decker Mine areas in southeastern Montana. The report is based on data obtained during 1988 through 1990 from intensive sampling and analysis of rock material and water at several points along flow paths extending from coal aquifers upgradient of each mine, through spoils aquifers to downgradient coal or other aquifers.

Data requirements included mineralogy, elemental chemistry, and ion-exchange capabilities obtained from solid-phase samples collected by core drilling during monitoring-well installation. These data were obtained by scanning electron microscopy (SEM), X-ray diffraction and other techniques. Other data include ground-water samples analyzed for major and minor chemical constituents, isotopic composition, and dissolved gases. The data were then analyzed with geochemical models.

Previous Investigations

Numerous geohydrologic studies have been conducted in the coal-producing areas of southeastern Montana by personnel of the U.S. Geological Survey, the Montana Bureau of Mines and Geology, and Montana State University. Davis (1984a) investigated the geochemistry and geohydrology of the Big Sky and West Decker Mine areas. Davis and Dodge (1986) reported the results of laboratory experiments related to spoils-aquifer water and coal in the same mine areas; the resulting report was the catalyst for this study. Dockins and others (1980) studied sulfate reduction in ground water of southeastern Montana. Davis (1984b) estimated ground-water inflow to the pits at the West Decker Mine area and Lee (1980) studied the regional geochemistry.

Geography

The study areas are in the coal-rich Powder River structural basin, which extends from southeastern Montana to northeastern Wyoming (fig. 1), in the northern Great Plains Physiographic Province. Both coal-mining areas are drained by tributaries of the Yellowstone River. The Big Sky Mine area, near the town of Colstrip, is drained by tributaries of Rosebud Creek; altitudes within this area range from about 3,600 ft above sea level near the northwest mine boundary to about 3,000 ft near Rosebud Creek. The West Decker Mine area is drained by the Tongue River; altitudes within the area range from about 4,000 ft at the west mine boundary to about 3,400 ft near the Tongue River.

The climate of most of the non-mountainous areas in southeastern Montana is semiarid. Figure 2 shows the annual precipitation at Colstrip and Decker from 1979-90, the time period of this and studies cited in the above Previous Investigations. Average annual precipitation for 1961-90 at Colstrip was 15.06 in., and at Decker was 12.69 in. About half of the annual precipitation occurs during April, May, and June, on the basis of records from the National Weather Service.

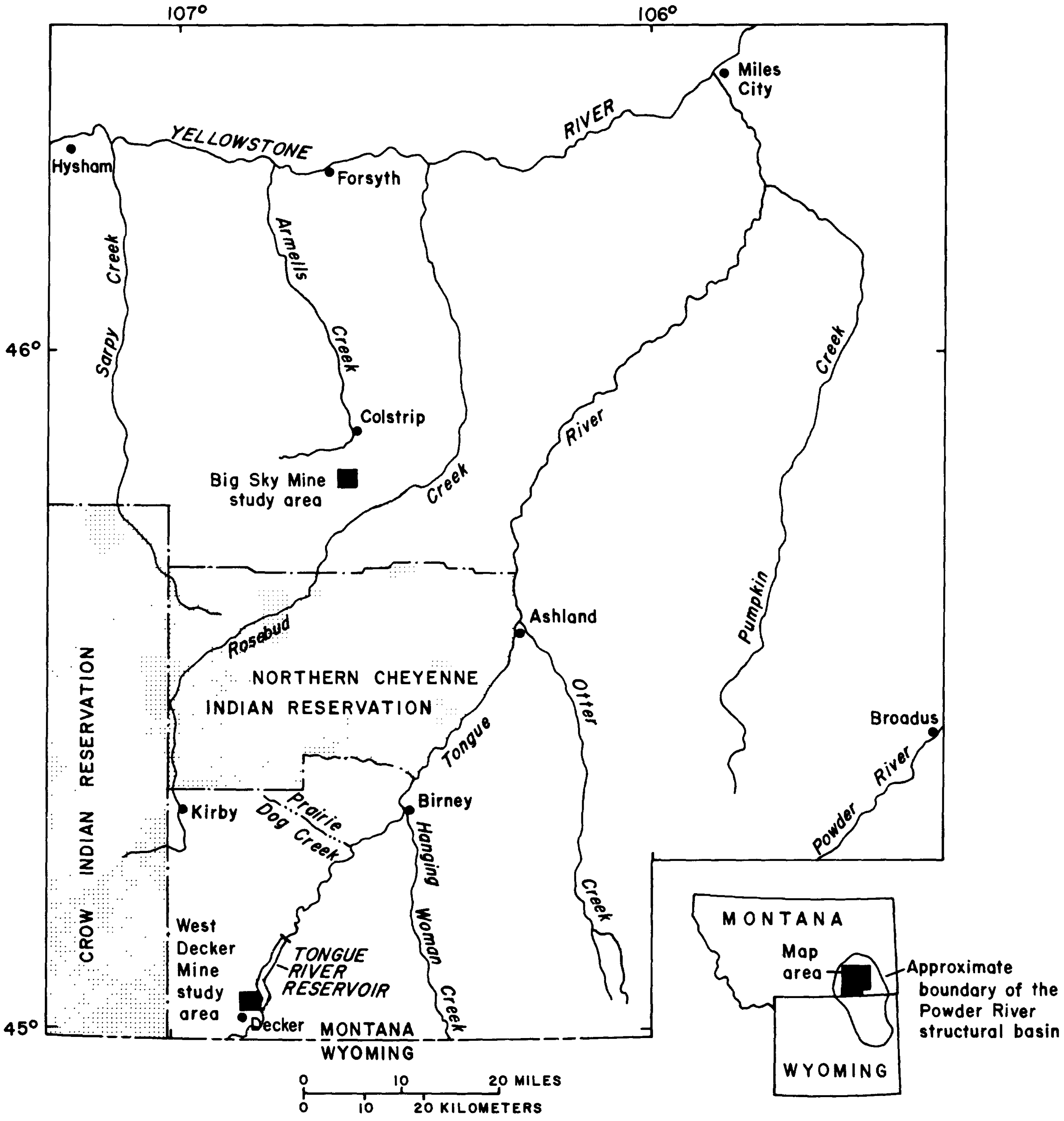


Figure 1. Location of study areas.

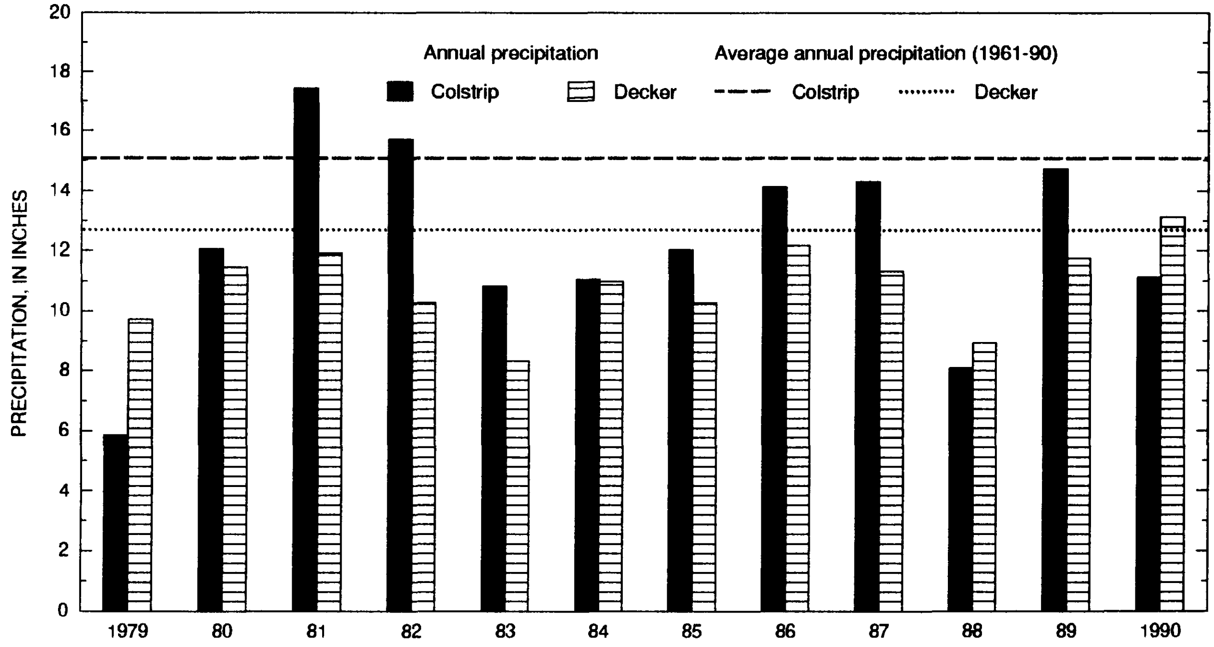


Figure 2. Annual and average annual precipitation at Colstrip and Decker, Montana.

Site-Numbering System

In this report, sites are numbered according to geographic position within the rectangular grid system used by the Bureau of Land Management (fig. 3). The site-identification number consists of 14 characters. The first three characters specify the township and its position north (N) or south (S) of the Montana Base Line. The next three characters specify the range and its position east (E) of the Montana Principal Meridian. The next two characters are the section number. The next four characters designate the quarter section (160-acre tract), quarter-quarter section (40-acre tract) quarter-quarter-quarter section (10-acre tract), and quarter-quarter-quarter-quarter section (2 1/2-acre tract), respectively, in which the well is located. The subdivisions of the section are designated A, B, C, and D in a counterclockwise direction, beginning in the northeast quadrant. The final two digits form a sequential number in order of inventory; for example, site 09S40E16BADC01 (fig. 3) is the first site inventoried in the SW1/4SE1/4NE1/4NW1/4 sec. 16, T. 9 S., R. 40 E.

Acknowledgments

The author appreciates the assistance and cooperation extended by employees of the Peabody Coal Company, the Decker Coal Company, and Peter Kiewit Sons, Inc. Many personnel of the U.S. Geological Survey also assisted in this study. In particular, acknowledgment is extended to Gene C. Whitney, Kenneth J. Esposito, and Joan J. Fitzpatrick, Branch of Sedimentary Processes (Denver, Colo.), for their assistance in the solid-phase sample analysis and interpretation. L. Neil Plummer and Donald C. Thorstenson (Reston, Va.) provided valuable assistance with the project design and data analysis and interpretation.

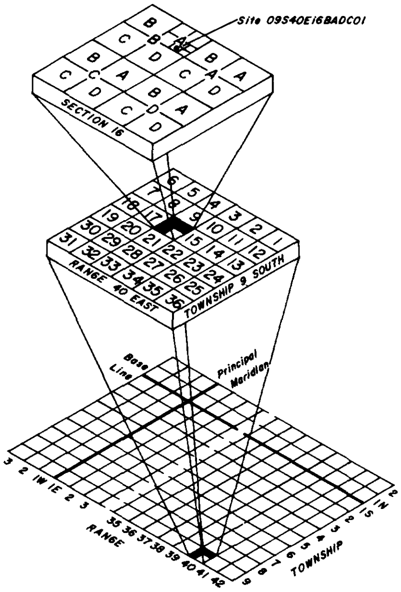


Figure 3. Site-numbering system.

METHODS OF STUDY

Changes in ground-water geochemistry within the coal mine areas were quantified primarily by the collection and analysis of solid- and aqueous-phase samples obtained through the drilling and installation of observation wells. At both mine areas, wells were completed in coal upgradient from the mine disturbance, mine spoils, and coal downgradient from saturated spoils. Details on well construction and measured water levels in the observation wells are shown in table 1. Solid-phase samples of spoils, unmined overburden, interburden, and coal were collected primarily from cores obtained during drilling. Water samples were collected by pumping or bailing after wells had been developed.

Solid-phase samples were analyzed for mineral constituents by X-ray diffraction, thin-section petrology, and scanning electron microscopy (SEM). Well-crystallized minerals were identifiable by X-ray diffraction if their abundance generally was greater than about 5 percent. Clay mineralogy was determined by X-ray diffraction of untreated samples, glycolated samples, and samples heated to 550 °C. Petrographic analysis and interpretations were completed for 10 rock samples, and petrographic analysis and analysis by SEM were completed for thin sections of selected coal samples. Solid-phase samples also were analyzed using SEM equipped with energy dispersive spectroscopy (EDS). Thin sections were prepared from cores of coal coated with a conducting layer of either carbon or gold. SEM photographs were taken and chemical constituents were analyzed with EDS for selected non-organic grains within the coal thin sections.

Cation and trace-element concentrations and exchangeable cations were determined for 20 selected core samples from overburden siltstone, sandstone, shale, clinker, and spoils by the Montana Bureau of Mines and Geology analytical laboratory. Nine coal samples collected from drill cores and one grab sample of coal were analyzed for 65 major and trace elements by the U.S. Geological Survey, Branch of Geochemistry laboratory. Selected coal samples were combusted at 800 °C to determine the percentage of ash. Fifteen mg of the ash were pulverized and sieved to pass 100 mesh and then chemically analyzed.

Ground-water samples were analyzed for a variety of properties and constituents. Analysis included major and trace dissolved constituents, onsite properties, dissolved gases, and isotopic composition. Water samples were analyzed for major and trace constituents by the Montana Bureau of Mines and Geology. Isotope and some trace-metal analyses were conducted by the U.S. Geological Survey National Water Quality Laboratory or private contractors.

Several properties and constituents including specific conductance, temperature, pH, dissolved oxygen, alkalinity, dissolved sulfide, and total and ferrous iron were measured onsite because of their potential instability. Specific conductance, temperature, pH and, where applicable, dissolved oxygen were measured in a flow-through sampling chamber after the values had stabilized. At least three well volumes were withdrawn before water-sample collection. Water generally was pumped slowly from the well head into the sampling chamber to prevent or minimize degassing or other atmospheric interference. The dissolved sulfide and iron species were measured semiquantitatively using a field colorimeter. Samples for laboratory analysis that required filtering generally were filtered through a 0.45-µm membrane filter; some samples analyzed for dissolved aluminum, iron, and manganese were filtered through a 0.10-µm membrane filter to remove colloidal material.

Dissolved gases were collected using a sampling apparatus illustrated and described in detail by Hobba and others (1977). A sample of the vapor phase was analyzed by gas chromatographic procedures for nitrogen, argon, oxygen, carbon dioxide, methane, and ethane. Dissolved gases in water were analyzed by Donald C. Thorstenson of the U.S. Geological Survey.

Isotopic composition can be a useful indicator of hydrologic and geochemical conditions. Isotopic fractionation might occur in many elements during phase transitions and chemical and biological reactions. These fractionations are due to slight variations in the physical and chemical properties of various isotopes of an element and are proportional to the differences in their masses. The hydrologically significant isotopes considered in this report are the stable isotopes of oxygen, hydrogen, carbon, and sulfur, and tritium, a radioactive isotope of hydrogen. Samples for the stable isotopes were collected according to guidelines established by the U.S. Geological Survey National Water Quality Laboratory. Samples for carbon-13 analysis were treated onsite with a reagent of ammoniacal strontium chloride. Sulfur-34 for the sulfide ion was determined on a silver sulfate sample precipitated onsite from an acidified sample using gas stripping and a solution of silver nitrate.

Stable-isotope composition is expressed in δ (Del) notation, written as: $\delta^{18}O$ for the heavy oxygen isotope; δD for the heavy hydrogen isotope (^2H) given the name deuterium and the symbol D; $\delta^{13}C$ for the heavy carbon isotope; and $\delta^{34}S$ for the heavy sulfur isotope. Del notation (δ) is typically expressed as the per mil (‰) difference in the measured isotopic ratios of a sample and a standard given by the equation:

$$\delta = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \times 1,000, \tag{1}$$

where R is the isotopic ratio of the element being considered. For example, the relation for sulfur isotopes is:

$$\delta^{34}S = \left[\frac{\left(^{34}S/^{32}S\right)\text{sample}}{\left(^{34}S/^{32}S\right)\text{standard}} - 1\right] \times 1,000. \tag{2}$$

The sulfur-isotopic ratios in the equation might be replaced by the ratios of $^{18}O/^{16}O$, D/H, or $^{13}C/^{12}C$ to obtain δ values for the other elements.

Stable carbon isotopes can be used to determine controlling chemical reactions and various sources of carbonate along an aquifer flow path. Dissolved carbon in ground water is derived primarily from carbonate sediments, soil organic matter, the decay of other organic material, and in some instances from atmospheric carbon dioxide (CO_2). Various sources of carbon generally have relatively distinct ranges of isotopic compositions. For example, the $\delta^{13}C$ is about 0 ± 3 ‰ for carbonate sediments, about -25 ± 5 ‰ for organic soil matter (wood and leaves), about -28 ± 4 ‰ for sedimentary organic carbon including coal, about -17 ‰ for soil CO_2 in arid climates, and about -7 ‰ for atmospheric CO_2 (Rightmire and Hanshaw, 1973, p. 959).

Sulfur isotopes can be used in geochemical studies to determine the amount of sulfate reduction that has occurred and to help define geochemical processes and flow paths. Sulfate-reducing bacteria such as *Desulfovibrio desulfuricans* reduce aqueous sulfate (SO_4^{2-}) to form hydrogen sulfide (H_2S or HS^-) in pH-neutral water. The sulfide is depleted in ^{34}S; therefore, the $\delta^{34}S$ of the remaining aqueous sulfate is enriched. When values of $\delta^{34}S$ are known for both sulfate and sulfide, the fractionation and the mass transfer of the sulfur system can be calculated. The primary source of sulfate in the study areas is $CaSO_4$, precipitated after the oxidation of pyrite and at least partly redissolved as the aquifer becomes saturated. At least part of the sulfide is derived from bacterial reduction of sulfate.

During an earlier study, Ferreira and others (1989) measured stable isotopes at 21 ground-water and 8 surface-water sites in the surface coal-mine areas of southeastern Montana in 1985. Stable-isotope ratios from the ground-water samples ranged from -21.7 to -16.5 ‰ for $\delta^{18}O$, -167 to -134 ‰ for δD, -13.0 to 0.4 ‰ for $\delta^{13}C$, and -9.3 to 6.2 ‰ for $\delta^{34}S$. The median ground-water values, including water from alluvial, overburden, coal, and spoils wells, were -6.5 ‰ for $\delta^{13}C$ and 1.7 ‰ for $\delta^{34}S$.

Tritium concentration also can be an indicator of hydrologic and geochemical conditions. Natural tritium in precipitation ranged from about 3 to 25 TU (tritium units) prior to 1952. From 1952 to the mid-1960's, large amounts of tritium were released to the atmosphere during atmospheric testing of thermonuclear weapons. This large input of man-made tritium to the atmosphere, and the subsequent input to ground water by recharge from precipitation, makes interpretation of some ground-water tritium data ambiguous. Examples of data that are not ambiguous include tritium concentrations less than 1 TU, which indicate no contribution of post-1952 water, and tritium concentrations larger than 50 TU, which indicate the presence of a significant portion of post-1952 water (T.B. Coplen, U.S. Geological Survey, written commun., 1989).

Geochemical processes were determined by interpretation of the data, including the use of geochemical models. Equilibrium speciation calculations were determined for water samples using the computer program WATEQF (Plummer and others, 1978). These calculations provide saturation indices (SI) of minerals that may be reacting in the system. The SI of a particular mineral is defined as:

$$\mathrm{SI} = \log \frac{\mathrm{IAP}}{K_T} \qquad (3)$$

where IAP is the ion-activity product of the mineral-water reaction and K_T is the thermodynamic equilibrium constant adjusted to the temperature of the given sample. Pertinent thermodynamic data used to calculate the saturation indices were revised from the original WATEQF (Plummer and others, 1978) and WATEQ4F (Ball and others, 1987) programs by Nordstrom and others (1990) and are summarized in table 2. The degree of saturation is expressed by the saturation indices; undersaturation is expressed as a negative saturation index, saturation is expressed as a value near zero, and supersaturation is expressed as a positive value. Saturation or supersaturation implies that the mineral might be present in the aquifer or unsaturated zone above the aquifer, whereas undersaturation implies limited contact between aquifer water and the mineral. Saturation indices, in conjunction with mineralogic information from the solid-phase samples, can be used to help determine the hydrological and geochemical processes that are important in the evolution of the observed ground-water quality.

Geochemical mass-balance models were constructed using the computer program NETPATH (Plummer and others, 1991) to determine the quantities of mineral or chemical species causing the observed changes in water quality. To solve the models, elemental concentrations and sets of plausible reacting phases for initial waters and plausible product phases for final waters are required. Mass-balance models simulate the net chemical reaction of the form:

Initial solution composition + reactant phases ⇒ final solution composition + product phases,

where reactant and product phases represent constituents that enter or leave the aqueous phase. Possible reactant or product phases were selected using solid-phase mineralogic data, speciation calculations, geologic and hydrologic inferences, and SEM analysis. Mass-balance calculations were made using Rayleigh distillation reactions calculated with equations developed by Wigley and others (1978, 1979) to determine if a particular reaction was occurring and the isotopic composition of the final solution.

GENERAL GEOCHEMICAL PROCESSES

The quality of water in the coal and spoils aquifers in the study areas generally is controlled by one or more major geochemical processes that can occur in the unsaturated zone, such as in recharge areas, or within the saturated zone. The major geochemical processes are:

- dissolution and precipitation of carbonate minerals,
- oxidation of sulfide minerals such as pyrite,
- precipitation and dissolution of sulfate minerals such as gypsum,
- ion-exchange and adsorption reactions on clay minerals and organic material,
- sulfate reduction,
- production of sulfide and carbon-dioxide gas, and
- precipitation of sulfide minerals such as amorphous iron sulfide.

The magnitude of any of these processes depends primarily on the hydrologic and geologic characteristics of the specific area.

Carbonate minerals such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), if present, might be dissolved in the near-surface unsaturated zone or in aquifers. Typical reactions might be expressed as:

$$CaCO_3 + H^+ \Leftrightarrow Ca^{2+} + HCO_3^- \tag{4}$$

and

$$CaMg(CO_3)_2 + 2H^+ \Leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- . \tag{5}$$

The hydrogen ions (H^+) in reactions 4 and 5 can result from oxidation of pyrite or from reactions of water with CO_2 gas. Carbon dioxide gas from the atmosphere or organic decay reacts with water:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \tag{6}$$

and the resulting carbonic acid (H_2CO_3) dissociates:

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- . \tag{7}$$

The overall effects of carbonate-mineral dissolution are to increase the concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) ions and to increase pH.

Dissolution and precipitation of carbonate minerals occur primarily within the unsaturated zone as water percolates below land surface. Dissolution of carbonates is ultimately limited by the ion-activity product of the particular mineral and whether the system is open or closed with respect to CO_2. Within the unsaturated zone, CO_2 derived from the atmosphere, from the decay of modern plants and coal, or from root respiration will dissolve in infiltrating water until the partial pressures of CO_2 in the vapor and liquid phases are equal. Dissolution of carbonate minerals will then proceed until the constraints of the ion-activity product and the vapor-liquid CO_2 pressure equality are simultaneously satisfied. In waters containing large concentrations of sodium sulfate, ion pairing reduces the free calcium- and carbonate-ion activities and permits further dissolution of calcite at a particular unsaturated-zone partial pressure of CO_2.

Oxidation of pyrite (FeS_2) or other iron-sulfide minerals might occur in the undisturbed unsaturated zone or within the overburden that has been disturbed by mining. The process initially requires the presence of oxygen, which is available from infiltrating recharge water or the atmosphere. The oxidation process consists of several steps, some of which are catalyzed by bacteria. The generalized reaction for the principal process involved is:

$$4FeS_2 + 15O_2 + 14H_2O \Leftrightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ . \tag{8}$$

If calcium ions are present, calcium sulfate can be formed:

$$Ca^{2+} + SO_4^{2-} \Leftrightarrow CaSO_4 . \tag{9}$$

The overall effect of the oxidation process is to increase the acidity and the concentration of sulfate ions in solution. The acid produced as a result of reaction 8 is buffered by the dissolution of carbonate minerals (reactions 4 and 5), which are present in the overburden and spoils. The sulfate ions produced in reaction 8 are either transported in solution to the aquifer or are precipitated as gypsum or other sulfate minerals as in reaction 9. These sulfate minerals might later be dissolved and transported to the aquifer by recharge water or, in a semiarid environment where annual evapotranspiration exceeds annual precipitation, might accumulate in the near-surface unsaturated zone. When disturbed by mining and replaced at depth, the sulfate minerals become available for dissolution in the saturated zone of the spoils.

Ion-exchange and adsorption reactions probably are an important process in the unsaturated zone and in the saturated spoils and coal aquifers. Generally, the process involves reactions on clay minerals where calcium, and in some cases magnesium, ions are exchanged for sodium ions:

$$\mathrm{Na_2\,(clay)} + X_{\mathrm{Mg}}\mathrm{Mg}^{2+} + (1 - X_{\mathrm{Mg}})\,\mathrm{Ca}^{2+} \Leftrightarrow \left[\mathrm{Ca}_{(1\text{-}X_{\mathrm{Mg}})}, \mathrm{Mg}_{(X_{\mathrm{Mg}})}\right]\mathrm{(clay)} + 2\mathrm{Na}^{+} \tag{10}$$

where X_{Mg} varies between 0 for pure Ca/Na cation exchange and 1 for pure Mg/Na cation exchange. When reaction 10 proceeds from left to right, it results in a decrease in calcium or magnesium ions and an increase in sodium ions in solution. The decrease in calcium ions in solution can cause further dissolution of calcium carbonate or calcium sulfate minerals to maintain equilibrium. Magnesium and potassium might also be involved in ion exchange or adsorption reactions. However, calcium generally has a greater affinity for exchange than magnesium, magnesium has a greater affinity than potassium, and potassium has a greater affinity than sodium. The extent to which exchange occurs largely depends on the cation-exchange capacity of the clay mineral or possibly organic material, and on the concentration of the ions in solution.

In anaerobic conditions, sulfate can be reduced to sulfide when organic material and sulfate-reducing bacteria are present. In reaction 11, organic material is represented compositionally as CH_2O, implying that nitrogen and phosphorus in the organic material are not present in sufficient quantities to affect the pH or alkalinity:

$$2\mathrm{CH_2O} + \mathrm{SO_4}^{-2} \xrightarrow{\text{sulfate-reducing bacteria}} \mathrm{H_2O} + \mathrm{CO_2} + \mathrm{HCO_3^-} + \mathrm{HS^-}. \tag{11}$$

The sulfate-reducing bacteria *Desulfovibrio desulfuricans* were found in relatively large numbers in 25 of 26 observation wells sampled by Dockins and others (1980, p. 6) in southeastern Montana and apparently most of the sulfide in those wells resulted from bacterial sulfate reduction. Reaction 11 results in an overall decrease in sulfate concentration, an increase in bicarbonate concentration, and the production of sulfide and carbon-dioxide gas. The sulfide ions produced as a gas in the reaction may then be removed from solution by precipitation of sulfide minerals, especially iron sulfide. Because sulfate reduction requires anaerobic conditions, it generally is not a factor in newly replaced spoils or in other oxygenated systems, such as some shallow ground water.

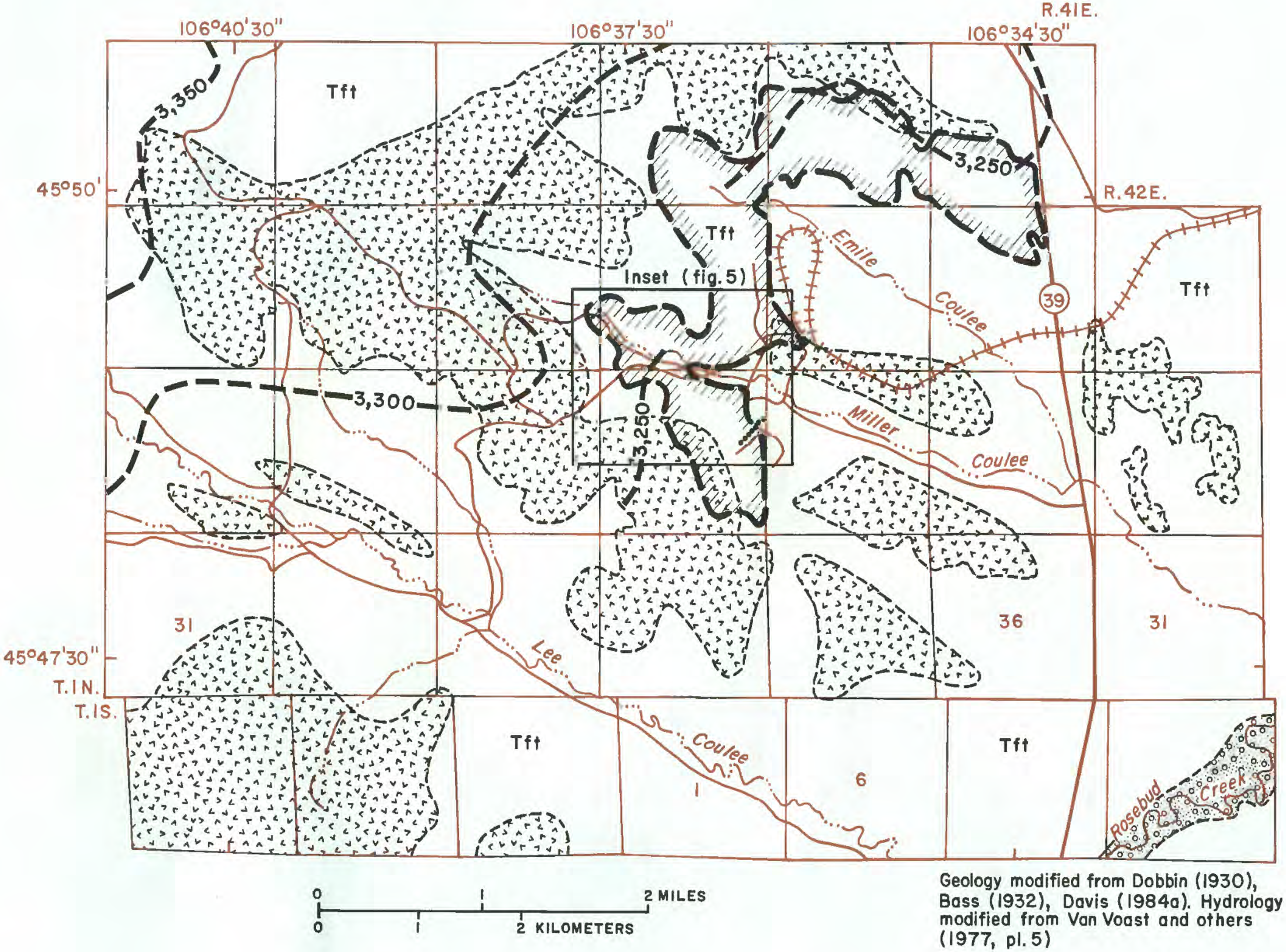
BIG SKY MINE AREA

In the Big Sky Mine area, ground-water flow is of a local nature with at least some recharge from direct infiltration of precipitation. The geochemical changes that occur as the calcium-magnesium sulfate type water moves from the unmined Rosebud coal bed into the spoils and then downgradient into the McKay coal bed and potentially offsite are the primary focus of this part of the study.

