GEOCHEMISTRY OF BATCH-EXTRACT WATERS DERIVED FROM SPOIL MATERIAL COLLECTED AT THE CORDERO COAL MINE, POWDER RIVER BASIN, WYOMING

By David L. Naftz

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CONVERSION FACTORS

For readers who prefer to use metric (International System) units, conversion of inch-pound units used in this report are listed below:

Multiply	By	To obtain
acre	0.4047	hectacre
atmosphere (atm)	1.01325	bar
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
foot per day (ft/d)	0.3048	meter per day
gallon (gal)	3.785	liter
gallon per minute (gal/min)	0.06309	liter per second
inch (in.)	0.2540	millimeter
pound (lb)	0.4536	kilogram
mile (mi)	1.609	kilometer
ton (short)	0.9072	metric ton

Temperature in degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) as follows:

$$°C = 5/9\ (°F-32)$$

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ABSTRACT

Batch-mixing experiments for possible use in predicting postmining water quality at the Cordero Mine were conducted by the U.S. Geological Survey during 1984 and 1985. Spoil-material samples and ground water from both the spoil aquifer and coal aquifer were used in the experiments. The results obtained from the experiments were used to identify possible chemical reactions that occurred during the laboratory simulations; to compare the chemical composition of the actual water to simulated postmining water; and to evaluate the use of the batch-mixing experiments to predict postmining water quality.

The relative changes in concentration of major elements during the experiments were greatly dependent on the source of the water used. Contact of water from the spoil aquifer with fresh spoil material caused only small changes in major-element concentrations and in pH, unless sulfide oxidation or contact with soluble salts, such as epsomite, occurred. In contrast, large changes in major-element concentrations resulted when water from the coal aquifer contacted the spoil material.

Seven reaction models were used to account for the changes in chemistry for a selected batch-mixing experiment conducted with water from the coal aquifer. Of the seven reaction models considered, only three were consistent with the thermodynamic and mineralogical data. The three models used to account for the water-quality changes derived potassium from potassium feldspar, magnesium from chlorite or epsomite or both, sodium from cation exchange and halite, chloride from halite, silica from potassium feldspar and chlorite, sulfate from gypsum or epsomite or both, and carbon from carbon dioxide.

Water-quality samples obtained from the batch-mixing experiments using water from the coal aquifer contained smaller concentrations of calcium, magnesium, sodium, chloride, and sulfate compared to the water in the spoil aquifer. Furthermore, pH and the concentrations of total inorganic carbon and alkalinity were larger in the waters derived from the batch-mixing experiments compared to the water quality in the spoil aquifer. These differences between the batch-extract water and actual postmining water quality can be explained by the limited amount of gypsum dissolution/volume of water used in the experiments. Mean correction ratios for major ions, calculated to normalize the batch-mixing results to the actual water quality of the spoil aquifer, ranged from 1.13 to 7.75. The correction ratios can be applied to results of batch-mixing experiments at other mines in the area to predict postmining

water quality. The major-ion concentrations and pH obtained from the batch-mixing experiments using water from the coal aquifer possibly represent the long-term postmining ground-water quality in the spoil aquifer.

INTRODUCTION

Surface coal mining in the Powder River basin of Wyoming has the potential to affect the water quality in near-surface aquifers. During 1982, surface-mine operations in eastern Campbell County, Wyoming, extracted 81.2 million tons of coal (Lowry, Wilson, and others, 1986, p. 34). Continental rocks of early Tertiary age within the Powder River basin of Wyoming contain numerous sandstone lenses and coal beds from which 10 to 20 gallons per minute of water can be obtained (Lowry, Wilson, and others, 1986, p. 91). The removal of coal from the area modifies near-surface aquifers by replacing the coal with overburden material that has been redistributed as a result of mining. Redistributed overburden material is commonly referred to as spoil. Spoil which becomes saturated after mining is referred to as the "spoil aquifer" in this report. During infiltration of water to the newly created spoil aquifer, the potential exists for changes in water quality.

As part of an ongoing program, the U.S. Geological Survey, in cooperation with the U.S. Bureau of Land Management, began a series of studies in 1984 to investigate the geochemical processes affecting the changes in ground-water quality resulting from surface coal mining. Solid-phase and water-quality data have been collected from mines in Wyoming, Montana, Colorado, Oklahoma, North Dakota, and Texas.

This report is the second of a series of reports describing data collected from selected surface coal mines in Wyoming. The first report in this series (Larson, 1988) is a data report containing solid-phase and water-quality data collected from two mines. The results of batch-mixing experiments at one mine are described in this report.

Various batch-mixing and column-leach experiments have been used by mine operators in Wyoming in an attempt to predict postmining ground-water quality. The batch-mixing experiments used in this study used a mixing ratio of two parts water to one part spoil material (by weight). Batch-mixing experiments with large water-to-rock ratios, such as the ratio used in this study, produce sufficient solution volumes to analyze for a variety of constituents. One disadvantage of batch-mixing experiments with large water-to-rock ratios is the limited quantity of soluble salts available for dissolution compared to the volume of water. The large water-to-rock ratios could yield diluted salt concentrations compared to the natural system (that is, water from the spoil aquifer). Chemical compositions of batch-extract water can then be compared to the chemical composition of the water in the spoil aquifer. The comparison of the chemical compositions of the batch-extract and spoil-aquifer water can then be used to calculate an empirical correction factor that transforms the chemical composition of the batch-extract water to the chemical composition of the water from the spoil aquifer.

Prior to this study, comparisons of laboratory simulations with actual postmining water quality in Wyoming had not been made. Furthermore, detailed mineralogical analyses were not included in the laboratory simulations designed to predict future postmining water quality. In this study, however, the mineralogical analyses of the spoil material were used in combination with comparisons of the batch-extract water quality to the postmining water quality to evaluate the predictive capability of the batch-mixing experiments.

Purpose and Scope

The purpose of this report is to describe the results obtained from batch-mixing experiments and to describe and define the possible geochemical reactions occurring during resaturation of spoil aquifers. Water samples and spoil material used in the batch-mixing experiments were collected from the Cordero Mine study area (fig. 1).

The results described in this report are related to the following objectives of the study:

1. To identify the possible chemical reactions that could have occurred during the batch-mixing experiments by using major- and minor-element variations, aqueous speciation, and mass-transfer calculations, along with the mineralogy of the spoil material.

2. To compare the chemical composition of the water taken from the spoil aquifer at the Cordero Mine with the chemical composition of water derived from batch-mixing experiments.

3. To evaluate the predictive capability of the batch-mixing experiments.

Study Area

The Cordero Mine, in the coal-rich Powder River structural basin, is located about 20 mi south of Gillette in Campbell County (fig. 1). The Cordero Mine will disturb 8,232 acres during mining (Cordero Mine personnel, written commun., 1983). Water and overburden samples for the study were collected in T. 47 N., R. 71 W., secs. 23, 26, and 27, within and adjacent to a disturbed area of the mine (fig. 2).

The Cordero Mine is drained by the Belle Fourche River. The average flow (since 1975) of the Belle Fourche past the mine area is less than 5 ft^3/s (Cordero Mine personnel, written commun., 1983). Periods of no flow occur during most years.

Rainfall at the Cordero Mine averages about 13 in. per year (Cordero Mine personnel, written commun., 1983). May and June usually are the months with the most rainfall; more than one-half of the annual precipitation usually falls during April, May, and June.

Acknowledgments

Appreciation is extended to Jim Sutherland of the Cordero Mining Company for the assistance and information he provided during the course of this study.

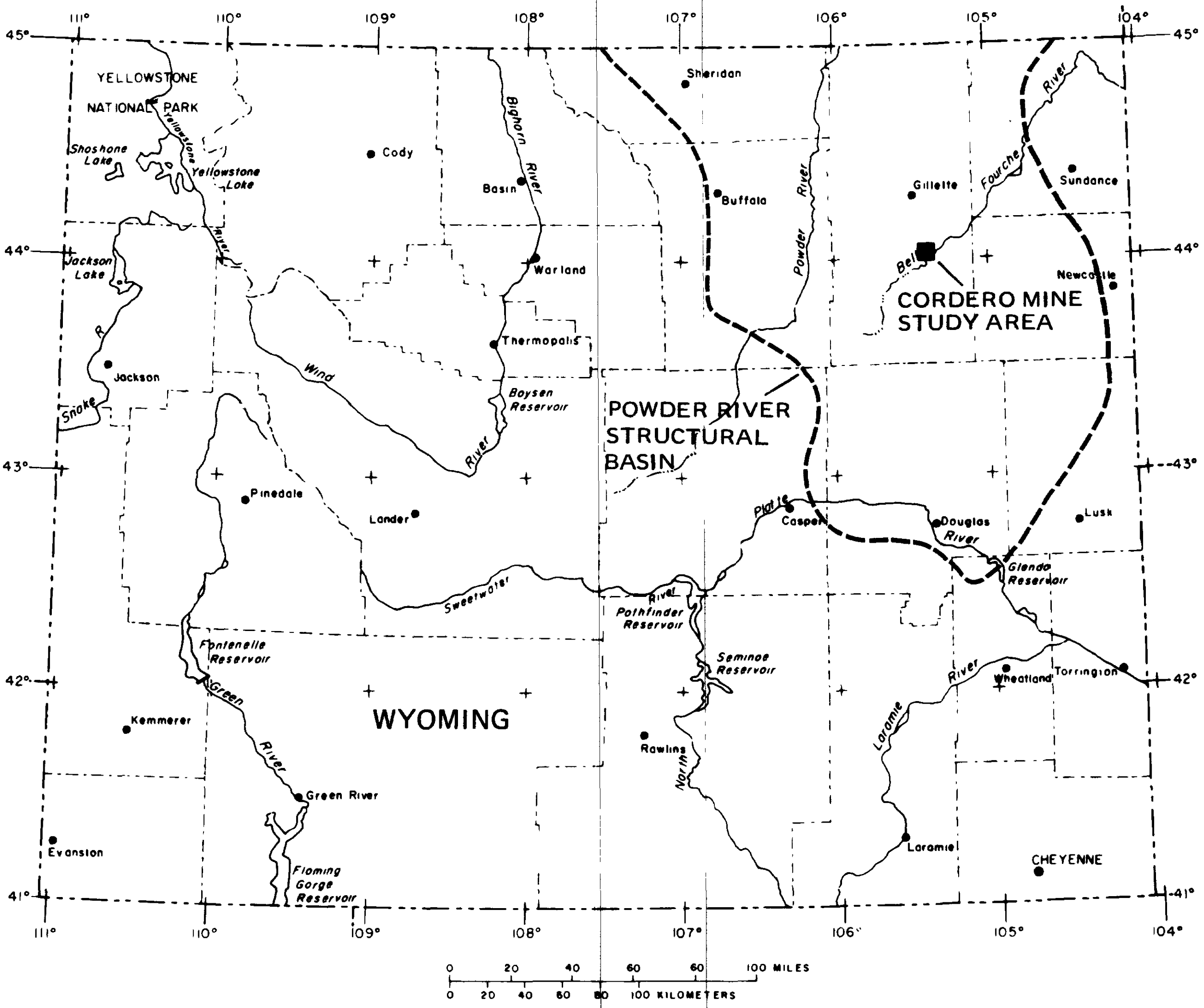


Figure 1.--Location of the study area.

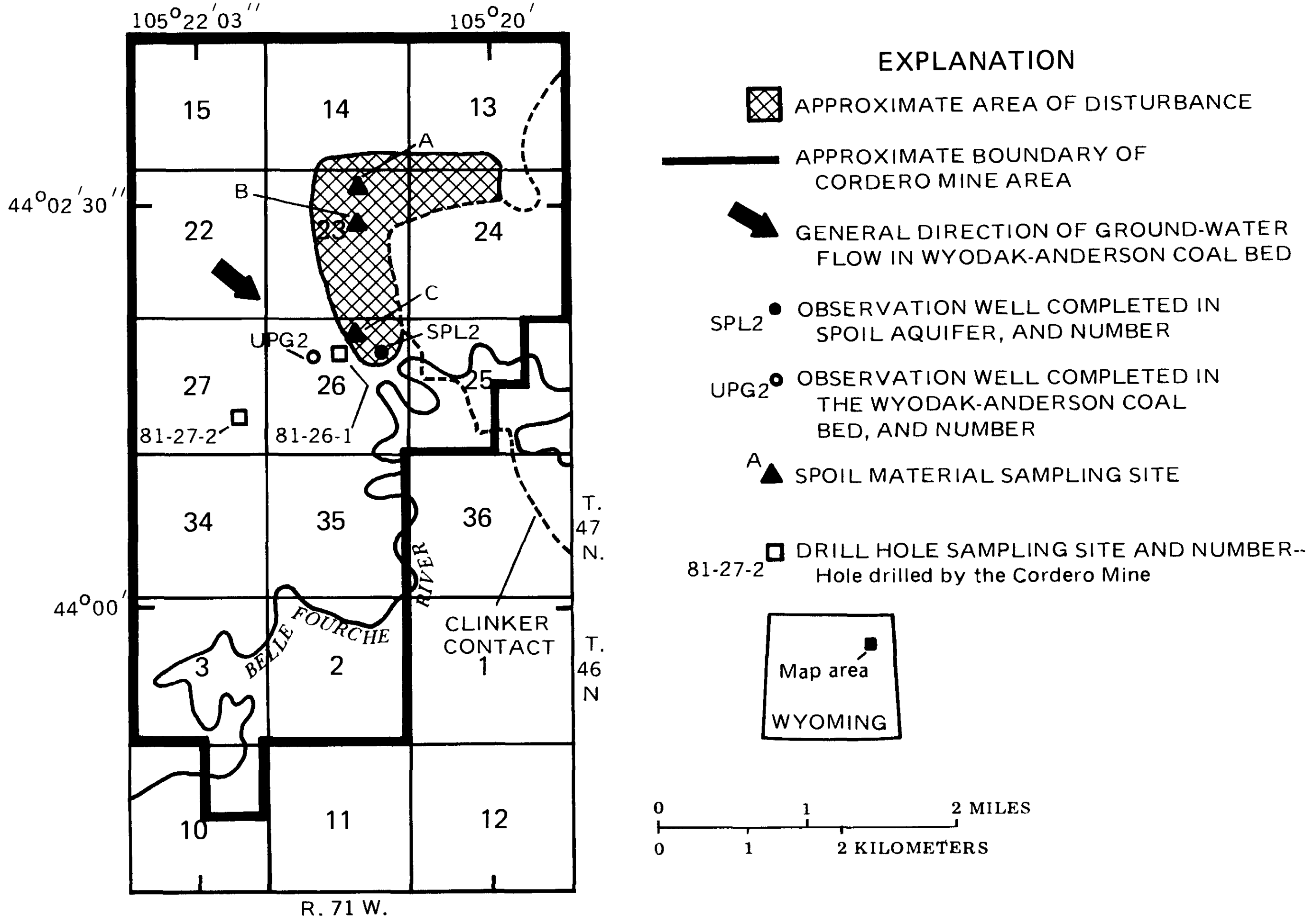


Figure 2.--Location of selected data-collection sites and general direction of water movement in the Wyodak-Anderson coal bed.

CONCEPT OF THE GEOHYDROLOGIC SYSTEM

Geology

Geologic units of interest in this study are the Fort Union and Wasatch Formations, of early Tertiary age. The uppermost member of the Fort Union Formation is the Tongue River Member of Paleocene age. The Tongue River Member consists of light-yellow to light-gray fine- to medium-grained thick-bedded to locally massive cross-bedded and lenticular sandstone and siltstone interbedded with gray and black shale. Within the Tongue River Member is the Wyodak-Anderson coal bed, which currently (1986) is being mined at the Cordero Mine. The thickness of the coal in the Wyodak-Anderson coal bed ranges from 25 to 175 ft and averages approximately 70 ft in the Powder River basin (Lowry, Wilson, and others, 1986, p. 26).

Overlying the Fort Union Formation is the Wasatch Formation of Eocene age. The Wasatch Formation consists of brownish-gray fine- to coarse-grained lenticular sandstone interbedded with shale and coal. During coal removal at the Cordero Mine, the overburden that is spoiled consists of rocks from the Wasatch Formation.

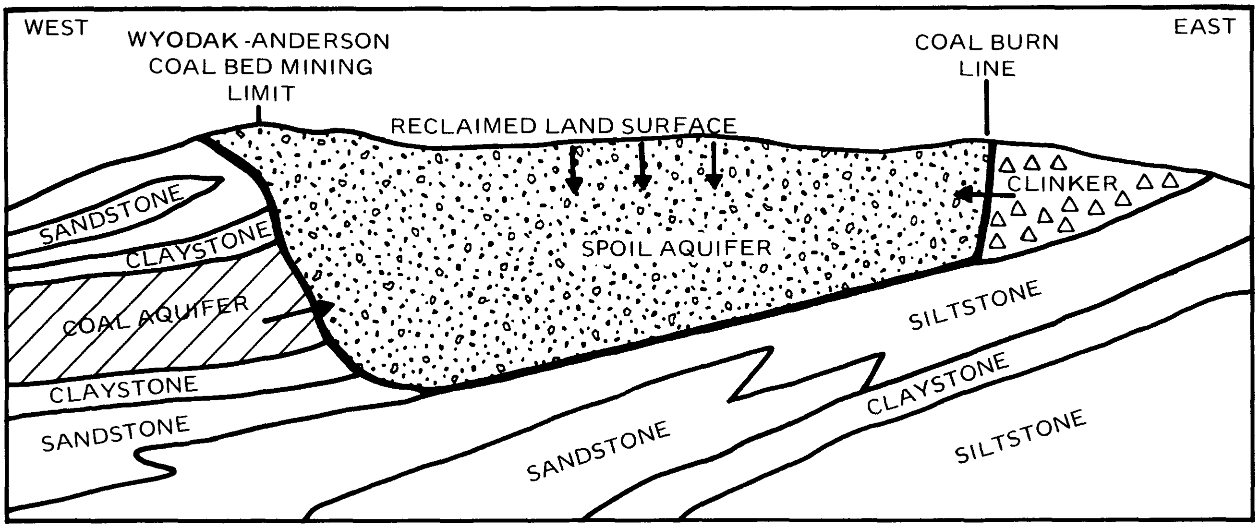
Along coal outcrops, clinker is present in both the Fort Union and Wasatch Formations. Clinker consists of fractured shale, siltstone, and sandstone that have been baked by the burning of underlying coal beds.

Hydrologic Flow System

The Wyodak-Anderson coal bed usually is sufficiently fractured to be a productive aquifer in the vicinity of the Cordero Mine (Keefer and Hadley, 1976, p. 15). In this report, the Wyodak-Anderson coal bed is referred to as the "coal aquifer." Surface mining of coal in the Powder River basin of Wyoming has the potential to alter water flow in the coal aquifer. During mining, pit dewatering will cause local water-flow patterns in the coal aquifer to be toward the mined area.

