

# EFFECTS OF SELECTIVE HANDLING OF PYRITIC, ACID-FORMING MATERIALS ON THE CHEMISTRY OF PORE GAS AND GROUND WATER AT A RECLAIMED SURFACE COAL MINE, CLARION COUNTY, PA, USA<sup>1</sup>

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**Abstract:** A change from dragline to “selective handling” mining methods at a reclaimed surface coal mine in western Pennsylvania did not significantly affect concentrations of metals in ground water because oxidation of pyrite and dissolution of siderite were not abated. Throughout the mine, placement of pyritic material near the land surface facilitated the oxidation of pyrite, causing the consumption of oxygen (O<sub>2</sub>) and release of acid, iron, and sulfate ions. Locally in the unsaturated zone, water sampled within or near pyritic zones was acidic, with concentrations of sulfate exceeding 3,000 milligrams per liter (mg/L). However, acidic conditions generally did not persist below the water table because of neutralization by carbonate minerals. Dissolution of calcite, dolomite, and siderite in unsaturated and saturated zones produced elevated concentrations of carbon dioxide (CO<sub>2</sub>), alkalinity, calcium, magnesium, iron, and manganese. Alkalinity concentrations of 600 to 800 mg/L as CaCO<sub>3</sub> were common in water samples from the unsaturated zone in spoil, and alkalinities of 100 to 400 mg/L as CaCO<sub>3</sub> were common in ground-water samples from the underlying saturated zone in spoil and bedrock. Saturation indices indicated that siderite could dissolve in water throughout the spoil, but that calcite dissolution or precipitation could occur locally. Calcite dissolution could be promoted as a result of pyrite oxidation, gypsum precipitation, and calcium ion exchange for sodium. Calcite precipitation could be promoted by evapotranspiration and siderite dissolution, and corresponding increases in concentrations of alkalinity and other solutes. Partial pressures of O<sub>2</sub> (P<sub>O<sub>2</sub></sub>) and CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub>) in spoil pore gas indicated that oxidation of pyrite and precipitation of ferric hydroxide, coupled with dissolution of calcite, dolomite, and siderite were the primary reactions affecting water quality. Highest vertical gradients in P<sub>O<sub>2</sub></sub>, particularly in the near-surface zone (0-1 m), did not correlate with concentrations of total sulfur in spoil. This lack of correlation could indicate that total sulfur concentrations in spoil do not reflect the amount of reactive pyrite or that oxidation rates can be controlled more by rates of O<sub>2</sub> diffusion than the amount of pyrite. Hence, if placed in O<sub>2</sub>-rich zones near the land surface, even small amounts of disseminated pyritic material can be relatively significant sources of acid and mineralized water.

## Introduction

Acidification and mineralization of ground water commonly result from the accelerated oxidation of pyrite (FeS<sub>2</sub>) and the consequent dissolution of other minerals exposed during surface coal mining. Innovative mining and reclamation techniques, such as “selective handling,” have potential to reduce water-quality degradation by minimizing these processes. Selective handling involves the segregation of pyritic, high-sulfur overburden during mining and the subsequent burial of this material in compacted pods in the backfill. In the Appalachian Coalfield of the Eastern United States, the pyritic pods commonly are encapsulated with alkaline materials and are placed below the plant-root zone but above the projected, postreclamation ground-water table within the backfill (Pionke and Rowgowski 1982; Phelps and Saperstein 1982; Geidel and Caruccio 1984). The objectives of selective handling are to (1) minimize transport of acid by preventing contact between ground water and pyritic materials or minimize oxidation of pyrite by limiting its exposure to oxygen, and (2) add alkalinity to infiltrating water, which can slow acid production, neutralize acid, and reduce the mobility of metals (Williams et al. 1982). If the objectives can be realized, mining with selective-handling techniques may be permitted in areas and on coal seams where traditional mining methods produced acidic ground water and mine drainage.

This paper evaluates the effects of selective handling of pyritic overburden materials on the chemistry of pore gas and ground water, and the mechanisms of producing alkalinity, at a reclaimed surface coal mine in western Pennsylvania. In a companion paper, Cravotta et al. (1994) give details of the geochemical and geohydrological characteristics of bedrock and spoil at the study area.

The study area is a reclaimed surface coal mine on two hilltops in southern Clarion County, PA (fig. 1). During 1980-86, the middle and lower Kittanning coals were mined (Glover 1987). The mined coalbeds were less than 1 m

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thick, dipped gently west-northwest, and were separated by about 18 to 20 m of medium- to dark-gray shale which graded upward to siltstone and claystone (Cravotta et al. 1994). The lower Kittanning coal and a 1.2-m-thick stratum of carbonaceous shale overlying the coal were pyritic, had total sulfur (S) concentrations greater than 2.5 weight percent (wt %), and were laterally continuous across the mine. Calcareous shale and siltstone above these strata had neutralization potential (NP) values as high as 125 grams as calcium carbonate per kilogram (g/kg CaCO<sub>3</sub>) and generally thinned northward across the mine. Most of the overburden had total S concentrations less than 1 wt % and NP values less than 25 g/kg CaCO<sub>3</sub>. Mass-weighted averages of net-neutralization potential (NNP) for spoil were negative and decreased northward (Cravotta et al. 1994).

Different methods were used to handle overburden and spoil at the mine (Cravotta et al. 1994). In the northern area, bulldozers and front-end loaders were used to selectively handle the pyritic shale overlying the lower Kittanning coal and to add crushed limestone (56 Mg/ha) to the pit floor and spoil. The selectively handled material was layered on benches of low-S (<0.2 wt %) material in the unsaturated zone. Disposal of the pyritic material below the water table would not have been practical because of the locally thin saturated zone in the backfill (Cravotta et al. 1994). In the southern area, a dragline was used. High-S (≥0.5 wt %) material was placed above intermediate-S material in the unsaturated zone. In the middle area, where mining methods used are uncertain, high-S material was placed near the surface and on the pit floor, within the zone of water-table fluctuation.