Geohydrologic Setting

The coal being mined at the Big Sky Mine area is part of the Tongue River Member of the Paleocene Fort Union Formation in the Powder River structural basin (fig. 1). The Big Sky Mine area opened to mining in 1969. The coal beds being mined are the Rosebud coal, generally about 25 ft thick, and the underlying McKay coal, about 10 ft thick. Around the mine disturbance area (fig. 4), the coal beds generally have been eroded or burned, leaving clinker or sandy material of the Tongue River Member. The burning of coal, commonly ignited by spontaneous combustion or range fires over the past hundreds of thousands of years, hardens, sinters, or sometimes melts the overlying sandstone, siltstone, and shale. The resultant rocks, collectively called clinker, are resistant to erosion because they are harder than the unbaked rocks and because baking causes increased fracture permeability, which allows water to infiltrate and, therefore, minimizes surface runoff.

Spoils consist primarily of overburden and interburden that have been removed and replaced as a result of mining. Overburden is the primary spoils material where only the Rosebud coal bed has been removed. The spoils consist of a mixture of overburden and interburden where both coal beds have been removed. The spoils might be composed entirely of interburden where the Rosebud coal has been eroded or burned.



Geology modified from Dobbin (1930), Bass (1932), Davis (1984a). Hydrology modified from Van Voast and others (1977, pl. 5)

Figure 4. Location, geology, and 1976 potentiometric surface of the Big Sky Mine area, Montana. (Explanation on following page.)

EXPLANATION FOR FIGURE 4

Qal	ALLUVIUM (HOLOCENE AND PLEISTOCENE)--Also includes uncorrelated gravel deposits
Tft	TONGUE RIVER MEMBER OF FORT UNION FORMATION (PALEOCENE)--Areas of clinker (baked and fused rock formed by the burning of coal beds) shown by pattern
– – – – – – – – –	APPROXIMATE GEOLOGIC CONTACT
— —3,300— —	APPROXIMATE POTENTIOMETRIC CONTOUR--Shows altitude at which water level would have stood in tightly cased wells completed in the Tongue River Member or reclaimed mine spoils. Contour interval 50 feet. Datum is sea level
//////////////	GENERAL BOUNDARY OF AREA MINED OR TO BE MINED
•	OBSERVATION WELL

The principal aquifers in the study area are the Rosebud and McKay coal beds, the spoils, and alluvium along Rosebud Creek. The coal aquifers have an average hydraulic conductivity of 8.8 ft/d and a median of 0.79 ft/d on the basis of nine aquifer tests (Davis, 1984a, p. 47). The spoils aquifer was created by placement of the removed overburden and interburden behind the advancing mine pit, creating a rubble zone of broken bedrock at the base overlain by granular material. The spoils aquifer is heterogeneous and has a large range of hydraulic-conductivity values, with an average value of 9.7 ft/d and a median of 0.028 ft/d on the basis of eight aquifer tests (Davis, 1984a, p. 47). Recharge in the Big Sky Mine area primarily is by infiltration of precipitation on nearby clinker outcrops. The relatively resistant and permeable clinker commonly caps the nearby knobs, ridges, and buttes and recharge water from these areas moves from the northwest to southeast as indicated by the potentiometric surface (fig. 4). The spoils are recharged primarily by lateral inflow from coal aquifers, and locally by infiltration of direct precipitation on sandy spoils material. Discharge from the spoils and coal aquifers primarily is by lateral flow southeastward to clinker or sand aquifers, with eventual discharge into alluvium along Rosebud Creek. Minor discharge from the coal aquifers is by domestic and stock-watering wells. Evapotranspiration from shallow parts of the aquifers might also be a source of some ground-water discharge.

The location of 10 wells drilled in the Big Sky Mine area during this study is shown in figure 5. Three wells (BSUMR1, BSUMSP1, and BSUMSP2) were drilled near the upper end of Miller Coulee with one well completed in coal and the other two wells completed in a downgradient spoils aquifer. The purpose of the wells was to quantify recharge into the mine area and geochemical changes that occur as water moves from the coal aquifer into the spoils aquifer. In this area, the Rosebud coal bed was mined during 1976 and 1977 and was replaced with spoils material that became saturated within a few years. Well BSUMR1 was completed in saturated Rosebud coal bed and the two other wells were completed in sandy spoils (table 3).

Seven wells were drilled along a downgradient flow path from the saturated spoils to the unmined McKay coal bed (fig. 5). In this area, the McKay coal was mined from 1969 to 1971, and the spoils material was replaced and became saturated within a few years. Wells BSLMSP3 and BSLMSP1 were completed in the spoils aquifer; wells BSLMMC1, BSLMMC2 and BSLMMC3 were completed in the aquifer in the unmined McKay coal bed; well BSLMMC5 was completed in an iron-rich sandstone at a depth contiguous with the McKay coal bed; and well BSLMSM1 was completed in gray sandstone of an interval stratigraphically lower than the McKay coal bed (sub-McKay) (table 3). The horizontal hydraulic gradient of about 0.01ft/ft might be at least partly controlled by an upgradient highwall pond, lateral flow from upgradient spoils (fig. 5), and infiltration of local recharge. Discharge from the unmined coal is offsite to stratigraphic equivalents and eventually to alluvium along Miller Coulee. Little or no water is thought to discharge to the sub-McKay. Additional information on the hydrology of the Big Sky Mine area is described by Davis (1984a).

Geochemistry and Geochemical Processes

The ground-water geochemistry at the Big Sky Mine area was studied to determine potential geochemical processes that might occur as water from the spoils flows into the downgradient aquifer in the McKay coal bed. Another objective was to determine processes related to changes in ground-water geochemistry as water flows from the aquifer in the unmined Rosebud coal bed into the spoils.

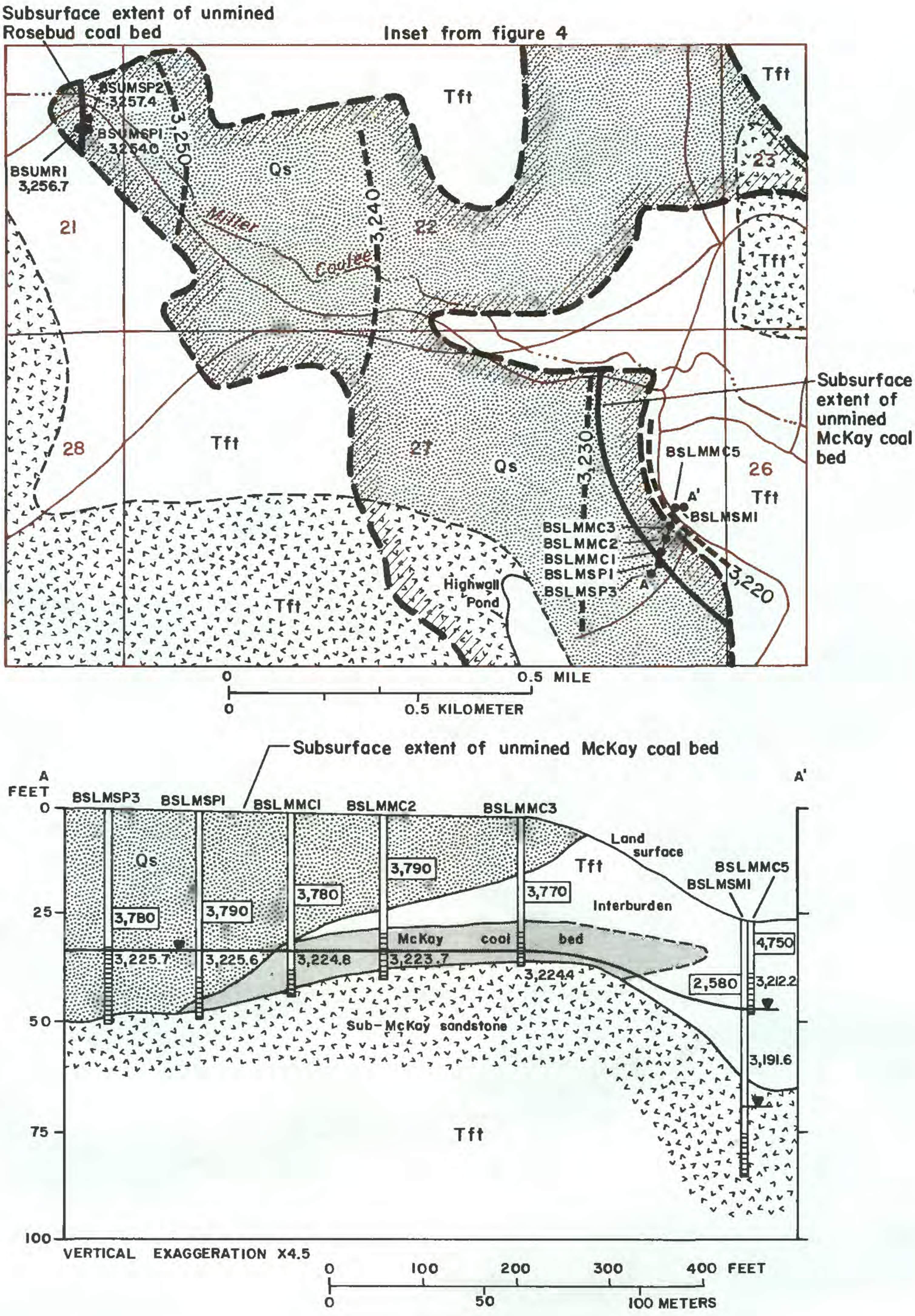


Figure 5. Location of wells, 1988 potentiometric surface, and geologic section of part of the Big Sky Mine area, Montana. (Explanation on following page.)

EXPLANATION FOR FIGURE 5

Qs	SPOILS (HOLOCENE)
Tft	TONGUE RIVER MEMBER OF FORT UNION FORMATION (PALEOCENE)--Areas of clinker (baked and fused rock formed by the burning of coal beds) shown by pattern
———— - - - -	GEOLOGIC CONTACT--Dashed where approximately located
— — —3,240— — —	APPROXIMATE POTENTIOMETRIC CONTOUR--Shows altitude at which water level would have stood in tightly cased wells completed in the Tongue River Member or reclaimed mine spoils. Contour interval 10 feet. Datum is sea level
//////////////	GENERAL BOUNDARY OF AREA MINED OR TO BE MINED
A ●——● A'	TRACE OF SECTION
——▼——	POTENTIOMETRIC SURFACE
3,790	DISSOLVED-SOLIDS CONCENTRATION--Units of milligrams per liter in water sample from well, October 1988
3,225.6	ALTITUDE OF WATER LEVEL, IN FEET ABOVE SEA LEVEL
	WELL AND NUMBER
BSLMMC3 ●	Map
BSLMMC3 ▯	Section Screened interval

Results of Solid-Phase Analysis

Detailed analyses of samples from unmined consolidated rocks, spoils, and coal beds were essential to determine geochemical processes and water-rock interactions. Solid-phase samples were analyzed for mineralogy and for concentrations of major and trace elements and exchangeable cations. The samples of overburden of the Rosebud coal bed was composed of clayey siltstone and calcareous, fine-grained sandstone and included abundant dolomite cement, feldspars, some calcite, and traces of pyrite and glauconite. Clay in the overburden consisted of kaolinite with minor quantities of smectite, illite, and chlorite (tables 4, 5, 6). Spoils in this area created from Rosebud overburden were mineralogically similar to the unmined overburden, except that the spoils contained more calcite and less dolomite (table 5).

The mineralogy of a calcareous clayey siltstone in interburden between the Rosebud and McKay coal beds (samples from BSLMMC2, BSLMMC3, and BSLMSM1) consisted of abundant quartz, dolomite and calcite cements, muscovite, biotite, and sericite. The predominant clays were kaolinite, illite, and chlorite. Feldspars were common in most samples, gypsum was detected in minor quantities, and strontianite, and possibly thenaderite, were detected in trace quantities. Pure, crystalline gypsum, most likely a result of evaporation, was detected in fractures in a siltstone sample. Samples of spoils consisting of interburden (samples from BSLMSP3 and BSLMSP1) were mineralogically similar to samples of the unmined interburden except that the spoils generally contained more quartz, chlorite, and smectite and less calcite (tables 5, 6).

The concentrations of cations and trace elements were determined from 11 drill-core samples of spoils and unmined consolidated rock collected in the Big Sky Mine area (table 7). The predominant elements were aluminum associated with the clay minerals, calcium and magnesium associated with the carbonate cements, and iron, potassium, and silica likely associated with silicate minerals. Generally, the concentrations from the samples of unmined consolidated rock and the spoils were indistinguishable. Solid-phase samples from four cores (consisting of spoils or siltstone) were analyzed for exchangeable cations. Calcium was the most prevalent exchangeable cation, with lesser quantities of magnesium, sodium, and potassium (table 8). Results from analysis of the one spoils sample (well BSLMSP1) did not differ greatly from the analysis of the three siltstone samples.

The concentrations of major and minor oxides and trace elements were determined from laboratory ash of four samples of McKay coal (table 9). The median concentrations of selected constituents were within the range of, and generally similar to, the mean concentrations from the analyses of 410 samples from throughout the Powder River structural basin (table 10).

Results of Ground-Water Analysis

Water samples were collected 3 times from 4 of the observation wells, twice from 1 of the wells, and once from the other 5 wells. Results of analyses for major ions and trace elements are given in table 11. Predominant cations and anions are depicted on trilinear diagrams (fig. 6) for samples collected during October 1988 to illustrate the similarity in the chemical types. Water from well BSUMR1 completed in the upgradient coal bed had a dissolved-solids concentration of 2,150 mg/L and was a magnesium-calcium sulfate chemical type (fig. 6). Water from wells completed in the spoils or downgradient coal bed had an average dissolved-solids concentration of about 3,800 mg/L and also was a magnesium-calcium sulfate chemical type. The dissolved-solids concentrations are similar to the mean dissolved-solids concentration of 2,700 mg/L from 19 coal wells and 3,700 mg/L from 18 spoils wells as reported by Davis (1984a, p. 51). Stiff diagrams of coal and spoils water (fig. 6) indicate that magnesium, calcium, and sulfate concentrations increase and bicarbonate concentrations decrease as water flows from the upgradient Rosebud coal bed (well BSUMR1) into the spoils of Rosebud overburden (well BSUMSP1). Major-ion concentrations in water from the spoils of Rosebud overburden, the interburden spoils (BSLMSP3), and the downgradient McKay coal bed (well BSLMMC2) are similar.

Water samples for laboratory determination of dissolved-gas concentration were collected from five observation wells (table 12). Oxygen, carbon dioxide, and methane were the gases of primary interest. Dissolved-oxygen concentrations larger than 1.0 mg/L were detected in water from wells BSUMR1 and BSUMSP2, whereas only a trace was detected in water from wells BSLMSP1, BSLMMC1, and BSLMMC2 in the downgradient flow path. Large concentrations of carbon dioxide were detected in water from wells BSLMSP1, BSLMMC1, and BSLMMC2, which are completed in the downgradient spoils and coal beds. Smaller concentrations were detected in water from wells BSUMR1 and BSUMSP2.

Water samples were collected for analysis of isotopic ratios or activities from five of the observation wells (table 13). Analytical results for the isotopes are virtually the same for water from the spoils well (BSLMSP1), and wells completed in the McKay coal bed (BSLMMC1 and BSLMMC2). The main isotopic dissimilarity is the difference in tritium activity between water from well BSUMR1 in the Rosebud coal bed (5.7 pCi/L) and water from well BSUMSP2 in the spoils (64 pCi/L).

Mineral-Water Equilibrium and Relation to Geochemical Processes

Thermodynamic equilibrium calculations for ground water from the Big Sky Mine area using the program WATEQF (Plummer and others, 1978) are listed in table 14. Calculations result in saturation indices of minerals that might be reacting in the system. Saturation indices denote that most water is saturated with respect to quartz, calcite, dolomite, and goethite, and is near saturation with respect to aragonite, gypsum, and celestite.

The oxidation-reduction (redox) state of the water was estimated based on dissolved-gas concentrations. Water from wells along the inferred downgradient flow path had concentrations of dissolved oxygen and hydrogen sulfide that were small and near the detection limits (table 11). Concentration of these parameters varied between samples collected from individual wells and showed no distinct differences between wells completed in spoils or coal, making it difficult to accurately determine the redox state of the water. For purposes of equilibrium calculations, an Eh value of -0.01 volt was estimated for all samples from the downgradient wells and an Eh value of 0.2 volt was estimated from dissolved-oxygen concentrations for the upgradient wells.

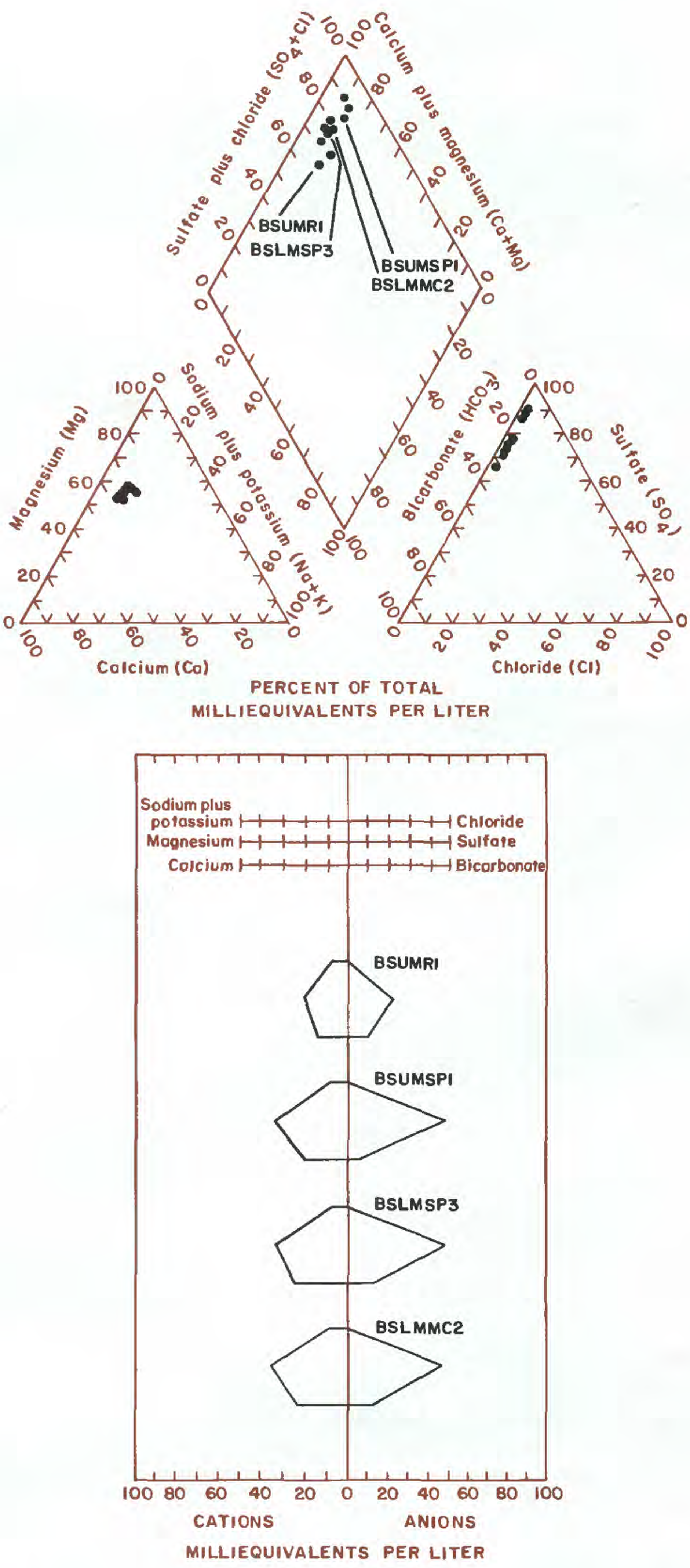


Figure 6. Trilinear and Stiff diagrams showing geochemical properties of ground water from the Big Sky Mine area, Montana.

Flow from Upgradient Coal Aquifer to Spoils Aquifer

The geochemical process of dedolomitization, the irreversible dissolution of gypsum at or near calcite-dolomite saturation, most likely occurred as water from the upgradient coal aquifer flowed into the spoils aquifer. Concentrations of calcium, magnesium, sodium, and sulfate increased and alkalinity decreased along the flow path from well BSUMR1 in the upgradient coal aquifer to wells BSUMSP1 and BSUMSP2 in the spoils aquifer (table 11). Water in the coal aquifer was saturated or nearly saturated with respect to calcite and dolomite and was undersaturated with respect to gypsum (table 14). Dissolution of gypsum added calcium to the water, which may have resulted in calcite precipitation, and caused the pH to decrease (Plummer and others, 1990, p. 1,987), owing to an increase in H^+ released from HCO_3^- during incorporation of CO_3^{2-} into the calcite. The decrease in pH and CO_3^{2-} probably caused the water to be undersaturated with dolomite, thereby increasing dissolution and increasing the concentration of dissolved magnesium. The amount of dolomite and gypsum dissolved normally would exceed the amount of calcite precipitated; therefore, the concentration of dissolved calcium normally would increase. As expected for the dedolomitization reaction (Plummer and others, 1990, p. 1,994, fig. 10), alkalinity decreased as sulfate increased. Calcite was more common in spoils samples from well BSUMSP1 than in the unmined overburden samples from well BSUMR1, whereas dolomite was more abundant in the overburden than in the spoils (table 5). This mineralization may have been due to precipitation of calcite and dissolution of dolomite within the spoils material as a result of dedolomitization. The increase in sodium concentration might have been the result of exchange of calcium ions for sodium ions on clay minerals or the dissolution of a sodium salt in the spoils material.

The dedolomitization reaction hypothesis was tested by constructing a mass-balance model to simulate the geochemical changes. The model is based on a set of probable reacting phases and the elemental concentrations corresponding to those phases for the initial and final waters. The phases selected were calcite, dolomite, gypsum, cation exchange, and carbon dioxide. Results of the simulated mass transfer, as calculated by the model NETPATH (Plummer and others, 1991), are given in table 15 and indicate the following geochemical processes: dolomite and gypsum dissolution with accompanying calcite precipitation, exchange of calcium ions for sodium ions, and transfer of carbon dioxide indicating an open system. In the overall dedolomitization reaction:

$$CaMg(CO_3)_2 + CaSO_4 \Rightarrow 2CaCO_3 + MgSO_4(aq), \qquad (12)$$

where 2 moles of calcite are precipitated and 1 mole of dolomite is dissolved for every mole of $CaSO_4$ irreversibly added to solution, in a ground-water system at equilibrium with calcite, dolomite, and gypsum (Plummer and others, 1990, p. 2,010). The waters were saturated with calcite and dolomite but undersaturated with gypsum, indicating that mass transfer of gypsum might increase disproportionately to that of dolomite and calcite.

Flow from Spoils Aquifer to Downgradient Coal Aquifer

As water flowed from the spoils aquifer to the downgradient coal aquifer, the dissolved-solids concentration essentially was unchanged (fig. 5). Only small differences in concentrations of major ions were detected between the spoils wells (BSLMSP3 and BSLMSP1) and two of the coal wells (BSLMMC1 and BSLMMC2) (table 11). Concentrations of a few constituents were noticeably different only between the spoils wells and coal well BSLMMC3, as iron increased substantially, dissolved silica nearly doubled, and bicarbonate, manganese, and potassium decreased slightly. A possible explanation for the differences in concentrations was an additional source of recharge to well BSLMMC3, as water levels in well BSLMMC3 were slightly higher than those in well BSLMMC2.

Results of samples collected in October 1988 show a gradual decrease in concentrations of most trace elements along the inferred flow path. However, results from subsequent sampling did not substantiate this trend, possibly because of changes in laboratory or sampling procedures or physical changes in the ground-water system, such as slight changes in ground-water flow rate or direction. If the initial results were accurate, then the trace-element concentrations most likely decreased due to sorption of the dissolved elements onto the coal or onto clay minerals within the coal.

WEST DECKER MINE AREA

At the West Decker Mine study area, several dissolved constituents had large changes in concentration as water moved along an inferred flow path from a spoils aquifer to a downgradient unmined coal aquifer. The types and quantities of changes, the possible causes and chemical reactions, and the mass transfer due to these geochemical changes are discussed in this section.

Geohydrologic Setting

The Decker Mine area consists of the East, North, and West Decker Mine areas (fig. 7). The West Decker Mine area was opened in 1972. The coal being mined is part of the Tongue River Member of the Paleocene Fort Union Formation. The main coal beds in descending stratigraphic order are the Anderson bed, the Dietz 1 bed, and the Dietz 2 bed. Within the West Decker Mine study area the Anderson and Dietz 1 are combined into one bed that generally is about 50 ft thick. This Anderson-Dietz 1 bed is separated from the 25-ft thick Dietz 2 bed by as much as 65 ft of interburden. The thickness of overburden above the Anderson-Dietz 1 bed varies within the mine area, ranging from tens of feet to about 100 ft. Also within the mine area is clinker which consists of shale, siltstone, and sandstone that has been fractured and baked by the burning of underlying coal beds (fig. 8).

The predominant lithologies in the overburden are siltstone, very fine-grained sandstone, some brown and gray to grayish-black shale, and several distinct layers of gray, calcareous siltstone (tables 3 and 4). These lithologic units generally were also identified in the spoils, which is composed of removed and replaced overburden.

The principal aquifers in the study area are clinker, coal beds, spoils, and alluvium. The clinker might be locally permeable as a result of fracturing and, thus, be a productive aquifer. The coal aquifer of principal interest is the Anderson-Dietz 1 coal bed. The spoils aquifer was created by placement of the removed overburden behind the advancing mine pit, creating a rubble zone at the base that might be at least partly confined by relatively impermeable clay in the overlying spoils. Alluvial aquifers in discharge areas generally are hydraulically connected to upgradient aquifers. The unmined shale and siltstone overburden is relatively impermeable and is not considered to be an aquifer. Davis (1984a, p. 19) reported hydraulic conductivities of the spoils aquifer ranging from 0.0033 to 8.4 ft/d, with a median of 1.8 ft/d determined from 6 aquifer tests, and hydraulic conductivities of the coal aquifer ranging from 0.46 to 29 ft/d, with a median of 2.2 ft/d determined from 16 aquifer tests.

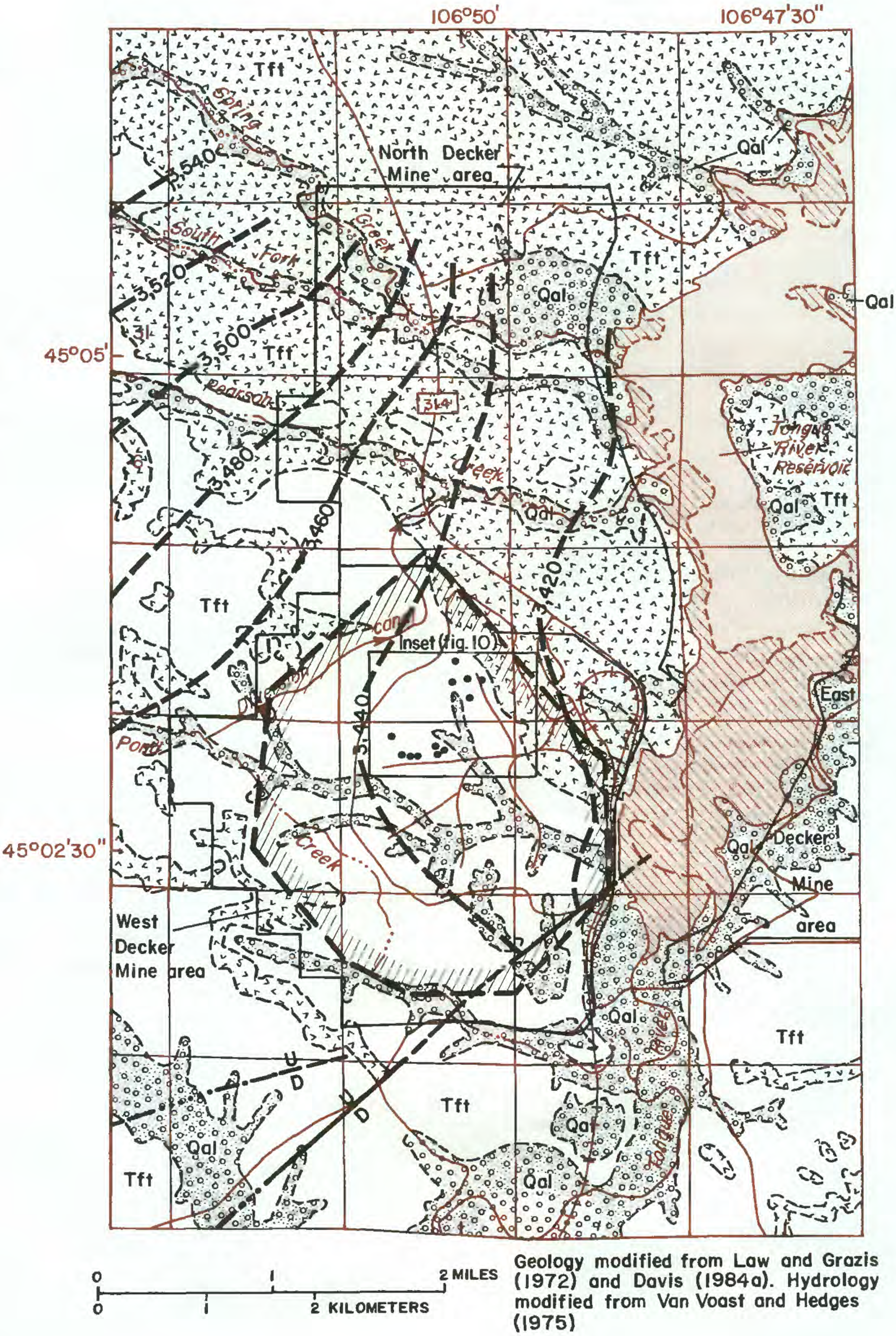
Recharge to aquifers undisturbed by mining primarily is from infiltration of precipitation on clinker outcropping in regional recharge areas (fig. 8). Natural discharge from the unmined coal aquifers primarily is to the Tongue River Reservoir or clinker and alluvium along the valley of the Tongue River.