Prior to mining, the sand lenses in the Wasatch Formation exhibit very poor water productivity (Cordero Mine personnel, written commun., 1983). As a result of mining and subsequent pit backfilling, the overburden sands will be mixed with finer grained overburden materials in a random manner. The resulting material comprising the spoil aquifer will allow adequate recharge from the coal aquifer, but will not support significant water production from wells open only to the spoil aquifer (Cordero Mine personnel, written commun., 1983).

Sources of recharge to the spoil aquifers include water from the coal and clinker and surface infiltration from precipitation (fig. 3). According to Bloyd and others (1986, p. 8), definitive data are not yet available to determine whether postmining recharge rates in the spoil aquifer will be greater or less than premining rates. According to Cordero Mine personnel (written commun., 1983), the potentiometric water levels in the coal aquifer probably will recover to the approximate premining elevation within 5 to 10



(Not to scale)

EXPLANATION

→ POSSIBLE DIRECTION OF WATER MOVEMENT FROM LAND SURFACE, CLINKER, AND COAL AQUIFER INTO THE SPOIL AQUIFER

Figure 3.--Schematic section showing possible sources of recharge to the spoil aquifer at the Cordero Mine.

years after reclamation. The rate of recovery in the spoil aquifer is dependent on the difference between the head (water level) in the spoil aquifer and the head (water level) in the adjacent coal aquifer.

The time required for the water level in the spoil aquifer to equal the water level in the adjacent coal aquifer is projected to be between 250 and 640 years (Cordero Mine personnel, written commun., 1983). The 250-year estimate assumes lateral recharge of the spoil from both the adjacent coal aquifer and from infiltration of precipitation through the spoil; but inflow from the coal aquifer will be the principal source of recharge. Flow in the spoil aquifer after equilibrium is expected to be toward the Belle Fourche River.

Ground-Water Quality

Important chemical reactions that could affect the ground-water quality in the aquifers within and adjacent to the study area were discussed in detail by Hounslow and others (1978); Thorstenson and others (1979); Davis (1984); Groenewold and others (1983); and Henderson (1984). These chemical reactions (table 1) include calcite [$CaCO_3$] dissolution by carbon dioxide (CO_2)-charged waters (reaction 8), calcium-sodium (Ca-Na) ion exchange (reaction 16), magnesium-sodium (Mg-Na) ion exchange (reaction 17), pyrite [FeS_2] oxidation (reaction 1), sulfate (SO_4) reduction (reaction 2), gypsum [$CaSO_4 \cdot 2H_2O$] dissolution and precipitation (reactions 11 and 12), dedolomitization (reaction 13), potassium feldspar ($KAlSi_3O_8$) hydrolysis (reaction 15), and dissolution of various efflorescent salts present within the spoils materials. Depending on the predominant hydrological, geochemical, and biological processes affecting the chemical character of premining and postmining ground waters, the water type can be calcium-magnesium bicarbonate, sodium bicarbonate, calcium-magnesium sulfate, or sodium sulfate (Davis, 1984, p. 10).

Surface coal mining can cause changes in the ground-water quality. During the coal-mining process, rock materials located above the coal are removed and redistributed with respect to their original stratigraphic order. Following saturation, redistributed overburden material can cause changes in the ground-water quality. As noted by Groenewold and others (1983, p. 138-139), redistribution of overburden sediment creates the potential for significant changes in the chemical reactivity of the spoil material. For example, contact of sediment from a previously reduced part of the overburden strata with oxidizing waters during resaturation of the spoil materials would increase sulfide oxidation (table 1, reaction 1) which in turn could drive other reactions such as calcite dissolution (table 1, reaction 9) as well as calcium-sodium and magnesium-sodium ion exchange (table 1, reactions 16 and 17). Furthermore, emplacement of sediments originally from the near-surface, oxidized part of the overburden in areas below the postmining water table could cause large increases in dissolved solids due to dissolution of gypsum, efflorescent salts, and other soluble constituents.

Table 1.--Pertinent chemical reactions

Reaction	Reaction number
Oxidation-reduction	
$FeS_2 + 3.5O_{2(g)} + H_2O = Fe^{2+} + 2.0SO_4^{2-} + 2H^+$ (pyrite)	(1)
$SO_4^{2-} + 2CH_2O + H^+ = HS^- + 2CO_{2\ (gas)} + 2H_2O$	(2)
$Fe^{2+} + 0.25O_2 + H^+ = Fe^{3+} + 0.5H_2O$	(3)
$CH_2O + O_2 = CO_{2(gas)} + H_2O$ (organic matter)	(4)
Dissolved carbonate equilibria	
$CO_{2\ (gas)} + H_2O = H_2CO_3^0$	(5)
$H_2CO_3^0 = HCO_3^- + H^+$	(6)
$CO_3^{2-} + H^+ = HCO_3^-$	(7)

Table 1.--Pertinent chemical reactions--Continued

Reaction	Reaction number
Mineral dissolution and weathering	
$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$ (calcite)	(8)
$CaCO_3 + H^+ = HCO_3^- + Ca^{2+}$ (calcite)	(9)
$Ca^{2+} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O$ (calcite)	(10)
$CaSO_4 \bullet 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$ (gypsum)	(11)
$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \bullet 2H_2O$ (gypsum)	(12)
$CaMg(CO_3) + CO_2 + H_2O = CaCO_3 + Mg^{2+} + 2HCO_3^-$ (dolomite) (calcite)	(13)
$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$ (ferric hydroxide)	(14)
$KAlSi_3O_8 + H^+ + 4.5H_2O = 0.5Al_2Si_2O_5(OH)_4 + K^+ + 2.0Si(OH)_4$ (potassium fedlspar) (kaolinite)	(15)
Ion exchange	
$Ca^{2+} + Na_2EX = 2Na^+ + CaEX^*$	(16)
$Mg^{2+} + Na_2EX = 2Na^+ + MgEX^*$	(17)

EX^* - Ion exchange site

The quality of water in the coal and spoil aquifers at the Cordero Mine is summarized in table 2. Median concentrations of all major constituents, except alkalinity, are much larger in waters from the spoil aquifer than in waters from the coal aquifer.

METHODOLOGY

Spoil material was collected at three sites within the Cordero Mine (fig. 2). Point samples of the spoil material used in the batch-mixing experiments were collected from surface spoil piles. At each site, three samples were collected--one near the base of the spoil pile, one near the top of the spoil pile, and one midway between the base and top of the spoil pile. Each sample consisted of approximately 30 lb of spoil material. Replicate samples were collected from one of the three sites (duplicate samples from top, middle, and base) to provide a basis for determining how representative the spoil samples were. Thus a total of 12 spoil samples were collected at the Cordero Mine. All spoil and water-quality data collected at the Cordero Mine were tabulated by Larson (1988).

The spoil-sample designation consists of two or three characters, such as B1D. The first character, a letter, designates the sampling site, and the second character, a numeral, designates the vertical location at a site (1 = base, 2 = midway, 3 = top). When used, the third character, the letter D, designates a duplicate sample.

Each sample was air-dried and thoroughly mixed. The dried and mixed samples were sent to the U.S. Geological Survey (Geologic Division) Laboratory in Denver, Colorado, for crushing and grinding. The samples then were analyzed (1) for sulfur content by the Geologic Division Laboratory, and (2) for whole-rock and clay mineralogy, using X-ray diffraction analysis, by the North Dakota Mining and Mineral Resources Research Institute in Grand Forks.

Water samples used in the batch-mixing experiments were collected from one well (UPG2) completed in the coal aquifer and from one well (SPL2) completed in the spoil aquifer (fig. 2). Approximately 30 gal of water was collected from each aquifer and was stored in plastic bottles (unfiltered and unpreserved) prior to being transported to the laboratory. Batch-mixing experiments utilizing the ground water collected from the Cordero Mine were conducted within 4 weeks after collection. Three subsamples of the ground water used in the batch-mixing experiments were analyzed for major and minor constituents immediately prior to use in the batch-mixing experiments.

In addition to the water samples collected for use in batch-mixing experiments, preserved and filtered water samples were collected from wells UPG2 and SPL2 (fig. 2) to help define in-situ water quality of the coal and spoil aquifers and to provide a comparison of batch-extract and actual postmining water quality. The samples were analyzed in the field for specific conductance, pH, temperature, and bicarbonate and carbonate concentrations. The samples were filtered through a 0.45-micrometer filter and analyzed by the U.S. Geological Survey National Water Quality Laboratory, Denver, Colo., for selected common and trace constituents. Water analyzed for silica, aluminum, iron, and manganese was filtered through a 0.10-micrometer filter to eliminate colloidal forms of these constituents from being analyzed.

Table 2.--**Summary of chemical quality of water in the coal and spoil aquifers, Cordero Mine**

[Concentration in milligrams per liter]

Constituent	Coal aquifer				Spoil aquifer			
	Number of samples	Median	Minimum	Maximum	Number of samples	Median	Minimum	Maximum
Calcium	98	58	8.8	501	16	520	470	560
Magnesium	98	32	5.1	170	16	346	280	400
Sodium	98	260	30	490	16	700	600	760
Potassium	98	9.7	4.5	19	16	35	28	40
Sulfate	98	140	.4	2,130	16	3,600	3,200	3,700
Chloride	98	12	3.1	34	16	110	92	130
Total alkalinity (as $CaCO_3$)	98	640	64	1,160	16	390	362	451
Dissolved solids (calculated)	98	1,050	320	3,400	16	5,600	5,100	5,700

The spoil material that was not crushed and ground was used in batch-mixing experiments according to the method outlined by Davis (1984). Water was added to the spoil material until a water:rock ratio of 2:1 by weight was obtained. Mixing of the spoil material with the water from either the spoil or coal aquifer was accomplished by affixing the mixture bottles, filled to exclude oxygen, to a vertical wheel 3 ft in diameter. The wheel was then rotated at three revolutions per minute for 2 hours. The mixtures then were allowed to settle. After a total contact time of about 24 hours, pH and alkalinity of the batch-extract waters were determined. Then samples of filtered and unfiltered batch-extract water were sent to the U.S. Geological Survey National Water Quality Laboratory for analysis for selected major and trace constituents.

The reproducibility of the batch-mixing experiments, using water from coal-aquifer observation well UPG2, was evaluated for the three sets of duplicate spoil samples. Calcium, magnesium, sodium, bicarbonate alkalinity, chloride, and sulfate concentrations in the duplicate batch-extract waters were very similar (fig. 4). Differences in the concentrations of calcium, magnesium, sodium, bicarbonate alkalinity, chloride, and sulfate in batch-extract waters derived from duplicate spoil samples are a combination of the variance between the duplicate spoil samples and the analytical variance associated with the analysis of the batch-extract waters.

The computer program WATEQF (Plummer and others, 1978) was used to calculate the activities of the aqueous species in the waters used in the batch-mixing experiments. Based on the activities calculated by WATEQF for

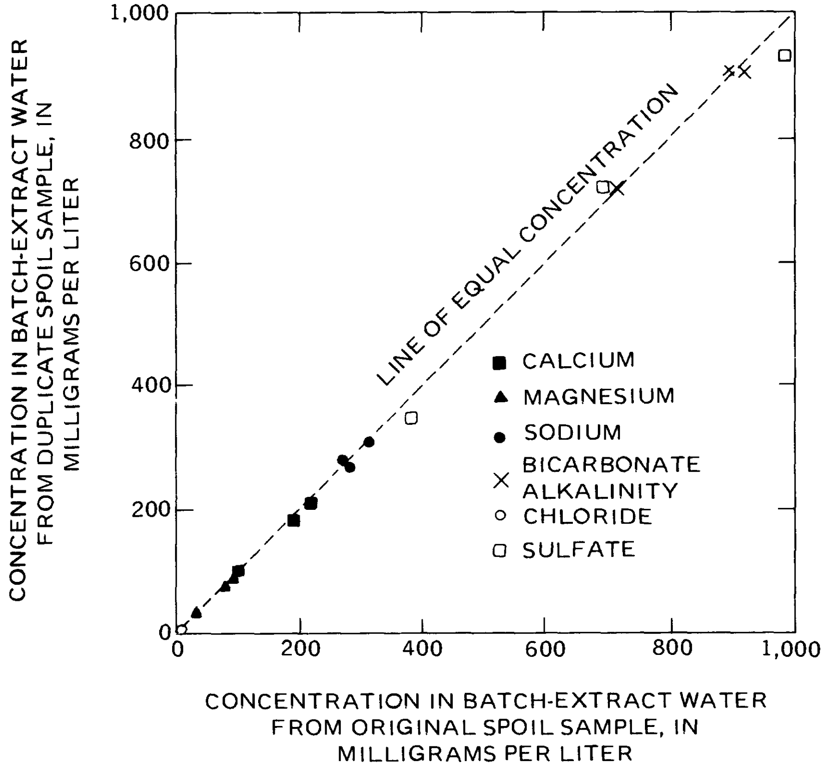


Figure 4.--Comparison of concentrations of major ions in batch-extract water from original and duplicate spoil samples using coal-aquifer initial water.

the various species of interest, the degree of saturation with respect to a particular mineral phase was determined for each water analysis. The degree of saturation with respect to a particular mineral phase is defined as the ratio of ion activity product divided by the equilibrium constant for the mineral of interest. Log transformation of this ratio is referred to as a saturation index (SI). A positive SI for a particular mineral phase denotes that the mineral will tend to precipitate from solution; whereas, a negative SI denotes that the mineral will tend to dissolve. An SI close to zero signifies that the solution is in equilibrium with respect to the mineral of interest.

One additional use of WATEQF involves the calculation of C_T (total inorganic carbon) concentrations from major-ion, pH, alkalinity, and temperature data for water samples. Because the relative concentrations of $H_2CO_3^0$, HCO_3^-, and CO_3^{2-} are dependent on the pH of the solution, increases or decreases in concentrations of HCO_3^- and CO_3^{2-} could be a function of pH changes instead of a function of dissolution or precipitation reactions involving the carbonate species. By calculating the C_T for the waters, both before and after the batch-mixing experiments, the sources for possible alkalinity changes during the batch-mixing experiments can be evaluated.

Stability diagrams were used to evaluate the possible aluminosilicate mineral phases formed during the batch-mixing experiments. Thermodynamic data from Tardy (1971) were used in constructing the phase boundaries. Activity ratios of calcium, sodium, and potassium to hydronium (H^+) ions for the waters used in the batch-mixing experiments were calculated by using WATEQF.

Mass-balance calculations, using the computer program BALANCE (Parkhurst and others, 1982a), were performed to determine the amounts of plausible phases that could enter or leave the waters during selected batch-mixing experiments based on the observed changes in water quality. The general chemical reaction is in the form of:

$$\text{Initial solution composition + reactant phases} \longrightarrow$$

$$\text{Final solution composition + product phases,}$$

where the terms "reactant phases" and "product phases" refer to constituents that enter or leave the aqueous phase during the course of a reaction. The possible "reactant and product phases" were determined by the mineralogical analysis of the spoil material as well as from speciation calculations and qualitative geological inferences derived from the overburden-material analyses.

Simulation of reactions and mass transfers that occurred during a selected batch-mixing experiment was accomplished using the computer program PHREEQE (Parkhurst and others, 1982b). Peterson and others (1983) have used reaction-path modeling techniques to evaluate and simulate the contact of acidic uranium-mill-tailings water with subsoil materials in laboratory situations, using a flow-through system. The PHREEQE program allows the user to add or subtract net stoichiometric amounts of mineral or gas phases while maintaining thermodynamic equilibrium with selected mineral or gas phases. Output from the PHREEQE program includes the final solution composition, and pH, as well as the associated mass transfer between solid, aqueous, and gas phases. Results of water-quality simulation using the PHREEQE program were compared to water-quality analyses obtained from a selected batch-mixing experiment.

As noted by Powell and Larson (1985), numerous reaction combinations can be used to explain reasonably the observed changes in water quality. Numerous reaction combinations can be used to explain the geochemical processes affecting water quality of the batch-extracts. However, without additional geochemical data, the reaction models proposed can be used as a "first guess," with modifications being incorporated as more data become available.

MINERALOGY OF THE SPOIL MATERIAL

X-ray diffraction (table 3) and sulfur-form analyses (table 4) were used to characterize the mineralogy of the spoil material used in the batch-mixing experiments. Based on the X-ray diffraction data, the predominant minerals present in the spoil material included mixed-layer clays, smectite, chlorite, muscovite/illite, kaolinite, gypsum, quartz, and potassium feldspar, and trace amounts of plagioclase feldspar, dolomite, and calcite (table 3). Comparison of sulfate determinations by sulfur-form analysis (table 4) and the amount of gypsum determined by X-ray diffraction analysis (table 3) imply X-ray bias. For example, sample A1 contains 0.22 weight percent sulfate according to the sulfur-form analysis and 13 percent gypsum by weight percent according to the X-ray diffraction analysis. The greater sulfate content of sample A1 suggested by the X-ray diffraction results implies efflorescent gypsum coatings on selected grains in the sample.

Although pyrite was not identified by X-ray diffraction, sulfide minerals (for example, pyrite) were inferred from the sulfur-form analyses (table 4). Measurable amounts of pyrite could have been oxidized prior to analysis of the spoil material.

GEOCHEMISTRY OF BATCH-EXTRACT WATERS

Results from the batch-mixing experiments were used to investigate probable geochemical reactions controlling the postmining water quality. Water from observation wells SPL2 and UPG2 (fig. 2) was used in the batch-mixing experiments to simulate possible water-quality changes that could have occurred during resaturation of the spoil aquifer. Finally, the predictive capability of the batch-mixing experiments was assessed by comparing the simulated water quality to the actual postmining water quality.