### Experimental Design and Methods

Different mining methods can have different effects on ground-water quality by altering the distribution of acid-forming and alkaline-producing materials, spoil permeability and pore-gas-exchange rates, and ground-water recharge and flow paths, because these factors determine the sequence and extent of water-rock interactions. Hence, a nested monitoring network was designed and installed to measure chemical variations in the unsaturated and saturated zones in areas mined by different methods.

### Monitoring Network

In each of the northern, middle, and southern areas, a minimum of four clusters of two or more boreholes were drilled in spoil and underlying bedrock by air-rotary methods during November 1991. At least one cluster, or monitoring nest, in each area included boreholes for ground-water (saturated-zone) sampling, pore-water (unsaturated-zone) sampling, and pore-gas sampling (fig. 1). Figure 2 shows construction details for monitoring nest components. At all monitoring nests, except at nest S4, where only one well was installed, two ground-water wells were installed in adjacent boreholes approximately 1.5 m apart; one well was screened in the horizon of the lower Kittanning coal to depths from 13.4 to 32.6 m, and the other well was screened in the unmined underlying bedrock at a 4.6-m greater depth (Cravotta et al. 1994). Each well was constructed of 5.1-cm-diameter, polyvinyl chloride (PVC) pipe with a slotted screen at least 3-m long. At many nests, PVC pressure-vacuum lysimeters with ceramic tips (Parizek and Lane 1970) and polyethylene gas-sampling tubes were installed in unsaturated mine spoil. Lysimeter tips and gas-sampling ports were placed at depths of 1 to 1.5 m, 4 to 4.6 m, 7 to 7.6 m, and 10.7 to 11 m below the spoil surface to enable comparison of chemical concentrations in pore-water and pore-gas samples, respectively, at comparable depths.

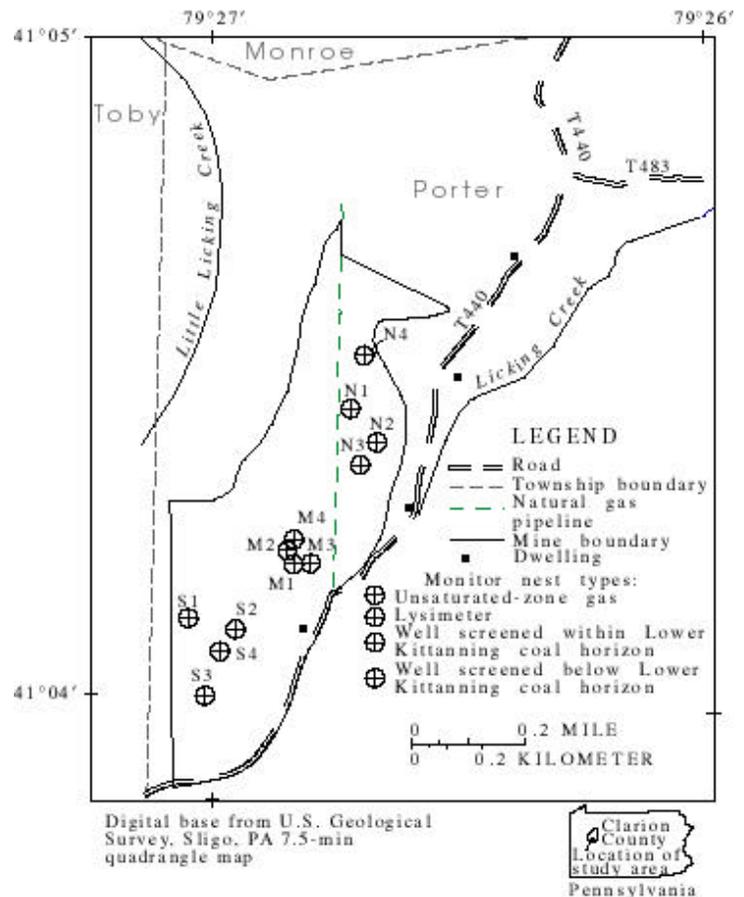


Figure 1. Location of monitoring sites at reclaimed surface coal mine in southern Clarion County, PA.

## Sampling and Analytical Methods

Rock samples from each borehole were collected as composites of drill cuttings over 1.5-m intervals and were logged for lithology. Rock samples from selected holes also were analyzed for mineralogical and chemical content, including total S, total C, and NP, as described by Cravotta et al. (1994).

During February-December 1992, samples of gas and water were collected monthly. Pore-gas and ambient air samples were collected directly into 1-L Tedlar bags within an airtight chamber that was evacuated with a hand-operated pressure-vacuum pump. Pore water from the unsaturated zone was collected into evacuated lysimeters, and samples were retrieved by applying pressure with a hand pump (Parizek and Lane 1970). Ground-water samples from spoil and bedrock were collected after purging water from each monitoring well with PVC bailers.

Field measurements and sample processing were conducted by use of methods of Wood (1976) and Claassen (1982). Before purging wells, ground-water levels, temperature, and dissolved oxygen were measured with downhole probes. After purging, specific conductance and redox potential (Eh) were measured by draining water from the bailer into a glass flow cell. Water samples were stored in polyethylene bottles on ice until laboratory analysis. One subsample for analysis of pH, acidity, alkalinity, sulfate, chloride, and nutrients was capped without head space. The second subsample for analysis of dissolved metals and silica was filtered through a 0.45- $\mu\text{m}$ -pore nitrocellulose filter, transferred to an acid-rinsed bottle, and preserved with nitric acid.

Chemical analyses were conducted at the Pennsylvania Department of Environmental Resources (PaDER) Bureau of Laboratories facility in Harrisburg, PA. Concentrations of  $\text{O}_2$  and  $\text{CO}_2$  in gas samples were measured by gas chromatography according to methods of Bremner and Blackmer (1982). Laboratory pH and concentrations of alkalinity, acidity, calcium, magnesium, sodium, potassium, nitrate, ammonia, phosphate, chloride, fluoride, sulfate, iron, manganese, aluminum, silica, and selected trace metals in water samples were analyzed by methods of Skougstad et al. (1979). Alkalinity and acidity were estimated by use of pH 3.9 and 8.2 titration endpoints, respectively. Chemical data for gas and water samples were reported by Lescinsky et al. (1993).