Ground-water inflow to the mine areas primarily is from adjoining clinker and coal beds. Infiltration of precipitation through the spoils probably is not a significant source of recharge. In many of the active mine areas, excavations are at a level lower than the Tongue River Reservoir at its normal stage of 3,412 ft. Because of the excavations, the natural gradient of the potentiometric surface might be reversed in local areas, especially near the reservoir, and water from the reservoir might be recharging the aquifers and discharging to the mine pits in those areas (fig. 8).

Water levels in spoils wells within about one-quarter mile of the Tongue River Reservoir apparently respond to seasonal fluctuations in the stage of the reservoir with water levels rising in summer in response to spring runoff refilling the reservoir. However, water levels in wells one-half mile or greater from the reservoir apparently do not respond to these seasonal reservoir fluctuations (data from Montana Bureau of Mines and Geology). Wells used during this study are at least one mile from the reservoir and water levels in these wells show no response to the seasonal changes in the reservoir stage.

Hydrographs of long-term water levels in the West Decker Mine area (fig. 9) indicate that when mining of the Anderson-Dietz 1 coal bed started in the early 1970's, water levels in that coal bed (well WR-01) (fig. 10) declined about 40 ft in 2 years. Water levels gradually declined in the Dietz 2 coal bed (well WR-07) (Van Voast and Reiten, 1988, sheet 2). Water levels in well WR-01 recovered partly during the late 1970's and early 1980's. When mining of the Dietz 2 coal in the southeast part of the mine area started in the early 1980's, water levels in that coal bed declined an additional 30 ft and water levels in the Anderson-Dietz 1 coal bed (well WR-01) declined gradually (fig. 9).

Figure 11 shows fluctuations of long-term water levels for a spoils well and two Anderson-Dietz 1 coal wells about one-quarter mile east and downgradient from the spoils well. Water levels in the spoils well, DS-6A, rose about 14 feet in 1976, and continued to rise another 10 feet in the next two years, most likely in response to initial saturation of the spoils aquifer. Water levels began to decline in 1981 and dropped about 20 feet in one year probably in response to mining of both the Anderson-Dietz 1 and the Dietz 2 coal southeast of the well. The hydrographs of the two coal wells WR-01 (104 feet deep) and WR-06 (135 feet deep), are similar to each other and show trends similar to the spoils-well hydrograph. The coal-well hydrographs indicate that water levels began to rise in 1977, about one year after the water-level rise in the upgradient spoils well, and began to decline in 1980, about 1-2 years before the water level declined in the spoils well. These water-level fluctuations may indicate the relative hydraulic



Geology modified from Law and Grazis (1972) and Davis (1984a). Hydrology modified from Van Voast and Hedges (1975)

Figure 7. Location, pre-mining geology, and pre-mining potentiometric surface of the Decker Mine area, Montana. (Explanation on following page.)

EXPLANATION FOR FIGURE 7

Qal	ALLUVIUM (HOLOCENE AND PLEISTOCENE)--Also includes uncorrelated gravel deposits
Tft	TONGUE RIVER MEMBER OF FORT UNION FORMATION (PALEOCENE)--Areas of clinker (baked and fused rock formed by the burning of coal beds) shown by pattern
◻	NORMAL RESERVOIR STAGE 3,412 FEET ABOVE SEA LEVEL
▧	MAXIMUM RESERVOIR STAGE 3,424 FEET ABOVE SEA LEVEL
- - - - - - - - - -	APPROXIMATE GEOLOGIC CONTACT
U/D — — — • • •	FAULT--Dashed where approximately located; dotted where inferred. U, upthrown side; D, downthrown side
— —3,440— —	APPROXIMATE POTENTIOMETRIC CONTOUR--Shows altitude at which water level would have stood in tightly cased wells completed in the Tongue River Member or reclaimed mine spoils. Contour interval 20 feet. Datum is sea level
————————	GENERAL BOUNDARY OF WEST, EAST, AND NORTH DECKER MINE AREAS
//////////////////	GENERAL BOUNDARY OF AREA MINED OR TO BE MINED, WEST DECKER MINE
●	OBSERVATION WELL

connection between the spoils aquifer and the coal aquifer. Water saturating the spoils aquifer in 1976 apparently then flowed into the coal, resaturating that aquifer within one year. Mining of the coal aquifers southeast of the wells resulted in water-level declines in the coal wells starting in 1980. Within 1-2 years water levels in the upgradient spoils wells began to decline. Assuming that water in the spoils aquifer recharged the coal aquifer and that the resaturation occurred within one year, then the water flowed at a rate of more than one foot per day, a relatively fast travel time.

The location of six wells drilled in the West Decker Mine area as part of this study is shown in figure 10. Three wells (WDFCL1, WDFD12, and WDFSP3) are near the active mine area boundary and the other three (WDESP1, WDESP2, AND WDED11) are in either the saturated spoils aquifer or the downgradient coal aquifer. Lithologies determined in drilling the wells are listed in table 3. Well WDFCL1, located near the boundary of active mining, is completed in about 30 ft of unmined Anderson-Dietz 1 coal. Well WDFD12, located within the mine disturbance area, also was completed in Anderson-Dietz 1 coal. Well WDFSP3, completed in the spoils, was downgradient of coal and clinker. Water levels in well WDFD12 recovered slowly after being pumped dry, and the hydraulic conductivity, although not measured, was assumed to be at the lower end of coal-aquifer values. Water levels in well WDFCL1 recovered relatively quickly upon cessation of pumping sustainable yields of over a gallon per minute, indicating a substantially larger hydraulic conductivity. Water levels in well WDFSP3 recovered very slowly after bailing small quantities of water, indicating a small hydraulic conductivity, assumed to be at the lower end of spoils-aquifer values.

Figure 10 illustrates a cross-sectional view of wells WDESP1, WDESP2, and WDED11. The wells were drilled through spoils material, overburden, or the Anderson-Dietz 1 coal bed, and a few feet into the underlying interburden. The approximate potentiometric surface of the water levels in the spoils aquifer and Anderson-Dietz 1 coal aquifer (fig. 10) indicates flow from the north toward the south-southeast. Dewatering effects of mining, the initial saturation of the spoils aquifers, and the consequent resaturation of coal aquifers have greatly changed the hydrologic processes at the West Decker Mine area. Even though water levels have dropped significantly in this

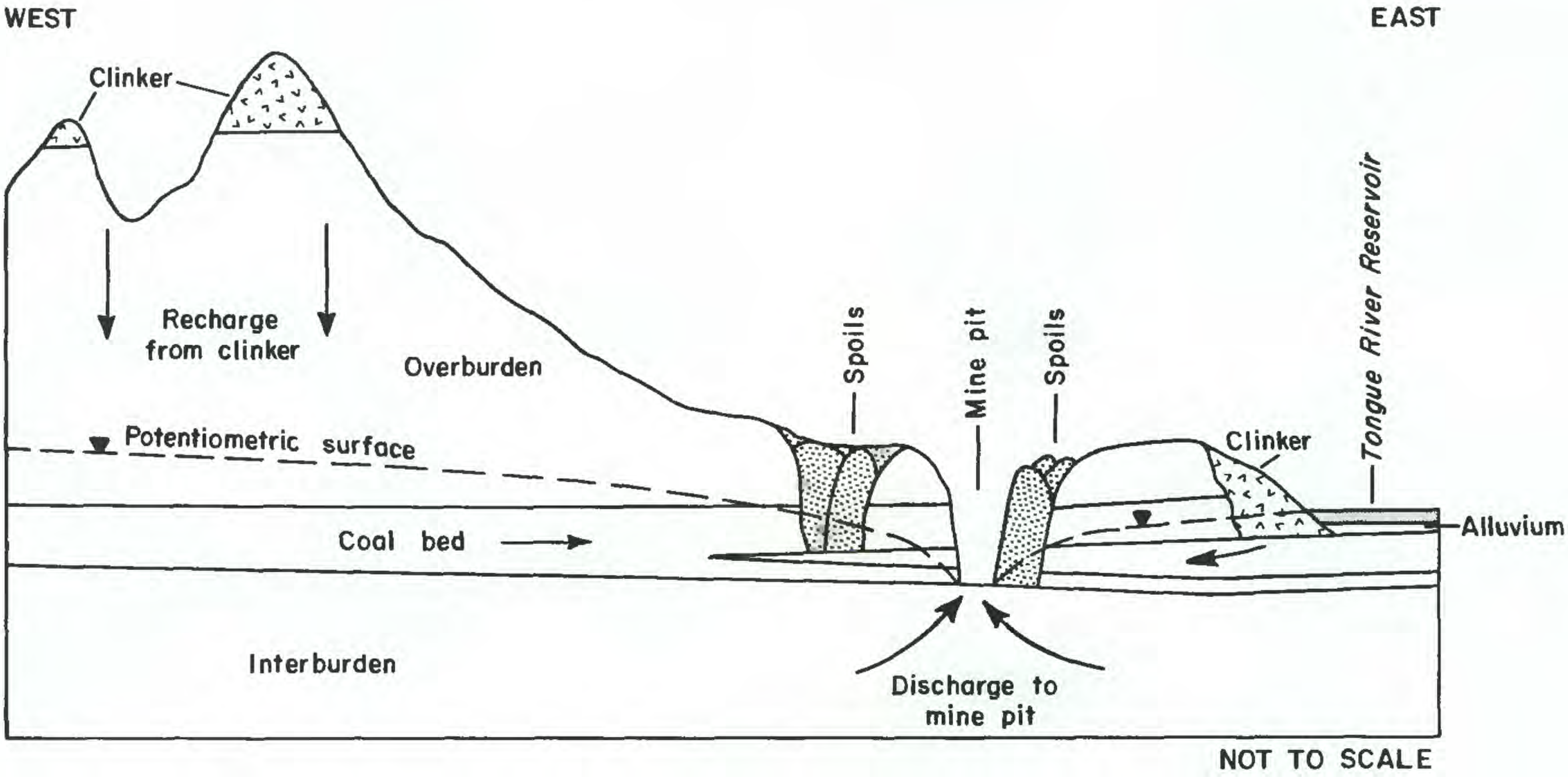


Figure 8. Generalized hydrogeologic section showing coal beds of the Fort Union Formation and associated strata after mining of the West Decker Mine area, Montana. Arrows indicate general direction of ground-water flow.

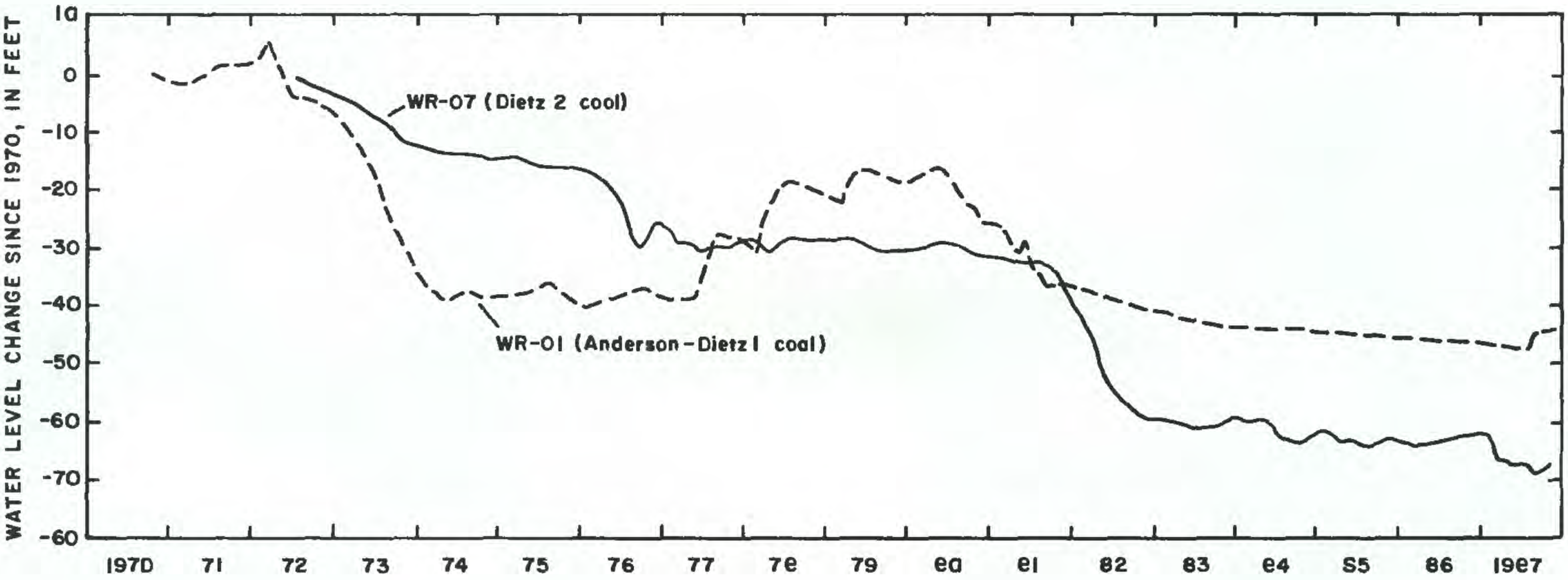


Figure 9. Water levels in wells in the West Decker Mine area, Montana, 1970-87 (data from Van Voast and Reiten, 1988, sheet 2).

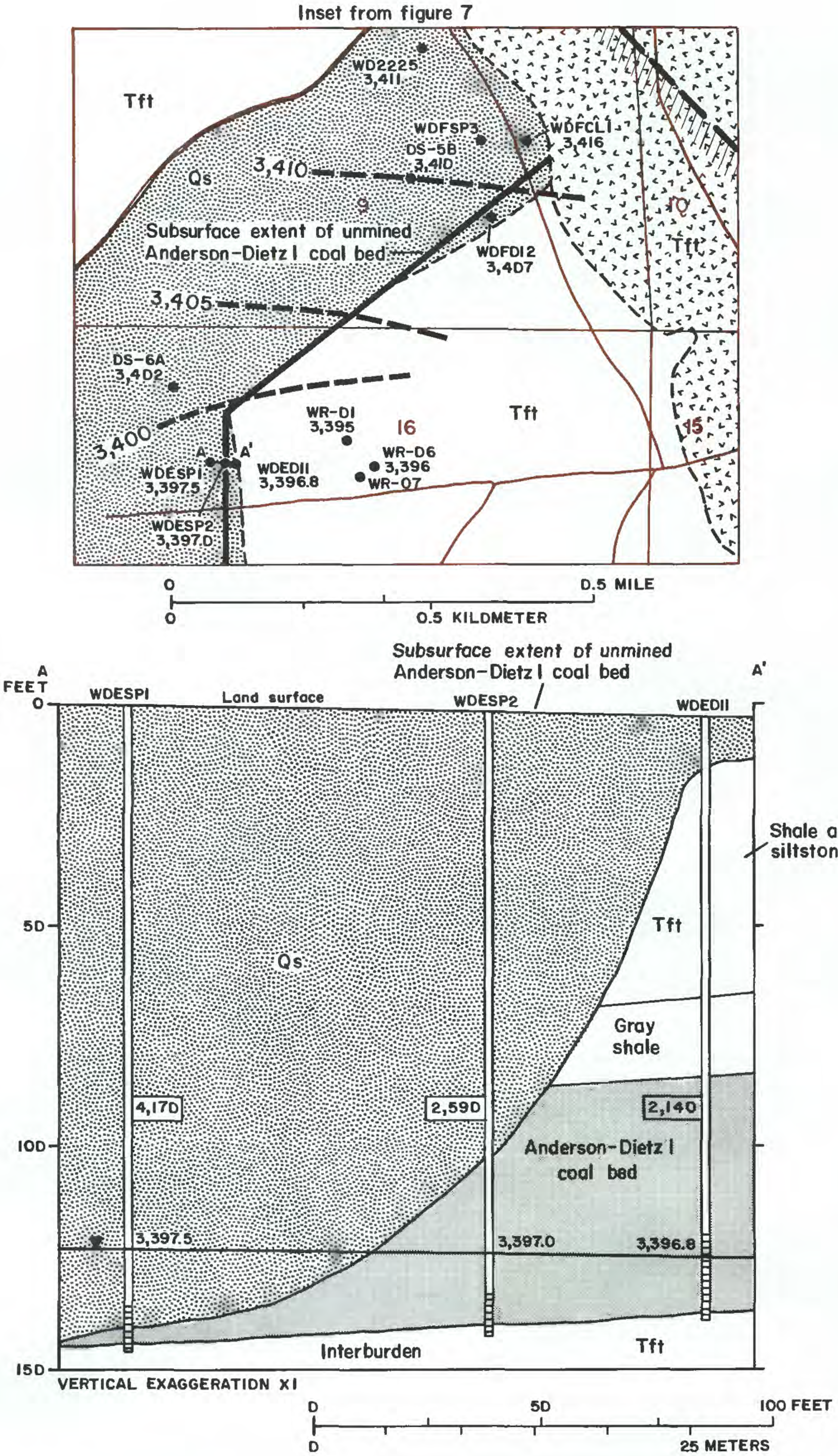


Figure 10. Location of wells, 1988 potentiometric surface, and hydrogeologic section of part of the West Decker Mine area, Montana. (Explanation on following page.)

EXPLANATION FOR FIGURE 10

Qs	SPOILS (HOLOCENE)
Tft	TONGUE RIVER MEMBER OF FORT UNION FORMATION (PALEOCENE)--Areas of clinker (baked and fused rock formed by the burning of coal beds) shown by pattern. May include some alluvium not disturbed by mining
———— – – – –	GEOLOGIC CONTACT--Dashed where approximately located
– – –3,405– – –	APPROXIMATE POTENTIOMETRIC CONTOUR--Shows altitude at which water level would have stood in tightly cased wells completed in the Tongue River Member or reclaimed mine spoils. Contour interval 5 feet. Datum is sea level
▨	GENERAL BOUNDARY OF AREA MINED OR TO BE MINED
A ●—● A'	TRACE OF SECTION
—▼——	POTENTIOMETRIC SURFACE
4,170	MEDIAN DISSOLVED-SOLIDS CONCENTRATION--Units in milligrams per liter in water sample from well, October 1988
3,397.5	ALTITUDE OF WATER LEVEL, IN FEET ABOVE SEA LEVEL
	WELL AND NUMBER
WDESPI ●	Map
WDESPI ▯	Section
▤	Screened interval

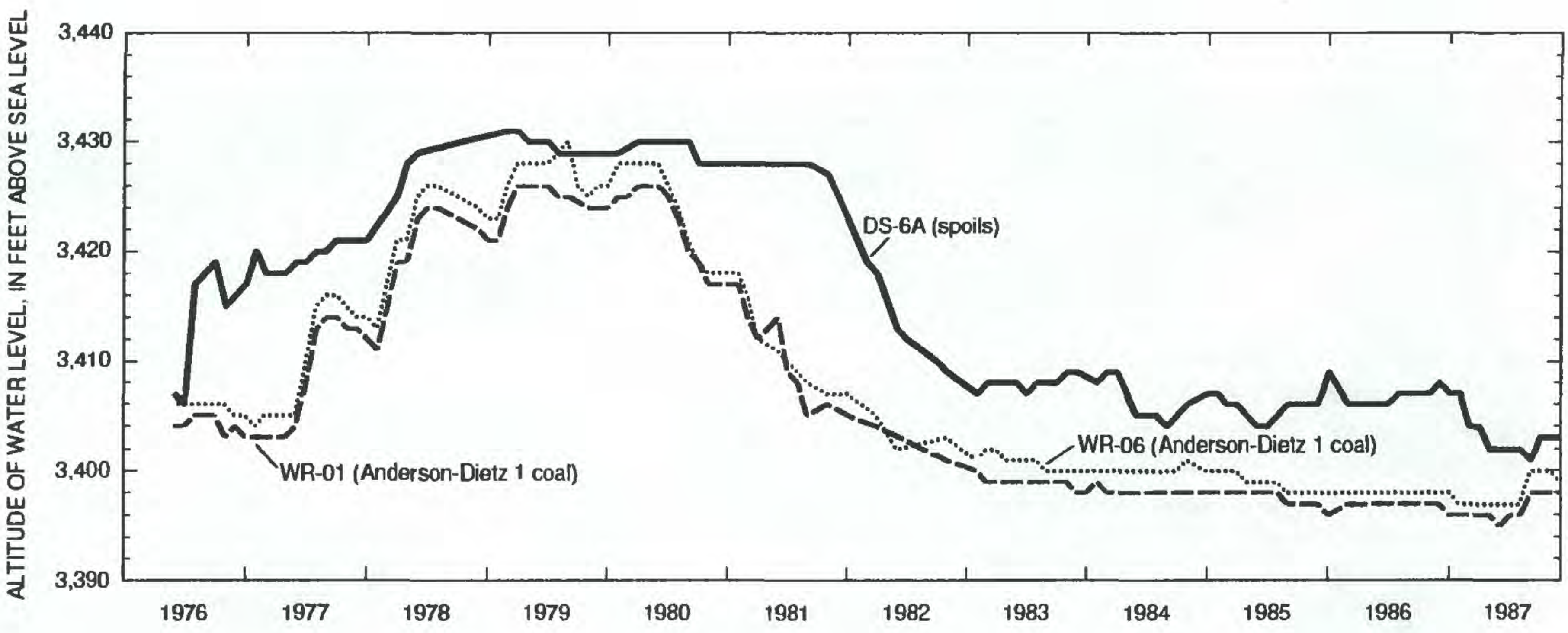


Figure 11. Water levels in three wells in the West Decker Mine area, Montana, 1976-87.

area since mining began in the early 1970's, the general configuration of the water table has not changed substantially. Prior to mining, water flowed from the recharge areas north and west of the mine area to discharge areas near the Tongue River Reservoir (fig. 7). The potentiometric surface in 1988 (fig. 10) is about 20 to 30 feet lower than the pre-mining potentiometric surface (fig. 7). The hydraulic gradient of the potentiometric surface shown in figure 10 is about 0.005, the change in head between the three wells shown in the cross-section is also about 0.005, whereas the pre-mining gradient in this area (fig. 7) is about 0.003 indicating that mining effects have steepened the gradient. Further information on the hydrology of the West Decker Mine area including a ground-water flow model is in Davis (1984a).

Water levels in wells shown in the hydrogeologic section (fig. 10) are higher in the spoils well and lower in the coal wells, indicating flow from the spoils into the coal. Although it is possible that wells WDESP1, WDESP2, and WDED11 might not be along a direct flow path, it is assumed for the purpose of this report that they are along a direct flow path. However, because of these uncertainties, this flow path will be referred to in this report as the inferred flow path.

Geochemistry

The major emphasis of the study of geochemistry at the West Decker Mine area was to determine the potential for geochemical changes as ground water flows from a spoils aquifer into an unmined coal aquifer. Results of analyses of solid-phase samples from spoils, unmined consolidated rock, and coal, and ground-water samples were essential to the determination of geochemical processes and water-rock interactions.

Results of Solid-Phase Analysis

The mineral content of the unmined consolidated rock (overburden and clinker) and spoils collected from drill-core samples is listed in tables 4, 5, and 6. The clinker sample, collected from well WDFCL1 at a depth of 50 ft, was a fine-grained clayey siltstone that primarily contained quartz, muscovite, feldspars, and trace amounts of iron (tables 4 and 5). Unmined overburden from well WDED11 included a slightly calcareous clayey siltstone with calcite and dolomite cement and trace amounts of gypsum, and a calcareous siltstone containing abundant calcite and dolomite and a trace of barite (tables 3 and 5).

The mineral content of mine spoils was determined by X-ray diffraction of 11 drill-core samples (tables 5 and 6). Quartz was the most abundant mineral in all samples. Carbonate minerals, particularly dolomite, and feldspars were common in most samples. Trace quantities of thenardite (a sodium-sulfate mineral), siderite, and celestite were detected in some samples. The clay content of the spoils included abundant kaolinite and smectite (table 6). This was markedly different from the clay content at the Big Sky Mine area, where the expandable clays of the smectite (montmorillonite) group were much less common. The expandable clays typically have a much larger cation-exchange capacity (CEC) than other clays and, therefore, a greater effect on ground-water chemistry. A range of CEC for clay minerals, as reported by Carroll (1959, p. 754) in meq/100 g, are: kaolinite, 3-15; illite, 10-40; chlorite, 10-40; and smectite, 70-100.

The chemical concentrations of cations and trace elements were determined from nine drill-core samples of unmined overburden, mine spoils, and clinker from the West Decker Mine area (table 7). The predominant elements are aluminum, silica, iron, and potassium, probably associated with clay minerals, and calcium and magnesium, associated with the carbonate minerals. The median sodium concentration in samples from the West Decker Mine area is much larger than the median sodium concentration in samples from the Big Sky Mine area. The range of values for most major constituents, except calcium, is small, and no substantial difference is indicated between the chemistry of the unmined overburden and mine-spoils samples.

Concentrations of exchangeable cations were determined on four drill-core samples from spoils and unmined overburden from the West Decker Mine area. Calcium and sodium were the most prevalent exchangeable cations, with lesser amounts of magnesium and potassium (table 8). The median concentration of exchangeable sodium ions from the West Decker Mine area samples is about 900 μg/g, whereas the median concentration of sodium ions from the Big Sky Mine area samples is about 60 μg/g, which demonstrates the more sodic nature of the rock material in the West Decker Mine area.

Two coal samples from the upgradient well WDFCL1 and four coal samples from wells WDESP2 and WDED11 downgradient from the spoils aquifer were analyzed for concentrations of major and minor oxides and trace elements (table 9). Concentrations from all coal samples are similar. The median concentrations of selected constituents were compared to the mean concentrations from analyses of 410 coal samples from throughout the Powder River structural basin (table 10). Concentrations of sodium, strontium, and barium at the West Decker Mine area are larger than or near the maximum values detected from the 410 Powder River coal samples. Concentrations of silica, aluminum, manganese, zinc, and percent of ash at the West Decker Mine area are near or less than the minimum values detected in the Powder River coal samples.

Results of Ground-Water Analysis

Water samples were collected three times from wells WDESP1, WDESP2, and WDED11 along the inferred flow path from the spoils aquifer to the downgradient coal aquifer, and once from wells WDFCL1, WDFD12, and WDFSP3. Results of the analyses for major ions and trace elements are shown in table 11. Ground water in the area was a sodium bicarbonate type, with large variations in dissolved-solids concentration. The dissolved-solids concentration in water from well WDFCL1, completed in the coal aquifer upgradient of the active mine area, was 1,430 mg/L, which is similar to that reported by Davis (1984a, p. 34). The dissolved-solids concentration in water from coal aquifer wells within the active mine area (WDED11, WDESP2, and WDFD12) ranges from about 2,100 to 2,800 mg/L. Dissolved-solids concentrations in water from two wells completed in the spoils aquifer range from about 4,100 to 5,700 mg/L, compared to an average concentration of 2,500 mg/L reported by Davis (1984a, p. 35) for a larger number of wells. The concentration of 5,700 mg/L in water from well WDFSP3 is much larger than the average concentration and is probably one of the largest concentrations in water from the spoils aquifer. The water having 4,100 mg/L concentration, although larger than the 2,500 mg/L average concentration, probably can be assumed to be representative, as the chemical character of this water is virtually the same as other spoils water with smaller dissolved-solids concentrations.

Predominant cations and anions are depicted on diagrams (fig. 12) for samples collected during October 1988. The data on the trilinear diagram for all six wells indicate the overall similarity of the ground water in the area, the predominance of the sodium and bicarbonate ions, and the paucity of calcium, magnesium, and chloride ions. Data for water samples from four selected wells, plotted as Stiff diagrams (fig. 12), indicate differences in the ground-water quality between the coal and spoils aquifers. Water from the spoils aquifer (well WDESP1) had larger concentrations of sodium, bicarbonate, and sulfate ions than water from the upgradient coal aquifer (well WDFCL1), which potentially recharged the spoils aquifer. Concentrations of all ions, particularly sulfate, decreased between the spoils well WDESP1 and the downgradient coal wells WDESP2 and WDED11.

Water samples for laboratory determination of dissolved-gas concentrations were collected from five wells, with oxygen, carbon dioxide and methane being the gases of primary interest (table 12). Oxygen was detected at trace levels in all five wells. Concentrations of carbon dioxide decreased substantially, from 280 to 51 mg/L, along the inferred flow path from well WDESP1 to WDED11. Methane concentrations of less than 1 mg/L were detected in samples from wells WDFCL1, WDFD12, and WDESP1, whereas concentrations of 8.8 and 6.6 mg/L were detected in samples from wells WDESP2 and WDED11.

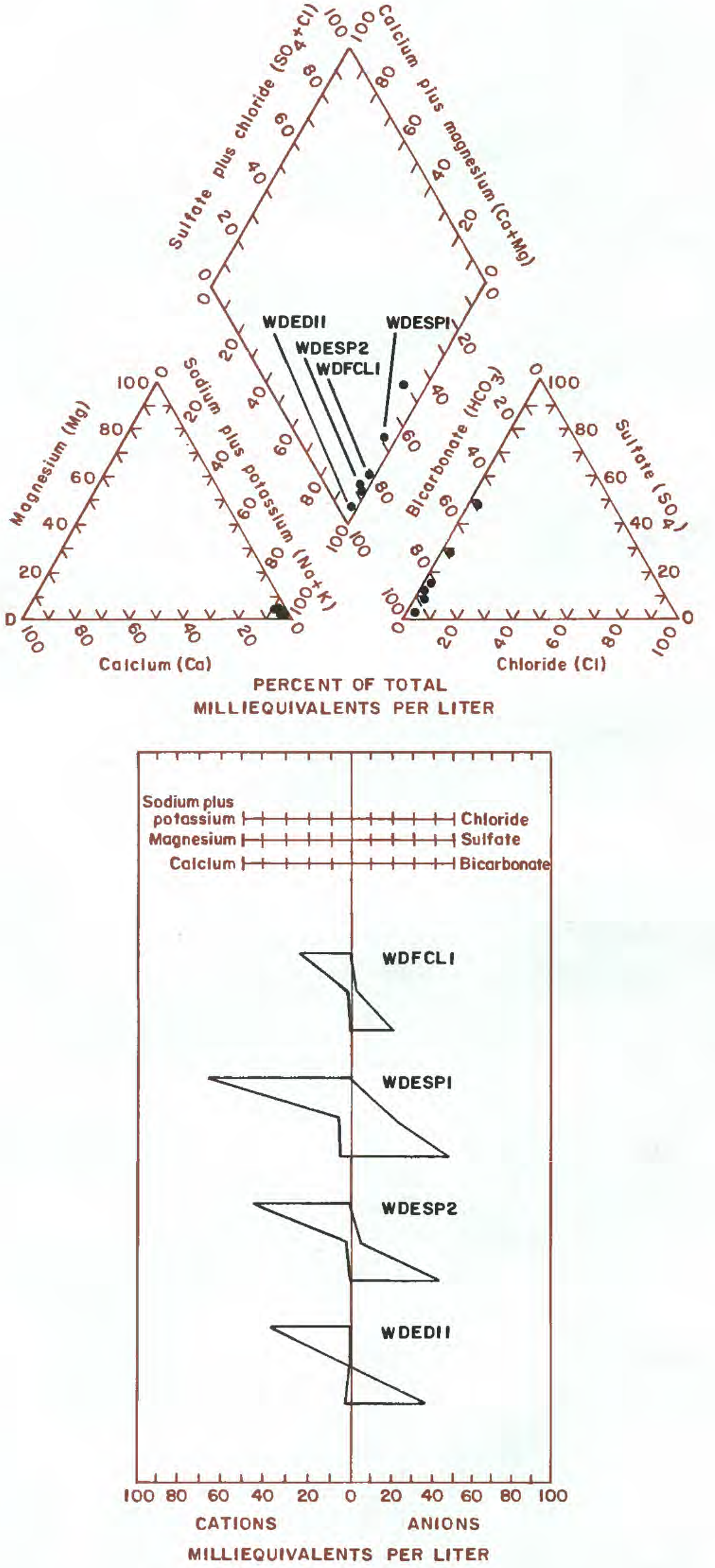


Figure 12. Trilinear and Stiff diagrams showing geochemical properties of ground water from the West Decker Mine area, Montana.