Table 3.--Mineral composition of spoil samples

[X-ray diffraction analyses by the North Dakota Mining and Mineral Resources Research Institute. Compositions in precent by weight. Sample number ending with D designates a duplicate sample. Abbreviation: <, less than]

Sample number	Mixed layer clays	Smectite	Chlorite	Muscovite/ illite	Kaolinite	Calcite	Dolomite	Gypsum	Quartz	Potassium feldspar	Plagio-clase feldspar	Total
A1	6	8	0	3	37	2	Trace	13	31	4	<1	105
A2	9	10	1	4	18	2	2	9	33	8	2	98
A3	0	0	0	1	44	0	<1	16	28	8	2	100
B1	15	26	2	7	15	0	Trace	4	24	5	0	98
B1D	13	24	2	11	19	0	0	<1	28	2	0	100
B2	13	21	3	8	23	0	0	0	30	2	0	100
B2D	8	16	3	8	38	0	0	0	28	1	0	102
B3	10	13	0	4	8	2	1	3	45	19	0	105
B3D	9	14	0	3	4	2	2	4	51	14	0	103
C1	5	9	3	5	31	0	<1	1	38	2	0	95
C2	7	36	1	5	16	7	Trace	1	27	2	0	102
C3	6	18	5	6	32	0	0	0	31	2	0	100

Table 4.--Sulfur-form analyses of spoil material

[Compositions are in percent by weight. Sample number ending in D designates a duplicate sample. Abbreviation: <, less than]

Sample number	Total sulfur	Sulfate sulfur	Sulfide sulfur	Organic sulfur
A1	0.24	0.22	<0.01	0.02
A2	.18	.22	< .01	.00
A3	.80	.86	< .01	.00
B1	.30	.08	.16	.06
B1D	.30	.08	.14	.08
B2	.08	.01	.03	.04
B2D	.09	.02	.03	.04
B3	.09	.10	< .01	.00
C1	.06	.08	< .01	.00
C2	.28	.23	.01	.04
C3	.04	.02	< .01	.02

Batch Tests Using Spoil-Aquifer Water

Variations in Major- and Minor-Ion Concentrations

Water-quality changes were determined for the batch-extract water using water collected from the spoil aquifer at the Cordero Mine. Changes in major- and minor-ion concentrations during the batch-mixing experiments were used to simulate probable controls affecting the water-quality in the spoil aquifer because postmining water continues to contact fresh spoil material during resaturation of the spoil aquifer.

Sulfate concentrations in most batch-extract waters were similar to the mean sulfate concentration in the initial leach (spoil-aquifer) water (fig. 5). Sulfate concentration in water sample A3 increased during the batch-mixing experiments (fig. 5). Accompanying the sulfate increase in batch-extract sample A3 was a pH decrease from 7.1 to 5.3, which could indicate sulfur oxidation (table 1, reaction 1). Based on sulfur-form analyses, all spoil samples contained trace amounts of either sulfide or organic sulfur that could be oxidized to lower the pH and increase the sulfate concentration in an unbuffered system that has abundant dissolved oxygen, as shown in table 4. Although gypsum was detected in 9 of the 12 spoil samples (table 3), the lack of significant increases in sulfate and calcium concentrations (fig. 5) in the remaining batch-mixing experiments suggests that the initial batch-mixing waters (before contact with the spoil material) were in equilibrium with gypsum.

In addition to gypsum and pyrite as possible sulfate sources during the batch-mixing experiments, efflorescent salts formed during wet-dry cycles could have contributed to increases in dissolved-solids concentrations. Saturated paste and mineralogical results from overburden samples collected from the unsaturated zones in the Northern Great Plains, Upper Colorado River basin, and Powder River basin areas indicate accumulations of soluble salts occur in the unsaturated zone. Magnesium-bearing minerals found within efflorescent crusts in the Upper Colorado River basin include epsomite ($MgSO_4 \bullet 10H_2O$), hexahydrite ($MgSO_4 \bullet 6H_2O$), pentahydrite ($MgSO_4 \bullet 5H_2O$), loewite ($Na_4Mg_2(SO_4)_4 \bullet 5H_2O$), starkeyite ($MgSO_4 \bullet 4H_2O$), kieserite ($MgSO_4 \bullet H_2O$), and bloedite ($Na_2Mg(SO_4)_2 \bullet 4H_2O$) (Whittig and others, 1982). Saturated paste-extract analyses from samples of cuttings taken at the Cordero Mine (figs. 6 and 7) indicated the largest salt concentrations were confined to areas about 10 ft below the land surface.

Continual wet-dry cycles over geologic time can increase the abundance of nonchloride salts within the overburden (Drever, 1982, p. 208-209). Due to the generally larger solubilities of chloride salts, the wetting fronts passing through the overburden profile will dissolve out the chlorides, leaving behind the less soluble (nonchloride) salts within the unsaturated zone.

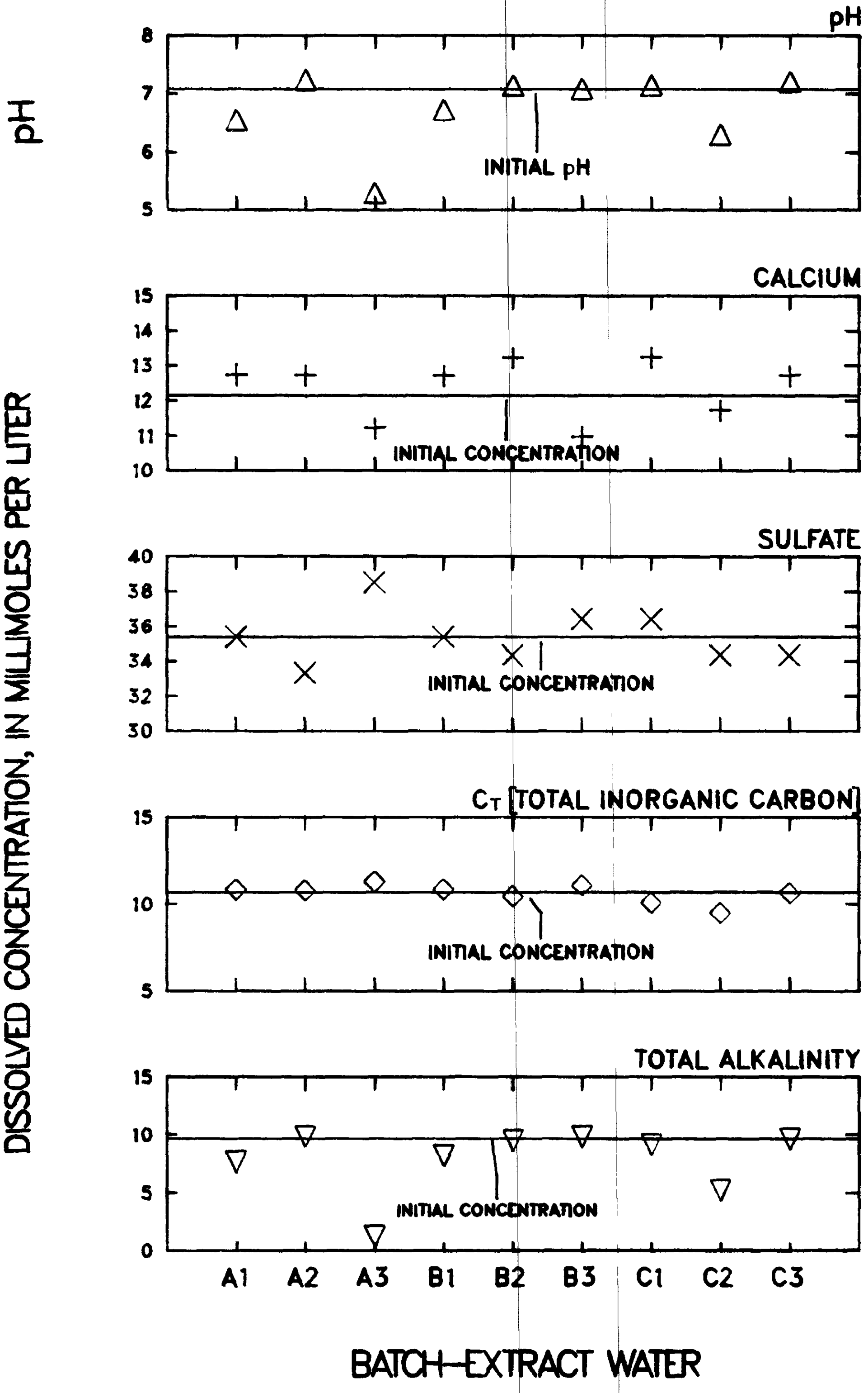


Figure 5.--pH and calcium, sulfate, total inorganic carbon, and total alkalinity concentrations in batch-extract water and spoil-aquifer initial water.

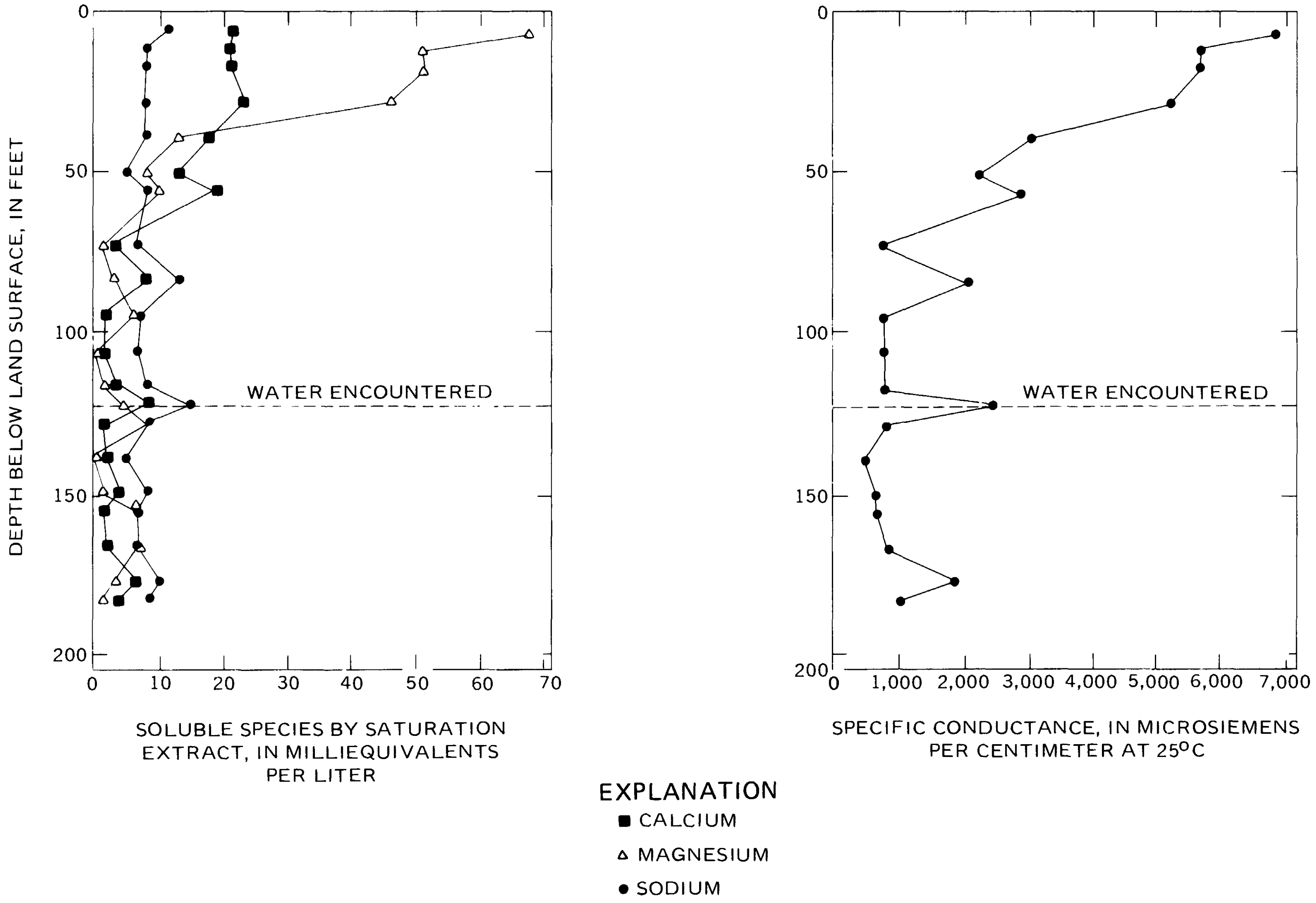


Figure 6.--Availability of leachable salts and specific conductance of overburden, with depth, in samples from drill hole 81-27-2.

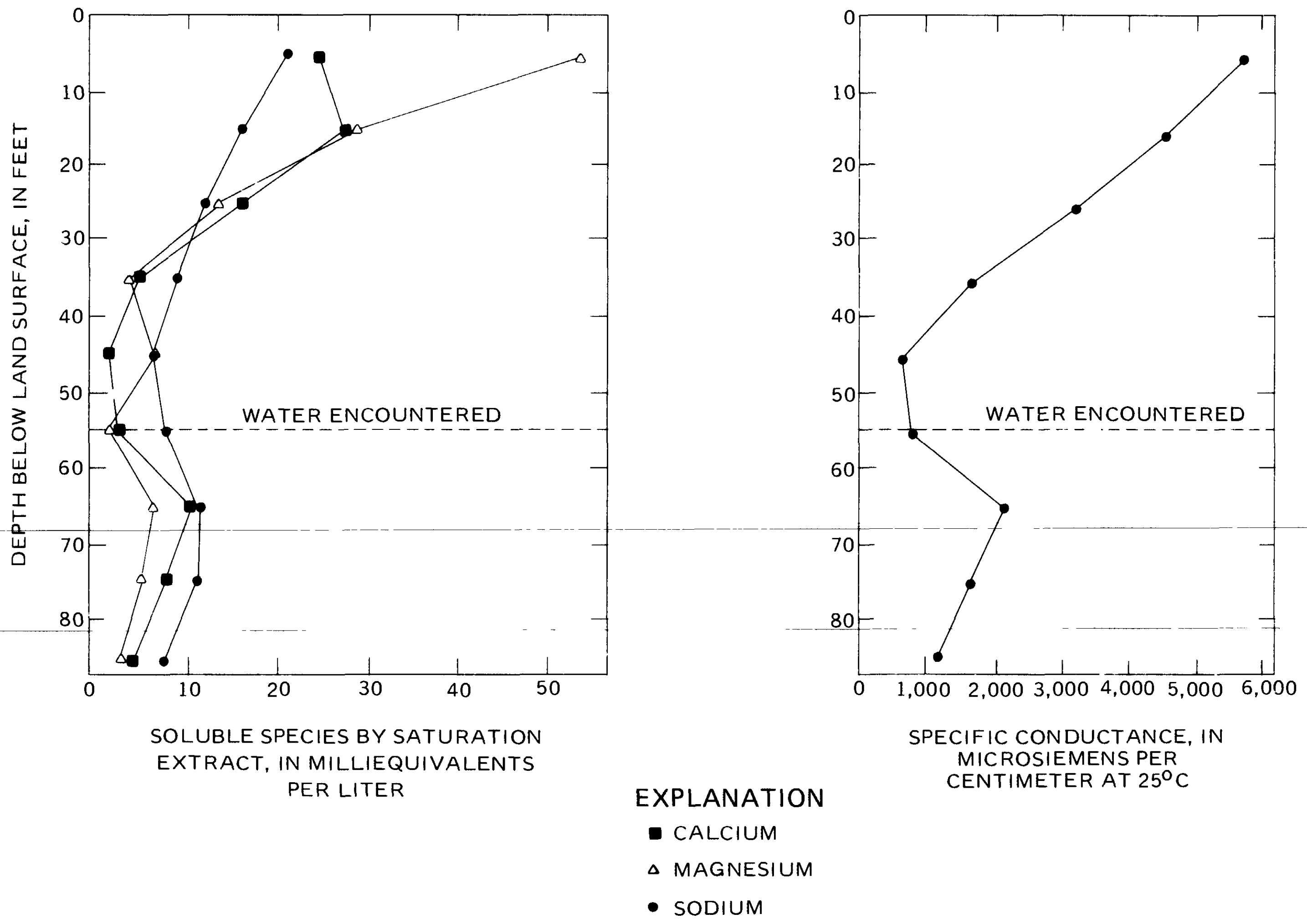


Figure 7.--Availability of leachable salts and specific conductance of overburden, with depth, in samples from drill hole 81-26-1.

Although the nonchloride efflorescent salts were not identified in the X-ray mineralogical analyses of the spoil samples collected at the Cordero Mine (table 3), it is possible that they were present in concentrations less than 1 percent by weight. For example, a sample containing 0.05 percent by weight of melanterite ($FeSO_4 \cdot 7H_2O$) would contain 9.0 mmol/L (millimoles per liter) of sulfate for dissolution in a batch-mixing experiment with a 2:1 water-to-rock ratio by weight. A melanterite content of 0.05 percent by weight would be sufficient as a sulfate source to explain the maximum observed sulfate increase of 5 mmol/L in the 2:1 batch-extract waters.

The C_T concentrations (calculated from WATEQF) in the water derived from the batch-mixing experiments had some deviations in concentration relative to the mean C_T concentrations in the initial batch-mixing waters before contact with the spoil material (fig. 5). Sources or sinks of C_T during the batch-mixing experiments included organic matter, carbon dioxide, and carbonate mineral phases.

As shown in figure 8, increases in calcium and magnesium concentrations occurred in several batch-extract waters. Although only one water sample had an increase in calcium concentration (compared to initial-water concentration) greater than 1 mmol/L, five of the nine batch-extract waters had increases in magnesium concentration greater than 1 mmol/L (fig. 8). Powell and Larson (1985, p. 7) have noted that the weathering of chlorite is a possible magnesium source. Chlorite was detected in most of the samples of the spoil material used in the batch-mixing experiments (table 3). Magnesium-bearing efflorescent salts also could be a source of magnesium during the batch-mixing experiments. Although trace amounts of dolomite were present in selected spoil materials, the inert activity of dolomite at low temperatures (Stumm and Morgan, 1970, p. 193; Drever, 1982, p. 53) eliminates dolomite dissolution as a plausible source for magnesium increases during the batch-mixing experiments.

Cation-exchange reactions probably influenced the concentrations of calcium, magnesium, and sodium during the batch-mixing experiments. The large amounts of clay minerals present within the spoil samples used in the batch-mixing experiments (table 3) could have acted as sources or sinks for calcium, magnesium, and sodium in the water. The plot of cation-exchange capacity of the spoil material compared to log-molar divalent/monovalent cation-activity ratios (LOG $[aCa^{2+}+aMg^{2+}]/[aNa^{+}]^{2}$) in waters from the batch-mixing experiments (fig. 9) indicates the importance of cation-exchange reactions on water-quality changes. Figure 9 shows that as the cation-exchange capacity of the spoil material increased, the cation-activity ratio (LOG $[aCa^{2+}+aMg^{2+}]/[aNa^{+}]^{2}$) in the corresponding batch-extract water decreased. Based on the relationship shown in figure 9, cation-exchange reactions (table 1, reactions 16 and 17) exert an important control on the water quality during the batch-mixing experiments.

