Department of Natural Resources

MARYLAND GEOLOGICAL SURVEY

Kenneth N. Weaver, Director

REPORT OF INVESTIGATIONS NO. 20

HYDROGEOLOGY OF THE FORMATION AND NEUTRALIZATION OF ACID WATERS DRAINING FROM UNDERGROUND COAL MINES OF WESTERN MARYLAND

by

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ABSTRACT

The flows from 18 underground mines for which mine maps are available in the bituminous coal basins of western Maryland were measured, and water samples were collected for determination of 27 major dissolved constituents and chemical properties and 28 minor elements. Natural neutralization is taking place in the underground environment and the most nearly neutralized acid mine drainage is associated with flow from an upper mine to a lower mine through the intervening rock strata.

The Problem

The coal of western Maryland was formed 300 million years ago as plant remains deposited in swamps under chemically reducing conditions. These conditions were favorable not only for the preservation of the plant remains, but also for the formation of iron sulfide minerals, particularly pyrite. Within the past 200 million years those coal deposits exposed at land surface have been subjected to erosion and oxidizing conditions. The pyrite, previously stable under reducing conditions has been oxidizing to sulfates with the production of ferrous iron and acid as part of the natural process of chemical weathering, thus:

$$2FeS_2(s)+7O_2(aq)+2H_2O = 4SO_4^{-2}+2Fe^{+2}+4H^{+1}$$

Under natural conditions it is possible that another 100 million years would have been required to erode all the coal measures and to oxidize the fixed tonnage of pyrite they contain. At the natural rate of chemical weathering the products of pyrite oxidation would be barely detectable in the streams of western Maryland.

Coal mining in Maryland during the past 100 years, however, has increased the rate of chemical weathering of the coal measures by several orders of magnitude by exposing vast surface areas of rock to weathering processes. Because of the nature of the distribution of minerals in the coal measures, mining almost inevitably disturbs more acid-producing rock than alkaline-producing rock as compared to the entire thickness of the coal measures. Under the new manmade conditions, it is possible that merely a few thousand years will be required to oxidize a considerable part of the fixed tonnage of pyrite in the coal measures. At the new rate of chemical weathering the products of pyrite oxidation are so abundant that they have created an acid mine drainage problem.

Maryland streams receiving mine drainage, in comparison to nearby streams that do not receive mine drainage, contain high concentrations of dissolved solids. Ions of calcium, magnesium, and sulfate are typically most abundant. In addition, streams receiving mine drainage in which the acidity has been only partly neutralized typically contain high concentrations of iron, manganese, aluminum, acid, and minor elements. As a result of the high concentration of these constituents, the water has excessive noncarbonate hardness, free mineral acidity, and low pH. Streams receiving mine drainage in which the acidity has been mostly neutralized typically lack high concentrations of iron, acid, some minor elements, free mineral acidity, and low pH. These streams, however, retain the unnaturally high concentrations of calcium, magnesium, and sulfate and continue to have excessive noncarbonate hardness. Bicarbonate may be present in the streams in which the acidity has been mostly neutralized.

The distribution and severity of the mine drainage problem in Maryland is best revealed by the load of sulfate ion in major streams receiving mine drainage. The only source of sulfate of any significance in western Maryland is in pyrite oxidation, and sulfate remains in solution under most conditions at concentrations normally encountered in mine drainage and streams. For this reason it is an excellent indicator of mine-drainage pollution. Table 1 summarizes calculations of loads of sulfate in major streams receiving mine drainage during a condition of approximately median streamflow. During May 1969, background concentrations of sulfate in streams not receiving mine drainage was between 5 and 15 mg/l (milligrams per liter). On the basis of sulfate loads, the table indicates that two-thirds of the mine drainage problem is in the North Branch Potomac River basin above Bloomington; one-quarter of the problem is in the Georges Creek basin (drained both by Hoffman Drainage Tunnel and by Georges Creek); and the remaining one-twelfth is in the Youghiogheny River, Jennings Run, Savage River, and Casselman River basins.

In addition, concurrent data on stream acidity indicate that the acid associated with the sulfate in North Branch Potomac River has undergone less neutralization than in Hoffman Drainage Tunnel or Georges Creek.

An abundance of mine-drainage constituents can seriously degrade the water for recreational, industrial, and municipal uses. Some constituents increase water-treatment costs and necessitate more frequent replacement of water-treatment facilities. Excessive dissolved solids and sulfate may have a laxative effect and in addition to iron and manganese, may have an unpleasant taste. Excessive iron and manganese stain stream bottoms, porcelain fixtures, and cloth. Excessive hardness produces insoluble "curd" when it reacts with soap and in addition to aluminum, may coat boilers

Table 1. Sulfate loads in major streams receiving mine drainage, Mav 1969

Stream	Streamflow		Sulfate Concentration, in milligrams per liter [2]	Sulfate Load,	
	Percentage of time that given discharge has been equaled or exceeded	Discharge, in cubic feet per second [1]		in tons per day	in percent of total
North Branch Potomac River at Bloomington	57	228.	140.	86.	67.
Hoffman Drainage Tunnel on Braddock Run at Clarysville	---	17.8	340.	16.	12.
Georges Creek at Westernport	57	26.	220.	15.	12.
Youghiogheny River at Friendsville	62	291.	6.0	4.7	3.6
Jennings Run at Corriganville	---	13.	116.	4.1	3.2
Savage River at Bloomington	80[3]	16.	44.	1.9	1.5
Casselman River at Grantsville	57	44.	12.	1.4	1.1
			Total	129.	100.