## Data-Analysis Methods

Computerized graphical, statistical, and geochemical modeling methods were used to evaluate the pore-gas and water-chemical data. Statistical tests for differences among data subsets were conducted by use of notched boxplots (Velleman and Hoaglin 1981) generated by the P-Stat EDA procedure (P-Stat 1989). If the notches on either side of medians in a pair of boxplots do not overlap, the medians for the two subsets are significantly different at the 95-percent confidence level (Velleman and Hoaglin 1981). Aqueous speciation and mineral saturation indices for selected water samples were computed by use of WATEQF (Plummer et al. 1976).

### Effects of Selective Handling of Pyritic, Acid-Forming Material

Segregation of pyritic, high-sulfur materials in pods surrounded by calcareous material and placed above the water table hypothetically can reduce the production of acidic ground water and increase the neutralization of acid and production of alkaline ground water. Oxidation of pyrite, the principal sulfur-bearing mineral at the mine (Cravotta et al. 1994), consumes  $\text{O}_2$  and releases acid, iron, and sulfate. Dissolution of carbonate minerals, predominantly calcite ( $\text{CaCO}_3$ ), dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], siderite ( $\text{FeCO}_3$ ), and manganosiderite [ $(\text{Fe,Mn})\text{CO}_3$ ], which were present in noncoal horizons at the mine (Cravotta et al. 1994), can neutralize acid and produce  $\text{CO}_2$ , alkalinity, and dissolved calcium, magnesium, iron, and manganese.

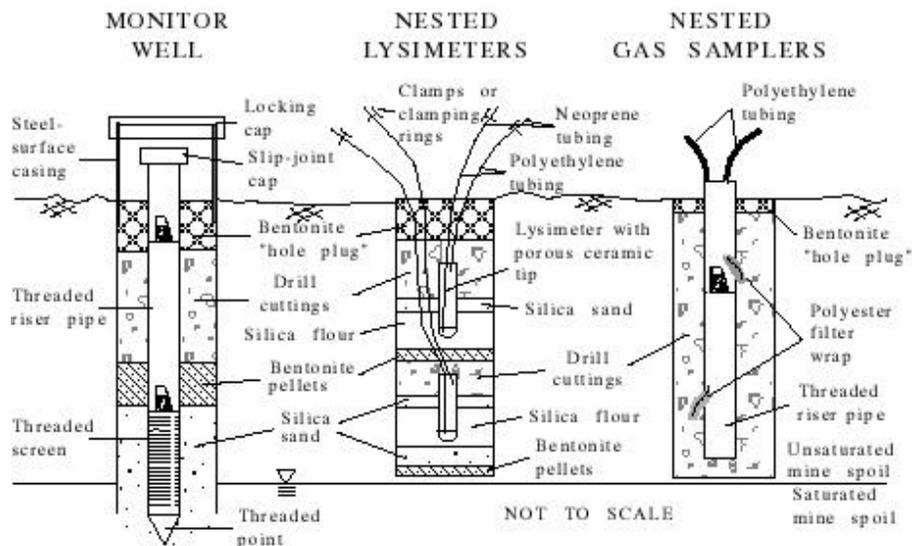
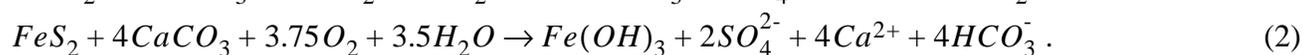
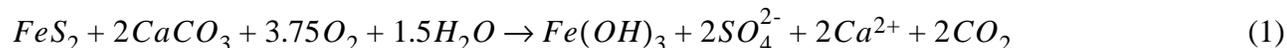


Figure 2. Schematic diagram showing nested monitoring design.

## Gas Chemistry

Partial pressures of O<sub>2</sub> and CO<sub>2</sub> in spoil are expected to vary depending on the predominant reactions involving the gases, relative rates of the reactions, and rates of gas exchange with surrounding zones (Jaynes et al. 1984a,b; Lusardi and Erickson 1985). In general, where pyrite-oxidation and carbonate-dissolution reactions are active, Po<sub>2</sub> will decrease and Pco<sub>2</sub> will increase. Data on pore-gas compositions at the mine (tables 1-2, fig. 3) indicate that Po<sub>2</sub> decreases from about 21 volume percent (vol %) at the land surface to less than 2 vol % at 10.7 m below the surface, with corresponding increases in Pco<sub>2</sub> with increasing depth in all three areas. Dissolution of carbonate minerals and production of alkalinity are favored by conditions characterized by elevated Pco<sub>2</sub> (Stumm and Morgan 1981; Bruno et al. 1992a,b). Because the pore water in spoil is extremely mineralized and dissolved solutes result primarily from mineral decomposition or weathering, oxidation of organic matter is not considered to be an important control of Po<sub>2</sub> and Pco<sub>2</sub>.

The observed changes in Po<sub>2</sub> proportional to Pco<sub>2</sub> in spoil (fig. 3) generally can be explained on the basis of theoretical stoichiometry of reactions involving pyrite, calcite, dolomite, and siderite. Two summary reactions can be written for the complete oxidation of pyrite combined with calcite dissolution (Cravotta et al. 1990):



Reactions 1 and 2 represent end-member reactions with respect to the quantity of calcite dissolved and its products. In both reactions, iron is presumed to oxidize and hydrolyze forming solid iron hydroxide [Fe(OH)<sub>3</sub>]. In reaction 1, CO<sub>2</sub> is a product, and the stoichiometric ratio of O<sub>2</sub> consumed relative to CO<sub>2</sub> produced (ΔPo<sub>2</sub>:ΔPco<sub>2</sub>) is 1.875. In reaction 2, bicarbonate (HCO<sub>3</sub><sup>-</sup>) is a product, not CO<sub>2</sub>. If ferrous iron (Fe<sup>2+</sup>) is produced instead of Fe(OH)<sub>3</sub>, ΔPo<sub>2</sub>:ΔPco<sub>2</sub> is 3.5 or larger. Similar reactions can be written with dolomite as a reactant instead of calcite that yield identical values of ΔPo<sub>2</sub>:ΔPco<sub>2</sub>. Hence, if predominant reactions involve oxidation of pyrite and neutralization by calcite or dolomite then values of ΔPo<sub>2</sub>:ΔPco<sub>2</sub> will be a minimum of 1.875.