The tritium-activity values in water from wells WDESP1, WDESP2 and WDED11 were similar (10, 11, and 8 TU) (table 13). The values might indicate a similar source for the water. Although similar values may not necessarily substantiate other data to indicate that the wells were along a flow path, the values do most likely indicate that the water in the wells has relatively similar ages. Tritium-activity values in water from wells WDFCL1 and WDFD12 were larger than values in water from the other wells, possibly indicating a younger source of recharge water to these wells. Conversely, the tritium data might indicate that some water recharging the spoils aquifer, represented by well WDESP1, originated from an older source having small tritium values, possibly from the aquifer in the Dietz 2 coal bed by way of unplugged exploration drill holes (Van Voast and Reiten, 1988, p. 4).

Thermodynamic speciation calculations for water from the West Decker Mine area were made using the program WATEQF (Plummer and others, 1978) (table 16). Saturation indices listed are for minerals considered to be potentially reacting in the ground water. Saturation indices demonstrate that, in general, the water was saturated with respect to quartz, calcite, aragonite, and barite, near saturation with respect to dolomite, and undersaturated with respect to strontianite, gypsum, anhydrite, and celestite. The saturation indices for the iron minerals siderite, goethite, and amorphous FeS demonstrate that the water might have been either saturated or undersaturated with respect to the minerals, depending on the concentration of dissolved iron and the redox state of the water. Eh values were not measured but were calculated by the WATEQF model based on ion pairs. An Eh value of 0.18 volts calculated from the dissolved-oxygen concentration was used for saturation calculations for water from well WDESP1 (table 11). The Eh values for the other samples which contain dissolved sulfide and Fe^{2+} were calculated from the sulfur-ion concentrations, and ranged from -0.24 to -0.16 volts.

Geochemical Processes Along an Inferred Flow Path From Upgradient Coal Aquifer to Spoils Aquifer

The geochemical processes along an inferred flow path from an upgradient, unmined coal aquifer to a spoils aquifer were studied using solid-phase, ground-water, and hydrologic data. Dissolved-solids concentrations in water from the spoils aquifer were more than three times the concentrations in the assumed recharge water from the coal aquifer (table 11). In water from the coal aquifer within the mine area (well WDFD12), the dissolved-solids concentration was about 50 percent more than the concentration in water from the upgradient coal aquifer.

No direct evidence was available to determine the amount of water, if any, that might have been recharged from the upgradient coal aquifer represented by well WDFCL1 to the spoils aquifer represented by well WDFSP3. Although the potentiometric-surface data (fig. 11) indicate that water flowed from the coal aquifer toward the mine area, hydrologic barriers may have prevented some water from entering the spoils. Some recharge water to the upgradient coal aquifer might have been from the Tongue River Reservoir, because mine dewatering has lowered aquifer water levels below the level of the reservoir. Primary recharge sources prior to mining were aquifers northwest of the mine area (Davis, 1984a, fig. 7), which potentially continue to be major sources of recharge. Upward migration from deeper aquifers through exploratory drill holes (Van Voast and Reiten 1988, p. 19) was another possible source of recharge.

The water in well WDESP1, completed in spoils, is assumed to be most representative of water in the spoils aquifer. Although actual dissolved concentrations might be larger or smaller than median values for the spoils aquifer, the reactions necessary to create the spoils water from upgradient coal aquifer water are assumed to be similar.

The changes in water chemistry between the recharge water and water in the spoils aquifer most likely were the result of only a few processes. The large increases in dissolved sulfate and sodium concentrations were likely a result of an initial dissolution of gypsum followed by the exchange of calcium or magnesium ions for sodium ions on the smectite clays in the spoils aquifer. The increase in bicarbonate concentration was likely the result of dissolution of the carbonate minerals calcite or dolomite.

Results of solid-phase analyses show that calcite and dolomite generally were common to abundant in the spoils. Gypsum was detected at only trace levels; however, it might have been concentrated in zones that were not sampled or it might have been in quantities too small for detection. Pyrite, which was abundant near the top and bottom of the coal bed, probably was oxidized when exposed by mining, thereby increasing acidity and the concentration of dissolved sulfate ions. The acidity probably was buffered by dissolution of the carbonate minerals. The sulfate ions were either transported to the aquifer or precipitated as gypsum or possibly other sulfate minerals in the unsaturated zone, and then dissolved and transported to the aquifer by recharge water.

Changes in isotopic composition of the waters could not be attributed to a specific or evident process. Differences in isotopic composition of water from well WDFCL1 and water from wells WDFD12 and WDESP1 (table 13) might have been the result of dilution or dissolution rather than isotopic fractionation.

Mass-balance models were used to simulate possible geochemical changes that might occur as water from the coal aquifer recharged the downgradient spoils aquifer. Simulations were made for paths from the coal aquifer, represented by well WDFCL1, to the spoils aquifer, represented by wells WDFSP3 and WDESP1. The results of the simulation indicate that the major geochemical processes were the dissolution of gypsum, calcite, and some dolomite; the exchange of calcium ions for sodium ions; the consumption of carbon dioxide gas; and the dissolution of minor quantities of strontianite and halite (table 17). The results of the simulations generally were supported by the solid-phase and gas analysis. Calcite, dolomite, and gypsum were detected by X-ray diffraction techniques and substantial quantities of carbon dioxide in the water were confirmed by gas analysis (table 12).

Geochemical Processes Along an Inferred Flow Path from Spoils Aquifer to Downgradient Coal Aquifer

The concentrations of major dissolved ions, some dissolved trace elements, stable isotopes, and dissolved gases were substantially different in water from well WDESP1 in the spoils aquifer than in water from wells WDESP2 and WDED11 in the downgradient coal aquifer. Selected median dissolved-ion concentrations for samples from each well are given in table 18. The dissolved-solids concentration decreased by nearly one-half, from 4,170 to 2,140 mg/L, along the inferred flow path from well WDESP1 to well WDED11 (fig. 10). Large decreases in median concentrations of major dissolved ions include sulfate, from 1,100 to 64 mg/L; bicarbonate, from 3,080 to 2,390 mg/L; and sodium, from 1,500 to 890 mg/L. Changes in concentrations of other ions along the inferred flow path include calcium, magnesium, manganese, strontium, all of which decreased to less than 30 percent of initial values, and barium which increased about 3,000 percent from the initial value. Although the relative concentrations of major ions decrease substantially along this inferred flow path, the chemical character of the water remained a predominantly sodium bicarbonate type (fig. 12).

This study was conducted as a follow-up to the laboratory experiments conducted by Davis and Dodge (1986). As a means of comparison, selected median values from the report by Davis and Dodge (1986) are included in table 18. A comparison between water from spoils and coal shows similar changes in laboratory and onsite results for most of the selected constituents, including decreases in concentrations of calcium, magnesium, sodium, bicarbonate, dissolved solids, manganese, and strontium, and increases in barium concentrations. Sulfate changed relatively little in the laboratory experiments but decreased substantially under onsite conditions because the experiments did not simulate the reducing environment found onsite. Davis and Dodge (1986, p. 7) concluded that the reactions causing the changes observed in the laboratory experiments included adsorption or ion-exchange reactions involving sodium ions exchanging for calcium ions and the precipitation of calcite.

Saturation indices calculated for minerals that might be reacting along the inferred flow path are given in table 16. The saturation state of dolomite and possibly goethite changed from saturated to near saturated or unsaturated as water flowed from the spoils aquifer to the coal aquifer. The saturation state of quartz, calcite, and strontianite was virtually unchanged, whereas the saturation state of the sulfate minerals gypsum, anhydrite, and celestite decreased substantially. Results for the remaining selected minerals generally were mixed.

The large change in the $\delta^{34}S$ isotopic ratio in sulfate of -0.2 to 62.5 ‰ along the inferred flow path was due to enrichment of the heavier sulfur isotope, whereas the change in the $\delta^{13}C$ in carbon of -0.8 to -9.4 ‰ was due to enrichment of the lighter carbon isotope (table 13). The magnitude of these isotopic changes is significant in that the changes occurred along a relatively short inferred flow path. Concentrations of carbon dioxide gas decreased substantially along the inferred flow path, and concentrations of methane increased (table 12).

Analytical results of solid-phase samples collected from drill cores were used to help substantiate potential geochemical reaction processes. Calcite and dolomite were relatively common to abundant in the spoils; gypsum, pyrite, siderite, and barite were identified in trace amounts; and smectite and kaolinite were the prevalent clay minerals (tables 4, 5, 6). Relatively large concentrations of sodium (table 7) and exchangeable sodium (table 8) demonstrate the sodic nature of the rock material in the West Decker Mine area. The presence of iron-bearing minerals such as goethite, pyrite, and siderite indicates that iron was available for the precipitation of iron-sulfide minerals.

Potential Reaction Processes

The changes in ground-water chemistry that occurred as water flowed from the spoils aquifer to the coal aquifer were likely the result of at least several reaction processes. The largest changes were decreases in the concentration of sodium, sulfate, and bicarbonate ions, and increases in dissolved sulfide. Possible reaction processes were the exchange of sodium ions for calcium ions on the surface of organic matter, bacterial reduction of sulfate which decreased sulfate concentrations and produced sulfide ions, removal of the produced sulfide ions by precipitation of sulfide minerals, and decreases in the concentration of bicarbonate by precipitation of carbonate minerals. For all these processes to proceed in the same system, specific hydrogeochemical reactions must have occurred.

Ion-Exchange and Adsorption Reactions

Ion-exchange and adsorption reactions within saturated coal might have been important processes resulting in the decrease in cations as water flowed from the spoils aquifer to the coal aquifer. Typically, calcium or magnesium ions exchange for sodium ions (equation 10). If the reaction is reversed, the concentration of sodium ions in solution decreases and the concentration of calcium or magnesium ions increases. The extent to which exchange occurs primarily depends on the cation-exchange capacity (CEC) of the solid and the ion concentrations in solution.

The CEC for specific clay minerals generally is well known (Carroll, 1959, p. 754). Although coal and other organic material potentially have a relatively large CEC, only sparse information is available. Data for lignite samples from the Tongue River Member of the Fort Union Formation at a mine area in North Dakota (Donald C. Thorstenson, U.S. Geological Survey, unpub. data, 1985) indicate that the CEC of the lignite averages about 70 meq/100g, which is similar to the value of 70-100 meq/100g for smectite, an expandable clay, as reported by Carroll (1959, p. 754).

Typically, divalent calcium or magnesium ions in solution will exchange preferentially for monovalent sodium ions. However, in some solutions containing large sodium concentrations (Drever, 1982, p. 84, Davis and DeWiest, 1966, p. 91) and in solutions containing virtually no dissolved calcium or magnesium and relatively large concentrations of dissolved sodium (Palmer and Cherry, 1984, p. 49), the sodium ions in solution tend to be exchanged for calcium or magnesium ions. Monovalent sodium ions in solution are unlikely to displace divalent ions unless the sodium percentage, which is the percentage of total cations in milliequivalents made up by sodium, is considerably greater than 50 (Hem, 1985, p. 161). The sodium percentage for the water from wells in the West Decker Mine area is considerably greater than 50 and generally greater than 90.

The possibility of the exchange of sodium ions for calcium ions in coal has been addressed in previous studies. Davis and Dodge (1986, p. 6) hypothesized about this exchange on the basis of experiments. During an earlier study of sodium and associated elements in the Anderson-Dietz 1 coal bed near Decker, Mont., Hildebrand (1988, p. 218) reasoned that the coal contains significantly larger concentrations of sodium, strontium, and barium and significantly smaller concentrations of potassium, calcium, and magnesium than samples from the Powder River structural basin owing to ion exchange. That study concluded that a large sodium percentage in the ground water causes chemical disequilibrium, which in turn causes sodium cations to be adsorbed by the coal in preference to other dissolved cations. The other adsorbed cations, particularly potassium, calcium, and magnesium, are then exchanged for the adsorbed sodium ions, resulting in a gradual increase in the sodium content in the coal. Large concentrations of barium and strontium in the coal could also be a result of cation adsorption.

Sulfate Reduction

Another major geochemical change along the inferred flow path was the substantial decrease in the concentration of dissolved sulfate from about 1,100 to 64 mg/L (table 17) and the subsequent increase in the concentration of dissolved sulfide. The removal of most of the sulfate is assumed to be the result of bacterial reduction with oxidation of organic carbon as the energy source. Dockins and others (1980, p. 6) found relatively large numbers of the sulfate-reducing bacteria *Desulfovibrio desulfuricans* in 25 of 26 observation wells sampled in southeastern Montana, and reported sulfide concentrations of about 1 mg/L. The occurrence of the sulfide in water in these coal aquifers probably can be attributed to bacterial reduction of sulfate and not to the slow kinetics of abiotic sulfate reduction.

Two assumptions are made for sulfate reduction and associated reactions to occur--the organic carbon source utilized is the subbituminous coal (represented compositionally by CH_2O) and the Fe_2O_3 is present as a source for iron and FeS_2 is present as a sink for sulfur (Thorstenson and others, 1979, p. 1,493). Using these assumptions, sulfate reduction with iron-sulfide precipitation can be represented by the following irreversible reaction:

$$15CH_2O + 2Fe_2O_3 + 8SO_4^{2-} + H_2CO_3 \xrightarrow{\text{sulfate-reducing bacteria}} 4FeS_2 + 16HCO_3^- + 8H_2O\,. \qquad (13)$$

With the completion of sulfate reduction, decomposition of the organic matter might continue according to the reaction:

$$2CH_2O \Rightarrow CH_4 + CO_2 \, . \tag{14}$$

On the basis of results of hypothetical geochemical models, Martin and others (1988, p. 91) indicate that an ideal situation for large decreases in dissolved-solids concentrations within a coal aquifer involves populations of sulfate-reducing bacteria, organic-carbon sources that can be utilized by the bacteria, and a source of iron that will facilitate removal of the produced sulfide by mineral precipitation. Because coal at the West Decker Mine area is subbituminous, and in some instances nearly lignitic, the source of organic carbon for the bacteria was assumed to be the coal itself, which likely contains an unlimited supply of aromatic carbon compounds available to the bacteria.

Both dissolved sulfate and methane were detected in water samples from the coal aquifer (tables 11, 12). This geochemical incongruity is potentially explained by the existence of microzones within the coal aquifer, where all dissolved sulfate has been removed by reduction and where methanogenesis predominates. Chapelle and others (1988, p. 170) suggest that such bacterial microenvironments produce a mosaic of redox conditions, resulting in apparent redox non-equilibrium conditions. Sulfate-reducing bacteria generally will outcompete the methanogens in the same system, primarily because both rely on the same fermentation products, including hydrogen, an intermediate product in the decomposition of organic matter. When sulfate concentrations are not limiting, the sulfate-reducing bacteria maintain hydrogen at a concentration so small that methane production from hydrogen is thermodynamically unfavorable (Loveley and Goodwin, 1988, p. 2,994). However, at minimal sulfate concentrations, the metabolism of the sulfate reducers is so limited that methanogens might be able to outcompete the sulfate reducers and prevent further sulfate reduction.

Precipitation of Sulfide and Carbonate Minerals

Potential products of the reaction processes are iron-sulfide and calcium-carbonate minerals. Plummer and others (1990, p. 1,994-1,998) report laboratory studies wherein reactions of sulfide gas with goethite ($HFeO_2$) at temperatures of 22 to 24 °C formed an iron-sulfide precipitate that was assumed to be either a form of very fine-grained pyrite or amorphous iron sulfide. If iron was available within the coal aquifer, either dissolved or as goethite, then the sulfide gas produced during sulfate reduction could have reacted with the iron and precipitated an iron-sulfide mineral. Therefore, in a system where sulfide concentrations are small, sulfate reduction might still occur at relatively fast rates because the sulfide is being precipitated. Results of petrographic analysis for this study (table 4) indicate the presence of iron oxides, chemical analyses of water (table 11) indicate relatively large concentrations of dissolved iron, and thermodynamic calculations (table 16) indicate that some water is supersaturated with respect to goethite. Therefore, sufficient iron was assumed to be available for the precipitation of iron-sulfide minerals. The form of the iron-sulfide minerals was not determined as part of this study.

Carbonate minerals, such as calcite or magnesian siderite, might have precipitated as a result of reaction processes. A relatively large decrease in bicarbonate concentration along the inferred flow path (table 11) was likely a result of carbonate-mineral precipitation. Even though concentrations of calcium decreased along the inferred flow path (table 11), speciation calculations (table 16) show that all waters were slightly oversaturated with respect to calcite. The degree of oversaturation required to precipitate calcite given the observed field conditions is unknown, but the calculated oversaturation was assumed to be sufficient for precipitation.

Results of Laboratory Experiment

A laboratory experiment was conducted to determine if the decrease in dissolved-sodium concentrations along the flow path could be the result of preferential exchange of sodium ions in solution for calcium and magnesium ions in the coal. The experiment was conducted using coal samples from the West Decker Mine area collected during the drilling of observation wells, and concentrated solutions of sodium sulfate (Na_2SO_4). The experiment was conducted using samples of coal collected from the saturated and unsaturated zones. Samples from each zone were used to determine the effect of soluble minerals in samples from each zone on the experiment results.

Four of five crushed coal samples were initially mixed with deionized wash water for 48 hours to determine the quantity of soluble minerals within the coal. The mixing water was then decanted, filtered through a 0.45-μm filter, and analyzed for major ions. The coal was air-dried for 48 hours. The fifth coal sample, used as a control, was not mixed with deionized water. The five coal samples were then mixed using a 1:1.5 weight ratio with a Na_2SO_4 solution in 500-mL bottles. Two concentrations of Na_2SO_4 solution, 0.05 and 0.1 M, were used. The bottles, filled completely to eliminate oxygen, were shaken periodically for 48 hours. The mixtures settled, and the coal and solutions were separated by decanting and filtering through a 0.45-µm filter. The filtered samples and the Na_2SO_4 solutions were analyzed for major ions.

Results of analyses of post-mixing wash water indicated substantial differences in the concentrations of the major constituents between mixtures using coal from the unsaturated zone and mixtures using coal from the saturated zone. The dissolved-solids concentration in the wash water from the unsaturated-zone mixtures was about twice that of the wash water sample from the saturated-zone mixtures (table 19). In addition, the wash water from the unsaturated-zone mixture was a sodium sulfate type, whereas the wash water from the saturated-zone mixture was a sodium bicarbonate type. These results might indicate that as water levels declined, soluble sodium-sulfate or sodium-carbonate minerals were precipitated above the water table.

When the sodium-sulfate solutions were added to the coal samples, analyses of the post-mixing solutions showed a general decrease in sodium concentrations and a large increase in the concentrations of calcium and magnesium ions. Sodium ions from the 0.05 M Na_2SO_4 solution apparently were exchanged for about 150 mg/L of calcium ions and about 60 mg/L of magnesium ions (table 19). Sodium ions from the 0.1 M Na_2SO_4 solution apparently were exchanged for about 340 mg/L of calcium ions and about 130 mg/L of magnesium ions, or approximately twice the amount exchanged from the 0.05 M Na_2SO_4 solution.

The results of the experiment indicate that sodium ions in solution can be preferentially exchanged on coal for calcium and magnesium ions. A large concentration of sodium ions in solution, especially when compared to small concentrations of calcium and magnesium ions, might control the direction of the exchange reaction (equation 10) and the quantity of exchange. The large concentration of sodium ions in the spoils water relative to the concentration of calcium and magnesium ions (table 11) indicates that the conditions for exchange of sodium ions for calcium or magnesium ions existed in the study area.

Mass-Balance Reaction Models

An objective of the geochemical modeling was to identify reactions or processes that resulted in the initial quality of ground water and caused chemical changes to occur along inferred flow paths. Ideally, the modeling would determine the quantities and types of minerals reacting in the system, either precipitating or dissolving, and would calculate speciation and isotopic effects as the reactions progressed. Geochemical mass-balance models were constructed to calculate the mass transfer of phases between water in the spoils aquifer and water in the downgradient coal aquifer. Possible reactant or product phases are listed in table 20.

The wells along the inferred flow path were sampled three times from October 1988 to May 1990. However, mass-balance calculations are presented only for the October 1988 samples, for which dissolved-gas analyses and full isotope analyses were available. Sulfur-isotope analyses for sulfate and sulfide in water collected in May 1989 from well WDESP2 were used in calculations. Mass-balance calculations were made using water-quality data for four wells (table 21).

Plausible Phases

Eight plausible reactant or product phases were considered for mass-balance reaction modeling (table 20). Organic matter was assumed to represent a carbon source and was included as a probable energy source and electron donor for bacterial reduction of sulfate. Sources of available iron species, such as goethite, are assumed to be present in sufficient quantities for the precipitation of pyrite or other iron-sulfide mineral forms such as amorphous FeS. Dissolved sulfide was included as a product of sulfate reduction because of the presence of sulfate-reducing bacteria. Carbon dioxide was included as a product of the oxidation of the organic matter. Calcite and magnesian siderite were included as plausible sinks for the removal of bicarbonate. Cation exchange of sodium ions for calcium or magnesium ions was included as a plausible phase for removing sodium ions from solution and for providing calcium and magnesium ions necessary to precipitate calcite, magnesian siderite, or other carbonate minerals.

Oxidation-reduction reactions are considered plausible along the inferred flow path, including sulfate reduction and the oxidation of organic matter and ferric hydroxide. The redox state (RS) shown in table 21 is a method of keeping track of electron transfer for redox reactions. The redox state is defined as follows:

$$RS = \sum_{i=1}^{I} m_i v_i \qquad (15)$$

where

I = the number of species in solution,
m_i = the molality of the i'th species in solution, and
v_i = the operational valance of the species.

Further description of operational valance and redox state is addressed by Plummer and others (1990, p. 1,991).

Isotopic Ratios

Stable-isotope data for dissolved carbon, sulfate, and sulfide were used in conjunction with other water-quality data to construct geochemical-reaction models for the inferred flow path from the spoils aquifer to the downgradient coal aquifer. Isotopic data were included in reaction modeling because they might provide an independent constraint without adding an additional phase. The sulfur- and carbon-isotope data were treated as Rayleigh distillation and not as dilution or isotope mass balance. Rayleigh distillation is a process where products in a chemical or physical reaction differ isotopically from the reactants and are isolated from the system after formation. Rayleigh distillation reactions were used to calculate the isotopic composition of the final solutions. The calculations were an independent check, because the correct reaction model would be among those predicting the observed isotope composition. The equation used for this report is described by Busby and others (1991, p. 43) and was adapted for Rayleigh distillation of the sulfur-isotope composition of dissolved sulfate from the equations developed by Wigley and others (1978, 1979).

To model fractionation and evolution of isotopes along the inferred flow path, isotopic values of initial sources and final products or isotopic sinks are needed. The value for a dissolved source, such as sulfate, can be determined from an aqueous sample. However, determining values for a solid source, such as an amorphous or microcrystalline precipitate, can be considerably more difficult. Some data are available in the literature for isotopic ratios of various sources and sinks.

Carbon

Dissolved carbon in ground water primarily is derived from carbonate sediments, soil organic matter, the decay of other organic material, and in some instances, atmospheric CO_2. The $\delta^{13}C$ of the dissolved carbon can vary widely depending on the source of the carbon. Values of $\delta^{13}C$ for coal range from -24 to -30 ‰ for samples collected from the Powder River structural basin, including the West Decker Mine area (Holmes, 1988, p. 211). Other values of $\delta^{13}C$ for coal include -28 ± 4‰ for sedimentary organic carbon (Rightmire and Hanshaw 1973, p. 959). The $\delta^{13}C$ of -0.8 ‰ in the initial water, well WDESP1 (table 13), was likely derived from dissolved carbonate or CO_2. The $\delta^{13}C$ of the dissolved carbon changed substantially along the inferred flow path to -8.8 and -9.4 ‰--potentially a result of bacterial fractionation of the carbon in the subbituminous coal.

The concentration of dissolved organic carbon (DOC) in water in the coal aquifers probably was significant. DOC samples were not collected during this study; however, concentrations in about 40 DOC and total organic carbon (TOC) samples collected by Lee (1979) from wells completed in the Tongue River Member of the Fort Union Formation ranged from 0.1 to 83 mg/L and had a median value of about 5 mg/L. This median value was assumed to be representative of DOC in the coal aquifer at the West Decker Mine area, and the $\delta^{13}C$ of the DOC was assumed to be the same as the $\delta^{13}C$ of the coal from which it presumably was derived.

Sulfur

The difference between the $\delta^{34}S$ values of the sulfide and sulfate ($^{34}\Delta$) determined in one sample was calculated by the equation:

$$^{34}\Delta = \delta^{34}S_{H_2S} - \delta^{34}S_{SO_4}. \qquad (16)$$

The $^{34}\Delta$ used for this study, as calculated from the values at well WDESP2 (table 13), was -41.2 ‰ at a temperature of 17 °C. The equilibrium value for $^{34}\Delta$ for this system is not known; however, various studies indicate an approximate value of about -65 ‰ (Back and others, 1983, p. 1,422). The value of -41.2 ‰ most likely represents non-equilibrium conditions controlled by microorganisms or, in other words, a kinetic fractionation mediated by bacterial action.

Plummer and others (1991, p. 19) present an equation:

$$\delta^{34}S_{H_2S} = \delta^{34}S_{SO_4} - 54 + 0.40t, \qquad (17)$$

to calculate $^{34}\Delta$ based on linear function of temperature (t in °C). Using the temperature of 17 °C in equation 17, the calculated $^{34}\Delta$ would be -47.2 ‰ which is in general agreement with the $^{34}\Delta$ determined for this study (-41.2 ‰). The value of -41.2 ‰ was therefore assumed to be the sulfur-isotope fractionation value representative of water from wells in the West Decker Mine area.

Water from 15 wells completed in alluvial, coal, shale, sandstone, and spoils aquifers in southeastern Montana was analyzed for $\delta^{34}S$ values for sulfide and sulfate (Dockins and others, 1980, p. 6). Values of $\delta^{34}S$ for sulfides ranged from -38.50 to 6.68 ‰ and averaged -23.80 ‰, whereas values for sulfate ranged from -0.20 to 45.17 ‰ and averaged 7.96 ‰. The $^{34}\Delta$ for these samples ranged from -9.54 to -48.13 ‰ and averaged -32.31 ‰.

Requirements for Preparing Mass-Transfer Models

The $\delta^{13}C$ value of organic matter (CH_2O) used in the models varied between -20 and -32 ‰, but generally ranged from about -28 to -30 ‰. Although this range is slightly isotopically lighter than the -25 ‰ that is commonly referenced, it does fall within the range of values reported by Rightmire and Hanshaw (1973, p. 959) and Holmes (1988, p. 211).

The initial $\delta^{34}S_{SO_4}$ was assumed to be equivalent to the value from well WDESP1 of -0.2 ‰. No additional input of $\delta^{34}S$ from other sources such as gypsum, anhydrite, or pyrite was likely because dissolved-sulfate concentrations decreased along the inferred flow path. The $^{34}\Delta$ fractionation of -41.2 ‰ was assumed to be the fractionation value along the inferred flow path; therefore, the $\delta^{34}S_{H_2S}$ used for samples from wells WDESP1 and WDED11 was calculated by subtracting the fractionation value from the values of $\delta^{34}S_{SO_4}$.

Amorphous iron sulfide (FeS) was included as a product because of the presence of H_2S, and goethite ($HFeO_2$) was included as a reactant. A laboratory study (Price and Shieh, 1979) indicated reactions of H_2S with goethite precipitated fine-grained pyrite, and the pyrite had only a slightly different $\delta^{34}S$ than that of the H_2S source, indicating little fractionation occurred between H_2S and the precipitated pyrite. Therefore, for the purpose of the mass-transfer model, the $\delta^{34}S$ of precipitated amorphous iron sulfide was assumed to be equal to that of dissolved H_2S.

Sulfate reduction was assumed to have occurred at relatively fast rates. Even though dissolved H_2S was detected in relatively minor quantities, the H_2S might have either degassed or precipitated as an iron-sulfide mineral in the presence of goethite. At least two products for the reduced sulfate were therefore considered in the model: H_2S gas, and precipitation of an iron-sulfide mineral in conjunction with the dissolution of an iron mineral such as goethite.

Another likely product was siderite, an iron-carbonate mineral detected in solid-phase samples from the West Decker Mine area (table 5). Siderite apparently is rarely found as pure $FeCO_3$ and the substitution of Fe^{2+} by other metallic ions such as magnesium (Mg) and manganese (Mn) is common (Deer and others, 1966, p. 487). Siderite might contain Mg in substitution for Fe to a complete solid solution as magnesite ($MgCO_3$). For the purpose of this mass-transfer model, magnesian siderite was assumed to precipitate at atmospheric temperatures and pressures with a composition of $Fe_{0.7}Mg_{0.3}CO_3$.

Ion exchange probably was an important reaction along the inferred flow path, as evidenced by results from the laboratory experiments and by the decrease in dissolved sodium ions. Ion exchange was calculated primarily for sodium ions exchanging for calcium ions, and to a lesser extent, for sodium ions exchanging for magnesium ions.