[1]Data from Maryland Water Resources Administration and U. S. Geological Survey

[2]Data from Maryland Water Resources Administration

[3]Regulated flow above mine drainage source

with insoluble scale. Other constituents are highly corrosive and attack both animate and inanimate components in the environment. Free mineral acidity and low pH severely restrict the number of species of aquatic life, and attack engineering structures and navigation equipment. Related problems may arise as a consequence of significant changes in water quality as a result of either mine drainage reclamation or natural causes. Significant changes in water quality might force existing water users, accustomed to treating and using mine drainage to replace their water treatment facilities.

Purpose and Scope

Several authorities have suggested that one solution to the mine drainage problem may develop from a better understanding of the geologic environment in which acid is formed and partly neutralized. The purpose of this investigation was to test the idea that there is a definitive relation between the chemical properties of mine drainage and the associated coal-measure stratigraphy. The assumption was made that if a definitive relation exists, then stratigraphic data could be used to predict the chemical properties of mine drainage prior to opening new mines or entering a new area. Accordingly, drainage treatment procedures or plants could be designed as part of the economic feasibility for a new mine. Considerable effort was devoted to the analysis of water samples for minor elements and to the interpretation of the analytical results to see if minor elements could be used to tag a mine discharge as to its source in a specific coal seam.

The purpose of this report is to present a hypothesis describing the formation and neutralization of acid waters draining from underground coal mines. The report is based largely upon detailed chemical analysis for dissolved solids in water samples collected at the point of surface discharge

of underground mines. These data are supplemented by available mine maps, published stratigraphic information, published chemical analyses of coal cores, and published analyses of water from wells and streams that do not receive mine drainage.

Field work for the investigation was limited to sampling the discharge from selected underground mines for which mine maps were available in the Georges Creek, Upper Potomac, and Castleman coal basins. The determination of chemical properties in the field omitted measurement of redox potential and discrimination between ferrous and ferric iron. Water samples were not analyzed for dissolved gases (except oxygen), suspended solids, or microbiologic content.

The scope of the report is limited to a discussion of those geologic and underground environmental factors that appear to have an effect upon the solutes in mine discharge. Discussion of research findings in the quantitative chemistry of pyrite oxidation and acid generation is beyond the scope of this report (Stephan and Lorenz, 1967; Singer and Stumm, 1970). The report discusses the occurrence of natural neutralization in the underground flow system and implies that a wholly new approach may be developed for treatment for mine drainage. Procedures are not proposed, however, for implementing the new approach.

Methods

Eight of the nine coal seams from which all recorded Maryland coal production was taken in 1968 (Buckley, 1968) were selected for sampling mine drainage. Underground or "deep" mines are the principal source of mine drainage loads in Maryland streams, and the chemical composition of drainage from these mines is less variable with time than drainage from strip mines. For these reasons underground mines, rather than strip mines, were selected as the sole target of the investigation. Available maps of the underground workings of deep mines in the eight coal seams were inspected, and 18 mines were selected for sampling drainage (appendix I, figure 9 through 16). In contrast to the usual method of walking streams to find mine discharges, in most cases the point location for collecting water samples at a mine portal was selected in advance on the basis of the most probable direction of water flow in the mine as judged from either floor elevations or drainage ways recorded on the mine maps.

A partly-successful attempt was made to apply the following additional criteria in the original selection of 12 of the 18 mines: 1) There were no other mines vertically above or below the mine to be sampled that could affect the quality or quantity of drainage; 2) Pooling of water in the mine was either shallow or absent; 3) The mine was large enough to have measurable discharge (at least 0.1 square mile); and 4) The mine augmented regional sampling within three coal basins. For the remaining six mines a successful attempt was made to select the largest underground mines in Maryland regardless of the local mining or hydrologic conditions. Although no criterion was established for mine activity, all but two of the 18 mines had been abandoned prior to the time of sampling.

At each site where water was collected from the 18 mines, measurements were made of the flow and of those properties of the water that can change following sampling. These included temperature, dissolved oxygen, specific electrical conductance, pH, and acidity and/or alkalinity (appendix II, table 4). A total of five bottles of water were collected at each site. These included four 1-liter samples in polyethylene bottles for laboratory analysis of 24 major dissolved constituents and chemical properties as well as arsenic and selenium. Of the four samples, two samples were collected without filtration; one of these was acidified. The remaining two samples were filtered; one of these was then acidified. Bottles were thoroughly rinsed with either the raw or filtered water as applicable. In addition to the four 1-liter samples, a 2-liter sample was collected in a polyethylene bottle for laboratory analysis of 30 minor dissolved constituents. This bottle was specially prepared according to standard methods for collecting samples for minor-element analysis (Barnett and Mallory, 1971, p. 1-2). This sample was filtered and acidified.

To all samples that were acidified in the field, sufficient hydrochloric acid was added to lower the pH below 2.0 in order to retard precipitation of metal hydroxides, particularly ferric hydroxide. A heavy plastic cylinder that could be pressurized with a hand air pump and containing a disposable 0.45-micrometer membrane filter was used for all sample filtration (Skougstad and Scarbro, 1968) in order to insure that suspended solids were eliminated from the sample.

The 0.45-micrometer membrane filters used at four of the 18 sites as well as the filter used on the distilled water samples were analyzed for common cations that might have been removed by filtration (appendix II, table 8). The filter papers were digested in nitric and sulfuric acids (Sandell, 1959). Individual dissolved constituents in the resulting solutions were analyzed by standard methods (Rainwater and Thatcher, 1960).

Common practice in mine drainage investigations requires that samples be analyzed for a limited set of indicator constituents such as pH and

acidity. In this investigation, however, the laboratory analysis for major constituents attempted to measure all major chemical properties and to achieve an acceptable balance between the equivalents of major cations and anions present in solution. Samples were analyzed for silica, aluminum, iron, manganese, calcium, magnesium, sodium, potassium, copper, zinc, sulfate, bicarbonate, chloride, fluoride, nitrate, phosphate, dissolved solids, calcium-magnesium hardness, non-carbonate hardness, specific conductance, pH, potential acidity, free acidity, and color (appendix II, table 5). Standard analytical methods of the U. S. Geological Survey (Brown, Skougstad, and Fishman, 1970) were used for all analyses.