Alkalinity and CO<sub>2</sub> also can be produced by the dissolution of siderite and manganoan siderite. Several reactions can be written for siderite dissolution with respect to the consumption of O<sub>2</sub> and the production of CO<sub>2</sub>. Under anoxic conditions, siderite dissolution can neutralize acid and produce alkalinity:



Neither O<sub>2</sub> nor CO<sub>2</sub> is involved in reaction 3. However, under acidic or oxic conditions, CO<sub>2</sub> can be a product:

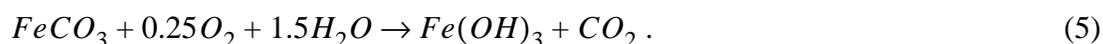


Table 1. Mean concentration of oxygen and carbon dioxide<sup>1</sup> in pore gas samples collected February-December 1992. [Values in volume percent, unless noted; <, less than; --, no data]

Depth (m)	Oxygen for gas well nest--					Carbon dioxide for gas well nest--				
	N2	M1	S1	S2	S4	N2	M1	S1	S2	S4
0	21.66	21.66	21.66	21.66	21.66	<0.50	<0.50	<0.50	<0.50	<0.50
1	14.62	17.79	14.59	12.55	16.26	5.82	3.27	6.17	6.31	5.72
4	10.37	10.70	3.39	11.08	14.29	8.70	9.20	12.66	8.36	7.69
7	6.80	4.32	4.56	6.79	12.98	11.87	16.61	14.17	13.02	8.57
11	3.18	5.00	4.28	3.34	--	13.63	15.78	15.72	16.44	--

<sup>1</sup>To compute mean, CO<sub>2</sub> concentration was assumed to be 0.2 if below detection (<0.5).

Table 2. Vertical gradient<sup>1</sup> of mean concentration of oxygen and carbon dioxide in pore gas samples collected February-December 1992. [Values in volume percent per meter, unless noted; --, no data]

Depth range (m)	Oxygen for gas well nest--					Carbon dioxide for gas well nest--				
	N2	M1	S1	S2	S4	N2	M1	S1	S2	S4
0-1	-7.70	-4.23	-7.73	-9.96	-5.90	6.15	3.35	6.53	6.68	6.04
1-4	-1.39	-2.33	-3.67	-.48	-.65	.94	1.95	2.13	.67	.65
4-7	-1.17	-2.10	.38	-1.41	-.43	1.04	2.43	.49	1.53	.29
7-11	-.91	.17	-.07	-.87	--	.44	-.21	.39	.86	--

<sup>1</sup>Gradient = (concentration at depth 2 - concentration at depth 1)/(depth 2 - depth 1). Negative value for gradient indicates decreasing concentration with increasing depth.

In reaction 4,  $O_2$  is not involved. In reaction 5,  $\Delta P_{O_2}:\Delta P_{CO_2}$  is 0.25. Hence, if siderite is the predominant reactant,  $\Delta P_{O_2}:\Delta P_{CO_2}$  will be a maximum of 0.25.

Absolute values of the slopes of the linear trends of  $O_2$  relative to  $CO_2$  in a gas nest (fig. 3) correspond to values of  $\Delta P_{O_2}:\Delta P_{CO_2}$  and range from 1.1 to 1.4. If reactions 1-2 predominated,  $\Delta P_{O_2}:\Delta P_{CO_2}$  values greater than 1.875 would be expected, whereas if reactions 3-5 predominated,  $\Delta P_{O_2}:\Delta P_{CO_2}$  values less than 0.25 would be expected. Hence, the gas data are consistent with the occurrence of some combination of reactions 1-5.

In general, the rapid decrease in  $P_{O_2}$  and the corresponding increase in  $P_{CO_2}$  at shallow depths (fig. 3, table 2), indicate that oxidation of pyrite and dissolution of carbonate minerals are most active in the unsaturated zone near the land surface. In all five gas-monitoring nests, the steepest  $O_2$  and  $CO_2$  gradients are indicated in the 0- to 1-m depth interval (table 2). Steep gradients are not restricted to the shallowest zone, however. For example, in nests M1 and S2, substantial  $O_2$  and  $CO_2$  gradients are indicated in the 4- to 7-m depth interval. Similar gradients were measured during nonrecharge periods in all seasons, which suggests biological respiration and decomposition are subordinate influences. Hence, mineral weathering is more extensive near the surface but can be active locally to depths of 7 m or more.

Zones exhibiting steep gradients in gas composition do not coincide with zones having highest acid-producing potentials in the mine spoil. For example, the total S concentration in rock sampled from the 0- to 1.5-m depth interval at gas-sampling nest S4 is  $<0.05$  wt % and that at nest M1 is 1.16 wt % (Cravotta et al. 1994). Because high vertical gradients may be independent of relative quantities of high-S material, pyrite oxidation rates could be controlled by rates of  $O_2$  diffusion, or total S concentrations in spoil may not reflect the amount of reactive pyrite. Hence, even small amounts of disseminated pyritic material can be relatively significant sources of acid and mineralized water.

### Water Chemistry

Ground water in spoil produced by the selective-handling method was neither less acidic nor more alkaline than ground water in spoil produced by the dragline method. Throughout the mine, overall ground-water quality was alkaline (figs. 4 and 5) despite overburden chemical data for spoil that indicated potential for development of acidic conditions (Cravotta et al. 1994). Median values of pH and concentrations of net alkalinity (= alkalinity - acidity) and alkalinity are significantly higher in ground water from mine spoil in the southern area relative to the middle and northern areas (fig. 4). This difference probably reflects an effect of decreasing concentration of NP in overburden from south to north across the mine (Cravotta et al. 1994). However, median concentrations of dissolved sulfate, iron, and manganese in the ground-water samples are not significantly different between the northern and southern areas, where selective-handling and dragline methods, respectively, were used.