Traces of methane (CH_4) were detected in dissolved-gas analyses (table 12). Although methane was not considered to significantly affect the overall geochemical results, it may have affected the calculated value of $\delta^{13}C$, and therefore was included in the geochemical modeling. Methane production was assumed to occur either in microzones where sulfate had been removed, or after sulfate reduction had virtually eliminated dissolved sulfate from the entire system. The $\delta^{13}C$ of methane was assumed to have a value of 50 ‰ less than the measured $\delta^{13}C$ in water from each well (Plummer and others, 1990, p. 1,999).

The supply of water from some wells was not adequate to accurately measure all parameters in a closed flow cell, including onsite measurement of some pH values. In such instances, the pH values were calculated using concentrations of alkalinity and CO_2 gas (table 12) (Pearson and others, 1978). A substantial difference between the onsite and calculated values was detected only for the sample collected from well WDED11 in October 1988. The onsite value of 7.2 was corrected to a calculated value of 7.8 for use in thermodynamic calculations (table 21).

Mass-Transfer Results

The results of mass-transfer calculations for calcite, magnesian siderite, organic matter, goethite, iron sulfide, H_2S gas, CO_2 gas, and ion exchange, in millimoles per kilogram of water, are listed in table 22. The calculated and observed $\delta^{13}C$ and $\delta^{34}S$ values, and the assumed isotopic composition of organic matter and sulfur-isotope fractionation values, are also listed in table 22. The mass-transfer results are listed for four combinations of wells along the inferred flow path. Path 1 has water from spoils well WDESP1 as the initial water and water from coal well WDED11 as the final water, path 2 has water from spoils well WDESP1 as the initial water and water from coal well WDESP2 as the final water, and path 3 has water from coal well WDESP2 as the initial water and water from coal well WDED11 as the final water. In addition, transfer was calculated along a fourth path, which included initial water from spoils well WDESP1 and mixing of water from an underlying coal bed and coal well WDED11 as the final water. When the results from paths 2 and 3 are added together, the sum generally should equal the results from path 1, excluding the isotopic ratios.

The computed mass transfer from the initial water to the final water (table 22) represents net millimoles of each phase entering (positive sign) or leaving (negative sign) a kilogram of water. For example, water from spoils well WDESP1 moving along path 2 to coal well WDESP2 (table 22) might evolve according to the following net reaction:

$$\begin{aligned}&\text{Water from well WDESP1}\ \overbrace{+\ 17.5\ CH_2O + 5.64\ HFeO_2 + 10.0\ CaMgX}^{\text{phases entering solution}} \Rightarrow\\ &\text{Water from well WDESP2}\ \underbrace{+\ 9.09\ CaCO_3 + 8.06\ Fe_{0.7}Mg_{0.3}CO_3 + 8.38\ H_2S + 11.8\ CO_2 + 10.0\ Na_2X}_{\text{phases leaving solution}} \qquad (18)\end{aligned}$$

The principal calculated mass transfers (table 22) were the oxidation of organic matter, the corresponding production of CO_2 gas, the exchange of sodium ions in solution for calcium and magnesium ions, and the corresponding precipitation of calcite and magnesian siderite. Two separate plausible reactions were calculated for the sulfur "sink": production of H_2S gas, and the dissolution of goethite with the corresponding precipitation of iron sulfide. Most likely, the sulfur "sink" was a combination of H_2S production, which was detected, and precipitation of iron sulfide.

Most of the mass transfer was calculated to occur between spoils well WDESP1 and coal well WDESP2 (path 2, table 22), where water from the spoils aquifer flows into the coal aquifer, and where sulfate reduction and exchange of sodium ions for calcium or magnesium ions is initiated. Calculated mass transfer along the path from coal well WDESP2 to coal well WDED11 indicate the same processes; however, the magnitude of the mass transfer was less than between wells WDESP1 and WDESP2. The results considered to be most representative of the inferred flow path are those calculated for the entire path from spoils well WDESP1 to coal well WDED11, path 1 in table 22.

To use the isotopic data as an additional modeling constraint, the mass-transfer results and the Rayleigh distillation equations of Wigley and others (1978, 1979) were included in the geochemical model NETPATH (Plummer and others, 1991) to predict observed values of $\delta^{13}C$ and $\delta^{34}S$ at the downgradient wells (table 22). An example of these detailed calculations is given in the NETPATH manual (Plummer and others, 1991).

Comparison of the calculated and observed $\delta^{13}C$ values helps in determining whether the predicted reactions might represent plausible reactions. The calculated and observed results for $\delta^{13}C$ along path 1 (table 22) were similar and based on representative isotopic values for the reacting and product phases. The results indicate that the isotopically light carbon of the subbituminous coal (-29.5 and -28 ‰) was likely utilized as an energy source by the sulfate-reducing bacteria. The utilization of the carbon caused the $\delta^{13}C$ in the water to become increasingly light along the path from a $\delta^{13}C$ value of -0.8 ‰ in the initial water to a value of -9.4 ‰ in the final water. The input values of $\delta^{13}C$ (-29.5 and 28 ‰) for both sets of mass-transfer calculations for path 1 are within an acceptable range of values. However, for the separate halves of the path (paths 2 and 3), the $\delta^{13}C$ values needed for the calculated values to approximate the observed values were unrealistically heavy, -21 ‰, or light, -31 ‰ (table 22).

Additional carbon inputs were dissolved organic carbon (DOC) and methane (CH_4). Both DOC and CH_4 were assumed to contribute carbon as an energy source for sulfate reduction. However, concentrations of both were relatively small compared to the quantity of carbon from organic matter necessary for the reactions to occur as postulated and therefore were not included in the mass-transfer calculations.

Mass-transfer results indicate that a large quantity of organic matter was oxidized and a correspondingly large quantity of CO_2 gas was outgassed. Although the quantity of CO_2 gas calculated to be outgassing was large, the quantity might not be unreasonable. The aquifer was relatively shallow and contained highly fractured coal, the overburden had been removed or replaced by spoils, and test holes which could vent CO_2 gas had been drilled throughout the area. In addition, relatively large concentrations of CO_2 gas were observed in samples collected in the West Decker Mine area (table 12).

Sulfur-isotope results were used to provide an additional constraint in the mass-transfer modeling. Sulfur-isotope values ($\delta^{34}S$) changed from -0.2 ‰ in water from spoils well WDESP1 to 33.2 ‰ in water from coal well WDESP2, to 62.5 ‰ in water from coal well WDED11. For the October 1988 samples, the dissolved-sulfate concentration decreased from 1,100 mg/L in water from WDEPS1, to 250 mg/L in water from WDESP2, to 51 mg/L in water from WDED11. This change was postulated to be the result of bacterially mediated sulfate reduction and not necessarily the result of another process such as dilution. Thermodynamically, the reduction of sulfate in the presence of reduced carbon (subbituminous coal) should proceed to the virtual disappearance of sulfate throughout the aquifer.

The magnitude of sulfate reduction observed is not unlikely when compared to other studies. Laboratory experiments performed by Fritz and others (1989, p. 103) induced sulfate reduction by *Desulfovibrio desulfuricans* bacteria in anaerobic water with a known initial sulfate concentration. Results indicated that the loss of dissolved sulfate during reduction was paralleled by increasing $\delta^{34}S$ values in the remaining sulfate (fig. 13). Experiments conducted for 211 to 228 days showed the largest isotope enrichment, whereas an experiment conducted for 50 days showed less isotope enrichment. The dissolved-sulfate concentration and isotope data from wells WDESP1, WDESP2 and WDED11 plotted on figure 13 show a similar pattern of decreasing sulfate and increasing enrichment of $\delta^{34}S$, indicating the loss in sulfate likely was due to sulfate reduction. The data from the experiments by Fritz and others (1989) including initial and final sulfate concentrations and $\delta^{34}S$ values closely match the data from the three wells. The time for the sulfate-reduction reaction for the experiments, 50 to 228 days, probably is similar to the time needed to produce the sulfate-reduction results observed in the three wells. These data would appear to provide further support for the assumption that wells WDESP1, WDESP2, and WDED11 are along a flow path.

Results of initial mass-transfer modeling using observed data and assumed values for input resulted in calculated $\delta^{13}C$ values closely approximating the observed $\delta^{13}C$ values. However, these same input data, including a $^{34}\Delta$ of -41.2 ‰, resulted in calculated $\delta^{34}S$ values that were about twice the observed $\delta^{34}S$ values. For the calculated values to approximate the observed values for the entire inferred flow path, a $^{34}\Delta$ factor of about -20 ‰, or about one-half the observed value, was needed. Additional model hypotheses were made in an attempt to have both carbon and sulfur isotope constraints result in calculated values that approximated observed values.

One hypothesis was adding a source for mixing water along the inferred flow path, causing the decrease in sulfate to be a result of both dilution and reduction. A potential source of mixing water is upward leakage from the underlying Dietz 2 (Dz2) coal bed. Upward leakage of water from the Dz2 coal bed into the Anderson-Dietz 1 (A-Dz1) coal bed is conceivable either through abandoned test holes or by diffuse seepage when water levels in the Dz2

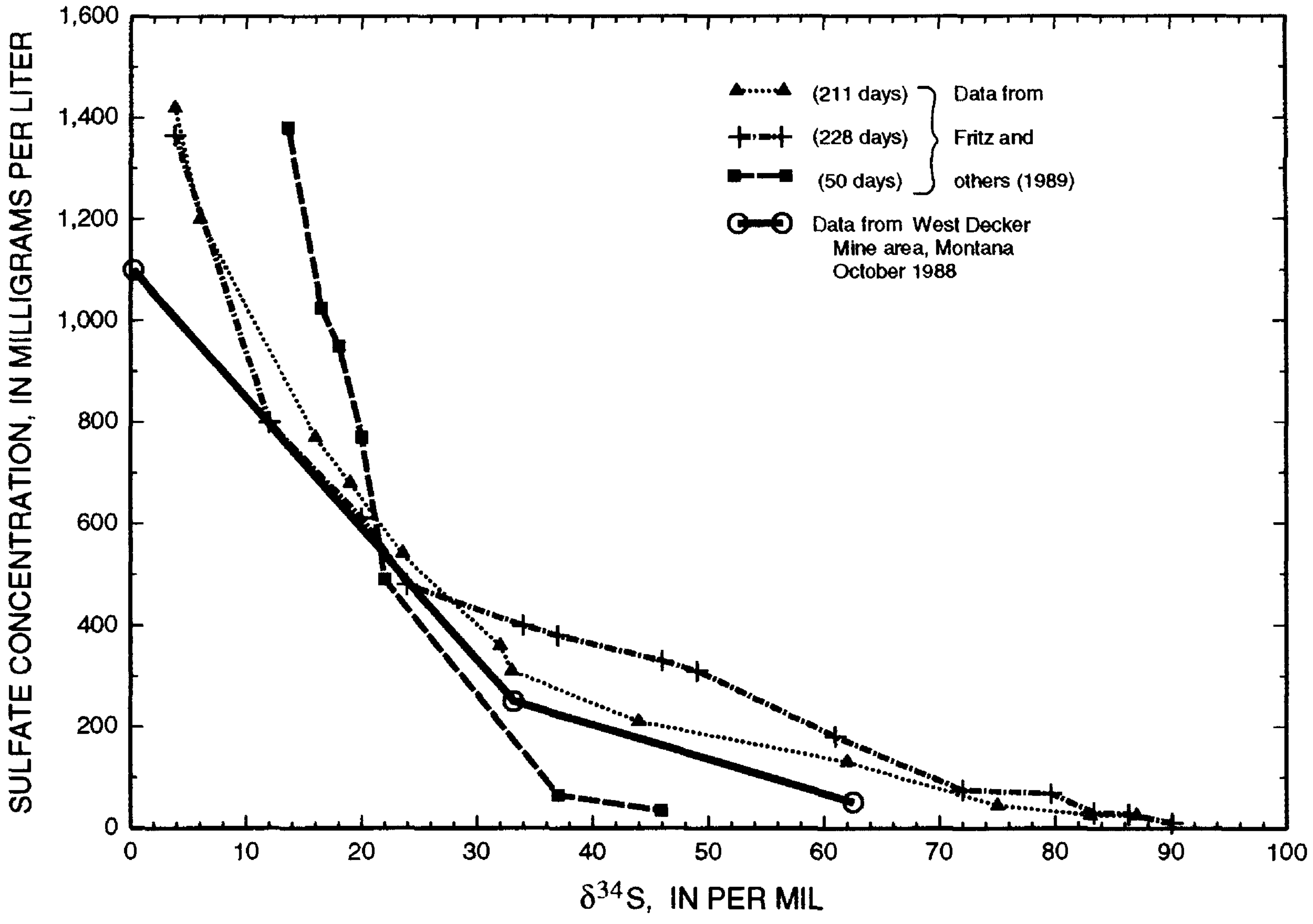


Figure 13. Relation of sulfate concentration in water to $\delta^{34}S$ values in residual sulfate after bacterial sulfate reduction.

coal bed were above the bottom of the A-Dz1 coal bed, and may have occurred during the late 1970's and early 1980's (Van Voast and Hedges, 1975, p. 14). Data from a ground-water flow model (Davis, 1984a) indicate the potential for a small quantity of premining vertical flow from the Dz2 to the A-Dz1 coal beds. Premining water-quality data from well WR-07 (tables 1 and 21) were considered to be representative of mixing water from the Dz2 coal bed. Isotopic values of $\delta^{13}C$ and $\delta^{34}S$ for the mixing water were assumed to be the same as the values from coal well WDED11, which contained the water with the smallest ion concentrations.

Mass-transfer model simulations were made with a range of mixing proportions, from about 10 percent Dz2 water and 90 percent spoils water to about 40 percent Dz2 water and 60 percent spoils water. Results from a model with 20 percent Dz2 water and 80 percent spoils water are given in table 22. When the results of path 4 are compared to path 1, a substantial decrease in the mass transfer of all reactant and product phases is indicated. In order for calculated values of $\delta^{13}C$ to match observed values, the addition of mixing water required changing the assumed $\delta^{13}C$ isotopic composition of the organic matter from -28 ‰ to -31 ‰, which is perhaps unrealistically light. Mixing the low-sulfate Dz2 water with the spoils water resulted in a slight change in the sulfur-isotope fractionation input factor from about -20 ‰ to about -23 ‰, which is still not close to the observed factor of -41.2 ‰. When a larger percentage of Dz2 water was used in the mixing models, the sulfur-isotope fractionation value that resulted was more negative, but the assumed $\delta^{13}C$ input value needed to be lighter and therefore even more unrealistic. Therefore, using mixing of waters in the mass-transfer models did not help solve problems related to the sulfur-isotope constraints.

Another possible explanation of the problem with the sulfur system is that water along the inferred flow path was not in chemical equilibrium. This explanation might mean that the sulfur concentration in the initial well, eventually reduced to the concentration in the final well, might have been considerably smaller than the observed 1,100 mg/L. However, results from mass-transfer models, wherein the sulfate concentration in the initial well was decreased from 1,100 to 500 mg/L or less, showed only a slight change in the sulfur-isotope fractionation factor and large discrepancies in the carbon-isotope results.

Mass-transfer models with isotopic constraints gave inconclusive results, especially with regard to the sulfur system. Observed and input data for the carbon-isotope system appear to be realistic; however, assumptions made about the sulfur system apparently are incomplete. If the sulfur-isotope fractionation factor were approximately -20 ‰ rather than -41.2 ‰, the model results would approximate observed results. Data in the literature support sulfur-isotope fractionation factors ranging from 0 to -65 ‰, and where the reaction is fast, kinetic fractionation is relatively small. However, no explanation is apparent as to why the observed difference between $\delta^{34}S$ of sulfide and sulfate was -41.2 ‰.

The most significant parameter in modeling error and inconsistency was $^{34}\Delta$, the sulfur-isotope fractionation factor, which was measured at only one of three wells along the flow path. In addition, unknowns about the $\delta^{13}C$ of the coal and the form of sulfide precipitate contributed to potential errors. Some parts of the modeling results, including the product and reactant phases, the proportions of the quantities transferred, and the carbon-isotope system, probably represent a reasonable solution to the geochemical processes that occurred along the inferred flow path. However, an almost unlimited number of small variations in isotopic composition, product phases, or minor changes in some analytical data due to uncertainties would also result in calculated values of $\delta^{13}C$ in close agreement with the observed values. Therefore, the calculated results are nonunique and semiquantitative. Possible reasons why the sulfur system could not be adequately modeled with observed data include that the water did not flow directly from the spoils aquifer to the coal aquifer without other influence, the water was not evolutionary, or additional isotopic data are needed to resolve the problem.

Verification of Results

Important phases in the mass-balance results were precipitation within the coal matrix of iron-sulfide minerals and the carbonate minerals, calcite and magnesian siderite. The quantity of either precipitate was likely very small in comparison to the mass of the coal matrix and therefore was difficult to confirm. The thermodynamic conditions and relatively short time frame probably equate to amorphous or microcrystalline mineral formation, making it unlikely that the quantities and size of precipitated iron-sulfide or carbonate minerals were large enough to be identified by standard techniques.

Minerals within fractures in the coal were extracted where possible, and analyzed by X-ray diffraction. Clay minerals were detected most frequently, including large quantities of almost pure crystalline kaolinite. In addition, significant quantities of pyrite, barite, and fibrous gypsum, apparently formed by the oxidation of microcrystalline pyrite, were found on the surface of the coal. In general, X-ray diffraction was not suitable for detecting the microscopic minerals expected to precipitate, primarily because of the lack of a method to extract the minerals from within the structure of the coal.

Scanning electron microscopy (SEM) also was used to quantify minerals precipitated within the coal. Thin sections prepared from coal having visible fracturing and from small fragments of coal affixed to slides were coated with a conducting layer of either carbon or gold for SEM analysis. Energy dispersive spectroscopy (EDS) was used to identify elements of non-organic material within the coal samples. Amorphous or microcrystalline minerals precipitated as a result of geochemical changes would likely be found in relatively porous areas of the coal such as fractures, cleats, or vugs. Therefore, SEM and EDS primarily were used to search cemented microscopic fractures for carbonate and iron-sulfide minerals. The SEM and EDS were used in an attempt to verify the existence of these minerals and not necessarily to quantify them.

A photomicrograph from SEM of a fracture in coal collected from well WDESP1 at a depth of 123 ft is shown in figure 14a and an enlargement of a section of that fracture is shown in figure 14b. The SEM was used with backscatter, which accentuates areas with heavy minerals such as iron sulfide. The lighter area around the fracture (fig. 14b) might be iron sulfide as the EDS graph for that area (fig. 14c) indicates a predominance of iron and sulfur. The physical structure of the material within the lighter area (fig. 14b) does not appear to be significantly different from the surrounding organic material, possibly indicating that the iron sulfide identified using EDS does not have a definite crystal structure but is instead amorphous. Similar SEM photomicrographs and EDS graphs indicating non-crystalline iron-sulfide were obtained for several other samples containing cemented fractures.

Carbonate-mineral precipitation was a major part of simulated water-quality changes along the inferred flow path. However, examples of precipitated calcite were difficult to locate and identify positively. If calcite did precipitate within the coal aquifer, the crystal form and association with organic or non-organic material would be unknown. Numerous samples observed using SEM and EDS contained crystals that were primarily calcium; however, these crystals were relatively large (5 to 20 µm) and not always within the structure of the coal. Other samples had non-organic material identified as predominantly silicon and calcium at various ratios, possibly indicating calcite associated with quartz. Examples of minerals containing both calcium and sulfur were fairly

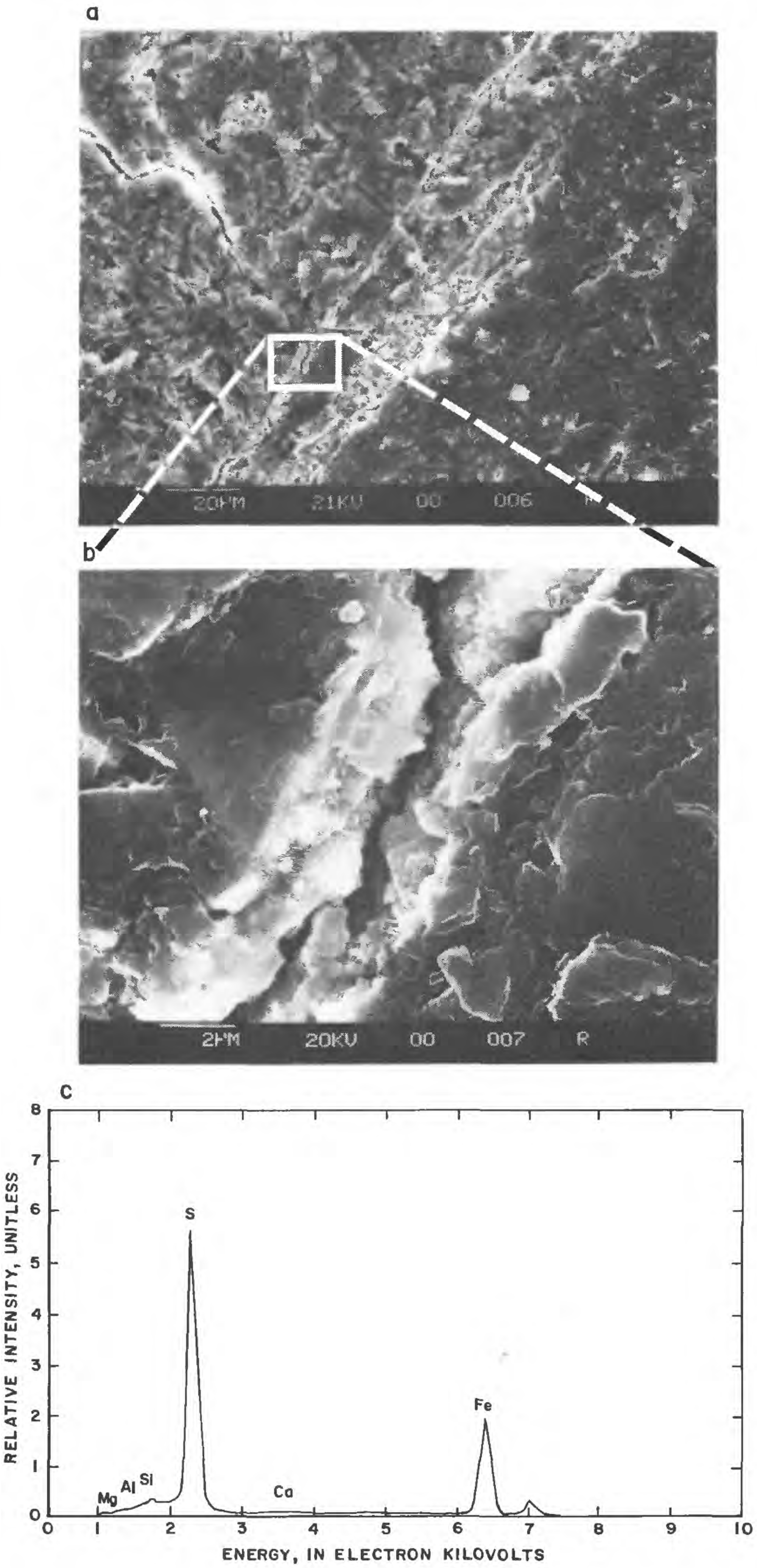


Figure 14. Photomicrographs (a,b) and graph showing elemental composition (c) of apparent amorphous iron-sulfide precipitate from a coal sample collected from the West Decker Mine area, Montana.

common, generally indicating gypsum; however, several samples contained ratios of calcium to sulfur substantially larger than the ratio expected for gypsum.

Several predominantly organic areas indicated by a large nondescript "hump" on the EDS graphs had substantial calcium associated with the organic material. Figure 15 shows an EDS graph of an area, about 2- to 4-µm in length, lining a small vug within the coal matrix of a sample collected from a depth of 123 ft in well WDED11. The figure shows that calcium and silicon are the predominant discernible ions within an organic matrix. In the center of a photomicrograph of another sample collected from well WDED11 at a depth of 123 ft is a 1-µm crystal (fig. 16). The crystal is most likely calcite; however, whether it was a primary or a secondary precipitate is unknown. Even though no definitive proof of secondary calcite precipitation as a result of mass transfer was found, there is substantial evidence from SEM and EDS of calcium within the coal that conceivably could be calcite.

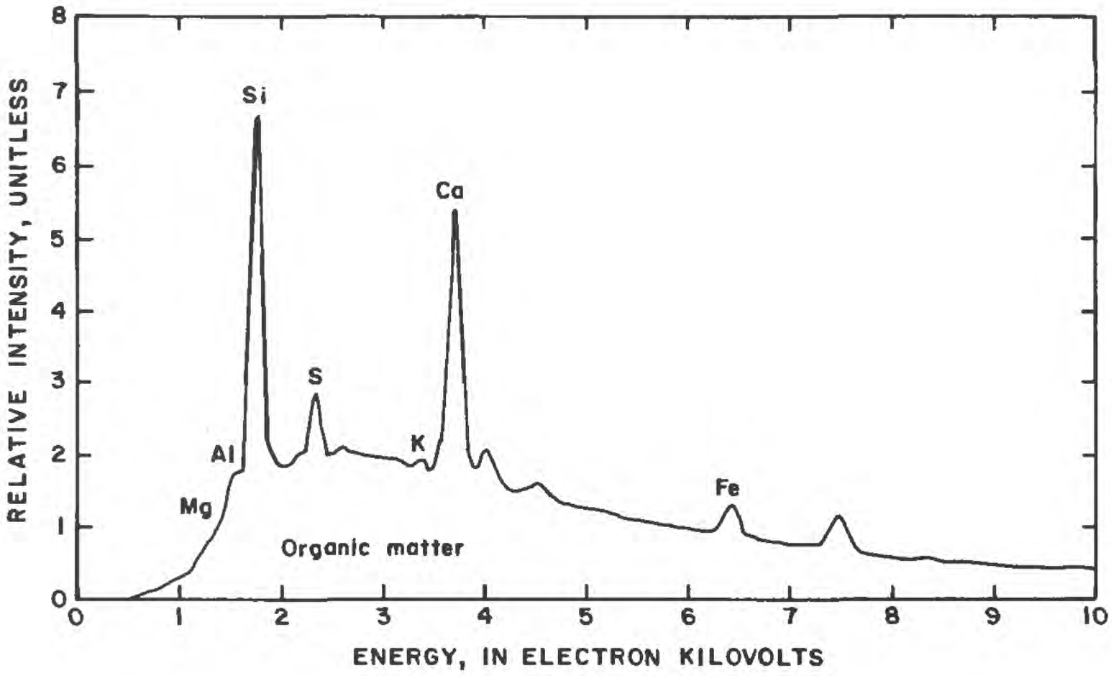


Figure 15. Elemental composition of apparent calcite crystal from a coal sample collected from the West Decker Mine area, Montana.

Processes Causing Geochemical Changes at the West Decker Mine Area

Processes postulated to cause geochemical changes in water as it moves along a potential flow path from the recharge area, to a spoils aquifer, and then to a downgradient coal aquifer at the West Decker Mine area are as follows:

1. Recharge Area
    - Entry of carbon dioxide into the system either by production in the soil or from the atmosphere.
    - Dissolution of carbonate minerals, primarily calcite and dolomite, resulting in an increase in the concentration of calcium, magnesium, and bicarbonate ions in solution.
    - Oxidation of pyrite, resulting in an increase in acidity and the concentration of sulfate ions in solution.
    - Precipitation of gypsum, or other salts, by evapotranspiration, resulting in an accumulation of sulfate minerals in the near-surface unsaturated zone.
2. Spoils Aquifer
    - Dissolution of gypsum, other salts, calcite, and dolomite resulting in a large increase in the concentration of dissolved solids.

   - Cation exchange on clays in the spoils. Calcium and magnesium ions from dissolved gypsum and carbonate minerals exchange for sodium ions on clays, resulting in sodium bicarbonate or sodium sulfate type water. Exchange allows additional dissolution of gypsum and carbonate minerals.

3. Downgradient Coal Aquifer
   - Reverse cation exchange within the coal--exchange of sodium ions in solution for calcium and magnesium ions--which decreases sodium ion concentration and increases calcium and magnesium ion concentrations in solution.
   - Sulfate reduction by *Desulfovibrio desulfuricans* bacteria, with the production of H_2S and CO_2 gas and the use of coal as an energy source by the bacteria, resulting in large decreases in dissolved-sulfate concentrations.
   - Precipitation of calcium and iron-magnesium carbonate resulting in a decrease in bicarbonate concentration, and precipitation of iron sulfide as a sink for the sulfide produced by sulfate reduction.

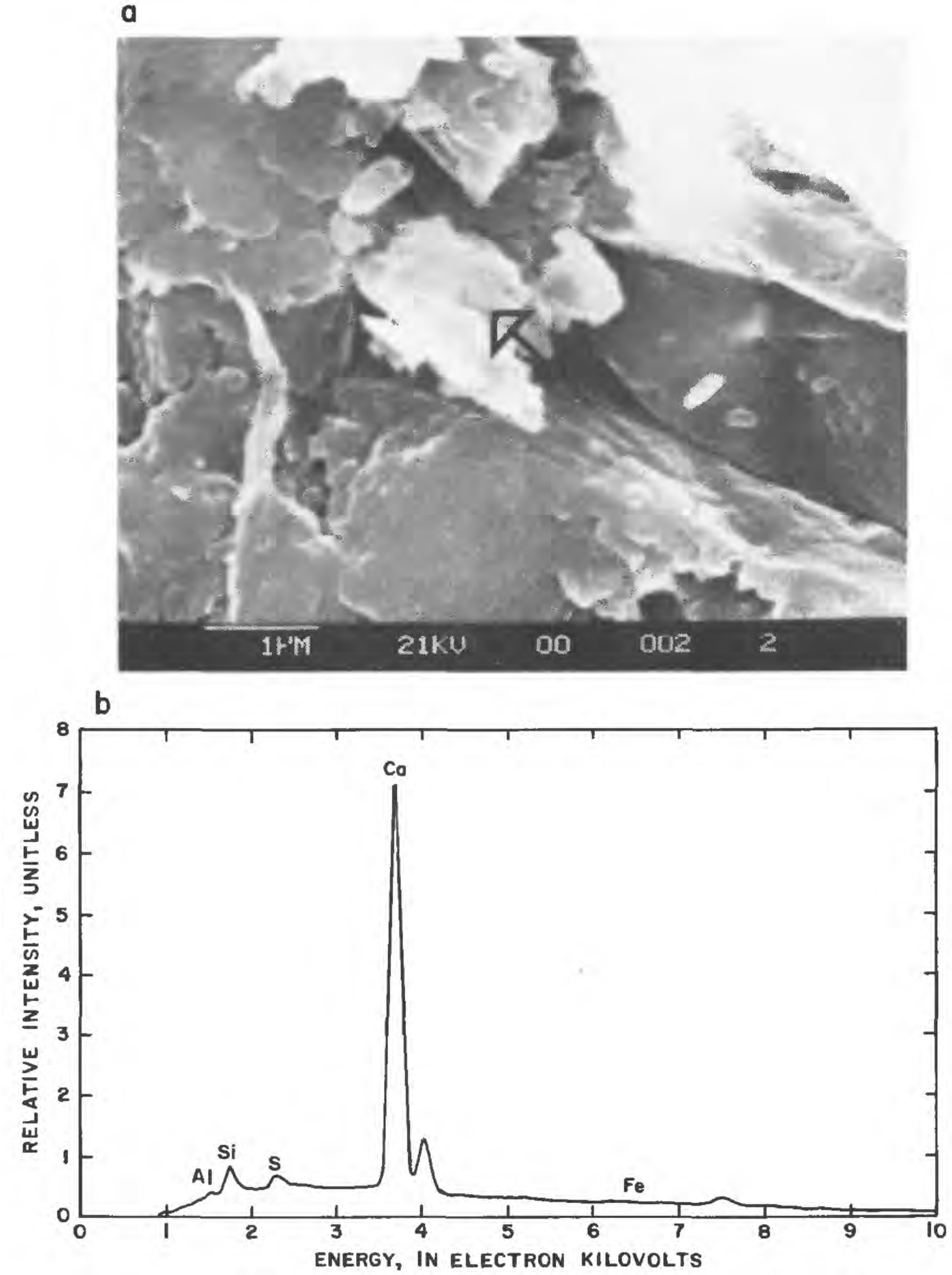


Figure 16. Photomicrograph (a) and graph showing elemental composition (b) of apparent calcite crystal from a coal sample collected from the West Decker Mine area, Montana. Arrow points to crystal.