The laboratory analysis for minor constituents included analysis for aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, chromium, cobalt, copper, gallium, germanium, lanthanum, lead, lithium, manganese, mercury, molybdenum, nickel, rubidium, scandium, selenium, silver, strontium, tin, titanium, vanadium, ytterbium, yttrium, zinc, and zirconium (appendix II, table 6). Standard analytical methods of the U.S. Geological Survey (Barnett and Mallory, 1971) employing emission spectroscopy and the precipitation method were used for all analysis with the exception of cadmium, mercury, and zinc which were analyzed by atomic absorption spectrophotometry and arsenic and selenium analyzed by wet chemical methods (Brown, Skougstad, and Fishman, 1970).

The results of chemical analysis were interpreted with the aid of published stratigraphic information, published analyses of coal cores, and published analyses of water from wells and streams that do not receive mine drainage.

Previous Work

Some previous attempts to relate the chemistry of coal-mine drainage to the associated geology and local stratigraphy have influenced the course of this investigation. Emrich and Thompson (1968) made an investigation of the regional trends in acidity and alkalinity in drainage from underground mines in each of ten producing coal seams in western Pennsylvania. The Pennsylvania Department of Health has published laboratory procedures for estimating the acid-producing potential of rock samples (Emrich, 1966). F. T. Caruccio attempted to relate the results of leaching experiments on rock samples collected from strip-mine highwalls with the mineralogy of the samples and with the general chemistry of local mine drainage (Caruccio and Parizek, 1967; Caruccio, 1968). Later he examined one process by which neutralization of mine drainage takes place by natural means and recommended a procedure for neutralization of strip-mine drainage (Caruccio, 1970).

The location and some of the chemical characteristics of many individual sources of drainage in Maryland from strip mines as well as underground mines have been reported in three volumes published by the Maryland Department of Water Resources (Hopkins, 1966 a, b, c). Preliminary results of investigation for the quantity or loads of mine drainage constituents in Maryland streams, as well as in the streams of the other Appalachian States, have been summarized by the Environmental Protection Agency (Federal Water Pollution Control Administration, 1969).

Published chemical analyses of water not containing mine drainage aid in the interpretation of the geochemistry of mine drainage. Thomas (1966) published data on the quality of water in all Maryland streams, most of which are not affected by mine drainage. Heidel and Frenier (1965) reported on trace elements as well as major constituents in streams of the Patuxent basin. Analyses of ground water not affected by mine drainage from wells in the coal basins are contained in the Bulletins of the Maryland Geological Survey (Amsden, Overbeck, and Martin, 1954; Slaughter and Darling, 1962).

Additional analyses as well as geochemical interpretations of ground water not affected by mine drainage from wells in the coal basins of western Pennsylvania are contained in the Bulletins of the Pennsylvania Geological Survey (Carswell and Bennett, 1963; Poth, 1963). These two reports also contain pertinent discussions of the natural groundwater flow system in less extensively mined parts of the Allegheny Plateau.

Investigations of the stratigraphy and economic resources of the coal measures in Maryland were begun before the turn of the century, and as a result the geology of the Pottsville and Allegheny Formations and the lower half of the Conemaugh Formation are known in considerable detail. The *Report on the Coals of Maryland* (Clark and others, 1905) remains a useful reference on measured sections of coal at many mines in each basin as well as measured sections of the intervening rocks and contains a detailed discussion of rock members within each formation. In addition the report contains records of the mines and mining companies and their drainage practice at turn of the century (Stockton, 1905).

The *Second Report on the Coals of Maryland* (Swartz and Baker, 1922) contains significant revisions to the stratigraphic designation of the coals and remains a principal reference on the upper half of the Conemaugh Formation, on the Monongahela Formation, and on rocks of the Dunkard Group.

In addition it contains records of the mines and drainage practice as of 1920 (Baker, 1922). Some of the first reported analyses of the composition of coal are also contained in this volume (Swartz and Fieldner, 1922).

Diamond-drill cores recovered during two investigations of coal reserves in the lower part of the coal measures by the U. S. Bureau of Mines provided valuable data for detailed interpretation and correlation of the coal measures below the base of the upper member of the Conemaugh Formation in the Castleman, Georges Creek, and northern part of the Upper Potomac coal basins. The reports of these investigations (Toenges and others, 1949, 1952) contain detailed descriptions of cores from the 66 drill holes, descriptions of operating and abandoned mines in the lower coals with small-scale maps of their underground workings, and analyses of the composition of coal cores.

The detailed stratigraphic work on the lower part of the coal measures by K. M. Waagé (1950) is thoroughly discussed in the *Refractory Clays of Maryland Coal Measures.* This volume is the principal reference on the geology of the Pottsville and Allegheny Formations and the lower half of the Conemaugh Formation.

Acknowledgments

The authors are grateful to H. B. Buckley and staff of the Maryland Bureau of Mines and James Coffroth of the Maryland Geological Survey who provided large-scale maps of the underground workings of many mines and who provided counsel that was instrumental in the selection of mines. The authors are grateful to George Steele and Paul Parsons of Island Creek Coal Company who allowed us to sample discharge from the Alpine Mine and who provided a small-scale map of the current extent of the mine workings.

Water samples were analyzed for major constituents by J. C. Chemerys and for arsenic and selenium by C. A. Watterson of the U. S. Geological Survey water quality laboratory in the District of Columbia under the direction of D. W. Fisher. Samples were analyzed for minor elements by P. R. Barnett, E. C. Mallory, Darwin Golden, and O. J. Feist of the U. S. Geological Survey analytical methods laboratory in Denver, Colorado, under the direction of M. W. Skougstad. Material collected on 0.45-micrometer filters was analyzed by S. L. Rettig through the courtesy of B. F. Jones, both of U. S. Geological Survey.