Water samples from spoil throughout the northern, middle, and southern areas of the mine are highly mineralized, with concentrations of sulfate that typically exceed 400 mg/L (fig. 4), presumably as a product of pyrite oxidation. Despite high sulfate concentrations, water samples from most intervals in the unsaturated and saturated zones of spoil are alkaline. Alkalinity concentrations of 100 to 400 mg/L as  $CaCO_3$  are common in ground-water samples from spoil, and alkalinities of 600 to 800 mg/L as  $CaCO_3$  are common in water samples from the overlying unsaturated zone (fig. 5). Locally in the unsaturated zone of the northern area, however, shallow pore water sampled

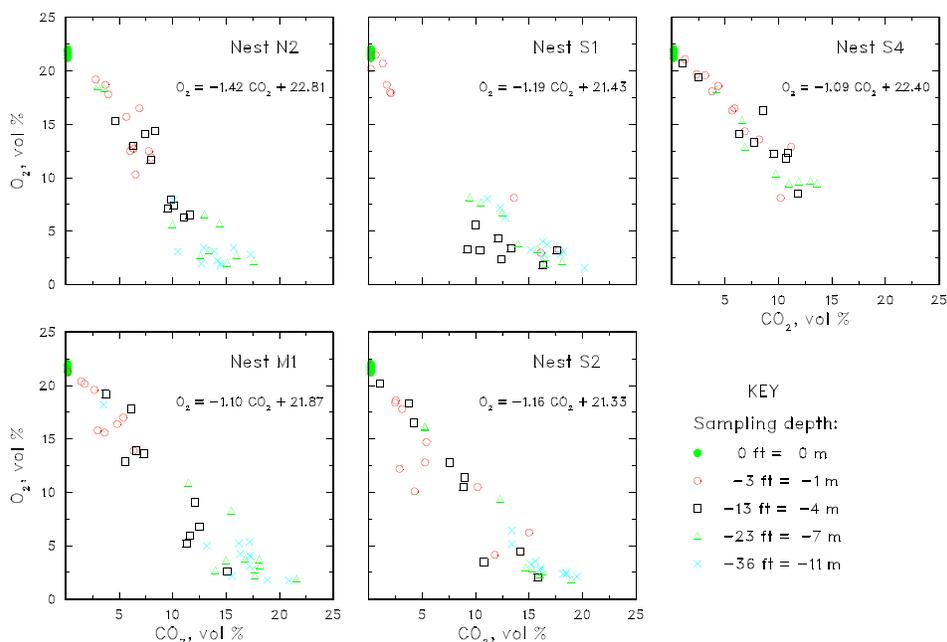


Figure 3. Concentration of oxygen ( $O_2$ ) relative to that of carbon dioxide ( $CO_2$ ) in pore-gas samples collected February-December 1992 from unsaturated spoil in Clarion County, PA (fig. 1). Regression equation calculated assuming  $O_2$  is independent variable.

within or near pyritic pods is acidic and has concentrations of sulfate exceeding 3,000 mg/L (fig. 5). For example, pore waters sampled in December 1992 (table 3) at nests N2 and N4 from a depth of 4.6 m have pH values less than 4 and sulfate concentrations greater than 5,000 mg/L. Despite substantial pyritic material within and below the 4.6-m depth interval, such as at nest N2 (see Cravotta et al. 1994), acidic conditions and high sulfate concentrations were only locally significant (table 3), and alkaline conditions prevail below the water table.

Dissolution of calcite and dolomite can produce alkalinity, calcium, and magnesium, and dissolution of siderite also can add these constituents plus iron and manganese. High concentrations of sodium relative to calcium and magnesium in pore waters and ground waters (table 3) can result from cation-exchange reactions (Foster 1950; Chapelle and Knobel 1985). Sodium bentonite, which was added to all boreholes containing lysimeters and wells (fig. 2), probably is not an important reactant because all water samples do not have elevated concentrations of sodium.

In general, pore-water samples have higher concentrations of alkalinity, sulfate, and base cations than in underlying groundwater samples (fig. 5, table 3). The trend of decreasing mineralization of pore waters with increasing depth probably results from intensive mineral weathering combined with evapotranspiration or freezing within shallow unsaturated mine spoil followed by dilution within the saturated zone. Evapotranspiration or freezing could produce elevated concentrations of solutes such as chloride (table 3). Dilution can result by mixing of waters with different residence times in chemically active zones and by mixing of waters from zones with different minerals or activities of reactions. Residence times and flow paths of percolating water can differ during recharge and nonrecharge periods (Diodato and Parizek 1988; Hawkins and Aljoe 1991).

Pyrite oxidation is a disequilibrium process that can occur as long as O<sub>2</sub> is available, whereas calcite dissolution and precipitation can achieve equilibrium (Geidel 1979). At this equilibrium condition, alkalinity accumulation will cease or be retarded. The potential for dissolution or precipitation of a solid phase by a pore-water or ground-water solution can be evaluated by use of water-quality data and thermodynamic data to compute a saturation index [SI = log (Q/K), where K is the solubility product constant and Q is the corresponding observed activity product] (Plummer et al. 1976; Stumm and Morgan 1981). Values of SI that are negative (<-0.1), zero (±0.1), or positive (>0.1) indicate the water is undersaturated, saturated, or supersaturated, respectively, with the solid phase. If undersaturated, the water can dissolve the solid phase. If supersaturated, the water cannot dissolve the solid phase, but can potentially precipitate it. Table 3 shows values of SI for calcite, siderite, amorphous Fe(OH)<sub>3</sub>, and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) plus corresponding values of measured pH and major solute concentrations in water samples collected during December 1992.