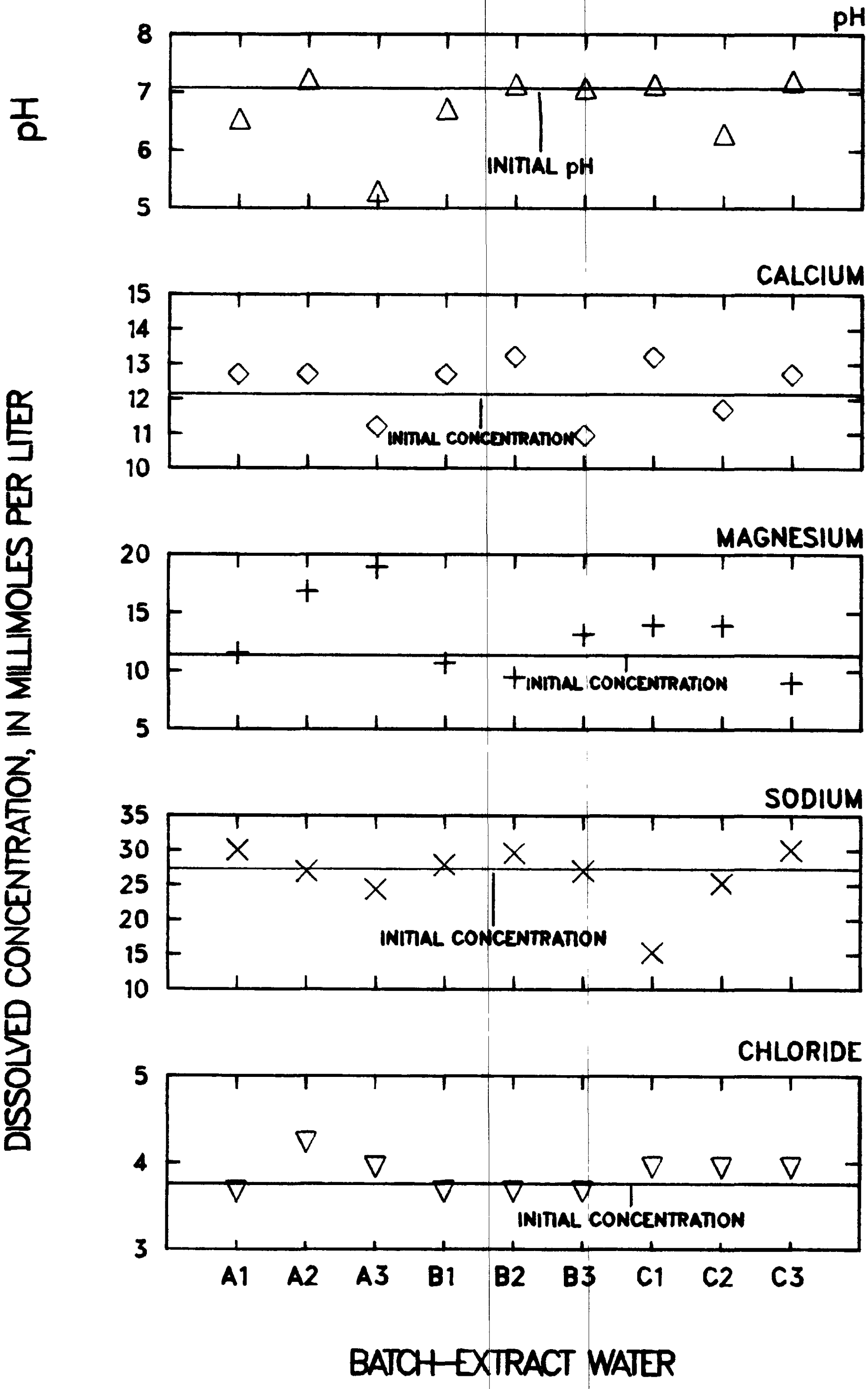


Figure 8.--pH and calcium, magnesium, sodium, and chloride concentrations in batch-extract water and spoil-aquifer initial water.

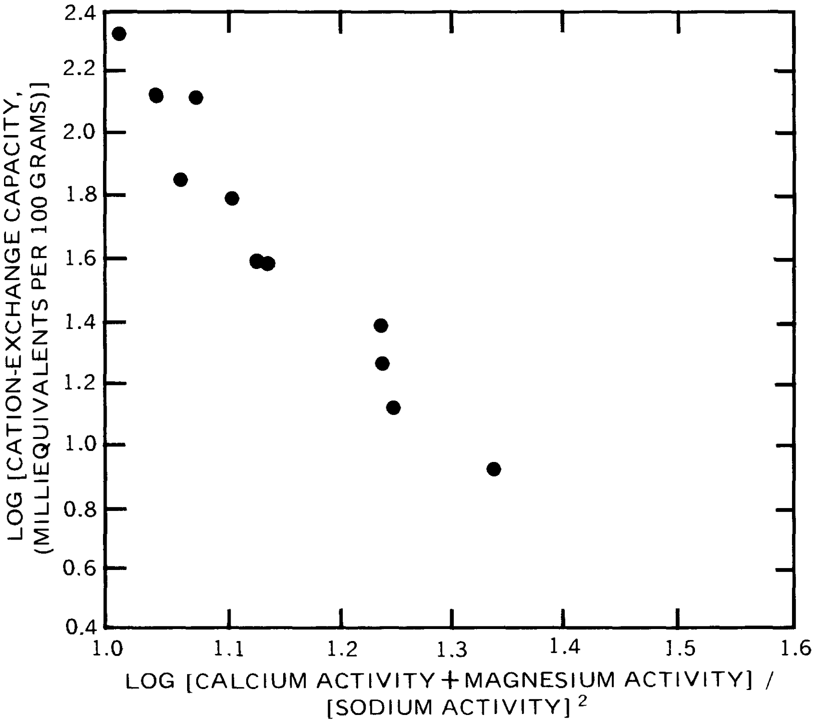


Figure 9.--Cation-exchange capacity of the spoil material compared to the ratio of calcium activity plus magnesium activity to sodium activity squared in batch-extract water using spoil-aquifer initial water.

Chloride concentrations increased only slightly in batch-extract waters (fig. 8). The largest increase in chloride concentration in the batch-extract waters was less than 0.5 mmol/L (18 mg/L). Possible sources for the chloride increases included dissolution of trace amounts of soluble salts and leaching of chloride from shale materials (Johns and Huang, 1967; Billings and Williams, 1967). The lack of increased chloride concentrations in batch-extract waters indicates absence of chloride salts or presence in limited amounts in the spoil material used. The absence of significant amounts of chloride salts in the overburden probably was the result of the wet-dry cycles washing away the chloride salts, as discussed previously. Once in solution, the chloride ion does not participate in adsorption or precipitation reactions during the batch-mixing experiments.

Variations in the pH and concentrations of aluminum, iron, manganese, and silica for the batch-extract waters after contact with spoil material are shown in figure 10. The pH had a marked effect on manganese and aluminum concentrations (fig. 10). When the pH of the batch-extract waters was less than 6.5, the concentrations of aluminum and manganese were substantially larger than their concentrations in higher pH waters. The concentration of iron in batch-extract waters did not exceed 0.004 mmol/L. According to Hem (1985, p. 80), low iron concentrations can be expected in moderately oxidizing waters that have a pH larger than 5, due to the stability of ferric hydroxide.

Geochemical Controls

Saturation indices calculated using the aqueous-speciation model WATEQF (Plummer and others, 1978) and stability diagrams were used to determine possible mineralogical controls during the batch-mixing experiments. Saturation indices for possible carbonate and sulfate minerals are listed in table 5. The stability of selected aluminosilcate phases during the batch-mixing experiments was evaluated with stability diagrams.

The initial leach waters, before contact with the spoil material, were oversaturated with respect to calcite, dolomite, and magnesite (table 5). As shown by the decrease in C_T during transport of the unpreserved water samples (table 6), CO_2 gas probably evolved from the unpreserved, initial leach waters after removal from the spoil aquifer. The degassing of carbon dioxide resulted in an increased pH that increased the activity of the carbonate ion. As a result, the saturation indices of specific carbonate mineral phases such as calcite and dolomite increased.

The carbonate present in selected spoil samples possibly was not available for acid neutralization. Based on the mineralogy of spoil sample C2 (table 3), sufficient amounts of carbonate were available to prevent pH decreases during the batch-mixing experiment. During the batch-mixing experiment (using spoil sample C2) the pH dropped 0.85 unit (fig. 5) and the batch-extract water was significantly undersaturated with respect to calcite (table 5). The lack of carbonate buffering during this batch-mixing experiment (using spoil sample C2) indicates that although carbonate was available within selected spoil materials, the spoil-material surface area available for neutralization reactions was not sufficient. Secondary coatings

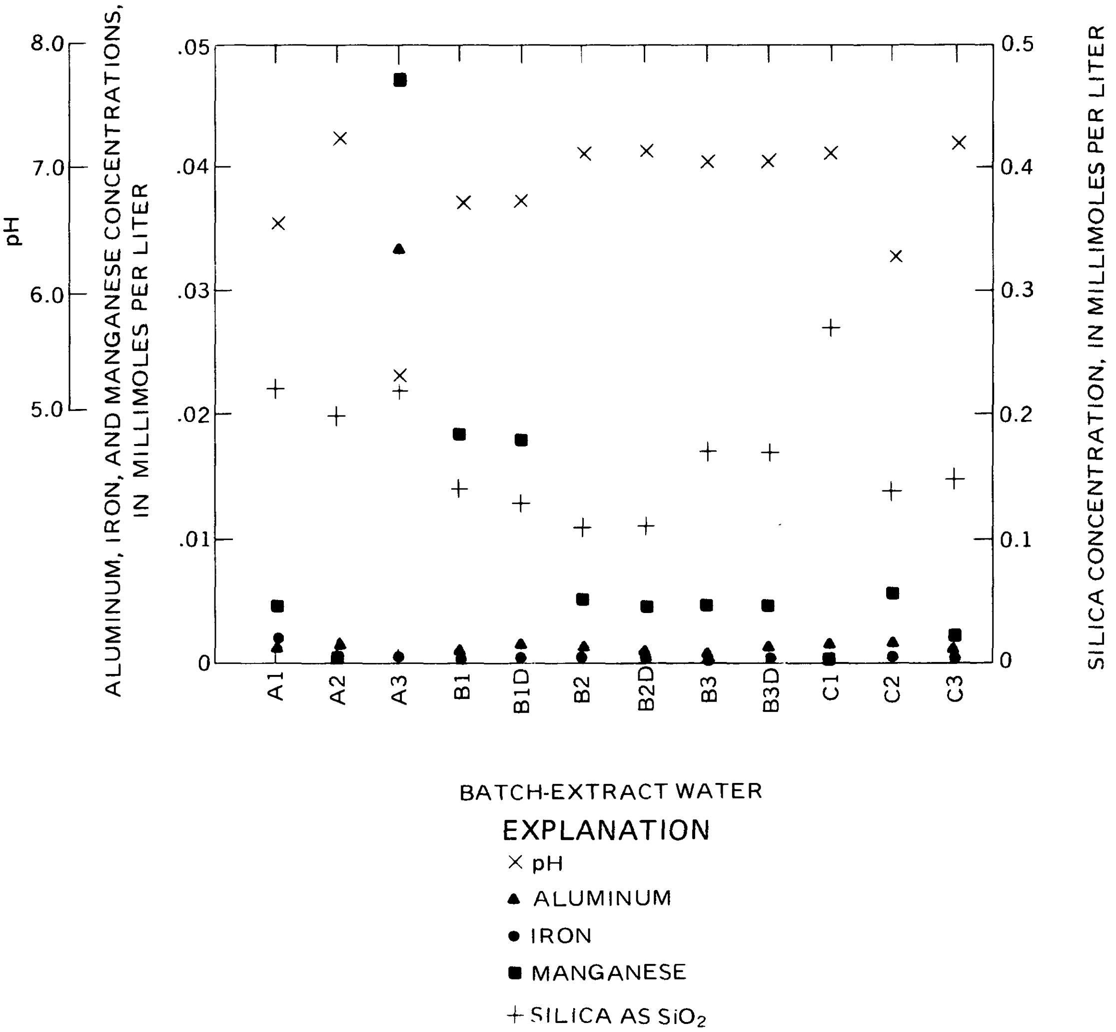


Figure 10.--pH and aluminum, iron, manganese, and silica concentrations in batch-extract water using spoil-aquifer initial water.

Table 5.--Saturation indices of carbonate and sulfate minerals for waters from the batch-mixing experiments using water from the spoil aquifer

Sample	Calcite	Strontium calcite ($Sr_{0.001}Ca_{0.999}CO_3$)	Dolomite	Strontianite	Magnesite	Gypsum
Preserved spoil-aquifer water						
	0.097	------	0.097	-1.274	-0.307	0.117
Initial leach water (unpreserved)						
Mean	0.528	0.372	1.227	-0.906	0.299	0.001
Standard deviation (three samples)	.072	.072	.124	.091	.100	.026
Water from the batch-mixing experiments						
A1	-0.043	0.200	0.039	-1.541	-0.288	0.019
A2	.667	.510	1.622	-.835	.585	-.018
A3	-2.189	-2.346	-3.984	-3.783	-2.165	-.023
B1	.088	-.071	.273	-1.298	-.186	.023
B1D	.072	-.087	.240	-1.304	-.203	-.018
B2	.669	.510	1.365	-.686	.325	.032
B2D	.640	.480	1.304	-.745	.294	.034
B3	.489	.331	1.228	-.931	.368	-.038
B3D	.491	.331	1.231	-.925	.370	-.039
C1	.638	.482	1.467	-.758	.460	.043
C2	-.535	-.692	.826	-1.984	-.661	-.020
C3	.654	.497	1.329	-.683	.305	.019

on the carbonate grains, such as iron or manganese oxyhydroxides, or both, could have decreased the amount of reactive surface area available during the batch-mixing experiments.

Excluding waters with a pH less than 7.0, dolomite, magnesite, and calcite oversaturation was maintained during the batch-mixing experiments (tables 5 and 6). The inert activity of dolomite can be used to explain why dolomite oversaturation was maintained during the batch-mixing experiments. According to Stumm and Morgan (1970, p. 193), formation rates of calcium-rich dolomite is on the order of hundreds of angstroms (less than 4×10^{-8} in.) per thousands of years. With these slow crystal growth rates, dolomite precipitation was not a chemical sink for calcium, magnesium, or C_T during the 24-hour mixing time used in the batch-mixing experiments.

The continued state of calcite oversaturation during the batch-mixing experiments probably can be explained by the effect elevated magnesium concentrations have on the rate of crystal growth for calcite. According to conclusions derived by Berner (1975), whenever the concentration of magnesium in artificial seawater exceeded 3 mmol/kg (millimoles per kilogram), the growth rate of calcite was depressed. In the experimental data derived by

Table 6.--Partial pressure of carbon dioxide, and pH and concentrations of total inorganic carbon and alkalinity for waters from the batch-mixing experiments using water from the spoil aquifer

Sample	Partial pressure of carbon dixoide (log atmospheres)	Total inorganic carbon	pH (units)	Alkalinity (milliequivalents per liter)
		Preserved spoil-aquifer water		
	-1.22	13.09	6.78	9.83
		Initial leach water (unpreserved)		
Mean	-1.43	10.93[1]	7.08	9.72
Standard deviation (three samples)	.10	.41	.08	.16
		Water from the batch-mixing experiments		
A1	-1.03	10.84	6.55	7.74
A2	-1.54	10.79	7.24	9.87
A3	-.52	11.29	5.30	1.37
B1	-1.10	10.85	6.73	8.24
B1D	-1.09	11.09	6.74	8.40
B2	-1.54	10.46	7.15	9.56
B2D	-1.54	10.47	7.17	9.56
B3	-1.42	11.09	7.09	9.89
B3D	-1.42	11.09	7.09	9.89
C1	-1.52	10.09	7.15	9.23
C2	-.90	9.50	6.31	5.27
C3	-1.53	10.65	7.22	9.72

[1] Geometric mean.

Berner (1975), a saturation index greater than 0.5 (dimensionless) was necessary before precipitation of calcite occurs in water with the composition of seawater. Although the batch-extract waters had a different composition than seawater, it is possible that the elevated magnesium concentrations in the batch-extract waters (average of 12.3 mmol/kg), coupled with the limited time for the batch-mixing experiments (24 hours), decreased the rate of calcite precipitation--thus, oversaturation was maintained during the batch-mixing experiments.

Another possible explanation for the continued oversaturation of calcite during the batch-mixing experiments was that of a solid-solution reaction with another carbonate mineral. Henderson (1984, p. 61) demonstrated a strontium-calcite solid-solution equilibrium in ground waters oversaturated with calcite and undersaturated with strontianite. For water samples without a large decrease in pH during the batch-mixing experiments, the calculated saturation index was negative with respect to strontianite (table 5). Holland and others (1964) reported a K_D (distribution constant, dimensionless) of 0.14 for the partitioning of strontium between an aqueous phase and calcite. The K_D relates the molalities (m) of strontium and calcium in solution to mole fractions of these elements in the solid phase according to the equation:

$$\frac{m^{x}_{Sr}}{m^{x}_{Ca}} = k_D \frac{m^{L}_{Sr}}{m^{L}_{Ca}} ,$$

where x denotes the solid phase and L denotes the solution phase.

The average calcium concentration in batch-extract waters was 12.37 mmol/L and the average strontium concentration was 0.106 mmol/L. Based on the previously defined equation, calcite that is in equilibrium with the batch-extract waters should have contained an average of 0.1 mole percent strontianite. For the reaction

$$Ca_{(1-x)}Sr_xCO_3 \longrightarrow (1-x)Ca^{2+} + xSr^{2+} + CO_3^{2-} ,$$

the free energy (G^0) of calcite containing 0.1 mole percent of strontianite was calculated using the equations derived by Berner (1975) for ideal mixing:

$$\Delta G^0_{\text{ideal mix}} = xRT\ln x + (1-x)RT\ln(1-x),$$

and

$$\Delta G^0_{f\ \text{Sr calcite}} = \Delta G^0_{f\ \text{ideal mix}} + \Delta G^0_{f\ \text{calcite}} +$$

$$x(\Delta G^0_{f\ Sr} - \Delta G^0_{f\ Ca} - RT\ln k_D),$$

where: x = mole fraction of Sr in solid solution,
R = gas constant,
T = temperature in degrees kelvin, and
ΔG^0_f = standard enthalpy of formation.

The calculated, free energy of formation for calcite containing 0.1 mole percent of strontianite was calculated to be -270.065 kilocalories per mole. The corresponding saturation indices calculated from this free-energy value are listed in table 5 for waters used in the batch-mixing experiments. Based on the calculated saturation indices for $Sr_{0.001}Ca_{0.999}CO_3$ (table 5), this solid-solution phase was not in equilibrium with the water during the batch-mixing experiments.