The investigation was conducted under the supervision of W. F. White, District Chief, U. S. Geological Survey, in cooperation with the Maryland Geological Survey, Kenneth N. Weaver, Director.

HYDROGEOLOGIC SETTING

Structure, Stratigraphy, and Mineralogy

The workable coal measures of Maryland lie within the Allegheny Plateau in Allegany and Garrett Counties and are situated in three elongated structural troughs that trend northeastward across the State (fig. 1). These three troughs have traditionally been subdivided into five coal basins. The eastern trough contains the Georges Creek basin in the north and the Upper Potomac basin in the south across Savage River. The Georges Creek basin is drained by Jennings Run and by Hoffman Drainage Tunnel in the north and Georges Creek in the south. The Upper Potomac basin, the western half of which is in Maryland and the eastern half in West Virginia, is drained to the northeast by North Branch Potomac River. The middle trough contains the Castleman basin in the north and Upper Youghiogheny basin in the south. The western trough contains the Lower Youghiogheny basin. The Castleman basin is drained to the northeast by the Casselman River and both the Upper and Lower Youghiogheny basins are drained to the north by the Youghiogheny River. The Upper and Lower Youghiogheny basins were omitted from this investigation because of an absence of detailed stratigraphic control and the relatively small number of deep mines.

Typical of many of the bituminous coal basins in the Allegheny Plateau, basinward-dipping strata become increasingly more steep away from the axis and generally reach a maximum between 10 and 15

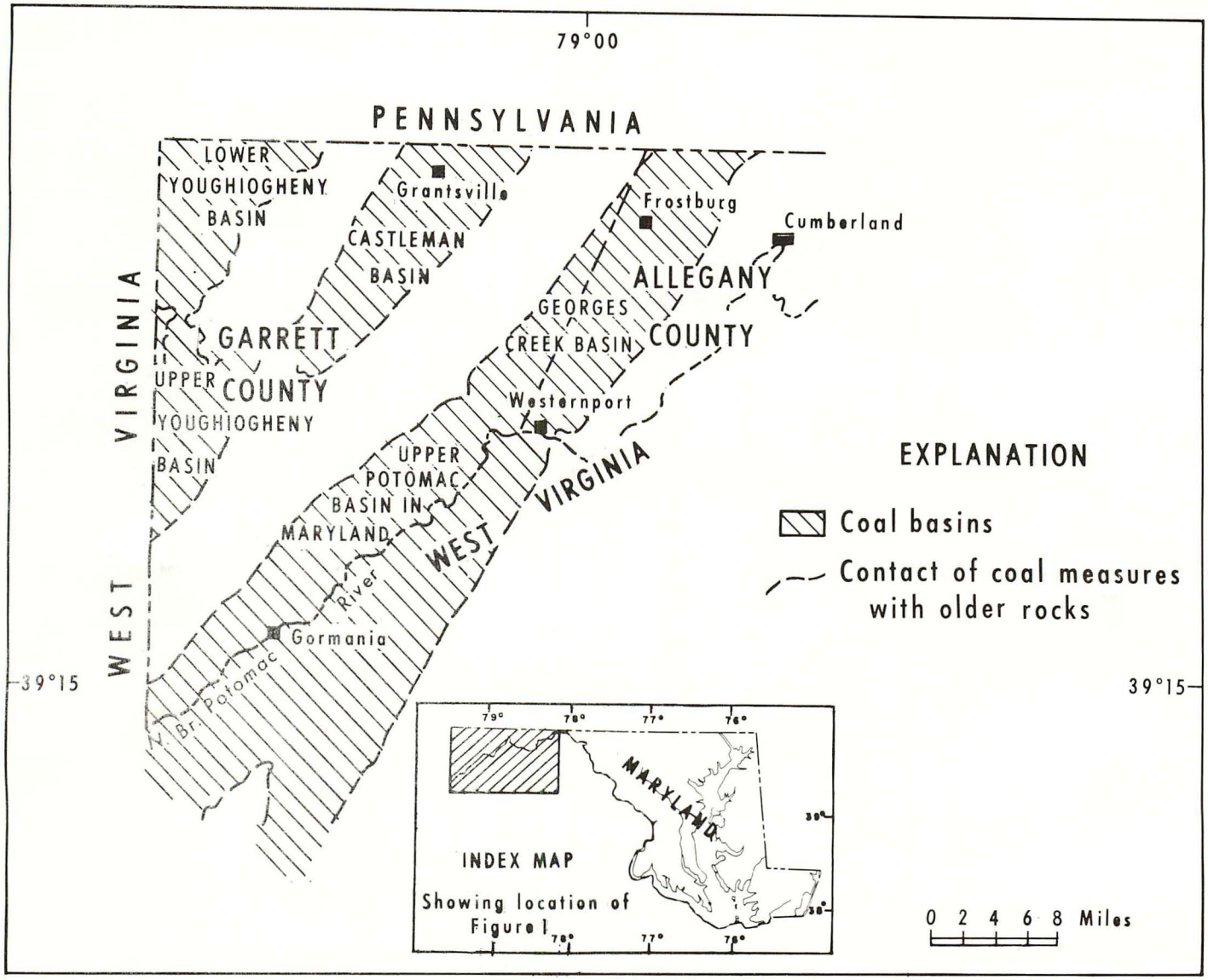

Figure 1.—Map of the coal basins in western Maryland.

degrees. Along the axis the strata plunge very gently toward structural lows. The structurally lowest part of the eastern trough is located at the underground, western entrance to the Hoffman Drainage Tunnel in the central part of the Georges Creek basin. From this point the axis of the eastern trough becomes more shallow to the northeast and southwest. The eastern trough is the deepest structure of the three and, therefore, the thickest section of the coal measures occurs near the middle of the Georges Creek basin. Because the intensity of folding decreases to the northwest, thinner sections lacking the Pittsburgh coal and younger formations occur in the Castleman and Youghiogheny basins.