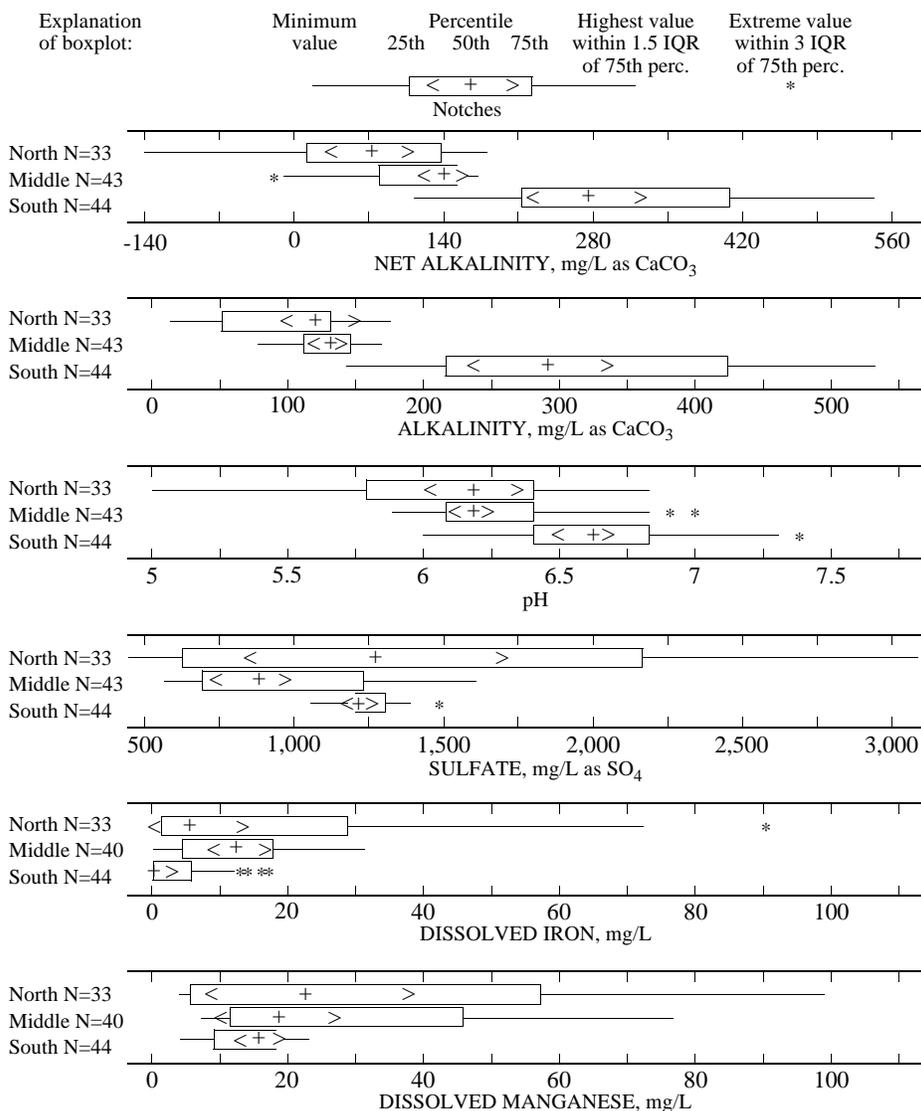


Figure 4. pH and concentrations of net alkalinity, alkalinity, sulfate, iron, and manganese in ground water from spoil. Data for monthly samples collected February-December 1992 from northern area wells N2-1, N3-1, and N4-1, middle area wells M1-1, M2-1, M3-1, and M4-1, and southern area wells S1-1, S2-1, S3-1, and S4-1 (fig. 1). IQR=75th-25th percentile.

Table 3. Measured composition and calculated saturation indices for water samples collected during December 1992. [Water-quality constituents in milligrams per liter, except for pH; saturation index, unitless; --, no data; <, less than]