Gypsum was at or near saturation for all the waters before and after use in the batch-mixing experiments (table 5), suggesting that gypsum was the dominant controlling phase for sulfate concentrations during the batch-mixing experiments. Although most of the spoil samples used in the batch-mixing experiments had enough gypsum to increase the sulfate concentrations more than 100 mmol/L (table 3), the largest sulfate increase during the batch-mixing experiments was approximately 5 mmol/L (sample A3). The sulfate increase during the batch-mixing experiment (using spoil material from site A3) was accompanied by a decrease in pH (fig. 5), which indicates possible sulfide oxidation (table 1, reaction 1).

Water samples before and after use in the batch-mixing experiments fell within the kaolinite stability field when plotted on activity diagrams (fig. 11). Based on the activity diagrams, kaolinite was considered to be the stable phase formed during hydrolysis of feldspars. During hydrolysis of the feldspars, H^+ is consumed while clays, dissolved silica, and metal ions are produced. Hydrolysis of potassium feldspar (found in the spoil material) could have occurred during the time frame of the batch-mixing experiments (table 1, reaction 15). According to studies of silicate-mineral dissolution (Freeze and Cherry, 1979, p. 273-274), a kinetically rapid dissolution (within minutes) is followed by a slower and gradually decreasing rate of mineral dissolution.

Batch Tests Using Coal-Aquifer Water

Variations in Major- and Minor-Ion Concentrations

Water-quality changes were determined for batch-extract waters using water collected from the coal aquifer at the Cordero Mine. Results of the changes in major- and minor-ion concentrations during the batch-mixing experiments were used to estimate probable controls affecting the postmining water quality as water from the coal aquifer recharged the spoil aquifer.

In general, increases in major-ion concentrations in batch-extract waters were larger when coal-aquifer initial water was used than when spoil-aquifer water was used. For example, the largest sulfate increase in the batch-extract water using spoil-aquifer water was less than 5 mmol/L; whereas, the largest sulfate increase in batch-extract water using coal-aquifer water was larger than 20 mmol/L.

Changes in sulfate concentration during the batch-mixing experiments were related directly to calcium concentrations and were inversely related to the pH of the batch-extract waters (fig. 12). Based on the mineralogy of the spoil material (table 3) and the composition of the waters derived from the batch-mixing experiments, pyrite oxidation (table 1, reaction 1) coupled with

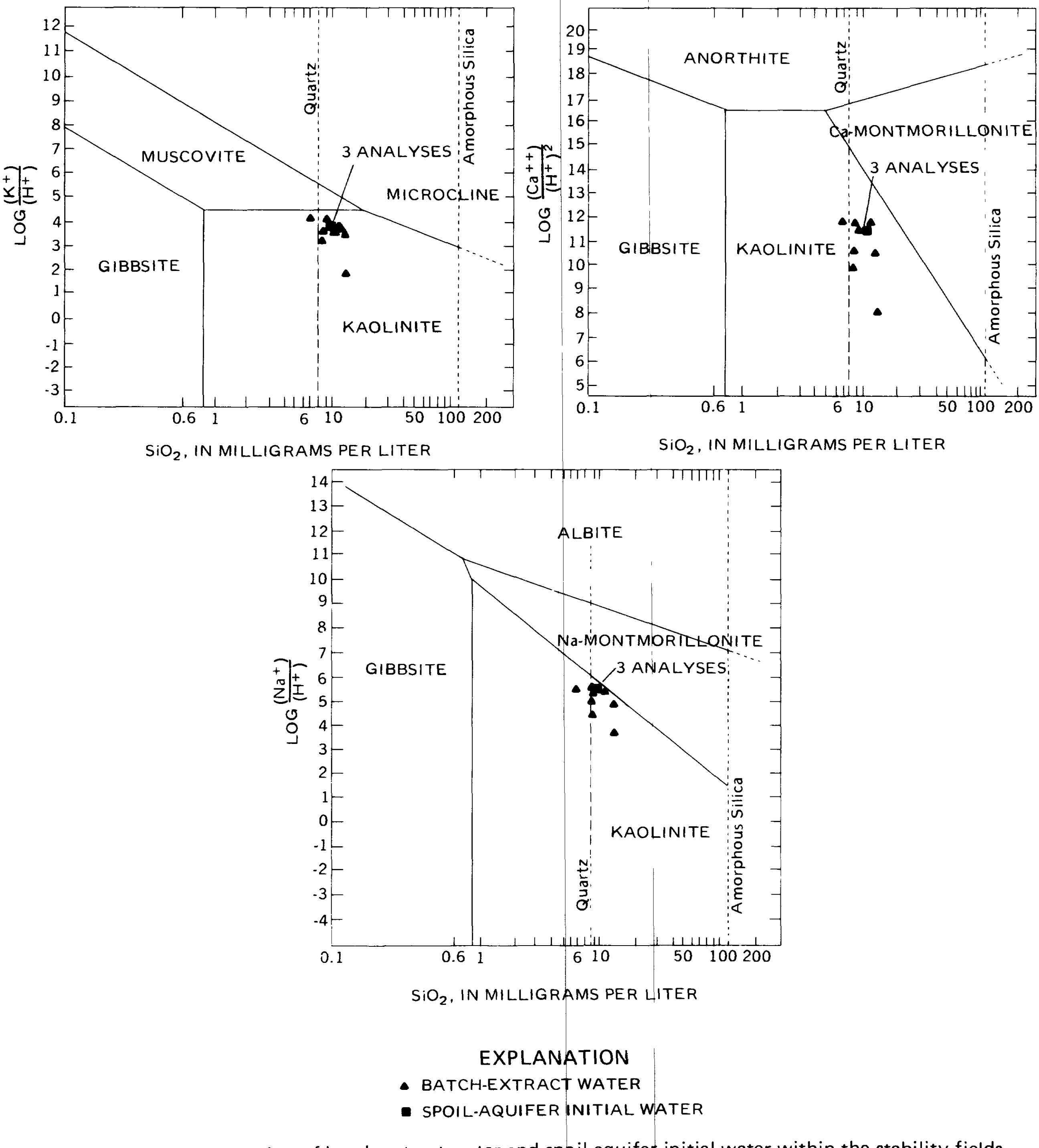


Figure 11.--Relation of batch-extract water and spoil-aquifer initial water within the stability fields of selected aluminosilicates at 25°C and 1 atmosphere (from Tardy, 1971).

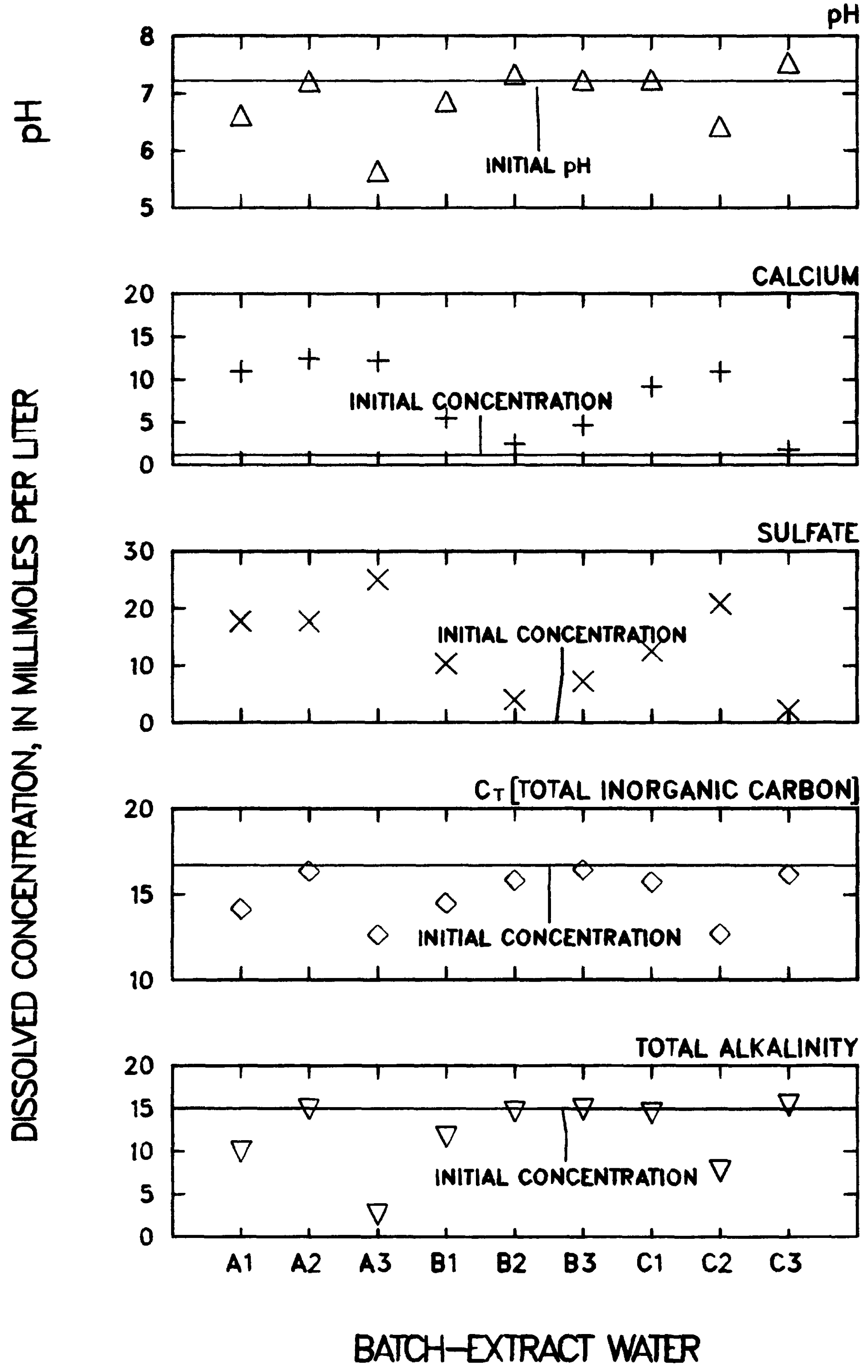


Figure 12.--pH and calcium, sulfate, total inorganic carbon, and total alkalinity concentrations in batch-extract water and coal-aquifer initial water.

gypsum dissolution (table 1, reaction 11) could have caused the observed decrease in pH, increase in calcium concentrations, and the increased concentration of dissolved sulfate. As mentioned previously, efflorescent salts that have accumulated in the spoil material also could have contributed to the observed sulfate increases during the batch-mixing experiments.

Sulfate concentrations in batch-extract waters were related directly to the amount of gypsum in the spoil material (fig. 13). Deviations from the observed trend of increasing sulfate concentration with increasing amounts of gypsum were observed for batch-extract water sample C2 that had a pH of less than 6.5 (fig. 13). Based on the mineralogical analyses of sample C2, it was determined that a part of the increased sulfate concentration during the batch-mixing experiment was due to sulfide oxidation.

The ratio of calcium plus sodium to sulfate concentrations ($[Ca]+[Na]/[SO_4]$) compared to the pH of batch-extract waters was used to evaluate the relative contributions of pyrite oxidation and gypsum dissolution to the observed sulfate increases (fig. 14). Sodium was considered in the ratio calculation due to the possible cation-exchange reaction with calcium (table 1, reaction 16), which could act as a calcium sink and subsequent source of sodium due to gypsum dissolution during the batch-mixing experiments. As indicated in figure 14, as pH increased in the batch-extract waters, the ratio of $[Ca]+[Na]/[SO_4]$ generally increased. The increase with increasing pH indicates that the observed sulfate increases primarily were due to gypsum dissolution (table 1, reaction 11), which would have contributed directly to increases in calcium and indirectly to increases in sodium concentrations. Decrease in pH from that of the initial coal water was coupled with a decrease in the equivalent ratio of $[Ca]+[Na]/[SO_4]$, indicating that a larger part of the sulfate increase was derived from nongypsum sources (for example, pyrite oxidation).

The concentrations of C_T (calculated by WATEQF), and pH in the waters derived from the batch-mixing experiments were closely related (fig. 12). The relationship possibly was due to the emission of CO_2 gas from the waters after the batch-mixing experiments had been completed.

Although the batch-mixing vessels were sealed from the atmosphere during the experiments, the vessels were opened to extract the water; thus the water was exposed to the atmosphere. During this exposure, it was possible that carbon dioxide could evolve, causing a decrease in the C_T in the waters. As the pH decreased during the batch-mixing experiments, bicarbonate ions were protonated, thus increasing the activity of $H_2CO_3^0$ (table 1, reaction 6). Because of the increase in the concentration of $H_2CO_3^0$, the partial pressure of carbon dioxide was increased within the batch-mixing container (table 1, reaction 5). Once the batch-mixing vessel was opened to the atmosphere, the concentration of $H_2CO_3^0$ could have equilibrated to atmospheric conditions and possibly could have emitted carbon dioxide; thus C_T in the batch-extract

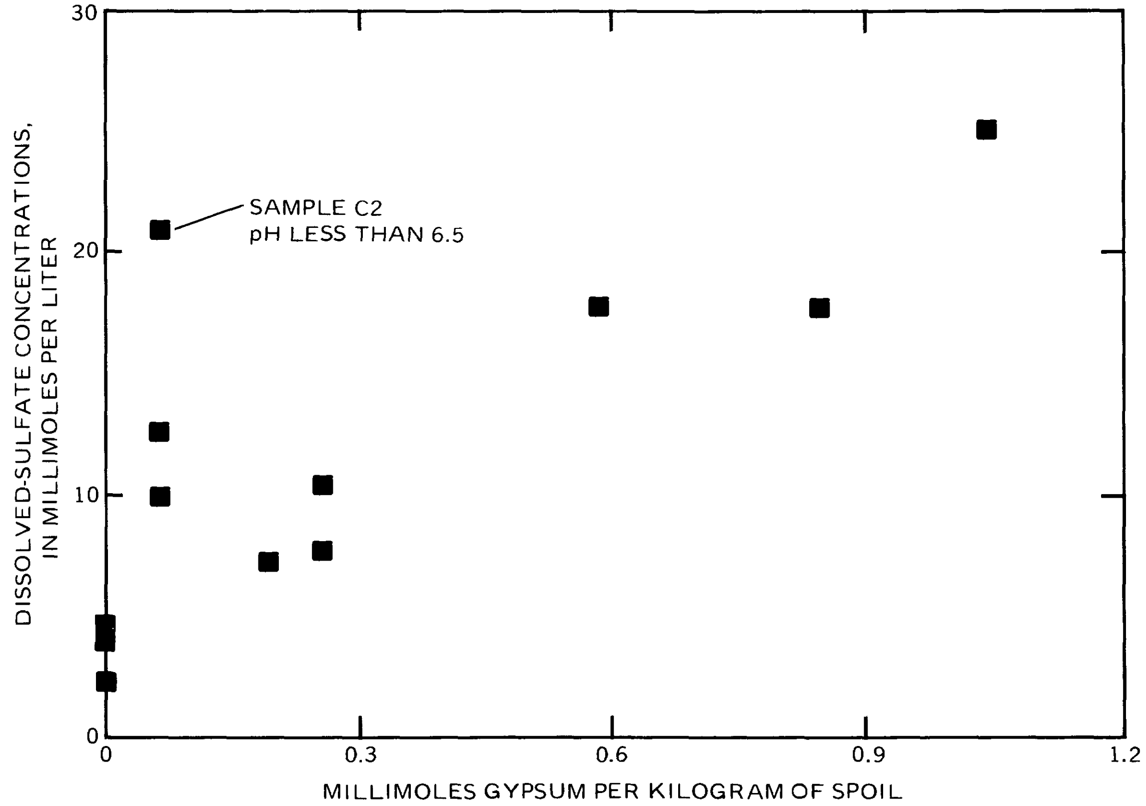


Figure 13.--Sulfate concentrations in batch-extract waters using coal-aquifer initial water compared to the concentration of gypsum in the spoil material.

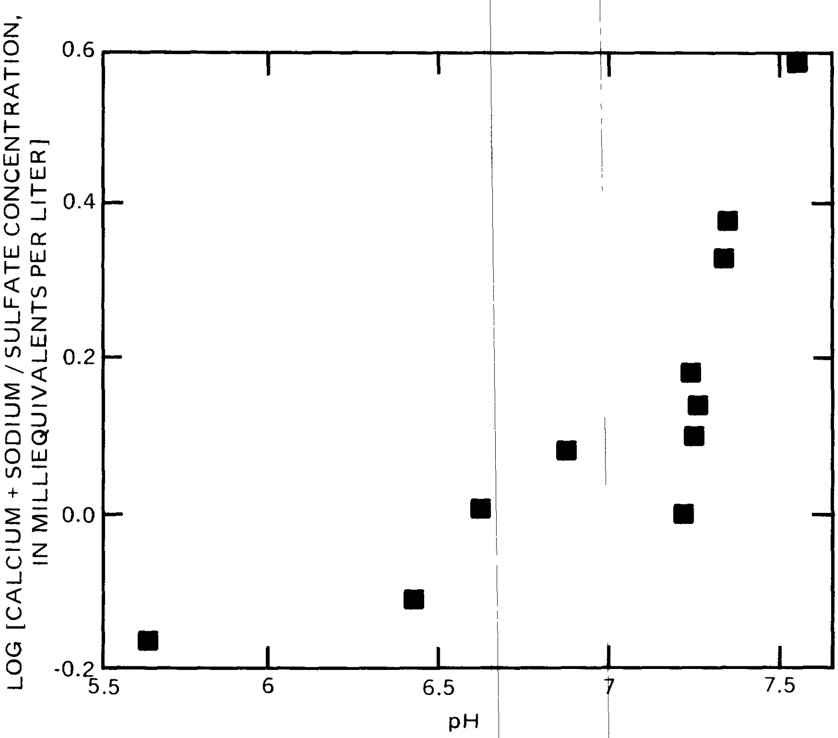


Figure 14.--Ratio of calcium plus sodium to sulfate concentrations compared to pH in batch-extract water using coal-aquifer initial water.

waters could have been decreased. The concentration of C_T in the initial leach waters from the previous set of batch-mixing experiments (spoil-aquifer water) was smaller (fig. 5), which possibly minimized CO_2 degassing when the mixing vessel was open to the atmosphere, compared to this set of batch-mixing experiments using water from the coal aquifer.

Cation-exchange reactions on the abundant clays in the spoil material possibly influenced the concentrations of calcium, magnesium, and sodium during the batch-mixing experiments. As shown in figure 15, increases in sodium concentrations in the waters derived from the batch-mixing experiments were accompanied by decreased calcium and magnesium concentrations. Concentration changes between the exchangeable cations is a trend characteristic of cation-exchange reactions (table 1, reactions 16 and 17). Results from the previous set of batch-mixing experiments (fig. 9) were similar--as the cation-exchange capacity of the spoil material increased, the exchangeable cation activity ratio ($\mathrm{LOG}\ [aCa^{2+}+aMg^{2+}]/[aNa^{+}]^2$) in the batch-extract water decreased (fig. 16).