Faults exposed in strip-mine highwalls commonly have less than a few feet of throw. At infrequent places where they have been observed along the outer edge of the basins, the strike of the faults is roughly parallel with the axis of the folds and the downthrown side is away from the axis of the fold. In areas of underground mining natural faults commonly are eclipsed by faulting and fracturing as a result of subsidence of the roofs of abandoned mines.

Secondary faulting and fracturing is especially significant to vertical flow of fluids in areas of underground mining. Secondary faults and fractures occur in those areas where insufficient sup-

port of the roof of an underground mine has led to roof failure and subsidence of the overlying strata and the land surface. Insufficient support commonly has occurred in those parts of old mines where pillars were removed as part of final mining operations. Mining practice at the turn of the century resulted in about 45 percent coal recovery in mined-out areas. Current practice results in 80 to 90 percent coal recovery and without backfilling or permanent artificial support subsidence in many cases is inevitable. The amount of surface subsidence is approximately 50 percent of the thickness of material removed from the mine when roof failure is 150 feet or less in depth(Davies, 1968). Surface subsidence is 25 to 30 percent of the thickness when roof failure is approximately 300 ft. in depth. Strata between the point of failure and the land surface subside in proportion to their distance above the point of failure. This subsidence commonly occurs within a matter of months after the coal has been removed.

The zone of secondary normal faults and fractures occurs within the boundary of the area of roof failure. Judging from model studies (Gieźyński, 1970), theoretical principles of rock mechanics would indicate that this zone in structurally isotropic materials should occupy a volume bounded by a 60-degree solid cone whose base corresponds to the area of roof failure. These faults and fractures tend to increase the vertical permeability of the strata within this zone by several orders of magnitude.

The strata of the coal measures consist of a repeating yet variable sequence of relatively thin units of sandstone, siltstone, and shale with subordinate amounts of coal, clay, and argillaceous limestone. In general from bottom to top the strata become more calcareous and contain a decreasing percentage of sandstone. The sandstone units are lenticular and rarely are continuous for more than a few miles. The standard subdivision from oldest to youngest units is Pottsville, Allegheny, Conemaugh, and Monongahela Formations of Pennsylvanian age and Dunkard Group of Pennsylvanian and Permian age (figure 2). The subdivision is based upon the relative abundance of coals in each formation and the boundaries are set at the areally more persistent coals.

There are two fundamental aspects to the lithology of the Maryland coal measures which are believed to have bearing on the geochemistry of mine drainage. One aspect contains strata that are markedly regular in lateral extent and thickness and exhibit a marked variety in lithologic types (Waagé, 1950, p. 9-11). By contrast, the other aspect contains strata that are quite irregular in lateral extent and thickness and exhibit relatively few lith-

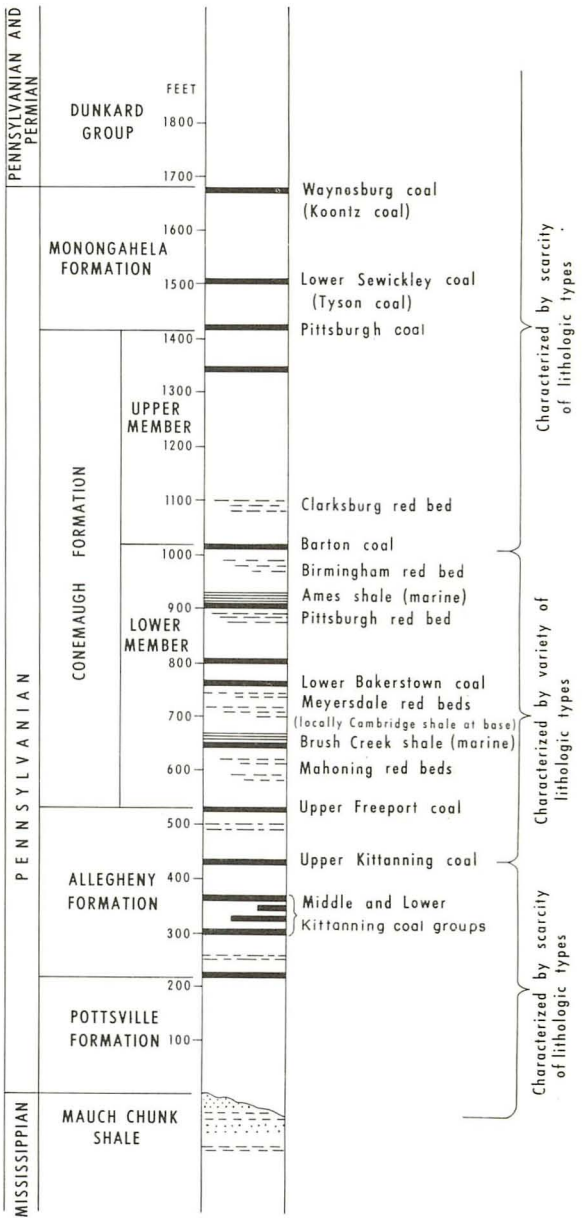

Figure 2.—Generalized stratigraphic column of the coal measures of Maryland.

ologic types. The latter aspect is characteristic of the Pottsville, lower two-thirds of the Allegheny, upper member of the Conemaugh, and the Monongahela Formation, and the Dunkard Group. The Pottsville and lower two-thirds of the Allegheny consists of sandstone and dark-gray siltstone with subordinate shale, clay, and a few laterally-discontinuous coals. The upper member of the Conemaugh, the Monongahela, and the Dunkard Group

are similar in lithology to the Pottsville and lower two-thirds of the Allegheny with the exception that fresh-water limestone may be present and the Monongahela contains several thick and persistent coals.