Sample site name <sup>1</sup>	Measured water-quality constituent									Saturation index <sup>2</sup>			
	pH	Ca	Mg	Na	Fe	Mn	Cl	SO <sub>4</sub>	Alkalinity, CaCO <sub>3</sub>	Calcite	Siderite	Fe (OH) <sub>3</sub>	Gypsum
Well N1-0	6.5	200	78	2.9	7.8	5.6	3	630	150	-0.8	-2.1	2.7	-0.6
Well N1-1	6.7	170	74	2.7	.6	5.9	3	570	130	-.7	-2.3	2.0	-.7
Lys N2-05	6.8	470	270	170.0	<.1	7.4	3	2,300	260	-.1	-2.3	-.7	-.0
Lys N2-15	4.0	490	1200	190.0	1.3	260.0	3	7,600	7	-4.8	-5.5	-5.3	.1
Lys N2-25	6.8	260	200	490.0	1.0	37.0	5	2,100	290	-.3	-.9	.3	-.3
Lys N2-35	6.8	210	120	460.0	.4	33.0	4	1,800	310	-.4	-1.3	-.0	-.4
Well N2-0	6.2	270	140	2.8	10.0	6.8	4	1,100	94	-1.3	-1.2	2.5	-.4
Well N2-1	6.1	320	240	6.4	30.0	59.0	4	2,200	120	-1.3	-.6	2.5	-.2
Lys N3-05	6.6	300	100	140.0	<.1	.3	3	1,300	130	-.7	-3.7	-2.1	-.3
Lys N3-15	6.8	460	400	620.0	<.1	20.0	13	3,500	430	-.0	-3.2	-2.0	.0
Lys N3-25	6.9	410	350	970.0	<.1	62.0	19	3,900	420	-.0	-3.1	-1.9	-.0
Well N3-0	6.8	170	35	3.9	1.5	.3	4	540	310	-.2	-1.5	2.5	-.7
Well N3-1	6.1	180	94	3.5	2.0	3.6	4	680	170	-1.2	-1.6	1.7	-.6
Lys N4-05	5.1	140	55	6.7	<.1	14.0	<1	580	12	-3.4	-5.2	-4.1	-.7
Lys N4-15	3.4	460	630	110.0	14.0	160.0	<1	5,000	0	--	--	-5.4	.1
Lys N4-25	6.7	470	290	98.0	<.1	20.0	6	2,300	230	-.3	-2.8	-1.5	-.0
Well N4-0	6.5	400	180	3.5	32.0	7.9	3	1,200	170	-.6	.0	3.0	-.2
Well N4-1	5.5	205	145	4.7	3.3	18.5	4	1,150	51	-2.4	-2.5	1.1	-.4
Lys M1-05	7.3	160	58	600.0	<.1	4.5	3	1,300	610	.3	-1.9	-.3	-.6
Lys M1-15	6.6	470	340	28.0	<.1	35.0	6	2,600	250	-.4	-2.7	-1.4	.0
Lys M1-25	6.5	510	310	31.0	1.8	14.0	4	2,300	390	-.2	-.8	.2	.0
Well M1-0	7.1	170	35	3.9	1.5	.3	3	270	220	-.0	-2.7	2.8	-.9
Well M1-1	5.9	260	240	25.0	21.0	58.0	5	1,600	130	-1.5	-.9	2.3	-.3
Lys M2-05	6.8	160	50	3.6	<.1	.4	3	520	70	-.9	-2.9	-.8	-.7
Lys M2-15	7.3	530	290	970.0	<.1	3.6	15	3,600	750	.7	-2.4	-.8	.1
Lys M2-25	6.9	55	38	300.0	2.3	10.0	9	670	230	-.8	-.4	1.2	-1.1
Well M2-0	7.5	100	27	6.8	1.0	.2	4	160	240	.2	-2.8	3.0	-1.3
Well M2-1	6.2	200	130	7.0	11.0	15.0	4	950	140	-1.2	-.9	2.5	-.5
Well M3-0	7.1	120	48	6.7	1.9	1.0	3	380	220	-.2	-1.6	2.9	-.9
Well M3-1	6.1	140	70	19.0	.5	7.2	4	750	84	-1.7	-3.5	1.4	-.7
Well M4-0	7.3	150	39	11.0	.9	.7	4	220	270	.2	-2.1	2.8	-1.0
Well M4-1	6.3	160	77	3.7	5.5	12.0	3	770	150	-1.2	-1.2	2.4	-.6
Lys S1-05	6.9	660	240	240.0	<.1	13.0	10	2,100	560	.4	-1.6	-.5	.1
Lys S1-15	6.9	610	220	230.0	1.8	19.0	14	1,600	600	.5	-.2	.9	-.0
Well S1-1	6.7	380	130	11.0	.8	5.1	8	1,300	500	.1	-2.1	2.2	-.2
Lys S2-05	7.0	560	210	550.0	<.1	6.6	39	2,300	750	.6	-1.7	-.4	.0
Lys S2-15	6.9	650	230	260.0	5.7	7.5	110	1,900	730	.5	.3	1.4	.0
Well S2-0	6.8	300	110	28.0	.2	1.7	4	1,300	220	-.3	-4.9	1.6	-.3
Well S2-1	6.3	290	140	7.5	8.2	17.0	4	1,200	230	-.8	-1.7	2.8	-.3
Well S3-0	7.3	110	40	57.0	<.1	.3	4	410	210	-.1	-4.7	1.7	-.9
Well S3-1	6.0	340	120	13.0	.6	16.0	8	1,300	150	-1.2	-2.9	1.4	-.2
Well S4-1	6.3	410	180	9.7	.7	16.0	4	1,400	360	-.5	-2.4	1.7	-.2

<sup>1</sup>Sample site name indicates sample type (well or lysimeter) and location (fig. 1). Well numbers with suffix “-1”, screened within horizon of mined coal; “-0”, screened below horizon of mined coal. Lysimeter number suffix indicates sample depth, in feet; metric equivalents are “-05” = 1.5 m, “-15” = 4.6 m, “-25” = 7.6 m, and “-35” = 10.7 m.

<sup>2</sup>Saturation index [SI=log (Q/K)] calculated with WATEQF (Plummer et al. 1976) and reported measured data (above), less abundant constituents (including fluoride, nitrate, ammonia, orthophosphate, aluminum, silica, strontium, and zinc), temperature, and measured Eh or computed Eh from Po<sub>2</sub>.

Most pore-water samples from shallow depths of 1.5 and 4.6 m, except those from or near pyritic pods (N2-15, N4-15), are saturated or supersaturated with calcite and gypsum and are undersaturated with siderite and  $\text{Fe}(\text{OH})_3$  (table 3). Underlying ground-water samples from the spoil generally are undersaturated with calcite, siderite, and gypsum, and are supersaturated with  $\text{Fe}(\text{OH})_3$ . These trends indicate that siderite can dissolve throughout the spoil; dissolution of siderite can add alkalinity and promote supersaturation with calcite. In systems at equilibrium with calcite, loss of calcium by ion-exchange for sodium and by precipitation of gypsum can promote calcite dissolution and the production of alkalinity. However, gypsum can precipitate on calcite and reduce its reactive surface area. Because shallow pore waters generally are undersaturated with  $\text{Fe}(\text{OH})_3$ , iron armoring of carbonate minerals is not likely. In deeper zones, where hydrolysis of iron and precipitation of  $\text{Fe}(\text{OH})_3$  may be active, additional acid and  $\text{CO}_2$  can be produced, which can promote the dissolution of carbonate minerals, hence buffering the ground water to be near neutral with median pH values of 6.2-6.6 (fig. 4).