Comparable to the previous set of batch-mixing experiments, the largest increase in chloride concentration (compared to the initial concentration) was less than 0.5 mmol/L (fig. 15). Although the initial leach water from the coal aquifer had a smaller chloride concentration compared to the water taken from the spoil aquifer, the relative increases, the sources, and the reactivity of chloride for both sets of batch-mixing experiments were the same.

Analogous to the results from the batch-mixing experiments using water from the spoil aquifer, aluminum and manganese concentrations decreased substantially when the pH of the batch-extract water was less than 6.0 (fig. 17). The larger pH of the batch-mixing experiments, using the larger-alkalinity water from the coal-aquifer (15.37 mmol/L compared to 9.83 mmol/L), caused smaller manganese and aluminum concentrations. The low concentration of iron in the waters derived from the batch-mixing experiments probably was due to the stability of ferric hydroxide in a moderately oxidizing water with a pH larger than 5.0.

Geochemical Controls

The initial leach waters before contact with the spoil material were oversaturated with calcite and dolomite (table 7). The decrease in C_T during transport of the unpreserved water samples (table 8) possibly was due to the evolution of CO_2 gas after removal of the water from the coal aquifer. The evolution of carbon dioxide from the water samples could have caused an increase in the saturation indices of calcite and dolomite.

Oversaturation with calcite and dolomite was maintained during the batch-mixing experiments where the pH was maintained above 6.5 (table 8). The undersaturated to near-equilibrium conditions with respect to calcite in low pH samples were a function of decreased carbonate activity due to pH decreases (table 1, reactions 6 and 7) rather than a carbonate-precipitation reaction decreasing the activity of calcium, magnesium, and carbonate during the batch-mixing experiments. The maintenance of calcite and dolomite oversaturation

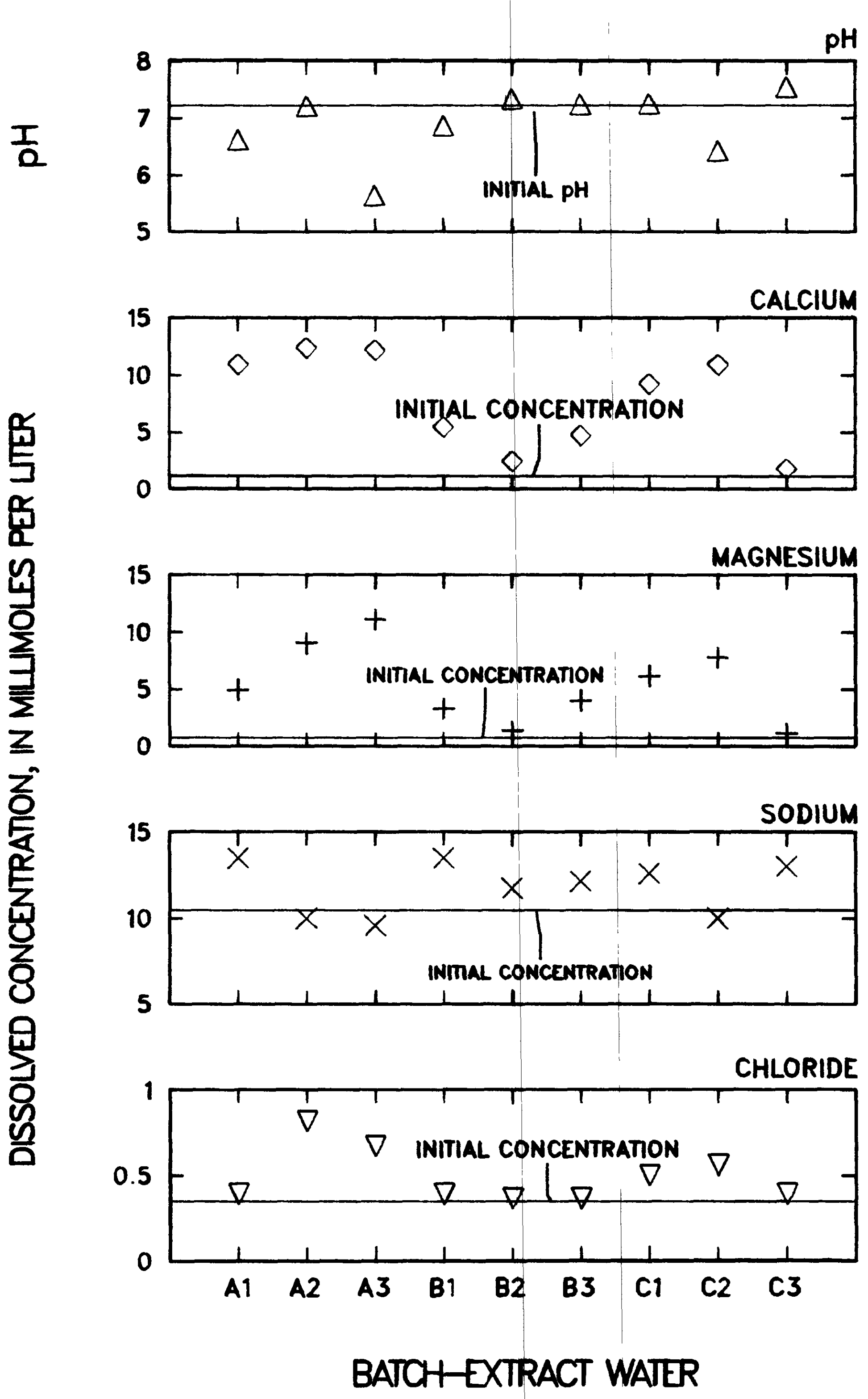


Figure 15.--pH and calcium, magnesium, sodium, and chloride concentrations in batch-extract water and coal-aquifer initial water.

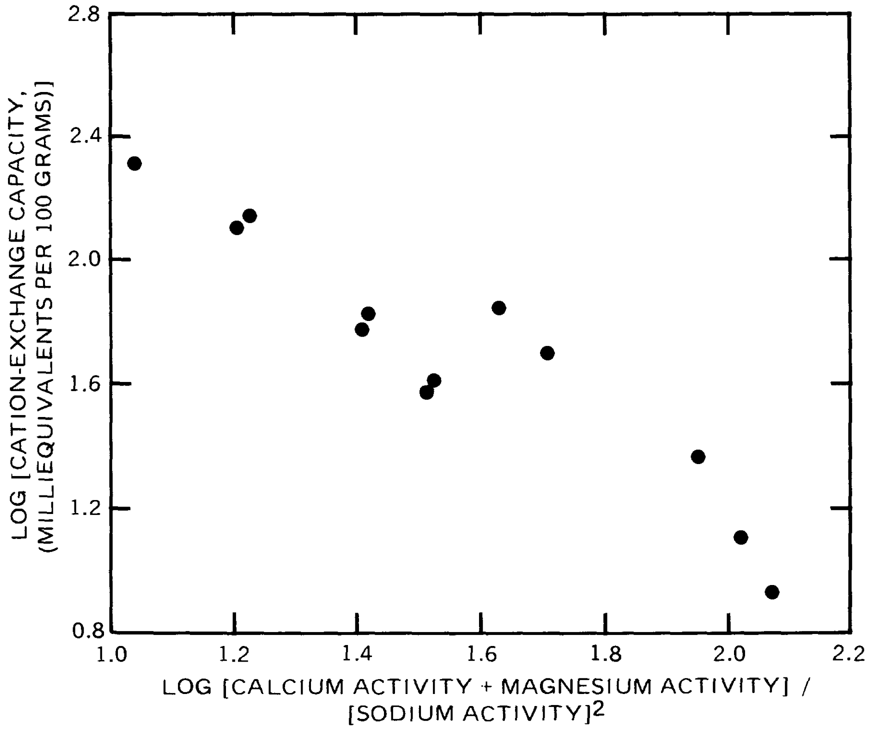


Figure 16.--Cation-exchange capacity of the spoil material compared to the ratio of calcium activity plus magnesium activity to sodium activity squared in batch-extract water using coal-aquifer initial water.

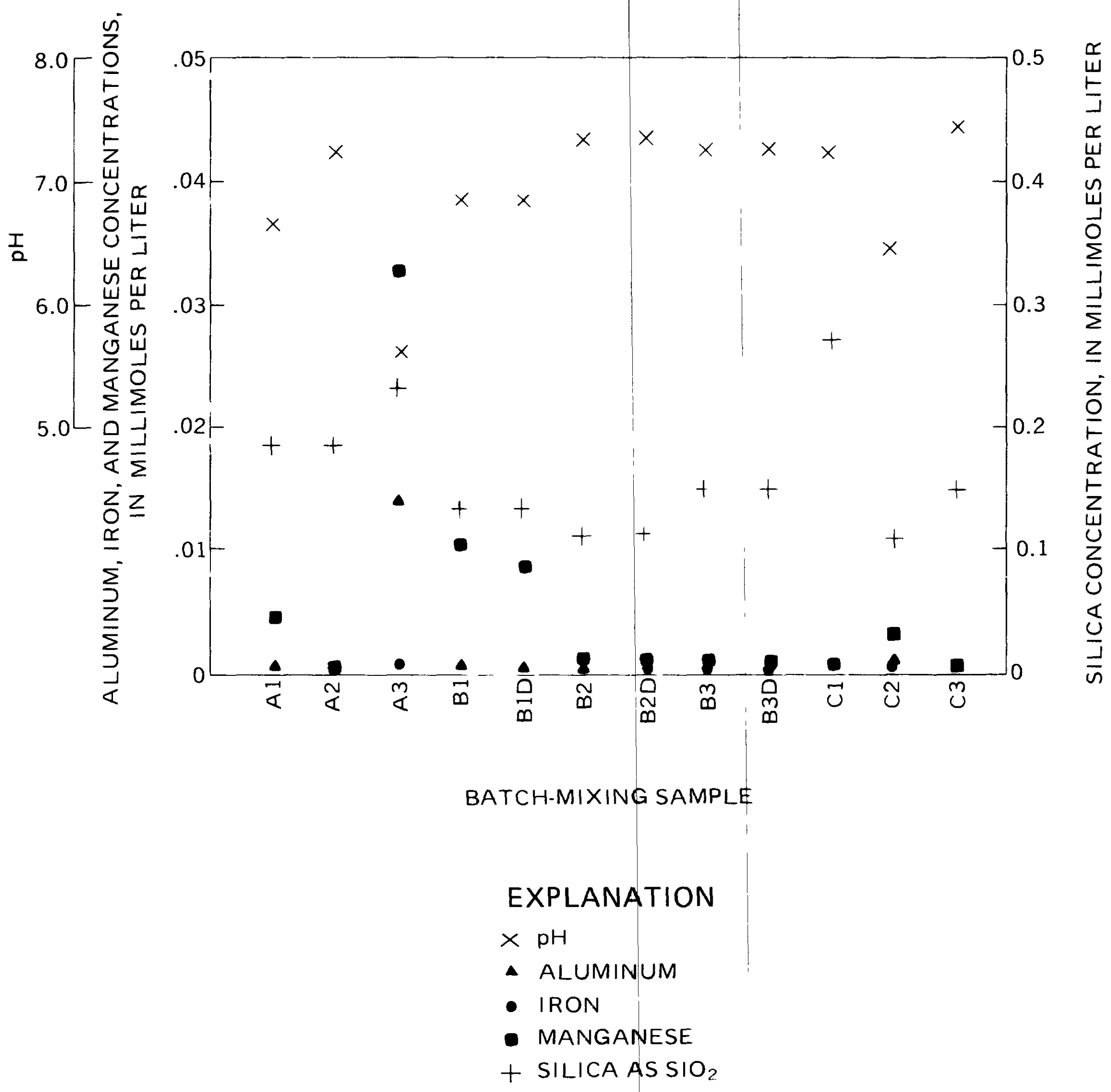


Figure 17.--pH and aluminum, iron, manganese, and silica concentrations in batch-extract water using coal-aquifer initial water.

Table 7.--Saturation indices of carbonate and sulfate minerals for waters from the batch-mixing experiments using water from the coal aquifer

Sample	Calcite	Strontium calcite ($Sr_{0.001}Ca_{0.999}CO_3$)	Dolomite	Strontianite	Magnesite	Gypsum
Preserved coal-aquifer water						
	0.113	------	-0.034	-1.094	-0.472	-3.401
Initial leach water (unpreserved)						
Mean	0.247	0.099	0.095	-1.006	-0.214	-3.566
Standard deviation (three samples)	.047	.048	.100	.050	.049	.084
Water from the batch-mixing experiments						
A1	0.149	-0.003	0.099	-1.495	-0.417	-0.151
A2	.965	.811	1.943	-.791	.610	-.144
A3	-1.405	-1.561	-2.694	-3.391	-1.657	-.042
B1	.243	.094	.402	-1.143	-.207	-.540
B1D	.239	.094	.404	-1.138	-.201	-.572
B2	.573	.426	1.006	-.739	.069	-1.117
B2D	.599	.452	1.074	-.688	.109	-1.150
B3	.693	.544	1.453	-.813	.393	-.723
B3D	.692	.544	1.457	-.816	.397	-.722
C1	.915	.758	1.810	-.576	.525	-.336
C2	-.192	-.338	-.390	-1.772	-.563	-.115
C3	.697	.550	1.316	-.473	.253	-1.469

during the batch-mixing experiments possibly was due to the slow precipitation kinetics involved with carbonate precipitation and to the limited time frame of the batch-mixing experiments.

In addition to possible kinetic influences causing carbonate oversaturation, the possibility of a strontium-calcite solid-solution controlling phase during the batch-mixing experiments was evaluated. Calcite with 0.1-mole percent of strontium could have been in equilibrium with selected batch-extract waters that have contacted the spoil material. This assumption was based on the distribution coefficient of 0.14 (as measured by Holland and others, 1964) for the partitioning of strontium between an aqueous and solid phase, and an average calcium concentration of 5.94 mmol/L and an average strontium concentration of 0.04 mmol/L in the batch-extract waters. The free energy of a $Sr_{0.001}Ca_{0.999}CO_3$ ideal solution is -270.065 kilocalories per mole. Saturation indices calculated from this value (table 7) indicated that batch-extract waters with a pH greater than 6.7 (table 8) remained oversaturated with respect to the calculated solid-solution phase. Batch-extract waters were not in equilibrium with respect to common carbonate phases due to the slow kinetics of carbonate precipitation and the limited time of the batch-mixing experiments.

Table 8.--Partial pressure of carbon dioxide and pH and concentrations of total inorganic carbon and alkalinity for waters from the batch-mixing experiments using water from the coal aquifer

Sample	Partial pressure of carbon dixoide (log atmospheres)	Total inorganic carbon	pH (units)	Alkalinity (milliequivalents per liter)
Preserved coal-aquifer water				
	-1.32	17.66	7.20	15.37
Initial leach water (unpreserved)				
Mean	-1.30	16.74	[1]7.22	14.99
Standard deviation (three samples)	.05	.28	.05	.10
Water from the batch-mixing experiments				
A1	-0.92	14.18	6.62	10.03
A2	-1.36	16.36	7.22	14.97
A3	-.53	12.66	5.64	2.63
B1	-1.09	14.51	6.87	11.66
B1D	-1.08	14.72	6.87	11.83
B2	-1.45	15.84	7.34	14.61
B2D	-1.45	16.16	7.35	14.94
B3	-1.35	16.45	7.24	14.95
B3D	-1.37	16.37	7.26	14.95
C1	-1.39	15.76	7.25	14.46
C2	-.85	12.71	6.43	7.73
C3	-1.63	16.19	7.55	15.43

[1] Geometric mean.

The waters from this set of batch-mixing experiments were consistently undersaturated with respect to gypsum (table 7). Although sulfate concentrations increased during the batch-mixing experiments, gypsum saturation never was attained. According to the X-ray diffraction analyses of the spoil material, sufficient gypsum is available to attain gypsum saturation in 8 of the 12 spoil samples (assuming that all the gypsum dissolves). However, X-ray bias of gypsum coatings on small grains could overestimate the total amount of gypsum present in the spoil material. Column-leach tests done by Johnson (1985) revealed that the total amount of sulfate leached from overburden samples was less than the amount of sulfate sulfur available based on sulfur-form analyses.

The limited amount of gypsum dissolution during the batch-mixing experiments possibly was a function of diffusion gradients established around the gypsum grains. Drever (1982, p. 124) noted that during dissolution of individual minerals in an aqueous solution, the solution immediately adjacent to the dissolving surface is possibly in equilibrium with the mineral and that the concentration decreases outwardly from the mineral grain. After the initial 2-hour rotating period to thoroughly mix the samples with the leach waters, the water and rock mixtures were not disturbed for approximately 22 hours. During this settling period, it is possible that concentration gradients could have been established adjacent to the gypsum grains, thereby decreasing the total amount of dissolved sulfate within the batch-extract waters.

The amount of reactive surface area also exerted an important control on gypsum dissolution during the batch-mixing experiments. Within the spoil material used in the batch-mixing experiments, it is likely that only a limited amount of the gypsum grains was available for dissolution reactions. Secondary mineral coatings could inhibit gypsum dissolution.

Batch-extract water using coal-aquifer initial water, similar to that using spoil-aquifer water, fell within the kaolinite stability field when plotted on activity diagrams (fig. 18). Small amounts of kaolinite could have formed during the limited water-to-rock contact time of the batch-mixing experiments.

Mass-Transfer Modeling

Mass-transfer calculations were performed to simulate the possible reactions between the coal-aquifer water and spoil sample B1 during the batch-mixing experiment. Mass-balance and thermodynamic calculations, in combination with the mineralogy of the spoil material, were used to establish a plausible set of chemical reactions that would simulate the observed changes in water quality during the batch-mixing experiment. The coal-aquifer water, before contact with the spoil material (sample B1), was considered to be the initial water, and the water derived from the batch-mixing experiment was considered to be the final water in the mass-balance calculations. The chemical data for the initial water and the water derived from the batch-mixing experiments are given in table 9. Numerous reaction combinations reasonably could be used to explain the observed changes in ground-water quality during the batch-mixing experiments.