By contrast, the upper third of the Allegheny and the lower member of the Conemaugh contain a significantly smaller percentage of sandy strata, larger percentage of claystone and fresh-water limestone, and have abundant coals that are laterally continuous. This aspect of the lithology has its maximum expression in the lower member of the Conemaugh. The variety in lithologic types in the lower member of the Conemaugh is increased by the only appearance in the Maryland coal measures of abundant red beds and fossiliferous marine shales.

It would appear significant to the geochemistry of mine drainage that three of the four red beds in the lower member of the Conemaugh have been found in part to be the lateral equivalents of discontinuous coal beds (Waagé, 1950b, p. 35-39, 47-48). In contrast to the coal, the red beds sometime in the geologic past have experienced chemically oxidizing conditions which are unfavorable to either the formation or preservation of iron sulfide minerals, particularly pyrite. The red beds are better developed and more regular in lateral extent in the Castleman basin as compared to red bed units in the eastern structural trough.

Among the eight coal seams selected for sampling mine drainage, four occur in the lithologic aspect that contains strata that exhibit relatively few lithologic types; these are the Middle Kittanning coal in the lower two-thirds of the Allegheny Formation, and the Pittsburgh, Sewickley, and Waynesburg coals in the Monongahela Formation (figure 2). The remaining four coal seams selected for sampling drainage occur in the lithologic aspect that contains strata that exhibit a marked variety in lithologic types; these are the Upper Kittanning coal and the Upper Freeport coal in the upper third of the Allegheny Formation, and the Lower Bakerstown coal and the Barton coal in the lower member of the Conemaugh Formation. With the exception of the Pittsburgh coal, which ranges in thickness between 9 and 14 feet, the eight selected coals are typically less than 6 feet thick including bony coal.

The mineralogy of the coal measures is dominated by common minerals and mineral groups such as quartz [SiO_2], the micas and clays, particularly kaolinite [$Al_2Si_2O_5(OH)_4$], and the carbonates, particularly calcite [$CaCO_3$] and dolomite [$CaMg(CO_3)_2$].

With regard to mine-drainage geochemistry, pyrite [FeS_2] is the most significant accessory mineral and is commonly reported from examination of cores (Toenges and others, 1949, 1952) in the coal, in carbonaceous shale, in and overlying the coal, and in calcareous clays underlying the coal. Pyrite forms a significant part of the total sulfur content of coal. The sulfur content of the Maryland coals below the Pittsburgh coal is relatively high and varies considerably within a single coal seam. The weighted average sulfur content of the five selected coals below the top of the lower member of the Conemaugh Formation in the Georges Creek and north part of the Upper Potomac coal basins ranges between 2.5 and 4.1 percent on a moisture-free basis (Toenges and others, 1949, p. 19). The comparable sulfur content of the four selected coals below the Barton coal in the Castleman basin ranges between 1.6 and 3.9 percent (Toenges and others, 1952, p. 19).

Another accessory mineral siderite [$FeCO_3$] or ferrous carbonate occurs as ironstone concretionary masses in all coal-measure lithologies except the coal. It is commonly reported from examination of cores in the redbeds and is more abundant than pyrite in the calcareous clays underlying the coal. Siderite is also more abundant in the Castleman basin than in the eastern structural trough. Siderite reacts more slowly than calcite [$CaCO_3$] reacts with dilute cold acids such as carbonic [H_2CO_3], hydrochloric [HCl], or sulfuric [H_2SO_4].

Gypsum [$CaSO_4 \cdot 2H_2O$] is one of the few common sulfate minerals in sedimentary rocks exclusive of evaporite deposits. In the Maryland coal measures, however, gypsum has been reported only from examination of cores in the calcareous clays underlying the coal where it is not a common accessory mineral. Here it occurs as coatings on partings and fractures in the clay, implying that at least in part it is secondary in origin and that possibly it could have formed as a result of the neutralization and concentration of coal-mine drainage.

All of the minerals that have been mentioned, in addition to others susceptible to attack by acid but whose stratigraphic distribution is presently unknown, are believed by the authors to be involved in mine-drainage geochemistry. The chemical data collected during this investigation, however, indicate that mine-drainage geochemistry is dominated by reaction of naturally occurring carbonates with the acid produced during pyrite oxidation.

Mining, Subsurface Drainage, and Sample-Site Evaluation

Mining practice and subsurface drainage in Maryland coal mines has been largely dictated by the structure and topography of the coal basins. Compared to the tightly folded and closely faulted

anthracite region of Pennsylvania, the Maryland bituminous coal basins are relatively shallow with simple, nearly horizontal structure which affects the topography and the regional flow of ground water. The land surface has been deeply dissected by the smaller streams which have left sloping hills a mile or more broad each of which typically is connected to a rim of a basin by a broad ridge or spur. As a result, coals crop out beneath mantling soil on the sides of the hills within the basins and springs are common in unmined areas. For these reasons the coals have been mined mostly from drift entries located near the axis of the basins above local stream base level.

From these entries the coals have been mined by the panel system of mining, on the rise (up dip) which permitted free draining and relatively dry working conditions without pumping. Even after these mines were abandoned, there has been only shallow pooling within the mines near the axis of the basins as a result of roof collapse or arching of the floor. Because pooling is shallow, dissolved gases in the deepest water in the mines are nearly in equilibrium with atmospheric pressure, and at constant temperature, the gases remain in solution when the water is discharged at land surface. Most abandoned mines with drift entries and open portals have a noticeable circulation of air through the portal.