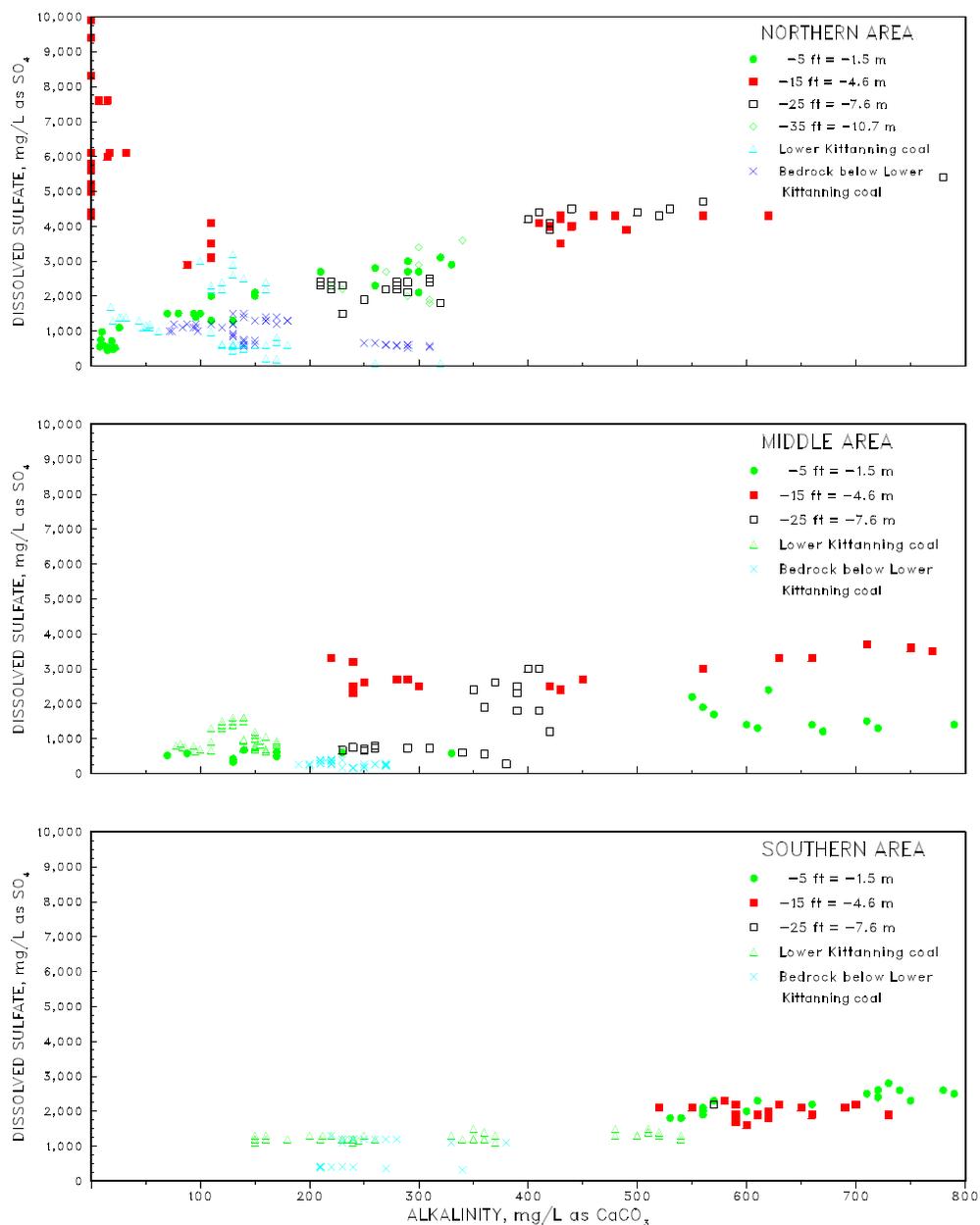


Figure 5. Concentration of sulfate relative to that of alkalinity in pore-water and ground-water samples from spoil and bedrock at a reclaimed coal mine in Clarion County, PA (fig. 1). Data for monthly samples collected February-December 1992 from lysimeters and wells.

### Conclusions

A change from dragline to selective-handling mining methods at a surface coal mine in Clarion County, PA, did not have a significant effect on concentrations of sulfate and metals in the ground water because oxidation of pyrite and dissolution of siderite were not abated. Throughout the mine, ground water was extremely mineralized, but it was more alkaline than expected on the basis of overburden chemical data. High concentrations of alkalinity in ground water from spoil indicate that both dragline and selective-handling mining methods may have promoted active dissolution of carbonate minerals. Dissolution of calcite and dolomite can result after pyrite oxidation, as a consequence of acid neutralization, and can be perpetuated by removal of dissolved calcium by ion exchange for sodium and precipitation of gypsum. Even at conditions of calcite supersaturation, increases in concentrations of alkalinity and other solutes can result as a consequence of evapotranspiration and freezing in shallow zones or dissolution of siderite. In addition, dissolved iron and manganese can be produced by dissolution of siderite. However, because calcareous minerals are not abundant in the spoil, the permanence of alkaline conditions at the mine is uncertain.

Although placement of pyritic material above the water table within mine spoil may be an effective means of isolating toxic material from ground water, its placement near the surface contributes to weathering and the consequent mineralization of ground water. Chemical data for pore-gas and water samples from mine spoil indicate that acid production and neutralization reactions are active in localized zones above the water table, particularly in the near-surface zone (0-1.5 m), regardless of the mining method used. High vertical gradients of pore-gas  $\text{Po}_2$  in the near-surface zone are independent of relative quantities of pyritic, high-S material in the shallow spoil. This indicates that pyrite oxidation rates may be controlled by rates of  $\text{O}_2$  diffusion, or total S concentrations in spoil may not reflect the amount of reactive pyrite. Hence, despite efforts to isolate spoil containing substantial amounts of pyrite, even small amounts of pyritic material may be significant sources of acid if placed in  $\text{O}_2$ -rich zones near the land surface.

Long-term monitoring, coupled with periodic determinations of quantities and identities of mineral sources of acidity and alkalinity, would aid in an evaluation of the persistence of alkaline conditions and potential for changes in water quality. Additional pore-gas and water-chemistry data, including unsaturated-zone temperature gradients, would be helpful to evaluate relative roles of calcite and siderite dissolution and the relative effect of depth of placement of pyritic and calcareous materials on reaction rates and ground-water quality. Enhanced production of alkalinity in mine spoil, particularly the potential for enhancement of calcite dissolution by cation exchange, can be important in aquifers and other systems, such as limestone drains. Additional work is needed to determine the nature of the minerals active in cation-exchange reactions and conditions that favor the process in mine spoil.

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