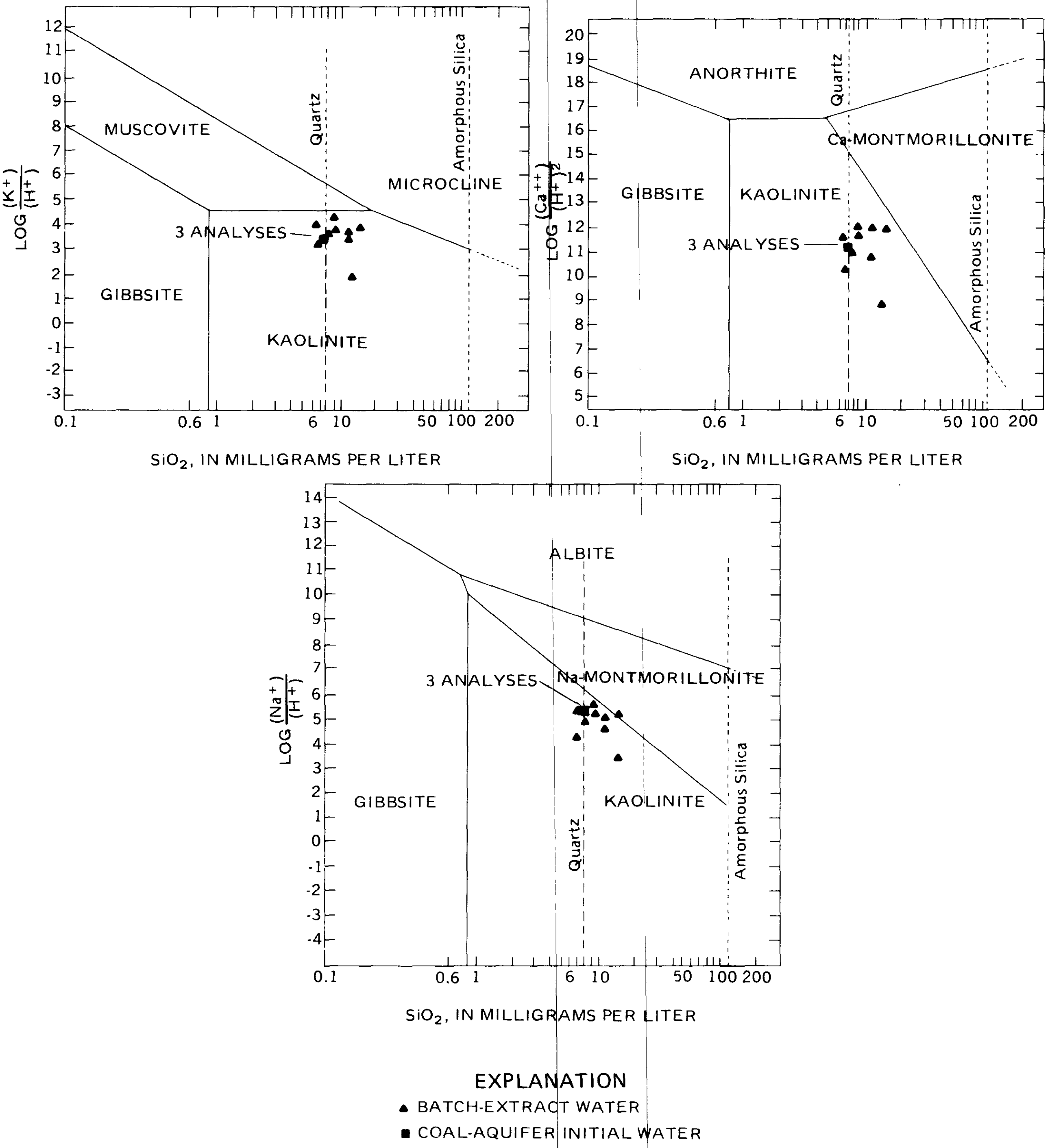


Figure 18.--Relation of batch-extract and coal-aquifer initial water within the stability fields of selected aluminosilicates at 25 °C and 1 atmosphere (from Tardy, 1971).

Plausible phases considered in the following geochemical reaction models for spoil sample B1 were based upon the mineralogical analyses of the spoil material. Seven sets of phases were considered (table 10). In each of the seven sets of phases considered, potassium was derived from the dissolution of potassium feldspar; magnesium from chlorite or epsomite, or both; sodium from cation exchange and halite dissolution; chloride from halite dissolution; and silica from potassium feldspar and chlorite. Chalcedony and kaolinite precipitation were the sinks for silica, and kaolinite was the sink for aluminum.

Table 9.--Chemical analyses of water before and after batch-mixing experiment B1 using water from the coal aquifer

[Concentration in milligrams per liter; abbreviation: <, less than]

Constituent	Initial water[1], mean concentration (three samples)	Final water[2] (one sample)
Calcium	45	220
Magnesium	17	80
Sodium	240	310
Potassium	7.5	25
Sulfate	2.0	990
Chloride	12	14
Fluoride	.9	.2
Silica	7.8	8.0
Aluminum	.020	.020
Iron	<.003	.012
Total alkalinity (as HCO_3^-)	910	710

[1] Water before contact with spoil material; pH = 7.22 (geometric mean).

[2] Water derived from the batch-mixing experiment; pH = 6.87.

Possible sources considered for the observed sulfate increases included the minerals pyrite, gypsum, and epsomite. In reaction set 1, pyrite oxidation was the only source of sulfate considered, whereas in reaction sets 2 and 3 gypsum also was considered. In reaction sets 4, 5, and 6, gypsum dissolution was the only source of sulfate considered, whereas in reaction set 7, epsomite also was considered in combination with gypsum.

Table 10.--Selected sets of plausible phases for mass-balance calculations for spoil sample B1

Reaction set	Plausible phases
1	Silica, goethite, kaolinite, potassium feldspar, halite, cation exchange, chlorite, carbon dioxide, oxygen, pyrite, calcite.
2	Silica, goethite, kaolinite, potassium feldspar, halite, cation exchange, chlorite, carbon dioxide, oxygen, pyrite, gypsum.
3	Silica, goethite, kaolinite, potassium feldspar, halite, cation exchange, chlorite, oxygen, pyrite, calcite, gypsum.
4	Silica, goethite, kaolinite, potassium feldspar, halite, cation exchange, chlorite, organic carbon, calcite, oxygen, gypsum.
5	Silica, goethite, kaolinite, potassium feldspar, halite, cation exchange, chlorite, calcite, oxygen, gypsum, carbon dioxide.
6	Silica, kaolinite, potassium feldspar, halite, cation exchange, chlorite, calcite, gypsum, carbon dioxide.
7	Silica, kaolinite, potassium feldspar, halite, cation exchange, chlorite, calcite, gypsum, epsomite.

The minerals pyrite and chlorite were considered as possible sources of iron; goethite was the only iron sink considered. Although the change in iron concentration during batch-mixing experiment B1 was essentially zero (table 9), iron was still considered as a reactant in selected mass-balance calculations. In reaction sets 1, 2, and 3 pyrite was the only iron source. Chlorite weathering was the source of iron in reaction sets 4 and 5. As noted by Powell and Larson (1985, p. 7), ferrous iron can substitute for magnesium in the chlorite structure. Reaction sets 6 and 7 did not include iron sources or sinks.

Carbon sources and sinks considered in the reaction sets included calcite, carbon dioxide, and organic matter (that is, carbon valence of 0). Reaction sets 1, 2, 5, and 6 were open to exchange with CO_2; reaction sets 3, 4, and 7 were not.

Both redox and nonredox reaction sets were considered as possible geochemical reaction models. Redox reactions were considered in reaction sets 1, 2, 3, 4, and 5. Redox reactions considered included pyrite oxidation (table 1, reaction 1), oxidation of ferrous iron (table 1, reaction 3), and oxidation of organic matter (table 1, reaction 4).

The results of the speciation calculations are given in table 11. These results include the total molality (mmol/kg water) of inorganic carbon, calculated from the alkalinity and pH of the waters.

The redox state (RS) is shown in table 11 and is a means of keeping track of electron transfer in the redox reactions which were considered. Redox state is defined as follows:

$$RS = \sum_{i=1}^{I} v_i m_i$$

where: I is the total number of species in solution,

m_i is the molality of the i'th species in solution, and

v_i is the operational valence of the species.

Plummer and others (1983, p. 665-686) addressed the definition of operational valence. The redox state of the initial water was calculated with an assumed dissolved-oxygen concentration of 8.0 mg/L due to the exposure of the water to the atmosphere before use in the batch-mixing experiments. The initial recharge waters entering the spoil aquifer possibly would have large concentrations of dissolved oxygen, similar to the initial water used in the batch-mixing experiments. As noted by Groenewold and others (1983, p. 138-139), large volumes of air are entrapped within the voids of the spoil aquifer that could dissolve into the initial recharge waters.

Mass-balance calculation results for the seven reaction sets of combined plausible phases (table 10) identified reaction models that can be used to explain water-quality changes that occurred during the batch-mixing experiment in which material from spoil-sample B1 was used (table 12). Each reaction model in table 12 represents the results of a particular combination of the plausible phases considered. The values in the columns indicate the quantity of each phase (in millimoles per kilogram of water) either entering or leaving the water. A positive value indicates dissolution of the phase; a negative value (-) indicates formation of the phase.

Water-quality changes that occurred during batch-mixing experiment B1 probably were not accurately represented by models 1, 2, 3, and 4 (table 12). Models 1, 2, 3, and 4 showed that additional oxygen be added to the water during the batch-mixing experiment to allow for the subsequent oxidation of pyrite or organic matter (table 12). Although small amounts of oxygen might have been available within the pore spaces of the spoil material used in the batch-mixing experiment, the lack of oxygen exchange with the atmosphere during the batch-mixing experiments prevented the large inputs of oxygen required in the mass-balance calculations. Furthermore, oxidation of large amounts of pyrite without buffering by carbonate dissolution (models 2 and 3) would have caused a large decrease in pH; however, such a decrease was not observed during this batch-mixing experiment. Finally, model 1 can be discounted because a large amount of calcite dissolution from an initial water oversaturated with respect to calcite (table 12) also would be required.

Table 11.--Results of speciation calculations for batch-mixing experiment B1 using the computer program WATEQF

[Data in millimoles per kilogram unless otherwise noted. Saturation index: a positive value indicates precipitation of the mineral phase; a negative (-) value indicates dissolution of the mineral phase]

Constituent or parameter	Initial water[1], mean concentration (three samples)	Final water[2]
Calcium	1.123	5.490
Magnesium	.699	3.292
Sodium	10.439	13.482
Potassium	.192	.639
Sulfur	.021	10.306
Chloride	.338	.395
Silica	.130	.133
Aluminum	.001	.001
Iron	.000	.000
Inorganic carbon (total)	16.691	14.513
Redox state	[3]67.140	119.888
Saturation index:		
Calcite	.25	.24
Gypsum	-3.57	-.54

[1] Water before contact with spoil material.

[2] Water derived from the batch-mixing experiment.

[3] Redox state calculated for the initial water, assuming a dissolved-oxygen concentration of 8.0 mg/L.

Reaction models 5, 6, and 7 were consistent with the saturation indices for calcite and gypsum and did not require that large amounts of oxygen dissolve during batch-mixing experiment B1 (table 12). Reaction models 5 and 6 did require that additional amounts of carbon dioxide dissolve. The source of the carbon dioxide during the batch-mixing experiment could be gas that was entrapped within the pore spaces prior to the spoil material being mixed with the water. Reaction model 7 was closed to carbon dioxide exchange and did not require additional amounts of oxygen. Reaction model 5, 6, and 7, or any combination of these models, may accurately represent the chemical system during the batch-mixing experiment.

Table 12.--Results of mass-balance calculations for the batch-mixing experiment using material from spoil-sample B1

[Data for phases shown in millimoles per kilogram of water;
a positive value indicates dissolution of the phase;
a negative value (-) indicates formation of the phase]

Plausible phases	Reaction model 1	2	3	4	5	6	7
Silica	-1.4096	-1.4096	-1.4096	-1.7553	-1.7553	-1.4096	-0.9602
Goethite	-5.1425	-2.2125	-1.1235	-1.7287	-1.7287	--	--
Kaolinite	-.7421	-.7421	-.7421	-1.0878	-1.0878	-.7421	-.2927
Potassium feldspar	.4470	.4470	.4470	.4470	.4470	.4470	.4470
Halite	.0570	.0570	.0570	.0570	.0570	.0570	.0570
Cation exchange	1.4930	1.4930	1.4930	1.4930	1.4930	1.4930	1.4930
Chlorite	.5186	.5186	.5186	.8643	.8643	.5186	.0692
Carbon dioxide	-8.0380	-2.1780	--	--	2.2470	2.2470	--
Oxygen	19.2219	8.2344	4.1506	2.6167	.3697	--	--
Pyrite	5.1425	2.2125	1.1235	--	--	--	--
Calcite	5.8600	--	-2.1780	-4.4250	-4.4250	-4.4250	-2.1780
Gypsum	--	5.8600	8.0380	10.2850	10.2850	10.2850	8.0380
Organic carbon	--	--	--	2.2470	--	--	--
Epsomite	--	--	--	--	--	--	2.2470

The reaction-path model PHREEQE (Parkhurst and others, 1982b) was used to simulate the water-quality changes during batch-mixing experiment B1. The initial water was saturated with oxygen. For the reaction simulation, halite, chlorite, gypsum, and epsomite were added in the stoichiometric proportions indicated in reaction set 7 (table 12). During the addition of these four phases, cation exchange and calcite precipitation were simulated.

Due to the short time involved in the batch-mixing experiments, oversaturation with respect to calcite was maintained at 0.25 (log ion activity product/equilibrium constant) during the reaction simulation. Calcite precipitation in solutions with a calcite saturation index of less than 0.5 is relatively slow when considering the short time of the batch-mixing experiments.

Selection and use of an exchange constant (K_{ex}) for the simulation of the Ca-Na exchange reaction considered in the reaction simulation has been discussed by Thorstenson and others (1979). As noted by Thorstenson and others (1979), Parkhurst and others (1982b), and Drever (1982, p. 82-85), K_{ex} values are not true equilibrium constants but change as the composition of the exchanger is modified. For the reaction simulation, the activity ratio of $(aNa^{2+})/(aCa^{2+})$ was fixed in order to simulate Ca-Na ion exchange. Three activity ratios bracketing the mean Na-Ca activity ratio of 0.057 in the 12 batch-extract waters were used in the following reaction-path-simulation calculations (table 13). The implications of using a fixed activity ratio to simulate cation exchange during reaction simulation have been discussed by Parkhurst and others (1982b, p. 49-50).

The results of the reaction-path simulation for batch-mixing experiment B1 compared favorably to the actual concentrations of selected constituents in batch-extract water B1 (table 13). The reaction simulation did not include the effects of hydrolysis of potassium feldspar and the formation of kaolinite. With the introduction of potassium feldspar hydrolysis, hydronium ions in solution would be replaced by potassium. Removal of hydronium ions from solution would increase the pH, decrease the pCO_2 (partial pressure of carbon dioxide), and increase the alkalinity of the water. Based on the small amount of potassium feldspar dissolution predicted by model 7 and the production of hydronium ions from additional calcite precipitation (table 1, reactions 5 and 10), exclusion of these parameters from the reaction simulation should not have a pronounced change on the simulated water quality.

Based on the saturation index for gypsum in batch-extract water B1 (table 11), additional amounts of gypsum could have dissolved. Using the same plausible reactions considered in the previous reaction-path simulation, further dissolution of gypsum in batch-extract water B1 would have caused further increases in calcium, sodium, and sulfate, while decreasing the concentration of bicarbonate and C_T, as well as pH, due to carbonate precipitation. These reactions, driven by gypsum dissolution, could have continued until gypsum saturation or the exchange capacity of the clays was reached.

COMPARISON OF BATCH-EXTRACT AND ACTUAL POSTMINING WATER QUALITY

The batch-extract water quality was compared with the actual postmining water quality in well SPL2, which was completed in the spoil aquifer. Major-ion concentrations and pH were used in the comparison. Concentrations were compared to evaluate how well the batch-mixing experiments using water from the coal aquifer simulated the postmining ground-water quality in the spoil aquifer. Furthermore, this comparison was used to infer possible reactions controlling the water quality in the spoil aquifer.

Sulfate in batch-extract waters was consistently smaller than actual sulfate concentrations in the water from the spoil aquifer (fig. 19). Due to the water-to-rock ratio (2:1, by weight) used in the batch-mixing experiments, the small sulfate concentration in the batch-extract waters, relative to the sulfate concentration in water from the spoil aquifer, possibly was related to the limited amount of gypsum and oxidizable sulfide available for dissolution or oxidation. Batch-extract waters from batch-mixing experiments using a 5:1 water-to-rock ratio by weight were smaller in sulfate concentration than waters from batch-mixing experiments using a 2:1 ratio (fig. 20). During

Table 13.--Summary of reaction-path simulation for batch-mixing experiment B1, using the plausible phases in model 7 from the mass-balance calculations

[Values shown are mean concentration in millimoles per kilogram of solvent unless noted. Abbreviations: meq/L, milliequivalents per liter; log atm., log atmosphere; pCO_2, partial pressure of carbon dioxide in atmospheres]

Constituent or characteristic	Initial leach water (three samples)	Batch-extract water		
		Analyzed (one sample)	Calculated concentration		
			Activity ratio of $(sodium)^2$ to calcium		
			0.079	0.063	0.050
Calcium	1.123	5.490	5.277	5.695	6.105
Magnesium	.699	3.292	3.292	3.292	3.292
Sodium	10.439	13.482	14.890	13.624	12.591
Sulfate	.021	10.306	10.306	10.306	10.306
Chloride	.338	.395	.400	.400	.400
pCO_2 (log atm.)	-1.299	-1.090	-1.090	-1.073	-1.058
Total inorganic carbon	16.691	14.513	14.890	14.774	14.667
Alkalinity (meq/L)	14.932	11.636	12.030	11.798	11.584
pH	7.22*	6.87	6.88	6.86	6.83

Plausible phases	Calculated mass transfer (mass balance calculations, model 7)†	Calculated mass transfer (reaction-path model)†		
		Activity ratio of $(sodium)^2$ to calcium		
		0.079	0.063	0.050
Epsomite ($MgSO_4 \cdot 7H_2O$)	2.247	2.247	2.247	2.247
Gypsum ($CaSO_4 \cdot 2H_2O$)	8.038	8.038	8.038	8.038
Calcium-sodium exchange	1.493	2.089	1.555	1.038
Calcite ($CaCO_3$)	-2.178	-1.801	-1.917	-2.024
Halite (NaCl)	.057	.057	.057	.057

*Geometric mean.

†Amount of each phase dissolved (positive value) or precipitated (negative value).