There are many hills within the coal basins that have only one mine with drift entries in one coal seam although other unmined seams may be present in the hill. Based upon available mine maps and reconnaissance of sites in the field, the following sites among the 18 mines sampled for drainage are believed by the authors to be such a single, isolated drift-entry mine: sites 1, 3, 4, 5, 6, and 10 (appendix I, figures 10, 11, and 12).

Other hills contain several mines, numerous drift entries and workings in more than one coal seam. Although there may be workings in more than one coal seam in a single hill this does not necessarily mean that a significant hydraulic connection exists between mining levels. Based upon the relative size and the stratigraphic and structural position of all the known mine workings in the hill, the following sites, although not physically isolated are believed to be hydraulically isolated to the extent that neither the quantity nor the quality of drainage sampled at the site is significantly affected by other mine workings: sites 11, 14, and 15 (appendix I, figures 13 and 14).

Some of the hills that contain workings in more than one coal seam provide evidence that a significant hydraulic connection exists between mining levels. As an example, U. S. Bureau of Mines Mine No. 178 (Toenges and others, 1949,

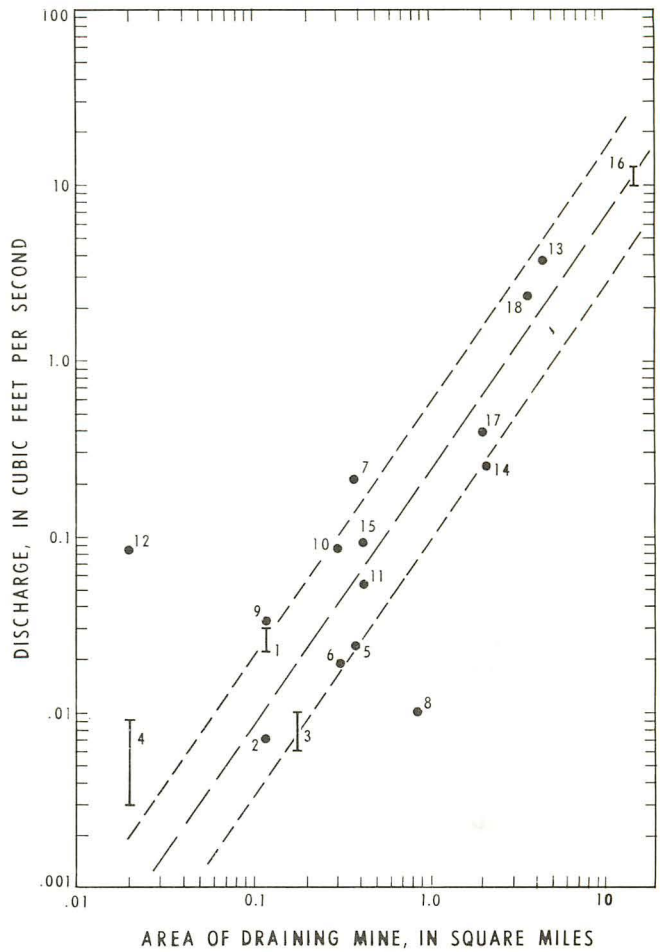

Figure 3.—Graph showing relation of measured discharge of mines to area of mine workings that contribute to flow at 18 sites.

and appendix I, figure 12, site 8) is part of an extensive mine in the Barton coal that is stratigraphically above Piedmont and Georges Creek Coal Company Washington No. 1 Mine (appendix I, figure 11, site 7) in the Upper Freeport coal. In addition Mine No. 178 is structurally up dip of Washington No. 1 Mine, the latter being situated over the axis of the eastern structural trough.

Figure 3 shows the relationship between the discharge measured at each sample site and the area of the mine workings shown in appendix I, figure 10, through 16, that drain to the sample site. The relationship is an approximation. It is based upon measurements of discharge made throughout the summer of 1970 (appendix II, table 4) when mine discharges were approximately in a low-flow condition. It is also based upon measurements of area of mine workings contributing to the discharge where the position of the underground drainage divides and the full extent of mine workings are not

accurately known. It should be noted from figure 3, however, that both sites 7 and 8 lie outside one standard error of estimate for the relationship, site 8 having too little discharge for its area and site 7 having too much discharge for its area. This relationship in discharges between 7 and 8 is the relationship that would be expected if site 8 were losing water by interflow to site 7.

U. S. Bureau of Mines, Mine No. 128 (appendix I, figure 12, site 9) has a hydrogeologic setting that is identical to the setting at site 7. Like the mine at site 7, Mine No. 128 also has excessive discharge indicating that a significant hydraulic connection may exist with mines above. Extensive mines, not sampled in this investigation, in the Barton and Pittsburgh coals are stratigraphically above Mine No. 128 in the Lower Bakerstown coal. In addition these mines are structurally up dip of Mine No. 128 the latter being just east of the axis of the eastern structural trough. It should be noted from figure 3 that site 9 lies outside one standard error of estimate for the relationship and has too much discharge for its area. The relationship in discharges between site 9 and the average for mines of its drainage area is the relationship that would be expected if site 9 were gaining water by interflow from extensive mines above.

A key point in regard to mine-drainage geochemistry in Maryland is that although more than one coal seam may have been mined in a single hill, vertical cross connections are rare in the underground between mining levels or coal seams worked from drift entries. As a result any vertical flow of water between mining levels is constrained to pass through the rock strata. The detailed chemical analyses for dissolved solids in water samples collected during this investigation (appendix II, tables 4, 5, and 6) indicate that this inferred, vertical flow of mine drainage through the rock strata is a critical control on the chemistry of drainage sampled at sites 7 and 9 as well as 16 and 17.