The geochemical processes postulated to occur in the West Decker Mine area are the results of detailed sample collection and analysis. Even though the processes enumerated are thought to be those most likely occurring, they are considered nonunique and might not be the only feasible processes. Questions about the sulfate system and the $^{34}\Delta$ factor, the rate of sulfate reduction, the presence of sulfate and methane in the same water, the $\delta^{13}C$ of the coal, the large quantity of CO_2 apparently produced, the verifiable existence of secondary calcite and amorphous iron-sulfide precipitates in the coal, and other questions need to be resolved before the geochemical processes occurring in the system are fully understood.

IMPLICATIONS OF THE STUDY

Changes in ground-water chemistry along several inferred flow paths in two surface-coal mine areas of southeastern Montana were analyzed during this study. The two areas studied, the Big Sky and West Decker Mine areas, have distinct differences in mineralogy and ground-water geochemistry, and some differences in ground-water flow processes. Results indicate substantial increases in dissolved-solids concentrations as water flowed from an upgradient, offsite coal aquifer to a spoils aquifer. The general processes along the inferred flow paths from coal to spoils were similar at both areas and predominantly were the result of simple dissolution of soluble minerals such as gypsum, cation exchange within the spoils material, and potentially precipitation of carbonate minerals.

Changes in ground-water geochemistry also can occur when water flows from a spoils aquifer to a downgradient coal aquifer. Results differ substantially between the two study areas. At the Big Sky Mine area, only minor changes in dissolved-solids concentrations occurred along this path, whereas at the West Decker Mine area, large decreases in the concentration of several dissolved ions occurred along the inferred flow path. It is not fully understood why geochemical processes resulted in changes at the West Decker Mine area but not at the Big Sky Mine area. Probable reasons include differences in the mineralogy of the spoils material, age of the reclamation, differences in redox conditions, and bacterial reduction of sulfate.

Water at the Big Sky Mine area primarily was a calcium-magnesium sulfate type, whereas water at the West Decker Mine area was a sodium bicarbonate type, reflecting the mineralogy of the spoils material and coal in each area. Gypsum, calcite, and dolomite in the spoils and unmined material at the Big Sky Mine area were controlling factors on the geochemistry. At the West Decker Mine area, the sodic nature of the spoils material affected cation exchange processes, and thereby increased dissolved-sodium concentrations in the water in the spoils.

The primary processes involved in the decrease in dissolved-solids concentrations at the West Decker Mine area were: reverse cation exchange within the coal, bacterial reduction of sulfate and the consequent production of H_2S and CO_2 gas, and precipitation of carbonate or iron-sulfide minerals. These processes might not have occurred at the Big Sky Mine area for several reasons. Concentrations of dissolved sodium greatly exceeded those of calcium at the West Decker Mine area (table 11) allowing reverse cation exchange within the coal. At the Big Sky Mine area, however, concentrations of dissolved calcium were substantially larger than those of sodium, which negated the possibility of reverse exchange.

At the Big Sky Mine area, sulfate reduction was not a major geochemical process within the coal aquifer, even though dissolved-sulfate concentrations were large (table 11). Dissolved oxygen and sulfide concentrations varied, even between samples at the same well (table 11), indicating that oxidizing and reducing conditions might have alternately existed in the coal aquifer, thereby decreasing the opportunity for sulfate reduction. In addition, it is unknown if a viable population of sulfate-reducing bacteria existed in the coal aquifer at the Big Sky Mine area.

The results of this study include probable geochemical processes responsible for major decreases in concentrations of several dissolved ions as water flowed from a spoils aquifer into an unmined coal aquifer at the West Decker Mine area. The processes indicated by this study are assumed to include all major processes, although additional processes might occur. The saturated coal bed, where the major decreases occurred, was about 10 ft thick and 50 ft in length. The results of this study indicate that, under certain conditions, concentrations of certain dissolved ions in spoils water will decrease if allowed to flow into a layer of coal. Some of the geochemical conditions that would most likely result in large decreases in dissolved-solids concentrations are:

1. An indigenous population of sulfate-reducing bacteria.

2. Organic carbon that can be utilized as an energy source by the sulfate-reducing bacteria.

3. A source of iron that can assist in the removal of sulfide by precipitation of iron-sulfide minerals.

4. The capacity of the coal, or other organic-carbon source, to exchange sodium ions for calcium or magnesium ions in order to reduce concentrations of dissolved sodium ions and facilitate carbonate-mineral precipitation.

SUMMARY

A potential hydrologic effect of surface mining of coal in southeastern Montana is a change in the quality of ground water. Dissolved-solids concentrations in water in spoils aquifers generally are larger than concentrations in the coal aquifers they replaced; however, laboratory experiments have indicated that the concentrations might decrease if ground water flows from a spoils aquifer to a coal aquifer. This study was conducted to determine if the decreases indicated in laboratory results occur onsite and, if so, which geochemical processes caused the decreases. The Big Sky and West Decker Mine areas were chosen for study as both contain coal of the Tongue River Member of the Paleocene Fort Union Formation but have differences in mineralogy, ground-water quality, and flow processes.

Solid-phase drill-core samples of spoil, unmined overburden, and coal and ground-water samples were collected from 16 observation wells at the two mine areas. Observation wells were installed along inferred flow paths to obtain samples for quantifying possible geochemical changes as ground water flowed from an upgradient coal aquifer to a spoils aquifer, and from a spoils aquifer to a downgradient coal aquifer. Selected solid-phase samples were analyzed for elemental concentrations, exchangeable cations, and mineral constituents. Water samples were analyzed for major and trace constituents, selected isotopes, and dissolved gases. Equilibrium relations and mass-balance calculations were determined for water samples using geochemical models.

In the Big Sky Mine area changes in ground-water chemistry varied according to the inferred path studied. Along a path from the upgradient coal aquifer to the spoils aquifer, dissolved-solids concentrations increased from about 2,200 to 3,800 mg/L. These changes probably were a result of dedolomitization caused by the irreversible dissolution of gypsum at or near calcite-dolomite saturation. In contrast, along a path from the spoils aquifer to the downgradient coal aquifer, dissolved-solids concentrations were unchanged and concentrations of most dissolved ions were relatively small and probably not solely related to geochemical processes.

In the West Decker Mine area dissolved-solids concentrations increased substantially as water from an upgradient coal aquifer potentially flowed into a spoils aquifer. Increases in the concentration of dissolved sulfate and sodium most likely were the result of dissolution of gypsum followed by exchange of calcium or magnesium ions in solution for sodium ions on the smectite clays in the spoils aquifer. An increase in bicarbonate concentration was likely due to dissolution of calcite or dolomite.

Along an inferred flow path from a spoils aquifer to a downgradient coal aquifer at the West Decker Mine area dissolved-solids concentrations apparently decreased from about 4,100 to 2,100 mg/L. Apparent decreases in selected constituent concentrations included: sodium, from 1,500 mg/L to less than 900 mg/L; bicarbonate, from about 3,000 mg/L to less than 2,400 mg/L; and sulfate, from 1,100 mg/L to less than 100 mg/L. Data for solid-phase and aqueous geochemical characteristics, including types of reactive minerals, isotopic ratios, and dissolved-gas concentrations, were used to develop geochemical models to analyze changes in water chemistry. Geochemical processes postulated to result in the decrease in dissolved-solids concentration along this inferred flow path include: bacterial reduction of sulfate utilizing the organic matter in coal as an energy source; reverse cation exchange with sodium ions in solution exchanging for calcium and magnesium ions within the coal; and precipitation of carbonate and iron-sulfide minerals. Results of geochemical modeling were substantiated by solid-phase analysis and by applying Rayleigh distillation equations to the fractionation of carbon isotopes as an additional mass-balance constraint. Geochemical-modeling results using sulfur-isotope data as an additional constraint were inconclusive, implying that assumptions may have been incorrect or additional data were required. Even though these geochemical processes are thought to be the most likely to occur, they are considered nonunique and might not be the only feasible processes. In addition to sulfur-isotope data, questions about the rate of sulfate reduction, the isotopic composition of the coal, the large quantity of CO_2 produced, the existence of secondary carbonates and amorphous iron-sulfide minerals in the coal, and other potential questions need to be resolved before the actual geochemical processes occurring in the system are fully understood.

On the basis of results from this study, it can be assumed that concentrations of some dissolved ions in spoils water will decrease if allowed to flow to a coal bed under certain geochemical conditions. Some of the geochemical conditions most likely to result in large decreases in dissolved-solids concentration include a population of sulfate-reducing bacteria, organic carbon suitable for use by sulfate-reducing bacteria as an energy source, a source of iron to facilitate the precipitation of iron-sulfide minerals, and the capacity of the coal to exchange sodium ions in solution for calcium or magnesium ions.

REFERENCES CITED

Back, William, Hanshaw, B.B., Plummer, L.N., Rahn, P.H., Rightmire, C.T., and Rubin, Meyer, 1983, Process and rate of dedolomitization--Mass transfer and 14C dating in a regional carbonate aquifer: Geological Society of America Bulletin, v. 94, no. 12, p. 1,415-1,429.

Ball, J.W., Nordstrom, D.K., and Zachmann, D.W., 1987, WATEQ4F--A personal computer FORTRAN translation of the geochemical model WATEQ2 with revised data base: U.S. Geological Survey Open-File Report 87-50, 108 p.

Bass, N.W., 1932, The Ashland coal field, Rosebud, Powder River, and Custer Counties, Montana: U.S. Geological Survey Bulletin 831-B, p. 19-105.

Busby, J.F., Plummer, L.N., Lee, R.W., and Hanshaw, B.B., 1991, Geochemical evolution of water in the Madison aquifer in parts of Montana, South Dakota, and Wyoming: U.S. Geological Survey Professional Paper 1273-F, 89 p.

Carroll, Dorothy, 1959, Ion exchange in clays and other minerals: Geological Society of America Bulletin, v. 70, no. 6, p. 749-780.

Chapelle, F.H., McMahon, P.B., Loveley, D.R., and Morris, J.T., 1988, Some impacts of bacterial metabolism on the ground-water geochemistry of deep coastal plain aquifers, *in* Ground-Water Geochemistry Conference Proceedings, Denver, Colorado: Dublin, Ohio, National Water Well Association, p. 153-174.

Davis, R.E., 1984a, Geochemistry and geohydrology of the West Decker and Big Sky coal-mining areas, southeastern Montana: U.S. Geological Survey Water-Resources Investigations Report 83-4225, 109 p.

____1984b, Example calculations of possible ground-water inflow to mine pits at the West Decker, East Decker, and proposed North Decker Mines, southeastern Montana: U.S. Geological Survey Water-Resources Investigations Report 84-4199, 29 p.

Davis, R.E., and Dodge, K.A., 1986, Results of experiments related to contact of mine-spoils water with coal, West Decker and Big Sky Mines, southeastern Montana: U.S. Geological Survey Water-Resources Investigations Report 86-4002, 16 p.

Davis, S.N., and DeWiest, R.J.M., 1966, Hydrogeology: New York, John Wiley, 463 p.

Deer, W.A., Howie, R.A., and Zussman, J., 1966, An introduction to the rock-forming minerals: London, Longman Group Limited, 528 p.

Dobbin, C.E., 1930, The Forsyth coal field, Rosebud, Treasure, and Big Horn Counties, Montana, *in* Contributions to economic geology, 1929, Part II, Mineral fuels: U.S. Geological Survey Bulletin 812-A, p. 1-55.

Dockins, W.S., Olson, G.J., McFeters, G.A., Turbak, S.C., and Lee, R.W., 1980, Sulfate reduction in ground water of southeastern Montana: U.S. Geological Survey Water-Resources Investigations Report 80-9, 13 p.

Drever, J.I., 1982, The geochemistry of natural waters: Englewood Cliffs, N. J., Prentice-Hall, 388 p.

Ferreira, R.F., Lambing, J.H., and Davis, R.E., 1989, Chemical characteristics, including stable-isotope ratios, of surface water and ground water from selected sources in and near East Fork Armells Creek basin, southeastern Montana, 1985: U.S. Geological Survey Water-Resources Investigations Report 89-4024, 32 p.

Fritz, P., Basharmal, G.M., Drimmie, R.J., Isben, J., and Qureshi, R.M., 1989, Oxygen isotope exchange between sulfate and water during bacterial reduction of sulphate: Chemical Geology (Isotope Geoscience Section) v. 79, p. 99-105.

Gat, J.R., 1980, The isotopes of oxygen and hydrogen in precipitation, *in* Fritz, Peter, and Fonte, J.C. eds., Handbook of environmental isotope geochemistry, part A--The terrestrial environment: New York, American Elsevier Publishing Co., p. 21-47.

Hatch, J.R., and Swanson, V.E., 1977, Trace elements in Rocky Mountain coals, *in* Murray, D.K., ed., Geology of Rocky Mountain coal, 1977: Colorado Geological Survey Resource Series 1, p. 143-164.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, 264 p.

Hildebrand; R.T., 1988, Sodium and associated elements in the Anderson-Dietz coal zone from the Decker area, Big Horn County, Montana, *in* Geological Society of America Field Trip Guidebook, 1988: Colorado School of Mines Professional Contributions 12, p. 217-219.

Hobba, W.A., Jr., Chemerys, J.C., Fisher, D.W., and Pearson, F.J., Jr., 1977, Geochemical and hydrologic data for wells and springs in thermal-spring areas of the Appalachians: U.S. Geological Survey Water-Resources Investigations Report 77-25, 36 p.

Holmes, C.W., 1988, Carbon isotopes in the Tertiary coals of the eastern Powder River and western Williston Basins--A regional perspective, *in* Geological Society of America Field Trip Guidebook, 1988: Colorado School of Mines Professional Contributions 12, p. 211-216.

Law, B.E., and Grazis, S.L.,1972, Preliminary geologic map and coal resources of the Decker quadrangle, Big Horn County, Montana: U.S. Geological Survey Open-File Map, scale 1:24,000.

Lee, R.W., 1979, Ground-water-quality data from the northern Powder River Basin, southeastern Montana: U.S. Geological Survey Water-Resources Investigations Open-File Report 79-1331, 55 p.

____1980, Geochemistry of water in the Fort Union Formation of the northern Powder River Basin, southeastern Montana: U.S. Geological Survey Water-Supply Paper 2076, 17 p.

Loveley, D.R., and Goodwin, Steve, 1988, Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments: Geochemica et Cosmochimica Acta, v. 52, p. 2,993-3,003.

Martin, L.J., Naftz, D.L., Lowham, H.W., and Rankl, J.G., 1988, Cumulative potential hydrologic impacts of surface coal mining in the eastern Powder River structural basin, northeastern Wyoming: U.S. Geological Survey Water-Resources Investigations Report 88-4046, 201 p.

Nordstrom, D.K., Plummer, L.N., Langmuir, Donald, Busenberg, Eurybiades, May, H.M., Jones, B.F., and Parkhurst, D.L., 1990, Revised chemical equilibrium data for major water-mineral reactions and their limitations, chap. 31, *of* Melchior, D.C., and Bassett, R.L., eds., Chemical modeling of aqueous systems II: Washington, D.C., American Chemical Society Symposium Series 416, p. 398-412.

Palmer, C.D., and Cherry, J.A., 1984, Geochemical evolution of groundwater in sequences of sedimentary rocks: Journal of Hydrology, v. 75, p. 27-65.

Pearson, F.J., Jr., Fisher, D.W., and Plummer, L.N., 1978, Correction of ground-water chemistry and carbon isotopic composition for effects of CO_2 outgassing: Geochemica et Cosmochimica Acta, v. 42, p. 1,799-1,807.

Plummer, L.N., Busby, J.F., Lee, R. W., and Hanshaw, B.B., 1990, Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota: Water Resources Research, v. 26, no. 9, p. 1,981-2,014.

Plummer, L.N., Jones, B.F., and Truesdell, A.H., 1978, WATEQF--A FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters: U.S. Geological Survey Water-Resources Investigations Report 76-13, 63 p.

Plummer, L.N., Prestman, E.C., and Parkhurst, D.L., 1991, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH: U.S. Geological Survey Water-Resources Investigations Report 91-4078, 227 p.

Price, F.T., and Shieh, Y.N., 1979, Fractionation of sulfur isotopes during laboratory synthesis of pyrite at low temperatures: Chemical Geology, v. 27, p. 245-253.

Rightmire, C.T., and Hanshaw, B.B., 1973, Relationship between the carbon isotope composition of soil CO_2 and the dissolved carbon species in groundwater: Water Resources Research, v. 9, no. 4, p. 958-967.

Thorstenson, D.C., Fisher, D.W., and Croft, M.G., 1979, The geochemistry of the Fox Hills-basal Hell Creek aquifer in southwestern North Dakota and northwestern South Dakota: Water Resources Research, v. 15, no. 6, p. 1,479-1,498.

Van Voast, W.A., and Hedges, R.B., 1975, Hydrogeologic aspects of existing and proposed strip coal mines near Decker, southeastern Montana: Montana Bureau of Mines and Geology Bulletin 97, 31 p.

Van Voast, W.A., Hedges, R.B., and McDermott, J.J., 1977, Hydrogeologic conditions and projections related to mining near Colstrip, southeastern Montana: Montana Bureau of Mines and Geology Bulletin 102, 43 p.

Van Voast, W.A., and Reiten, J.C., 1988, Hydrogeologic responses--Twenty years of surface coal mining in southeastern Montana: Montana Bureau of Mines and Geology Memoir 62, 30 p.

Wigley, T.M.L., Plummer, L.N., and Pearson, F.J., Jr., 1978, Mass transfer and carbon isotope evolution in natural water systems: Geochemica et Cosmochimica Acta, v. 42, p. 1,117-1,139.

_____1979, Errata: Geochemica et Cosmochimica Acta, v. 43, p. 1,395.

(p. 45 follows)

SUPPLEMENTAL INFORMATION

Table 1. Records and water levels of observation wells from the Big Sky and West Decker Mine areas, Montana

[Site-identification numbering system described in text. Altitude of measuring point: Accuracy variation due to surveying method. Aquifer zone--Big Sky Mine area: R, Rosebud coal bed; Sr, spoils from mining of the Rosebud coal bed; Sm, spoils from mining of the McKay coal bed; Mc, McKay coal bed; sub-Mc, sandstone below the McKay coal bed; Se-Mc, stratigraphic equivalent of the McKay coal bed. West Decker Mine area: A-Dz1, combined Anderson-Dietz 1 coal bed; Sp, spoils from mining of the Anderson-Dietz 1 coal bed; Dz2, Dietz 2 coal bed]

Observation well no.	Site identification no.	Altitude of measuring point above sea level (feet)	Depth of well below land surface (feet)	Screened interval (feet)	Aquifer zone	Depth to water below measuring point (feet)	Altitude of water level above sea level (feet)	Date water level measured
Big Sky Mine area								
BSUMR1	01N41E21DADB01	3,325.43	104	84-108	R	69.5	3,255.93	09-22-88
						68.79	3,256.64	10-05-88
						68.74	3,256.69	10-20-88
						68.54	3,256.89	04-19-89
						67.69	3,257.74	05-10-90
BSUMSP1	01N41E21DADA01	3,321.14	75	55-75	Sr	70.4	3,250.74	09-22-88
						67.13	3,254.01	10-20-88
						67.02	3,254.12	04-19-89
						67.03	3,254.11	05-10-90
BSUMSP2	01N41E21DADA02	3,322.94	78	58-78	Sr	65.37	3,257.57	10-04-88
						65.58	3,257.36	10-20-88
						65.59	3,257.35	04-19-89
						65.59	3,257.35	05-10-90
BSLMSP3	01N41E27ADDB01	3,261.34	50.5	32-50	Sm	35.63	3,225.71	10-05-88
						35.64	3,225.70	10-18-88
						35.38	3,225.96	04-19-89
						35.49	3,225.85	05-23-89
						35.42	3,225.92	05-09-90
BSLMSP1	01N41E27ADDB02	3,259.35	51	41-51	Sm	33.68	3,225.67	09-15-88
						33.76	3,225.59	10-05-88
						33.72	3,225.59	10-18-88
						33.68	3,225.67	04-19-89
						33.58	3,225.77	05-23-89
						33.49	3,225.86	05-09-90
BSLMMC1	01N41E27ADAC01	3,257.49	44.5	38-44	Mc	32.60	3,224.89	09-15-88
						32.69	3,224.80	10-05-88
						32.68	3,224.81	10-18-88
						32.58	3,224.91	04-19-89
						32.19	3,225.30	05-22-89
						32.44	3,225.05	05-09-90
BSLMMC2	01N41E27ADAC02	3,256.55	40.5	30-40	Mc	33.05	3,223.50	09-15-88
						33.18	3,223.37	10-05-88
						32.89	3,223.66	10-18-88
						32.46	3,224.09	04-19-89
						32.47	3,224.08	05-22-89
						32.19	3,224.36	05-09-90
BSLMMC3	01N41E27ADAC03	3,257.93	37	29-37	Mc	33.40	3,224.53	09-15-88
						33.49	3,224.44	10-05-88
						33.54	3,224.39	10-18-88
						33.36	3,224.57	04-19-89
						33.29	3,224.64	05-23-89
						33.28	3,224.65	05-09-90

Table 1. Records and water levels of observation wells from the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Site identification no.	Altitude of measuring point above sea level (feet)	Depth of well below land surface (feet)	Screened interval (feet)	Aquifer zone	Depth to water below measuring point (feet)	Altitude of water level above sea level (feet)	Date water level measured
Big Sky Mine area--Continued								
BSLMSM1	01N41E27ADAB01	3,233.09	62	52-62	sub-Mc	41.67	3,191.42	09-15-88
						41.66	3,191.43	10-05-88
						41.44	3,191.65	10-19-88
						40.85	3,192.25	04-19-89
						41.44	3,191.65	05-10-90
BSLMMC5	01N41E27ADAB02	3,232.11	22	12-22	Se-Mc	19.94	3,212.17	10-19-88
						19.45	3,212.66	04-19-89
						19.50	3,212.61	05-10-90
West Decker Mine area								
WDFCL1	09S40E09DACD01	3,498.0	96	84-96	A-Dzl	82.25	3,415.75	10-26-88
						83.82	3,414.18	03-27-89
						84.12	3,413.88	05-10-89
						85.68	3,412.32	05-09-90
WDFSP3	09S40E09DACC01	3,492.5	94	83-94	Sp	83.7	3,408.8	09-12-88
						88.64	3,403.86	10-26-88
						87.56	3,404.94	03-27-89
						88.53	3,403.97	05-10-89
						90.17	3,402.33	05-09-90
WDFD12	09S40E09DDBC01	3,507.3	108	98-108	A-Dzl	100.49	3,406.8	10-26-88
						99.66	3,407.6	03-27-89
						99.77	3,407.5	05-10-89
						100.38	3,406.9	05-09-90
WDESP1	09S40E16BADC01	3,522.0	144	134-144	Sp	125.7	3,396.3	09-12-88
						124.49	3,397.5	10-25-88
						125.31	3,396.7	03-27-89
						125.39	3,396.6	05-10-89
						128.04	3,394.0	05-08-90
WDESP2	09S40E16BADC02	3,521.2	135	125-135	A-Dzl	126.8	3,394.4	09-12-88
						124.18	3,397.0	10-25-88
						125.08	3,396.1	03-27-89
						125.35	3,395.8	05-10-89
						128.24	3,393.0	05-08-90
WDED11	09S40E16BADC03	3,519.8	136	116-136	A-Dzl	123.1	3,396.7	09-12-88
						122.98	3,396.8	10-25-88
						124.05	3,395.8	03-27-89
						124.28	3,395.5	05-10-89
						127.6	3,392.2	05-08-90
WD 2225	09S40E09DBAD01	3,517	120	100-120	Sp	106.63	3,410	09-29-88
DS-5B	09S40E09DCAB02	3,506	140	100-140	Sp	96.28	3,410	09-10-88
						96.06	3,410	05-10-89
WR-01	09S40E16ABCA01	3,498	104	--	A-Dzl	103.22	3,395	05-10-89
WR-06	09S40E16ABCD01	3,499	135	115-135	A-Dzl	103.07	3,396	05-10-89
WR-07	09S40E16ABCD02	3,498	207	180-200	Dz2	107.12	3,391	05-10-89
DS-6A	09S40E16BABD01	3,515	157	142-154	Sp	112.76	3,402	05-10-89

Table 2. Summary of revised thermodynamic data

[Data from Nordstrom and others (1990) except where noted. Abbreviation: ΔH°_r, enthalpy of reaction; log K, equilibrium constant; Kcal/mol, kilocalorie per mole. Symbol: --, no data]

Mineral	Reaction	ΔH°_r (kcal/mol)	log K
Quartz	$SiO_2 + 2H_2O = H_4SiO_4$	5.99	-3.980
Calcite	$CaCO_3 = Ca^{3+} + CO_3^{2-}$	-2.297	-8.480
Aragonite	$CaCO_3 = Ca^{2+} + CO_3^{2-}$	-2.589	-8.336
Dolomite[1]	$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	-9.436	-17.09
Strontionite	$SrCO_2 = Sr^{2+} + CO_3^{2-}$	-.40	-9.271
Siderite[2]	$FeCO_3 = Fe^{2+} + CO_3^{2-}$	--	-10.89
Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	-.109	-4.58
Anhydrite	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	-1.71	-4.36
Celestite	$SrSO_4 = Sr^{2+} + SO_4^{2-}$	-1.037	-6.63
Barite	$BaSO_4 = Ba^{2+} + SO_4^{2-}$	6.35	-9.97
Goethite	$HFeO_2 + 3H^+ = Fe^{3+} + 2H_2O$	--	-1.0
FeS(ppt)[3]	$FeS = Fe^{2+} + S^{2-}$	--	[4]-3.915

[1] Thermodynamic data are for ordered dolomite.

[2] Thermodynamic data are for crystalline siderite.

[3] Amorphous iron-sulfide precipitate.

[4] Data from Plummer and others (1978).