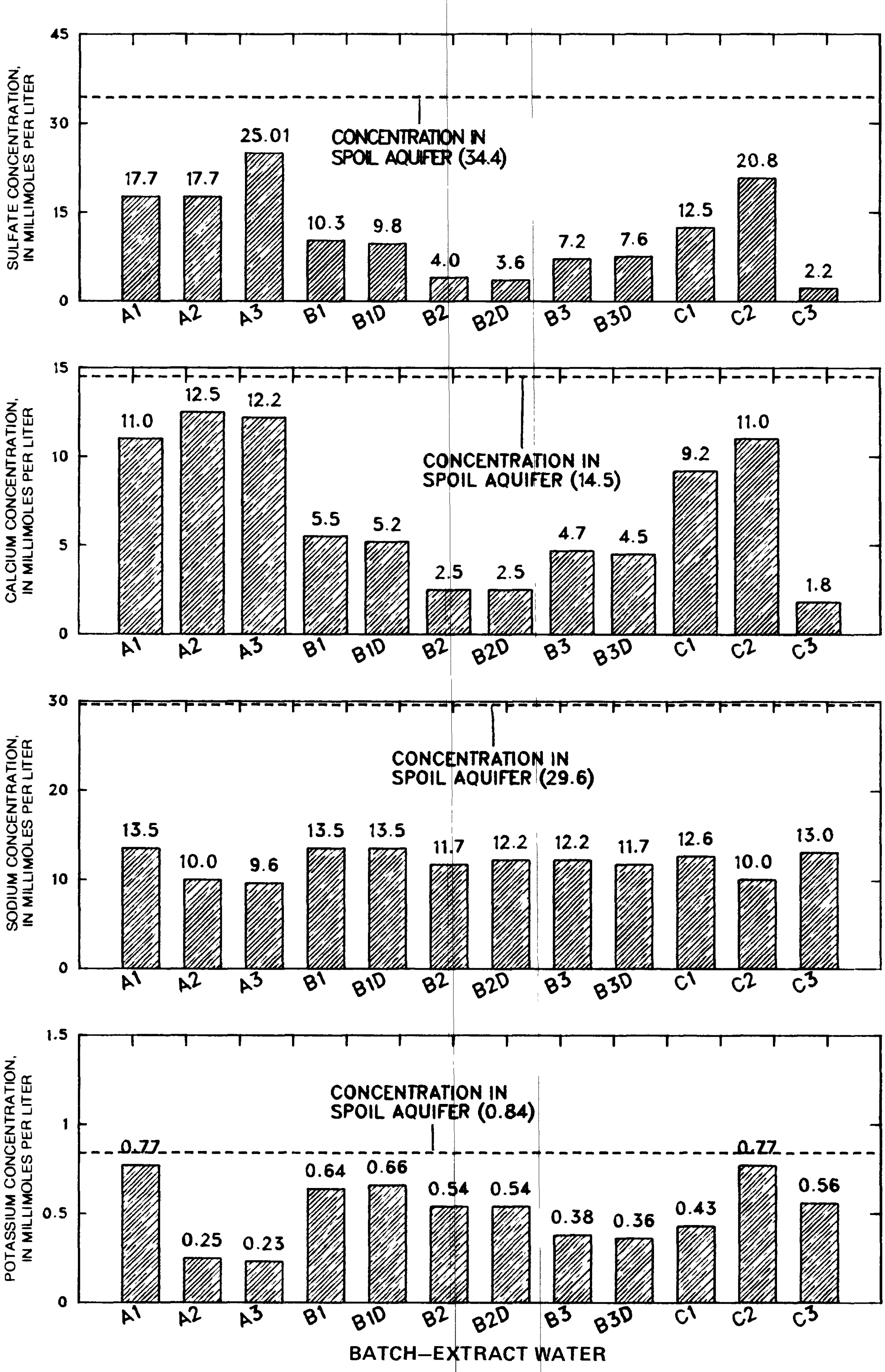


Figure 19.--Comparison of batch-extract and actual concentrations of sulfate, calcium, sodium, and potassium in water from the spoil aquifer.

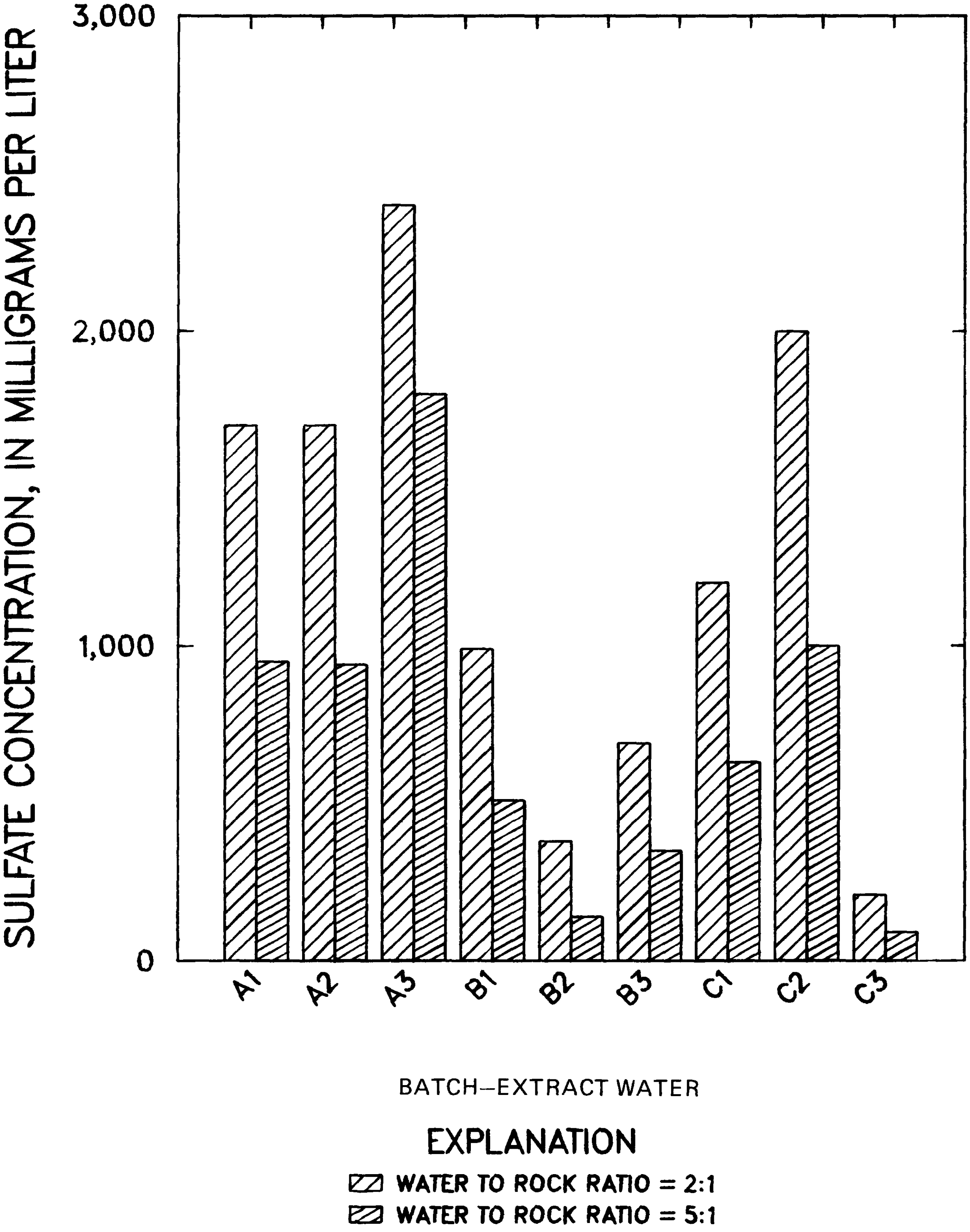


Figure 20.--Sulfate concentrations in batch-extract water derived from 2:1 and 5:1 water-to-rock ratios, by weight.

recharge of the spoil aquifer, the initial recharge waters contacting the spoil material had the potential to contact large amounts of reactive minerals, resulting in saturation with respect to gypsum and correspondingly large sulfate concentrations.

The smaller amount of gypsum dissolution during the batch-mixing experiments also affected the concentrations of calcium and sodium in the batch-extract waters. Due to the large water-to-rock ratio used in the batch-mixing experiments, the amount of gypsum dissolution in the batch-mixing experiments was decreased resulting in calcium concentrations in the batch-extract waters that were smaller than that observed in the water from the spoil aquifer (fig. 19). The depressed sodium concentrations in the batch-extract waters (fig. 19) probably were the result of limited calcium-sodium ion exchange due to decreased calcium input from gypsum dissolution.

Potassium concentrations in the batch-extract water were less than the actual postmining ground water (fig. 19). Assuming the principal source of potassium was from hydrolysis of potassium feldspar, it is possible that the 24-hour limit of the batch-mixing experiments prevented additional inputs of potassium. As mentioned previously, silicate hydrolysis has a kinetically rapid dissolution step (minutes) followed by a gradually decreasing rate of dissolution.

Alkalinity and C_T concentrations, as well as pH values, generally were larger in the batch-extract waters relative to their concentrations in the water from the spoil aquifer (fig. 21). The large alkalinity C_T and pH in the batch-extract waters largely was due to the lack of carbonate precipitation driven by the limited amount of gypsum dissolution during the batch-mixing experiments. Furthermore, in contrast to the batch-extract waters, the water from the spoil aquifer had a longer time to reach a steady state with respect to kinetically slower reactions such as carbonate precipitation. Additional carbonate precipitation could have resulted in decreases in bicarbonate alkalinity and C_T concentrations as well as pH.

Magnesium and chloride concentrations were consistently smaller in the waters obtained from the batch-mixing experiments than in the water collected from the spoil aquifer (fig. 21). A possible source of magnesium and chloride within the batch-extract waters included dissolution of efflorescent salts. Because of the 2:1 water-to-rock ratio used in the batch-mixing experiments, a relatively small amount of efflorescent salts per volume of water could explain the smaller magnesium and chloride concentrations. However, the water collected from the spoil aquifer could have had contact with larger amounts of efflorescent salts for a specified volume of water, resulting in elevated concentrations in magnesium and chloride. Surface waters recharging the spoil aquifer could have increased concentrations of chloride due to evaporation. Water sometimes is collected or pumped to surface ponds for use in dust suppression during normal mining operations at the Cordero Mine.

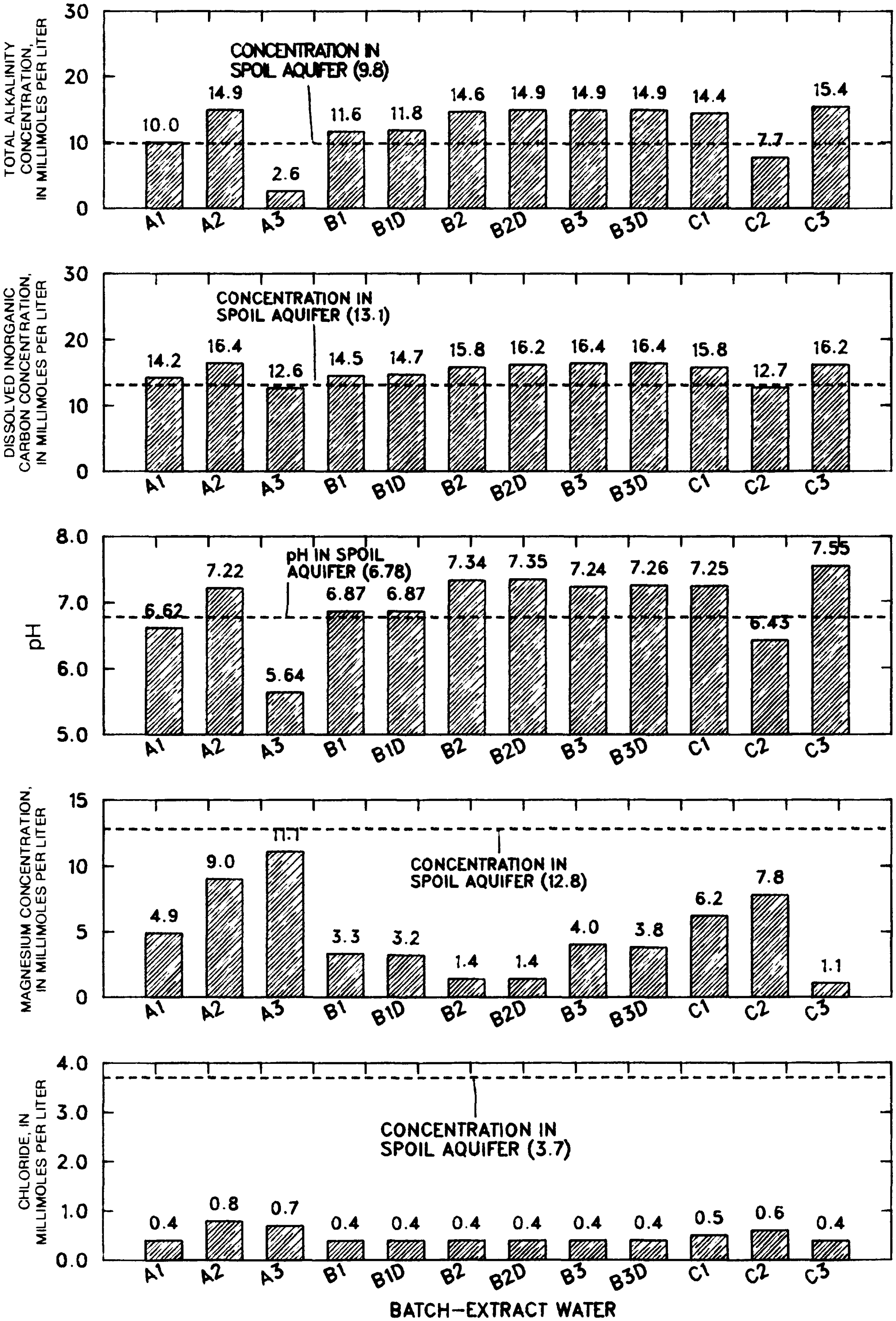


Figure 21.--Comparison of batch-extract and actual pH and concentrations of total alkalinity, dissolved inorganic carbon, magnesium, and chloride in water from the spoil aquifer.

Mean correction ratios were calculated for selected constituents in the batch-extract waters (table 14). Correction ratios were calculated by

$$R_c = \frac{C_s}{C_b} ,$$

where R_c is the correction ratio (unitless), C_s is the concentration of a particular constituent in the spoil aquifer, and C_b is the concentration of the same constituent in the batch-extract water. A correction ratio greater than 1.00, indicates that the concentration of a particular constituent is smaller in the batch-extract water than in the natural system (that is, spoil aquifer). A correction ratio less than 1.00, indicates that the concentration of a particular constituent is greater in the batch-extract waters than in the spoil aquifer.

Mean correction ratios calculated for the 2:1 (water to rock) batch-extract waters range from 1.13 for alkalinity to 7.75 for chloride (table 14). Mean correction ratios greater than 1.00 for the batch-extract waters verify the dilute nature of the batch-extract waters compared to the water from the spoil aquifer at the Cordero Mine. The large standard deviations associated with the mean correction ratios are due to the nonhomogeneous nature of the spoil aquifer material.

The initial recharge waters to the spoil aquifer at the Cordero Mine have contacted relatively large amounts of soluble salts on the spoil material. Future recharge waters to the spoil aquifer will contact lesser amounts of soluble materials due to the flushing effect of the previous recharge waters, resulting in decreasing concentrations of dissolved solids. Additional study is needed to address possible mixing and chemical reactions that occur as the postmining ground water moves offsite and possibly flows through a coal aquifer.

Batch-mixing experiments in combination with correction ratios could be a useful method for predicting the water quality of postmining ground water at other coal mines in the Powder River basin of Wyoming. If additional batch-mixing experiments were conducted at other mines with existing spoil aquifers, a more accurate estimation of correction ratios for each chemical constituent could be made. These correction ratios then could be used in combination with batch-mixing experiments at future lease areas or mines without existing spoil aquifers to predict the quality of the ground water after mining.

Table 14.--Mean correction ratios for selected chemical constituents in waters derived from batch-mixing experiments using water from the coal aquifer

[Correction ratio equals dissolved concentration in spoil aquifer divided by the dissolved concentration in batch-extract water]

Chemical constituent	Mean correction ratio (nine samples)	Standard deviation
Calcium	2.68	2.56
Magnesium	4.08	3.73
Sodium	2.55	.35
Potassium	1.97	.95
Sulfate	4.66	4.68
Chloride	7.75	1.93
Alkalinity	1.13	1.01

CONCLUSIONS

1. Results obtained from the batch-mixing experiments were related to the type of water used (that is, water from the spoil aquifer or water from the coal aquifer). On the basis of results of experiments that use water from the spoil aquifer, it is concluded that contact of postmining ground water with fresh spoil material will cause small changes in major-element concentrations and pH, unless sulfide oxidation or contact with soluble salts, such as epsomite, occurs. The initial leach water from the spoil aquifer was saturated with respect to gypsum, preventing further gypsum dissolution during the batch-mixing experiments using water from the spoil aquifer. In contrast, large changes in major-element concentrations were observed in batch-extract water using coal-aquifer initial water. The initial leach water from the coal aquifer was undersaturated with respect to gypsum (saturation index less than -3.0) and allowed additional gypsum dissolution during the batch-mixing experiments.

2. Mass-transfer modeling using U.S. Geological Survey computer programs WATEQF and BALANCE was applied to batch-mixing experiment B1 (using water from the coal aquifer) in order to evaluate possible water and rock interactions. In the seven reaction models considered, potassium was derived from potassium feldspar; magnesium from chlorite or epsomite, sodium from cation exchange and halite; chloride from halite; silica from potassium feldspar and chlorite; sulfate from pyrite, gypsum or epsomite, or both; iron from pyrite and chlorite; and carbon from calcite, carbon dioxide, and organic matter. Only three of seven reaction models were consistent with all the data. In the three models used to account for the observed water-quality changes, potassium was derived from potassium feldspar; magnesium from chlorite or epsomite, or both; sodium from cation exchange and halite; chloride from halite; silica from potassium feldspar and chlorite; sulfate from gypsum or epsomite, or

both; and carbon from carbon dioxide. Once the probable reactions were identified, the U.S. Geological Survey computer program PHREEQE was used to simulate the water-quality changes that occurred during batch-mixing experiment B1. The simulated water quality closely approximated the quality of water derived from batch-mixing experiment B1.

3. Comparison of the batch-extract waters using coal-aquifer initial water with the actual postmining ground-water quality at the Cordero Mine reveals large differences in major-ion concentrations and pH. These differences can be explained on a qualitative scale by the limited amount of gypsum dissolution/volume of water used in the batch-mixing experiments. Mean correction ratios for major ions, calculated to normalize the batch-mixing results to the observed water quality of the spoil aquifer, ranged from 1.13 to 7.75. The major-ion concentrations and pH values obtained from the batch-mixing experiments using water from the coal aquifer possibly represent the long-term postmining ground-water quality in the spoil aquifer. If additional batch-mixing experiments were conducted at other mines that have existing spoil aquifers, a more accurate estimation of correction ratios for each chemical constituent could be made. These correction ratios then could be used in combination with batch-mixing experiments at future lease areas or mines without existing spoil aquifers to predict the quality of the ground water after mining.

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