Table 3. Logs of observation wells from the Big Sky and West Decker Mine areas, Montana

[Thickness penetrated is in feet. Bottom of depth interval is in feet below land surface]

Lithology	Thickness penetrated	Bottom of depth interval
Big Sky Mine area		
Observation well BSUMR1; drilled September 22, 1988		
Fill, topsoil	5	5
Mine spoils, gray, sandy	30	35
Mine spoils, sandy, clinker, calcareous	15	50
Mine spoils, grayish-green, sandy	17	67
Siltstone, gray	2	69
Sandstone, gray, very fine grained, calcareous	2	71
Sandstone; wet	12	83
Coal (Rosebud); water	21	104
Shale, gray; dry	1	105
Observation well BSUMSP1; drilled September 21, 1988		
Fill, topsoil, clinker, shale	5	5
Mine spoils, sandy; moist	5	10
Mine spoils, sandy, contains gravel, calcareous	12	22
Mine spoils, sand, clinker, coal; moist	38	60
Mine spoils, sand; wet	34	94
Shale	1	95
Observation well BSUMSP2; drilled September 21, 1988		
Mine spoils, sandy; moist	20	20
Mine spoils, sand, clinker, coal; moist	65	85
Mine spoils, sand; wet	12	97
Shale	1	98
Observation well BSLMSP3; drilled September 21, 1988		
Mine spoils, coal	10	10
Mine spoils, sand	10	20
Mine spoils, sandy, dark	5	25
Mine spoils, coal; wet	13	38
Mine spoils, siltstone, sandy, coal; water	12	50
Sandstone (sub-McKay)	.5	50.5
Observation well BSLMSP1; drilled September 13, 1988		
Mine spoils, clinker, coal	5	5
Mine spoils, sandy, calcareous	19	24
Mine spoils, sandy	8	32
Mine spoils; water	10	42
Mine spoils, coal, shale; water	7	49
Sandstone (sub-McKay)	2	51

Table 3. Logs of observation wells from the Big Sky and West Decker Mine areas, Montana (Continued)

Lithology	Thick-ness pene-trated	Bottom of depth interval
Big Sky Mine area--Continued		
Observation well BSLMMC1; drilled September 13, 1988		
Mine spoils, yellowish-brown	10	10
Mine spoils, sand	5	15
Mine spoils, sand, rocks, brown	9	24
Mine spoils, sand, coal, clinker	8	32
Mine spoils, siltstone, sandy	3.5	35.5
Coal (McKay)	8.5	44
Sandstone (sub-McKay)	.5	44.5
Observation well BSLMMC2; drilled September 14, 1988		
Mine spoils	23	23
Siltstone, gray	6	29
Coal (McKay)	10	39
Sandstone (sub-McKay)	1.5	40.5
Observation well BSLMMC3; drilled September 14, 1988		
Mine spoils	5	5
Mine spoils, clinker	5	10
Mine spoils, calcareous	5	15
Siltstone, calcareous	3	18
Siltstone, grayish-green, calcareous	5	23
Siltstone, yellowish-brown, sandy	2	25
Organic, dark, non-coal	2.5	27.5
Coal (McKay)	9	36.5
Sandstone (sub-McKay)	.5	37
Observation well BSLMSM1; drilled September 14, 1988		
Fill, clinker	8	8
Shale, light-brown	5	13
Siltstone and sandstone, hard, red	2	15
Siltstone, sandy	15	30
Sandstone	7.5	37.5
Siltstone, gray, slightly calcareous (sub-McKay)	12.5	50
Siltstone, gray, some sand (sub-McKay)	5	55
Sand, gray (sub-McKay); water	7	62
Observation well BSLMMC5; drilled September 20, 1988		
Fill, clinker	5	5
Shale	14	19
Sandstone and siltstone, red; moist	1	20
Siltstone, gray	2	22

Table 3. Logs of observation wells from the Big Sky and West Decker Mine areas, Montana (Continued)

Lithology	Thickness penetrated	Bottom of depth interval
West Decker Mine area		
Observation well WDFCL1; drilled September 12, 1988		
Fill, shale and siltstone, calcareous	5	5
Mine spoils, clinker	4	9
Mine spoils, brown shale, calcareous	3	12
Mine spoils, coal and sand	24	36
Mine spoils, sand and clinker	1	37
Mine spoils, sand	2	39
Mine spoils, coal	2	41
Mine spoils, sand and coal	6	47
Clinker	13	60
Clinker, sandy; moist	7	67
Coal (Anderson-Dietz 1)	18	85
Coal (Anderson-Dietz 1), contains some pyrite; wet	10	95
Shale; dry	1	96
Observation well WDFSP3; drilled September 11, 1988		
Mine spoils	30	30
Mine spoils, gray siltstone, calcareous	5	35
Mine spoils, gray shale	17	52
Mine spoils, gray siltstone, calcareous	1	53
Mine spoils, coal and clinker	2	55
Mine spoils, gray shale	3	58
Mine spoils, contains some clinker	7	65
Mine spoils, gray shale	5	70
Mine spoils, coal, and siltstone, calcareous	4	74
Mine spoils, brown shale, clinker, and coal	6	80
Mine spoils, gray shale	4	84
Mine spoils; contains some coal	8	92
Shale	2	94
Observation well WDFD12; drilled September 10, 1988		
Mine spoils	25	25
Mine spoils; wet	2	27
Mine spoils, gray, calcareous; contains coal; dry	3	30
Mine spoils, brownish-gray	11	41
Mine spoils, siltstone, calcareous	8	49
Shale	5	54
Coal (Anderson-Dietz 1)	43	97
Coal (Anderson-Dietz 1); wet	10	107
Shale	1	108

Table 3. Logs of observation wells from the Big Sky and West Decker Mine areas, Montana (Continued)

Lithology	Thickness penetrated	Bottom of depth interval
West Decker Mine area--Continued		
Observation well WDESP1; drilled September 8, 1988		
Mine spoils	6	6
Mine spoils, calcareous	2	8
Mine spoils	5	13
Mine spoils, calcareous	2	15
Mine spoils, rocks, coal, calcareous	35	50
Mine spoils, coal	5	55
Mine spoils, gray siltstone, calcareous	10	65
Mine spoils, dark shale	18	83
Mine spoils, brown shale, calcareous	19	102
Mine spoils, gray siltstone, calcareous	2	104
Mine spoils, brown, soft	12	116
Mine spoils, rock	3	119
Mine spoils, gray, fine-grained	13	132
Mine spoils; water	7	139
Mine spoils, coal	3	142
Shale; dry	2	144
Observation well WDESP2; drilled September 10, 1988		
Mine spoils, fine-grained, slightly calcareous	45	45
Mine spoils; contains some coal	19	64
Mine spoils, powdery, contains some coal	31	95
Mine spoils; soft, coal	7	102
Coal (Anderson-Dietz 1)	32	134
Coal (Anderson-Dietz 1), pyrite	1	135
Shale	.5	135.5
Observation well WDED11; drilled September 9, 1988		
Mine spoils	11	11
Siltstone, yellowish-brown, slightly calcareous	7	18
Siltstone, gray, calcareous	3	21
Siltstone, brown	6	27
Shale, grayish-black	10	37
Siltstone, gray, calcareous	2	39
Shale, grayish-black	4	43
Siltstone, gray, calcareous	2	45
Shale, gray	17	62
Siltstone, gray, calcareous	2	64
Shale, gray	16	80
Coal (Anderson-Dietz 1)	50	130
Coal (Anderson-Dietz 1); water	5	135
Shale, whitish-brown; dry	1	136

Table 4. Petrographic analyses of selected core samples from mine spoils and unmined consolidated rock from the Big Sky and West Decker Mine areas, Montana

[Depth of sample: in feet below land surface. Symbol: --, no data]

Observation well no.	Depth of sample (feet)	General lithology	Major identifiable mineral (5 percent or more of total)	Minor identifiable mineral (less than 5 percent of total)
		Big Sky Mine area		
BSUMR1	68	Siltstone, clayey, coarse-grained.	Clay, dolomitic cement, quartz, fine-grained lithics, feldspar.	Muscovite, biotite, coalified debris.
BSUMR1	71	Sandstone, clayey, calcareous, very fine grained.	Quartz, dolomitic cement, fine-grained lithics, clay, biotite, feldspar.	Muscovite, glauconite, pyrite.
BSLMSP1	50	Sandstone, clayey, kaolinitic, very fine grained.	Fine-grained lithics, quartz, clay.	Feldspar, carbonates, biotite, muscovite, heavy minerals, glauconite.
BSLMMC2	28-29	Siltstone, clayey, calcareous, very fine grained.	Illite, carbonates, quartz/ feldspar, sericite, biotite.	--
BSLMMC3	21-23	Siltstone, clayey, calcareous, medium-grained.	Clay, carbonate cement, quartz/feldspar, muscovite.	Biotite.
BSLMSM1	13-15	Siltstone, and sandstone, containing iron,very fine grained.	Iron oxides, fine-grained lithics, quartz, carbonates.	Dolomite, feldspar, muscovite.
		West Decker Mine area		
WDFCL1	50-52	Siltstone, clayey, containing iron, fine-grained.	Quartz/feldspar, biotite, illite, carbonates, muscovite, hematite.	--
WDESP1	103	Siltstone, and sandstone, calcareous, fine-grained.	Dolomite, quartz/feldspar, chert, schist, fine-grained lithics.	Calcite, muscovite, biotite.
WDESP1	117-119	Siltstone, clayey, calcareous.	Illite, calcite, quartz/feldspar, organics.	Biotite, muscovite, framboidal pyrite.
WDED11	13	Siltstone, clayey, calcareous, fine-grained.	Illite, quartz/feldspar, muscovite, carbonates.	Manganese and iron oxides.

Table 5. Bulk mineralogy determined by X-ray diffraction analysis of samples of mine spoils and unmined consolidated rock from the Big Sky and West Decker Mine areas, Montana

[Depth of sample: in feet below land surface. Type of material: Ms, mine spoils; Um, unmined consolidated rock. Bulk mineralogy content: MA, most abundant, greater than 40 percent; A, abundant, 10-40 percent; C, common, 5-10 percent; M, minor, 1-5 percent; T, trace, less than 1 percent; ND, not detected. Other minerals: BA, barite; CE, celestite; GO, goethite; PY, pyrite; SD, siderite; SR, stronianite; TH, thenaderite. The detection limit using X-ray diffraction is about 1-2 weight percent. Symbols: --, no data; ?, probable detection]

Observation well no.	Depth of sample (feet)	Type of material	Bulk mineralogy										Other minerals
			Quartz	Calcite	Dolomite	Gypsum	Potassium feldspar	Plagioclase feldspar	Smectite	Muscovite/ illite	Kaolinite	Chlorite	
						Big Sky Mine area							
BSUMR1	68	Um	MA	M	A	ND	T	M	M	C	C	M	--
	71	Um	MA	T	A	ND	M	T	T	M	C	T	--
BSUMSP1	80	Ms	MA	C	C	ND	T	M	M	M	C	M	TH
BSLMSP3	45	Ms	MA	M	A	T	T	M	M	C	C	M	--
BSLMSP1	32	Ms	MA	M	A	ND	T	M	T	C	C	M	TH,SD?
	41	Ms	MA	T	C	ND	T	C	M	T	M	M	--
BSLMMC2	28	Um	A	ND	A	M	M	C	ND	C	C	C	TH, SR
BSLMMC3	18	Um	A	MA	A	ND	T	M	M	C	C	M	--
BSLMSM1	13	Um	MA	M	A	M	M	M	M	M	C	M	GO, PY
	50	Um	MA	C	A	ND	M	M	M	M	C	T	TH?
						West Decker Mine area							
WDFCL1	50	Um	MA	ND	ND	ND	ND	C	ND	A	ND	ND	--
WDFSP3	72	Ms	MA	M	M	T?	T	C	M	C	C	M	--
	80	Ms	MA	C	C	ND	T	C	C	C	C	C	TH
	85	Ms	MA	C	C	ND	M	C	C	C	C	C	TH,SD?
WDESP1	13	Ms	MA	M	C	ND	M	C	M	C	C	M	TH,CE
	65	Ms	MA	A	C	ND	T	C	M	C	C	M	TH
	75	Ms	MA	M	C	ND	M	C	M	A	C	M	--
	103	Ms	MA	A	C	ND	M	A	M	C	C	M	--
	115	Ms	MA	M	A	ND	M	C	M	C	C	M	TH
	117	Ms	MA	M	C	ND	M	C	M	C	C	M	TH
	123	Ms	MA	C	C	ND	T	C	M	C	C	M	TH?
WDESP2	85	Ms	MA	M	C	T?	T	C	M	C	C	M	TH, SD?
WDED11	13	Um	MA	C	C	T?	M	C	C	C	C	C	--
	63	Um	MA	A	A	ND	M	C	M	M	C	M	BA

Table 6. Bulk mineralogy determined by X-ray diffraction analysis of the less than 2-micron size fraction from samples of mine spoils and unmined consolidated rock from the Big Sky and West Decker Mine areas, Montana

[Depth of sample: in feet below land surface. Type of material: Ms, mine spoils; Um, unmined consolidated rock. Bulk mineralogy content: MA, most abundant, greater than 50 percent; A, abundant, 20-50 percent; C, common, 10-20 percent; M, minor, 1-10 percent; T, trace, less than 1 percent; ND, not detected. Other minerals: CA, calcite; CL, iron chlorite; DO, dolomite; PL, plagioclase. The detection limit using X-ray diffraction is about 1-2 weight percent. Symbol: --, no data]

Observation well no.	Depth of sample (feet)	Type of material	Bulk mineralogy					Other minerals
			Smectite	Muscovite /illite	Kaolinite	Chlorite	Quartz	
			Big Sky Mine area					
BSUMR1	68	Um	A	M	MA	M	T	DO
BSLMSP1	32	Ms	M	A	MA	A	T	--
BSLMMC2	28	Um	ND	A	A	C	M	DO
BSLMMC3	21	Um	ND	A	MA	C	M	--
			West Decker Mine area					
WDFSP3	80	Ms	C	C	MA	M	M	--
WDESP1	13	Ms	A	C	MA	C	M	--
	75	Ms	MA	C	A	C	M	--
	103	Ms	MA	M	A	M	M	CA, DO
	117	Ms	A	C	MA	M	M	--
	123	Ms	A	C	A	C	M	CL
WDESP2	85	Ms	C	A	MA	C	T	--
WDED11	13	Um	A	A	A	C	M	CA, DO, PL

Table 7. Cation and trace-element concentrations in core samples from mine spoils and unmined consolidated rock from the Big Sky and West Decker Mine areas, Montana

[Analyses by Montana Bureau of Mines and Geology. Depth of sample: in feet below land surface. Type of material: Cl, clinker; Ms, mine spoils; Sh, shale; Slt, siltstone; Ss, sandstone]

Observation well no.	Depth of sample (feet)	Type of material	Concentration, in micrograms recovered per gram of solid										
			Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Silica (SiO_2)	Phosphorous (P)	Aluminum (Al)	Boron (B)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)
						Big Sky Mine area							
BSUMR1	68	Slt	42,000	26,000	6,200	20,000	22,000	630	56,000	1,100	7.1	68	25
BSUMR1	71	Ss	36,000	22,000	5,700	17,000	14,000	610	48,000	650	4.9	72	13
BSUMSP1	80	Ms	38,000	15,000	5,600	17,000	8,000	510	48,000	280	5.8	54	12
BSLMSP3	45	Ms	37,000	21,000	4,700	21,000	12,000	570	58,000	580	5.8	54	12
BSLMSP1	32-34	Ms	38,000	25,000	6,200	21,000	25,000	650	57,000	1,400	5.2	89	20
	41-42	Ms	42,000	19,000	5,000	20,000	23,000	570	52,000	920	5.9	100	21
	49-50	Ss	4,800	8,500	5,600	21.000	6,000	880	65,000	330	3.6	81	28
BSLMMC2	28-29	Slt	32,000	30,000	6,400	29,000	35,000	570	75,000	1,800	6.5	78	32
BSLMMC3	18	Sh	190,000	21,000	4,100	15,000	41,000	450	39,000	2,000	4.9	43	23
	21-23	Slt	73,000	33,000	5,400	22,000	40,000	600	59,000	1.800	5.1	57	27
BSLMSM1	13-15	Slt, Ss	24,000	17,000	4,900	14,000	28,000	590	44,000	1,400	17	48	16
Median			38,000	21,000	5,600	20,000	23,000	590	56,000	1,100	5.8	72	13
						West Decker Mine area							
WDFCL1	50-52	Cl, Slt	29,000	14.000	9,900	26,000	37,000	1,000	91,000	1,700	10	93	56
WDFSP3	72-74	Ms	8,300	11,000	8,500	26,000	17,000	700	90,000	780	10	90	50
	80-82	Ms	26,000	15,000	8,300	24,000	15,000	810	80,000	660	6.3	79	46
WDESP1	103	Ms	130,000	16,000	9,000	12,000	44,000	570	48,000	2,200	8.9	49	50
	117-119	Ms	31,000	17,000	8,900	24,000	24,000	830	80,000	1,200	7.9	87	50
	123	Ms	30,000	16,000	9,900	23,000	36,000	840	80,000	1,700	8.0	120	48
WDESP2	85	Ms	25,000	16,000	8,300	23,000	26,000	860	82,000	1,200	7.2	85	47
WDED11	13-15	Slt	28,000	20,000	10,000	24,000	56,000	850	80,000	2,800	8.8	82	46
	63	Slt	110,000	21,000	8,600	12,000	41,000	540	49,000	2,200	5.0	81	41
Median			29,000	16,000	9,000	24,000	36,000	830	80,000	1,700	8.0	85	48

Table 7. Cation and trace-element concentrations in core samples from mine spoils and unmined consolidated rock from the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Concentrations, in micrograms recovered per gram of solid										
	Iron (Fe)	Lead (Pb)	Lithium (Li)	Manganese (Mn)	Molybdenum (Mo)	Nickel (Ni)	Strontium (Sr)	Titanium (Ti)	Vanadium (V)	Zinc (Zn)	Zirconium (Zr)
					Big Sky Mine area						
BSUMR1	20,000	43	25	340	16	23	77	1,700	77	59	66
BSUMR1	12,000	44	21	210	8.1	27	62	2,200	60	50	87
BSUMSP1	30,000	72	22	580	14	23	110	1,700	61	57	65
BSLMSP3	27,000	100	32	450	16	25	81	1,400	68	61	48
BSLMSP1	22,000	72	30	380	16	24	72	1,500	65	52	59
	22,000	62	28	420	14	25	93	1,300	63	53	56
	17,000	54	22	130	9	37	86	1,900	83	92	60
BSLMMC2	29,000	72	46	520	17	37	55	2,400	83	95	88
BSLMMC3	25,000	27	23	730	14	19	200	990	51	44	43
	27,000	53	33	670	14	27	110	2,100	74	70	89
BSLMSM1	130,000	47	14	1,300	14	45	74	1,700	60	83	68
Median	25,000	54	25	450	14	25	81	1,700	65	59	65
					West Decker Mine area						
WDFCL1	43,000	123	39	1,100	21	56	290	3,500	140	140	60
WDFSP3	24,000	50	43	280	24	42	170	3,100	140	110	75
	27,000	62	39	740	19	50	170	2,200	120	110	51
WDESP1	22,000	4.7	20	500	14	13	370	1,700	51	57	59
	39,000	83	38	1,000	13	41	190	2,500	130	97	65
	34,000	60	35	830	26	70	210	2,800	120	120	81
WDESP2	38,000	87	39	820	13	46	180	2,600	130	110	68
WDED11	56,000	83	40	1,200	22	47	340	2,100	140	120	71
	25,000	77	20	530	13	17	370	1,400	52	48	52
Median	34,000	77	39	820	19	46	200	2,500	130	110	65

Table 8. Exchangeable cations in core samples from mine spoils and unmined consolidated rock from the Big Sky and West Decker Mine areas, Montana

[Analyses by Montana Bureau of Mines and Geology. Depth of sample: in feet below land surface. Type of material: Ms, mine spoils; Slt, siltstone. Symbol: <, less than]

Observation well no.	Depth of sample (feet)	Type of material	Exchangeable cations, in micrograms per gram of solid									
			Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Silica (SiO_2)	Phosphorus (P)	Aluminum (Al)	Boron (B)	Cadmium (Cd)	Chromium (Cr)
						Big Sky Mine area						
BSUMR1	68	Slt	2,400	380	20	78	250	<2	<0.6	1.6	<0.04	<0.04
BSLMSP1	32-34	Ms	3,900	850	110	35	170	<2	<.6	5.8	<.04	<.04
BSLMMC2	28-29	Slt	1,300	930	76	55	61	<2	<.6	2.3	<.04	<.04
BSLMMC3	21-23	Slt	4,800	420	38	37	45	<2	<.6	.83	<.04	<.04
						West Decker Mine area						
WDFSP3	80-82	Ms	3,400	280	760	120	38	<2	<.6	.44	<.04	<.04
WDESP1	123	Ms	2,100	360	1,000	130	4.9	<2	<.6	<.4	<.04	<.04
WDESP2	85	Ms	2,200	330	750	110	33	<2	<.6	<.4	<.04	<.04
WDED11	13-15	Slt	2,700	830	1,300	100	37	<2	1.7	.82	.088	.048

Table 8. Exchangeable cations in core samples from mine spoils and unmined consolidated rock from the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Exchangeable cations, in micrograms per gram of solid											
	Copper (Cu)	Iron (Fe)	Lead (Pb)	Lithium (Li)	Manganese (Mn)	Molybdenum (Mo)	Nickel (Ni)	Strontium (Sr)	Titanium (Ti)	Vanadium (V)	Zinc (Zn)	Zirconium (Zr)
					Big Sky Mine area							
BSUMR1	0.50	0.12	<0.8	<0.04	12	<0.4	0.66	8.2	0.23	0.073	1.2	<0.08
BSLMSP1	.15	.17	<.8	<.04	4.6	<.4	<.2	11	.29	<.04	.24	<.08
BSLMMC2	.12	.17	<.8	.098	3.4	<.4	<.2	4.5	.11	<.04	.28	<.08
BSLMMC3	.14	.18	<.8	<.04	14	<.4	<.2	15	.33	.070	.11	<.08
					West Decker Mine area							
WDFSP3	.32	.096	<.8	.22	23	<.4	1.0	39	.25	<.04	.94	<.08
WDESP1	.21	.15	<.8	.12	17	<.4	.25	47	.17	<.04	.48	<.08
WDESP2	.23	.18	<.8	.12	19	<.4	.24	37	.14	<.04	.73	<.08
WDED11	.077	2.4	<.8	.35	4.8	<.4	<.2	81	.37	.11	<.06	.10

Table 9. Ash content and concentrations of selected major and minor oxides and selected trace elements in laboratory ash of coal samples from the Big Sky and West Decker Mine areas, Montana

[Analyses by U.S. Geological Survey, Branch of Geochemistry. Depth of sample: in feet below land surface. Coal ashed at 800 degrees Celsius. Source of coal: Mc, McKay; A-Dzl, combined Anderson-Dietz 1. Symbols: <, less than; >, greater than]

				Concentration in laboratory ash, in percent								
Observation or location well no.	**Depth of sample (feet)**	**Source of coal**	**Ash content (percent)**	**Calcium (CaO)**	**Magnesium (MgO)**	**Sodium (Na_2O)**	**Potassium (K_2O)**	**Silica (SiO_2)**	**Phosphorous (P_2O_5)**	**Aluminum (Al_2O_3)**	**Iron (Fe_2O_3)**	**Titanium (TiO_2)**
						Big Sky Mine area						
BSLMMC1	36-37	Mc	5.9	6.9	7.6	0.26	<0.06	26	<0.16	9.6	1.1	0.25
BSLMMC1	37-38	Mc	6.4	6.7	6.0	.23	.12	28	<.16	9.3	1.4	.48
BSLMMC2	37-39	Mc	2.6	11	8.6	.51	.11	8.8	<.16	6.6	5.7	.14
Mine wall[1]		Mc	6.1	6.6	5.8	.22	.27	21	<.16	4.7	.56	.25
						West Decker Mine area						
WDFCL1	87-88	A-Dzl	2.0	18	4.0	12	.40	1.1	.32	4.5	2.9	.57
WDFCL1	88-89	A-Dzl	2.2	20	4.5	10	.30	3.9	1.1	4.5	3.1	1.2
WDESP2	124-125	A-Dzl	2.4	15	4.3	12	.45	6.2	.32	3.2	1.2	1.4
WDESP2	133-134	A-Dzl	3.5	14	4.1	7.8	.25	11	.34	3.2	1.7	.62
WDED11	125	A-Dzl	2.3	17	3.7	12	.41	6.2	.30	2.5	1.1	.52
WDED11	129	A-Dzl	3.6	15	4.3	8.1	.22	11	1.6	3.8	1.7	1.5

---

[1] Sample collected from upgradient mine wall, Big Sky Mine.

Table 9. Ash content and concentrations of selected major and minor oxides and selected trace elements in laboratory ash of coal samples from the Big Sky and West Decker Mine areas, Montana (Continued)

Observation or location well no.	Concentration in laboratory ash, in percent													
	Barium (Ba)	Beryllium (Be)	Boron (B)	Cadmium (Ca)	Cerium (Ce)	Chromium (Cr)	Cobalt (Co)	Copper (Cu)	Europium (Eu)	Gallium (Ga)	Germanium (Ge)	Holmium (Ho)	Lanthanum (La)	Lead (Pb)
						<u>Big Sky Mine area--Continued</u>								
BSLMMC1	300	7.2	720	<22	<63	22	7.3	28	<0.7	24	<5	<2	49	8.8
BSLMMC1	190	26	720	<22	80	21	37	100	2.9	40	51	<2	50	64
BSLMMC2	300	54	>1,000	<22	79	34	140	39	7.9	150	27	7.2	70	20
Mine wall[1]	130	31	550	<22	170	71	22	89	7.4	94	26	9.0	64	56
						<u>West Decker Mine area--Continued</u>								
WDFCL1	17,000	2.0	680	<22	<63	28	18	34	<.7	32	<5	<2	<10	28
WDFCL1	13,000	2.2	550	<22	190	39	19	230	<.7	31	<5	<2	73	28
WDESP2	14,000	<2	420	<22	<63	35	17	440	<.7	33	<5	<2	32	23
WDESP2	11,000	2.0	380	<22	<63	44	19	84	<.7	24	<5	<2	29	28
WDED11	14,000	<2	540	<22	<63	29	16	33	<.7	34	<5	<2	30	26
WDED11	17,000	<2	300	<22	190	54	13	490	2.7	43	<5	<2	79	37

Table 9. Ash content and concentrations of selected major and minor oxides and selected trace elements in laboratory ash of coal samples from the Big Sky and West Decker Mine areas, Montana (Continued)

Observation or location well no.	Concentration in laboratory ash, in percent														
	Lithium (Li)	Manganese (Mn)	Molybdenum (Mo)	Nickel (Ni)	Niobium (Nb)	Samarium (Sm)	Scandium (Sc)	Silver (Ag)	Strontium (Sr)	Tin (Sn)	Vanadium (V)	Ytterbium (Yb)	Yttrium (Y)	Zinc (Zn)	Zirconium (Zr)
							Big Sky Mine area--Continued								
BSLMMC1	72	290	10	34	6.3	6.4	8.3	0.22	2,100	<5	28	1.7	19	84	150
BSLMMC1	47	250	7.9	83	13	7.3	14	.32	2,800	5.9	49	7.7	64	60	260
BSLMMC2	<10	230	18	210	1.5	12	11	.20	6,600	10	33	11	170	110	88
Mine wall[1]	69	670	34	57	23	11	33	.33	1,000	7.7	110	16	180	460	340
							West Decker Mine area--Continued								
WDFCL1	20	160	12	30	7.1	<4	24	.38	16,000	14	94	3.2	24	<15	120
WDFCL1	20	190	12	31	9.1	9.1	27	.61	23,000	<5	110	3.0	25	<15	150
WDESP2	31	150	13	24	14	<4	28	.55	14,000	<5	120	2.0	18	15	200
WDESP2	26	170	11	46	4.5	<4	35	.23	9,300	<5	120	2.6	27	<15	160
WDED11	29	130	14	19	3.3	<4	24	.26	18,000	8.8	88	1.7	13	140	130
WDED11	22	120	7.1	34	11	11	32	.81	15,000	11	130	3.1	24	<15	170

Table 10. Comparison of median values of ash content, selected major and minor oxides, and selected trace-element concentrations in laboratory ash of coal samples from the Big Sky and West Decker Mine areas, Montana, to analyses of coal samples from throughout the Powder River structural basin

[Symbol: <, less than]

	Concentration, in percent								Concentration, in parts per million				
	Ash	Calcium (CaO)	Magnesium (MgO)	Sodium (Na_2O)	Silica (SiO_2)	Aluminum (Al_2O_3)	Iron (Fe_2O_3)		Barium (Ba)	Copper (Cu)	Manganese (Mn)	Strontium (Sr)	Zinc (Zn)
Big Sky Mine area (4 samples)													
Median[1]	6.0	6.8	6.8	0.24	24	8.0	1.2	Median[1]	240	64	270	2,400	97
West Decker Mine area (6 samples)													
Median[1]	2.4	16	4.2	11	6.2	3.5	1.7	Median[1]	14,000	160	160	16,000	<15
Powder River Structural Basin (410 samples)													
Minimum[2]	3.2	.36	.28	.03	5.8	2.6	.39	Minimum[3]	100	24	100	150	15
Mean[2]	9.9	18	4.0	1.8	30	14	7.3	Mean[3]	3,000	110	510	2,000	200
Maximum[2]	85	49	12	8.7	69	30	77	Maximum[3]	20,000	760	4,430	7,000	2,200

[1] Calculated from table 9.

[2] Hatch and Swanson, 1977, p. 156.

[3] Recalculated from a whole-coal basis to a laboratory-ash basis, on the basis of the ash mean of 10 percent (Hatch and Swanson, 1977, p. 157).

Table 11. Properties and concentration of chemical constituents in water from observation wells in the Big Sky and West Decker Mine areas, Montana

[Aquifer zone--Big Sky Mine area: R, Rosebud coal bed; Sr, spoils from mining of the Rosebud coal bed; Sm, spoils from mining of the McKay coal bed; Mc, McKay coal bed; sub-Mc, sandstone below the McKay coal bed; Se-Mc, stratigraphic equivalent of the McKay coal bed. West Decker Mine area: A-Dzl, combined Anderson-Dietz 1 coal bed; Sp, spoils from mining of the Anderson-Dietz 1 coal bed. Laboratory analyses by Montana Bureau of Mines and Geology except as noted. Concentrations are dissolved except as noted. Abbreviations: µS/cm, microsiemens per centimeter at 25 °C; °C, degrees Celsius; ND, not detected. Symbols: --, no data; <, less than; >, greater than]

Observation well no.	Aquifer zone	Date of sample	Specific conductance (onsite) (µS/cm)	pH (onsite) (units)	Water temperature (onsite) (°C)	Concentration, in milligrams per liter							
						Dissolved oxygen (onsite)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (onsite) (HCO_3)	Bicarbonate (laboratory) (HCO_3)	Carbonate (CO_3)
					Big Sky Mine area								
BSUMR1	R	10-20-88	2,740	7.0	11.0	--	240	230	100	7.3	780	670	0
BSUMSP1	Sr	10-20-88	3,900	7.0	11.0	--	370	400	150	20	510	490	0
BSUMSP2	Sr	10-20-88	--	7.2	12.0	--	390	450	170	20	420	400	0
BSLMSP3	Sm	10-19-88	4,170	6.7	12.0	--	470	390	130	15	920	720	0
		05-23-89	4,000	6.5	13.0	0.35	470	390	120	14	910	900	0
		05-09-90	3,900	6.6	12.5	ND	460	390	130	16	960	880	0
BSLMSP1	Sm	10-18-88	3,780	6.5	12.0	--	460	410	130	15	930	820	0
		05-23-89	4,000	6.5	12.5	.5	470	410	130	15	930	900	0
		05-09-90	3,900	6.6	12.5	.05	450	390	130	15	950	880	0
BSLMMC1	Mc	10-18-88	3,800	6.5	12.0	--	440	420	130	11	1,000	940	0
		05-22-89	3,950	6.5	13.5	ND	450	430	120	10	970	950	0
		05-10-90	4,100	6.6	12.5	ND	450	430	130	11	980	940	0
BSLMMC2	Mc	10-18-88	3,800	6.5	12.0	--	440	420	140	9.6	930	860	0
		05-22-89	4,120	6.4	14.0	1.5	450	440	120	9.6	890	880	0
BSLMMC3	Mc	10-19-88	4,200	6.4	11.5	--	450	410	100	9.1	770	690	0
		05-22-89	4,050	6.3	13.5	.35	460	440	90	7.8	740	750	0
		05-10-90	4,000	6.4	12.5	--	440	430	110	9.7	780	740	0
BSLMSM1	sub-Mc	10-19-88	3,240	7.0	11.5	--	240	280	160	11	720	610	0
BSLMMC5	Se-Mc	10-19-88	5,100	7.2	12.5	--	600	480	150	9.7	460	430	0

Table 11. Properties and concentration of chemical constituents in water from observation wells in the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Concentration, in milligrams per liter								Concentration, in micrograms per liter						
	Alkalinity (onsite) (as $CaCO_3$)	Sulfide (onsite) (H_2S)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (Fl)	Silica (SiO_2)	Dissolved solids, calculated	Nitrate (as N)	Aluminum (Al)	Aluminum[1] (Al)	Barium (Ba)	Boron (B)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)
						Big Sky Mine area--Continued									
BSUMR1	638	0.13	1,200	6.3	0.3	18	2,150	0.13	80	<10	--	410	<2	17	15
BSUMSP1	418	.05	2,400	9.9	.2	17	3,630	.10	60	20	--	370	6	14	23
BSUMSP2	344	.03	2,700	10	.2	15	3,980	.11	60	20	--	330	<2	17	25
BSLMSP3	751	.15	2,400	16	.1	13	3,780	.19	60	10	--	970	8	18	25
	749	ND	2,200	17	<.1	14	3,680	.32	<30	--	13	830	7	15	<4
	790	ND	2,200	15	.1	14	3,710	.07	<40	--	<10	700	<5	<5	<4
BSLMSP1	761	.04	2,300	17	.1	13	3,790	.48	<30	10	--	1,100	<2	13	22
	761	ND	2,300	17	<.1	14	3,800	.39	<30	--	7	870	19	24	9
	776	ND	2,200	16	.1	14	3,630	.07	<40	--	<10	780	<5	<5	<4
BSLMMC1	769	.02	2,300	17	.2	15	3,780	.19	<30	20	--	1,700	<2	10	21
	793	.04	2,300	18	<.1	14	4,000	.39	<40	--	<1	1,400	<5	<5	<4
	804	.2	2,300	17	.2	15	3,800	<.05	<40	--	<10	1,200	<5	<5	<4
BSLMMC2	761	.1	2,300	18	.1	17	3,790	.07	<30	20	--	1,500	<2	6	19
	728	ND	2,300	17	<.1	16	3,830	.22	<40	--	1	1,200	<5	<5	<4
BSLMMC3	630	.05	2,400	18	.1	26	3,770	.13	<30	30	--	1,300	<2	3	14
	610	.19	2,400	17	<.1	25	3,840	.39	60	--	3	1,000	7	<5	<4
	641	ND	2,400	16	.2	24	3,810	.07	<40	--	<10	950	<5	<5	<4
BSLMSM1	590	.05	1,600	10	.2	18	2,580	.10	50	20	--	380	<2	14	20
BSLMMC5	377	.04	3,300	21	.1	20	4,750	2.1	100	20	--	2,200	<2	23	48

Table 11. Properties and concentration of chemical constituents in water from observation wells in the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Concentration, in micrograms per liter														
	Iron, total (onsite) (Fe)	Iron (Fe)	Iron[1] (Fe)	Iron, ferrous (onsite) (Fe)	Lithium (Li)	Manganese (Mn)	Manganese[1] (Mn)	Molybdenum (Mo)	Nickel (Ni)	Silver (Ag)	Strontium (Sr)	Titanium (Ti)	Vanadium (V)	Zinc (Zn)	Zirconium (Zr)
						Big Sky Mine area--Continued									
BSUMR1	80	22	40	40	40	340	260	<20	20	11	7,800	18	20	10	24
BSUMSP1	60	16	40	40	48	2,500	2,100	50	32	12	4,400	83	78	130	190
BSUMSP2	30	11	40	10	51	2,000	1,700	90	40	15	4,200	18	23	78	29
BSLMSP3	--	16	40	70	71	940	650	<20	28	12	11,000	16	22	7	22
	30	4	--	ND	68	1,100	--	<40	42	7	11,000	<4	11	24	11
	15	27	--	ND	69	1,100	--	<40	<20	<4	11,000	28	9	<6	<6
BSLMSP1	120	110	90	80	70	870	620	<20	19	7	12,000	15	17	19	12
	250	63	--	250	69	880	--	<40	60	30	10,000	5	36	23	42
	250	140	--	250	71	820	--	<40	<20	<4	11,000	32	11	<6	<6
BSLMMC1	200	100	90	130	54	210	160	<20	20	3	13,000	15	15	15	<4
	300	150	--	300	50	220	--	<40	37	4	11,000	<4	6	14	<6
	300	250	--	300	59	230	--	<40	<20	<4	12,000	29	10	<6	<6
BSLMMC2	>2,000	1,800	1,900	>2,000	46	180	150	<20	18	<2	14,000	15	12	24	<4
	14,000	2,400	--	1,800	46	190	--	<40	43	9	12,000	<4	9	54	11
BSLMMC3	--	6,800	6,700	>2,000	76	490	370	<20	19	<2	12,000	11	5	13	<4
	8,800	6,400	--	7,200	69	520	--	<40	42	11	10,000	<4	17	30	13
	8,000	6,100	--	4,800	70	540	--	<40	<20	<4	11,000	32	11	<6	<6
BSLMSM1	>2,000	1,200	1,000	1,200	57	60	50	<20	25	13	8,100	19	20	12	26
BSLMMC5	50	20	60	30	85	90	60	23	44	19	4,400	17	28	9	38

Table 11. Properties and concentration of chemical constituents in water from observation wells in the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Aquifer zone	Date of sample	Specific conductance (onsite) (μS/cm)	pH (onsite) (units)	Water temperature (onsite) (°C)	Concentration, in milligrams per liter							
						Dissolved oxygen (onsite)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (onsite) (HCO_3)	Bicarbonate (laboratory) (HCO_3)	Carbonate (CO_3)
					West Decker Mine area								
WDFCL1	A-Dz1	10-26-88	2,200	6.7	14.0	ND	7.5	2.5	560	3.9	1,360	1,260	0
WDFSP3	Sp	10-26-88	8,000	7.1	13.0	--	98	46	1,900	24	3,150	2,560	0
WDFD12	A-Dz1	10-26-88	3,310	7.1	13.5	ND	16	4.7	850	5.8	2,210	2,090	0
WDESP1	Sp	10-25-88	6,150	7.1	14.0	ND	42	30	1,500	14	3,080	2,940	0
		05-11-89	7,500	7.1	17.5	.6	59	47	1,700	19	3,330	3,260	0
		05-08-90	7,000	7.2	15.5	.5	48	35	1,500	16	3,080	3,000	0
WDESP2	A-Dz1	10-25-88	4,080	7.5	15.0	ND	19	8.3	1,000	8.0	2,680	2,480	0
		05-11-89	4,650	7.2	17.0	--	24	12	1,100	9.5	2,890	2,760	0
		05-09-90	3,800	7.3	12.5	--	21	9.4	1,000	9.1	2,620	2,580	0
WDED11	A-Dz1	10-25-88	3,150	7.2	15.0	ND	12	4.5	890	6.0	2,390	2,330	0
		05-11-89	3,550	7.4	15.0	--	13	5.2	850	6.7	2,340	2,220	0
		05-08-90	3,600	7.6	12.5	--	14	6.2	920	7.7	2,450	2,330	0

Table 11. Properties and concentration of chemical constituents in water from observation wells in the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Concentration, in milligrams per liter								Concentration, in micrograms per liter						
	Alkalinity (onsite) (as $CaCO_3$)	Sulfide (onsite) (H_2S)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (Fl)	Silica (SiO_2)	Dissolved solids, calculated	Nitrate (as N)	Aluminum (Al)	Aluminum[1] (Al)	Barium (Ba)	Boron (B)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)
							West Decker Mine area--Continued								
WDFCL1	1,100	0.18	200	9.5	3.4	22	1,430	0.12	<30	30	--	90	<2	<2	<2
WDFSP3	2,580	.03	2,400	14	.1	8.0	5,720	.30	<30	20	--	110	<2	<2	<2
WDFD12	1,810	.08	190	15	2.6	13	2,130	.26	<30	40	--	90	<2	<2	<2
WDESP1	2,520	.05	1,100	18	.4	13	4,120	.17	<30	20	--	80	<2	<2	<2
	2,730	ND	1,200	52	.9	14	4,710	<.01	<30	--	<1	60	<5	<5	<4
	2,520	ND	1,000	42	1.2	15	4,170	.11	220	--	37	80	<5	<5	<4
WDESP2	2,200	.26	250	18	1.8	13	2,590	.10	<30	<10	--	90	<2	<2	<2
	2,370	8.0	220	18	1.7	16	2,760	<.07	<40	--	150	70	<5	<5	<4
	2,150	1.2	200	17	2.2	16	2,560	.04	160	--	180	120	<5	<5	<4
WDED11	1,960	.28	51	15	2.0	14	2,140	.19	<30	30	--	60	<2	<2	<2
	1,920	.68	64	14	1.9	15	2,060	.23	100	--	670	70	<5	<5	<4
	2,010	2.0	90	15	2.6	17	2,220	.13	85	--	450	100	<5	<5	<4

Table 11. Properties and concentration of chemical constituents in water from observation wells in the Big Sky and West Decker Mine areas, Montana (Continued)

Observation well no.	Concentration, in micrograms per liter														
	Iron, total (onsite) (Fe)	Iron (Fe)	Iron[1] (Fe)	Iron, ferrous (onsite) (Fe)	Lithium (Li)	Man-ganese (Mn)	Man-ganese[1] (Mn)	Molyb-denum (Mo)	Nickel (Ni)	Silver (Ag)	Stron-tium (Sr)	Tita-nium (Ti)	Vana-dium (V)	Zinc (Zn)	Zirco-nium (Zr)
						West Decker Mine area--Continued									
WDFCL1	250	90	80	150	120	4	10	<20	<10	<2	490	<1	<1	23	<4
WDFSP3	80	40	50	50	510	360	260	<20	<10	<2	6,400	<1	<1	4	<4
WDFD12	510	180	140	200	180	30	40	<20	<10	<2	810	<1	<1	<3	<4
WDESP1	60	120	140	50	350	80	70	<20	<10	<2	3,500	<1	<1	23	<4
	1,200	57	--	220	440	95	--	<40	<20	<4	4,000	<4	<4	25	<6
	--	990	--	--	460	94	--	<40	<20	<4	3,900	<4	<4	19	<6
WDESP2	1,200	70	10	170	240	10	10	<20	<10	<2	1,200	<1	<1	16	<4
	350	420	--	350	280	17	--	<40	<20	<4	1,300	<4	<4	11	<6
	--	300	--	--	300	27	--	<40	<20	<4	1,300	<4	<4	<6	<6
WDED11	--	30	50	--	190	3	20	<20	<10	<2	820	<1	<1	<3	<4
	250	180	--	250	200	7	--	<40	<20	<4	790	<4	<4	<6	<6
	200	160	--	100	240	6	--	<40	<20	<4	950	<4	<4	<6	<6

[1] Analyses by U.S. Geological Survey, filtered through 0.10 micrometer membrane filter.

Table 12. Results of analyses for dissolved gases in ground water from the Big Sky and West Decker Mine areas, Montana

[Analyses by U.S. Geological Survey. Abbreviations: °C, degrees Celsius; T, trace present; ND, not detected]

Observation well no.	Date of sample	Onsite temperature (°C)	Partial pressure of dissolved gas, in atmospheres at onsite temperature						Concentration of dissolved gas, in milligrams per liter					
			Nitrogen (N_2)	Argon (Ar)	Oxygen (O_2)	Carbon dioxide (CO_2)	Methane (CH_4)	Ethane (C_2H_6)	Nitrogen (N_2)	Argon (Ar)	Oxygen (O_2)	Carbon dioxide (CO_2)	Methane (CH_4)	Ethane (C_2H_6)
						Big Sky Mine area								
BSUMR1	10-20-88	11.0	0.75	0.008	0.023	0.037	ND	ND	17	0.60	1.2	84	ND	ND
BSUMSP2	10-20-88	12.0	.77	.010	.036	.012	ND	ND	18	.68	1.9	26	ND	ND
BSLMSP1	10-18-88	12.0	.89	.010	T	.13	0.001	ND	20	.71	T	290	0.023	ND
BSLMMC1	10-18-88	12.0	.84	.009	T	.12	ND	ND	19	.67	T	260	ND	ND
BSLMMC2	10-18-88	12.0	.77	.009	T	.15	ND	ND	17	.64	T	330	ND	ND
						West Decker Mine area								
WDFCL1	10-26-88	14.0	.76	.009	T	.10	.002	ND	16	.59	T	210	.060	ND
WDFD12	10-26-88	13.5	.62	.008	T	.10	.032	ND	14	.51	T	210	.89	ND
WDESP1	10-25-88	14.0	.87	.011	T	.14	.012	ND	19	.73	T	280	.32	ND
WDESP2	10-25-88	15.0	.54	.007	T	.055	.33	0.001	11	.47	T	110	8.8	0.089
WDED11	10-25-88	15.0	.65	.008	T	.026	.25	.001	14	.53	T	51	6.6	.069

Table 13. Isotopic ratios for oxygen, hydrogen, carbon, and sulfur and activity of tritium in water samples from observation wells at the Big Sky and West Decker Mine areas, Montana

[Analyses by U.S. Geological Survey. Aquifer: R, Rosebud coal bed; Sr, spoils from mining of the Rosebud coal bed; Sm, spoils from mining of the McKay coal bed; Mc, McKay coal bed; A-Dzl, combined Anderson-Dietz 1 coal bed; Sp, spoils from mining of the Anderson-Dietz 1 coal bed. Abbreviations: δ^{18}O, oxygen-18/oxygen-16 isotopic ratio; δD, deuterium/hydrogen isotopic ratio; δ^{13}C, carbon-13/carbon-12 isotopic ratio; δ^{34}S, sulfur-34/sulfur-32 isotopic ratio; TU, tritium units. Symbol: --, no data]

Observation well no.	Aquifer	Date of sample	Isotopic ratio, in per mil					Tritium (TU)[2]
						Sulfur		
			Oxygen (δ^{18}O)[1]	Hydrogen (δD)[1]	Carbon (δ^{13}C)[1]	Sulfate (SO_4) (δ^{34}S)[1]	Sulfide (H_2S) (δ^{34}S)[1]	
			Big Sky Mine area					
BSUMR1	R	10-20-88	-19.20	-151.5	-3.6	5.0	--	5.7
BSUMSP2	Sr	10-20-88	-18.85	-148.5	-5.8	4.7	--	64
BSLMSP1	Sm	10-18-88	-17.65	-139.5	-6.2	1.4	--	36
BSLMMC1	Mc	10-20-88	-17.65	-140.0	-6.4	1.2	--	38
BSLMMC2	Mc	10-20-88	-17.60	-140.0	-6.7	.9	--	40
			West Decker Mine area					
WDFCL1	A-Dzl	10-26-88	-19.85	-154.0	-3.4	2.6	--	33
WDFD12	A-Dzl	10-26-88	-19.25	-151.0	2.7	8.0	--	18
WDESP1	Sp	10-25-88	-19.00	-151.5	-.8	-.2	--	10
WDESP2	A- Dzl	10-25-88	-19.75	-155.5	-8.8	33.2	--	11
	A- Dzl	05-11-89	--	--	--	36.4	-4.8	--
WDED11	A-Dzl	10-25-88	-20.00	-156.5	-9.4	62.5	--	8.0

[1] Per mil values of δ^{18}O and δD are reported relative to Vienna-SMOW (Standard mean ocean water). δ^{13}C and δ^{34}S are in per mil relative to the PDB (Peedee belemnite) and CDT (Canyon Diablo troilite) standards, respectively.

[2] One TU is one atom of tritium in 10^{18} atoms of hydrogen.

Table 14. Results of thermodynamic calculations for water from aquifers at the Big Sky Mine area, Montana

[Abbreviation: Log P_{CO_2}, logarithm of the partial pressure of carbon dioxide; FeS-ppt, amorphous iron-sulfide precipitate. Symbols: --, concentration of barium less than minimum reporting level; -, not calculated]

Observation well no.	Date of sample	Calculated log P_{CO_2}	Saturation Index											
			Quartz (SiO_2)	Calcite ($CaCO_3$)	Aragonite ($CaCO_3$)	Dolomite [$CaMg(CO_3)_2$]	Strontianite ($SrCO_3$)	Siderite ($FeCO_3$)	Gypsum ($CaSO_4 \cdot 2H_2O$)	Anhydrite ($CaSO_4$)	Celestite ($SrSO_4$)	Barite ($BaSO_4$)	Goethite ($HFeO_2$)	FeS-ppt
BSUMR1	10-20-88	-1.23	0.69	0.24	0.09	0.56	-0.71	-1.41	-0.47	-0.72	-0.25	--	6.95	-1.90
BSUMSP2	10-20-88	-1.75	.60	.26	.11	.72	-1.16	-2.05	-.12	-.37	-.37	--	7.79	-4.40
BSUMSP1	10-20-88	-1.51	.66	.26	.04	.52	-1.19	-1.56	-.16	-.41	-.37	--	6.99	-3.57
BSLMSP3	10-19-88	-.87	.53	.19	.03	.41	-.91	-1.74	-.08	-.34	.00	--	6.67	-2.43
	05-23-89	-.67	.54	.01	-.14	.07	-1.11	-2.86	-.11	-.36	-.04	0.20	-.90	-
	05-09-90	-.77	.54	.14	-.01	.34	-.95	-1.89	-.11	-.36	-.02	--	.30	-
BSLMSP1	10-18-88	-.69	.54	.01	-.14	.09	-1.06	-1.54	-.10	-.35	.01	--	6.83	-3.43
	05-23-89	-.69	.56	.03	-.13	.13	-1.17	-1.66	-.10	-.36	-.05	-.05	6.28	-
	05-09-90	-.78	.54	.14	-.02	.33	-.96	-1.33	-.11	-.36	-.02	--	7.49	-
BSLMMC1	10-18-88	-.69	.59	.06	-.10	.21	-.94	-1.46	-.13	-.38	-.05	--	6.55	-4.21
	05-22-89	-.71	.54	.08	-.07	.30	-1.01	-1.21	-.14	-.39	-.04	--	6.49	-2.60
	05-10-90	-.82	.57	.18	.03	.47	-.86	-.88	-.13	-.38	.01	--	6.23	-1.38
BSLMMC2	10-18-88	-.71	.64	.01	-.14	.11	-.97	-.18	-.12	-.37	-.08	--	7.84	-1.28
	05-22-89	-.61	.60	-.08	-.24	-.03	-1.16	-.28	-.12	-.37	.00	-.93	8.42	-
BSLMMC3	10-19-88	-.72	.83	-.15	-.30	-.23	-1.17	.25	-.10	-.35	.06	--	7.80	-1.16
	05-22-89	-.61	.78	-.24	-.40	-.36	-1.37	.10	-.10	-.35	-.03	-.43	8.25	-.60
	05-10-90	-.70	.79	-.14	-.29	-.16	-1.20	.21	-.12	-.37	.01	--	7.62	-
BSLMSM1	10-19-88	-1.30	.68	.19	.04	.57	-.74	.02	-.43	-.68	-.18	--	8.24	-1.27
BSLMMC5	10-19-88	-1.69	.72	.45	.30	.94	-1.15	-1.57	.08	-.17	-.33	--	7.76	-4.75

Table 15. Simulated mass-transfer results for flow from the Rosebud coal aquifer to the spoils aquifer at the Big Sky Mine area, Montana

[Transfer is negative for precipitation or degassing, positive for dissolution. Ion exchange: calcium ion exchanged for sodium ion]

Observation well no.		Date	Millimoles per kilogram of water				
Inititai water	Final water		Calcite	Dolomite	Gypsum	Ca/Na ion exchange	Carbon dioxide (gas)
BSUMR1	BSUMSP2	10-20-88	-20.1	9.14	15.9	1.36	-6.08
BSUMR1	BSUMSP1	10-20-88	-15.5	6.95	12.7	1.01	-4.22

Table 16. Results of thermodynamic calculations for water from aquifers at the West Decker Mine area, Montana

[Aquifer zone: A-Dz1, combined Anderson-Dietz 1 coal bed; Sp, spoils from mining of the Anderson-Dietz 1 coal bed. Abbreviations: Log P_{CO_2}, logarithm of the partial pressure of carbon dioxide; FeS-ppt, amorphous iron-sulfide precipitate. Symbols: --, concentration of barium less than minimum reporting level; -, not calculated]

Observation well no.	Aquifer zone	Date of sample	Calculated log P_{CO_2}	Saturation Index												
				Quartz (SiO_2)	Calcite ($CaCO_3$)	Aragonite ($CaCO_3$)	Dolomite [$CaMg(CO_3)_2$]	Strontianite ($SrCO_3$)	Siderite ($FeCO_3$)	Gypsum ($CaSO_4 \cdot 2H_2O$)	Anhydrite ($CaSO_4$)	Celestite ($SrSO_4$)	Barite ($BaSO_4$)	Goethite ($HFeO_2$)	FeS-ppt
WDFCL1	A-Dz1	10-26-88	-0.67	0.71	-1.10	-1.25	-2.53	-1.73	-0.71	-2.48	-2.74	-1.93	--	-1.38	-1.42
WDFSP3	Sp	10-26-88[1]	-.71	.31	.38	.23	.56	-.13	-.52	-.80	-1.07	-.14	--	8.15	-2.12
WDFD12	A-Dz1	10-26-88	-.86	.50	-.24	-.40	-.89	-1.00	.07	-2.26	-2.53	-1.85	--	-.51	-.91
WDESP1	Sp	10-25-88	-.75	.51	.16	.01	.34	-.32	-.37	-1.37	-1.64	-.67	--	8.12	-1.92
		05-11-89	-.70	.49	.36	.21	.85	-.22	-.28	-1.21	-1.46	-.59	--	5.67	-
		05-08-90	-.79	.53	.29	.14	.63	-.29	.99	-1.33	-1.59	-.65	0.49	7.01	-
WDESP2	A-Dz1	10-25-88	-1.20	.46	.29	.14	.41	-.34	-.58	-2.17	-2.41	-1.62	--	-1.02	-1.03
		05-11-89	-.89	.54	.18	.03	.27	-.56	.01	-2.13	-2.38	-1.67	.68	-.45	.94
		05-09-90	-1.04	.62	.14	-.01	.05	-.53	.63	-2.20	-2.47	-1.70	.83	.41	.84
WDED11	A-Dz1	10-25-88[2]	-1.53	.52	.36	.21	.50	-.26	.40	-2.99	-3.25	-2.43	--	.04	.10
		05-11-89	-1.18	.54	.06	-.09	-.09	-.63	.57	-2.84	-3.10	-2.34	.96	.44	.60
		05-08-90	-1.32	.64	.22	.07	.20	-.41	.47	-2.66	-2.93	-2.13	.96	.41	1.00

---

[1] Laboratory bicarbonate analysis used in calculations.

[2] pH of 7.8 used, calculated from measurements of P_{CO_2} and onsite alkalinity.

Table 17. Mass-transfer results for flow from the upgradient coal aquifer to the spoils aquifer in the West Decker Mine area, Montana

[Transfer is positive for dissolution. Ion exchange: calcium ion exchanged for sodium ion]

Observation well no.			Mass transfer, in millimoles per kilogram of water						
Initital water	Final water	Date of sample	Calcite	Dolomite	Gypsum	Stron-tianite	Halite	Ca/Na ion exchange	Carbon dioxide (gas)
WDFCL1	WDFSP3	10-26-88	6.74	1.80	22.9	0.07	0.14	29.2	6.81
WDFCL1	WDESP1	10-25,26-88	11.3	1.15	8.93	.03	.24	20.5	12.9

Table 18. Comparison of selected median dissolved-ion concentrations in water from spoils and coal to results from laboratory experiments for the West Decker Mine area, Montana

[All values in milligrams per liter except as noted. Source of data: Onsite; Spoils, median values for well WDESP1; Coal 1, median values for well WDESP2; Coal 2, median values for well WDED11; Laboratory, median values from tables 1 and 2 (Davis and Dodge, 1986); Abbreviation: µg/L, micrograms per liter]

Source of data	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Silica (SiO_2)	Dissolved solids	Barium (Ba) (µg/L)	Boron (B) (µg/L)	Manganese (Mn) (µg/L)	Strontium (Sr) (µg/L)
						Onsite							
Spoils	48	35	1,500	16	3,080	1,100	42	14	4,170	18	80	94	3,900
Coal 1	21	9.4	1,000	9.1	2,680	220	18	16	2,590	160	90	17	1,300
Coal 2	13	5.2	890	6.7	2,390	64	15	15	2,140	560	70	6	820
						Laboratory							
Spoils	22	8.0	860	8	1,700	680	7.8	12	2,330	40	100	36	1,000
Coal	9.6	3.7	790	6	1,460	660	6.4	12	2,070	200	240	3	640

Table 19. Properties and concentration of chemical constituents in water from coal samples from the West Decker Mine area, Montana, used in laboratory experiments

[Analyses by Montana Bureau of Mines and Geology. Sample: Unsaturated, coal sample collected from the unsaturated zone; Saturated, coal sample collected from the saturated zone. Type of treatment: W, washed with deionized water; U, not washed; 0.05M, sample in contact with 0.05 M Na_2SO_4 for 48 hours; 0.1M, sample in contact with 0.1 M Na_2SO_4 for 48 hours. Concentrations in milligrams per liter except as noted. Abbreviations: µS/cm, microsiemens per centimeter at 25 °C; °C, degrees Celsius; M, molar sodium sulfate (Na_2SO_4). Symbols: <, less than; --, no data or not applicable]

Sample	Type of treatment	Specific conductance (µS/cm)	pH (units)	Temperature (°C)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)
Unsaturated	W	2,000	7.2	25	11	5.1	463	5.0
Unsaturated	W, 0.05M	9,000	6.8	25	153	65	2,200	13
Unsaturated	W, 0.1M	16,000	6.8	25	362	135	4,400	15
Unsaturated	U, 0.1M	16,000	6.8	25	323	120	4,200	18
Saturated	W	1,000	8.1	25	3.0	1.2	246	2.9
Saturated	W, 0.05M	9,000	7.3	25	148	61	2,200	11
Saturated	W, 0.1M	16,000	7.1	25	340	130	4,300	15
0 .05M	--	--	--	--	--	--	2,300	--
0 .1M	--	--	--	--	--	--	4,600	--

Sample	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (Fl)	Silica (SiO_2)	Dissolved solids, calculated	Nitrate (as N)	Iron (Fe)	Manganese (Mn)
Unsaturated	220	740	0.8	<2	5.8	1,340	0.02	0.12	0.016
Unsaturated	94	5,100	1.1	<2	3.3	7,670	<.04	.075	.12
Unsaturated	95	10,000	.4	<4	3.3	15,100	<.05	.072	.28
Unsaturated	133	9,600	.7	<4	3.4	14,300	.04	.037	.25
Saturated	450	134	2.1	1.5	7.1	620	.48	.76	.016
Saturated	180	4,900	1.4	<2	1.9	7,420	.04	.11	.15
Saturated	160	9,900	.7	<2	2.0	14,800	.02	.055	.31
0.05M	--	4,800	--	--	--	--	--	--	--
0.1M	--	9,700	--	--	--	--	--	--	--

Table 20. Selected reactant or product phases for mass-balance reaction modeling for the West Decker Mine area, Montana

Phase	Composition	Operational valence
Organic matter	CH_2O	0.0
Goethite	$HFeO_2$	3.0
Iron sulfide	FeS	.0
Dissolved sulfide	H_2S	.0
Carbon dioxide	CO_2	4.0
Calcite	$CaCO_3$	4.0
Magnesian siderite	$Fe_{0.7}Mg_{0.3}CO_3$	5.4
Cation exchange	$(Na_2\text{-}Ca/Mg)X$	.0

Table 21. Concentrations of the major elements and redox state used in mass-balance models for water from the West Decker Mine area, Montana

[Abbreviation: °C, degrees Celsius]

Observation well no.	Date of sample	pH (units)	Water temper-ature (°C)	Concentration, in millimoles per liter						
				Calcium (Ca)	Sodium (Na)	Carbon, total (C)	Sulfur, total (S)	Iron (Fe)	Magnesium (Mg)	Redox state
WDESP1	10-25-88	7.19	14.0	1.049	65.624	59.173	11.027	0.0025	1.258	300.89
WDESP2	10-25-88	7.52	15.0	.466	45.596	47.717	2.642	.0002	.343	200.45
WDED11	10-25-88	[1]7.8	15.0	.288	38.670	41.245	.541	.0009	.186	163.04
WR-07[2]	08-13-71	8.2	14.0	.115	17.992	19.276	.032	.0009	.041	67.98

[1] Calculated.

[2] Concentrations converted from Davis (1984a, table 2).

Table 22. Mass-transfer results for an inferred flow path from spoils aquifer to downgradient coal aquifer, October 1988, in the West Decker Mine area, Montana

[Path: 1. Well WDESP1 to well WDED11; 2. Well WDESP1 to well WDESP2; 3. Well WDESP2 to well WDED11; 4. Well WDESP1 to well WDED11, 80 percent of water from well WDESP1, 20 percent of water from vertical flow from Dietz-2 coal bed. $\delta^{13}C$, Carbon 13 isotope ratio: 1. calculated; 2. observed. $\delta^{34}S$, Sulfur 34 isotope ratio: 1. calculated 2. observed. Transfer is negative for precipitation or degassing, positive for dissolution. Ion exchange: negative, Na exchange for Ca and Mg on coal. All isotope values are per mil. Symbol: --, phase not included in calculation]

	Mass transfer, in millimoles per kilogram of water													
Path	Calcite ($CaCO_3$)	Magnesian siderite ($Fe_{0.7}Mg_{0.3}CO_3$)	Organic matter (CH_2O)	Goethite ($HFeO_2$)	Iron sulfide (FeS)	H_2S (gas)	CO_2 (gas)	Na/CaMg ion exchange	Input isotopic composition ($\delta^{13}C(CH_2O)$)	Input sulfur fractionation factor ($^{34}\Delta$)	$\delta^{13}C$ Calculated	$\delta^{13}C$ Observed	$\delta^{34}C$ Calculated	$\delta^{34}C$ Observed
1	-12.2	-10.3	21.4	7.22	--	-10.5	-16.8	-13.5	-29.5	-19.9	-9.3	-9.4	61.5	61.9
1	-12.2	-10.3	23.8	17.7	-10.5	--	-19.2	-13.5	-28.0	-19.9	-9.4	-9.4	61.5	61.9
2	- 9.09	-8.06	17.5	5.64	--	-8.38	-11.8	-10.0	-31.0	-23.1	-8.2	-8.8	33.3	33.1
2	- 9.09	-8.06	19.4	14.0	-8.38	--	-13.7	-10.0	-31.0	-23.1	-8.8	-8.8	33.3	33.1
3	- 3.12	-2.26	3.93	1.58	--	-2.10	-5.02	-3.46	-21.0	-17.4	-9.4	-9.4	61.9	61.9
3	- 3.12	-2.26	4.41	3.68	-2.10	--	-5.50	-3.46	-21.0	-17.4	-9.4	-9.4	61.9	61.9
4	- 5.16	-5.00	13.4	3.49	--	-6.82	-7.85	-5.54	-31.0	-23.1	-8.8	-9.4	62.1	61.9
4	- 5.16	-5.00	14.9	10.3	-6.82	--	-9.40	-5.54	-31.0	-23.1	-9.3	-9.4	62.1	61.9

☆ U.S. GOVERNMENT PRINTING OFFICE: 1995 - 673-211 / 00070 REGION NO. 8