Drainage from strip mines frequently enters the underground workings of deep mines in the same coal seam. This phenomenon is most common where the strip mine is structurally up dip of the underground mine. Big Laurel Run Mine (appendix I, figure 13, site 12) is an example of a drift-entry mine receiving drainage from a large strip mine up dip of the underground mine. As a result the discharge at site 12 exceeds the average discharge of mines of the same drainage area by several orders of magnitude. Data for site 12 were accordingly omitted from calculation of the regression line by method of least squares shown in figure 3. Site 12 is also unique in that the drainage from the strip mine passes through the base of a solid-refuse dump prior to seeping into the underground workings. As a result the chemical quality of the drainage (appendix II, tables 4, 5, and 6) is not representative of coal-mine drainage. Murphy Coal Company Susanne No. 1 Mine (appendix I, figure 10, site 2) is an example of a drift-entry mine receiving drainage from a small strip mine up dip of the main portal of the underground mine. In contrast to the drainage from site 12, the chemical quality of drainage from site 2 (appendix II, tables 4, 5, and 6) is more representative of dilute coal-mine drainage.

In contrast to the abundance of drift-entry mines, only a few vertical shaft entries have been used to mine the thickest coals on the axis of the eastern structural trough in those areas where the coals may be several hundred feet below local stream base level. Mining from the shaft entries was conducted in combination with mining from drift entries near the margin of the trough from which the coal was mined on the slope (down dip). Both types of entries required pumping to keep the workings dry and were subject to flooding and eventual deep pooling whenever the pumps were not operating. As work progressed, drifts on the slope were eventually connected to drifts on the rise from the shaft and then all water was collected at a central sump at the bottom of the shaft from which it was pumped to the surface. Local pools in the mine were either ditched or drained to the sump with small pumps.

Only three large underground mines in the Maryland part of the eastern structural trough were worked from both shaft and slope entries. These are the Davis Coal and Coke Company Mine No. 42 in the Upper Freeport coal at Kempton, Maryland (appendix I, figure 14, site 13), the Island Creek Coal Company Alpine Mine (formerly Davis Coal and Coke Company Mine No. 22) in the Lower Bakerstown coal at Henry, West Virginia (appendix I, figure 16, site 18), and the Consolidation Coal Company workings in the Pittsburgh and Sewickley coals in the central part of the Georges Creek basin (appendix I, figures 15 and 16, sites 16 and 17).

One of these three, the Davis Coal and Coke Company Mine No. 42, has been abandoned since 1950. Elevations on the mine maps indicate that pooling is only 30 feet deep at the point of discharge (sample site 13) outside an air shaft near the north edge of the mine. Elevations near the east edge of the mine, however, indicate that pooling may be as deep as 370 ft. The Upper Freeport was the only coal worked in this mine. The workings extend into other mines to the south, and (as is the case with several of the mines investigated) the exact position of the underground drainage divide is not known. The Upper Freeport coal has been strip mined adjacent to the northwest edge of the underground mine and structurally up dip of the

underground mine. Drainage from the strip mines may be increasing the flow from the underground mine. In addition along two-thirds of its length, the main heading of the underground mine is within 300 feet of the North Branch Potomac River.

The Island Creek Coal Company Alpine Mine was worked from two shafts at Henry, Grant County, West Virginia, when the mine was owned by Davis Coal and Coke Company. Workings were opened in both the Upper Freeport and Lower Bakerstown coals, but the workings in the Upper Freeport were abandoned sometime between 1901 and 1920. Workings in the Lower Bakerstown coal extend beneath the Maryland side of the Potomac River and were being actively worked by Davis Coal and Coke Company in 1920. The Alpine Mine is presently worked in West Virginia on the rise as well as the slope by the Island Creek Coal Company from a drift entry on the east side of the mine. The old workings of the Davis Coal and Coke Company Mine No. 22 are used as a sump from which the water is pumped periodically through a deep well (at sample site 18) that was drilled into the old workings. It is believed that the old, deeper workings in the Upper Freeport coal were not extensive enough to have a significant effect upon either the quantity or quality of drainage from this mine.

The abandoned mines of the Consolidation Coal Company in the Pittsburgh and Sewickley coals between Frostburg and Midland (appendix I, figure 15, and 16) have a unique drainage system. In 1903 pumping costs became burdensome, and the Company decided to drive a tunnel 10,646 feet long from Braddock Run (a tributary of Wills Creek) near Clarysville to the lowest workings in the Pittsburg coal immediately east of the Pumping Shaft. The Hoffman Drainage Tunnel (sample site 16) was completed in 1906 and subsequently all 17 square miles of workings except those in the extreme northeastern and southern ends of the properties were connected to the tunnel by means of 13 miles of auxiliary tunnels and ditches in the floor of the mine. The Allegany Water Ditch (appendix I, figure 16, site 17) still effectively drains the northeastern part of the properties to Jennings Run northeast of Frostburg. Prior to 1903, the Midland Drainage Tunnel was driven from the right bank of Georges Creek opposite Midland west to the center of the Georges Creek basin in order to drain parts of five mines. This tunnel, however, no longer functions, and the drainage is diverted to Hoffman Drainage Tunnel.

Workings in the Sewickley coal, 100 feet or more stratigraphically above the Pittsburgh coal, were drained by bore holes that were drilled from the ground surface down through depressions in the floor of the Sewickley workings, down through the intervening strata, and into workings in the Pittsburgh coal. In this way the Sewickley coal as well as the Pittsburgh coal was drained by the Hoffman Drainage Tunnel and Allegany Water Ditch.

The southern property boundary of the Consolidation Coal Company workings in the Pittsburgh coal is believed to be approximately in the location of the underground drainage divide between these workings and mines north of Lonaconing (appendix I, figure 15). This estimate is based upon the location and volume of flow from known points of discharge from the Pittsburgh coal in Oak Hill north of Lonaconing. Seepage out of Georges Creek may constitute a significant part of the flow of Hoffman Drainage Tunnel. Baker (1922, p. 179) reports that the removal of pillars in the workings of the Pittsburgh coal caused fracturing and subsidence of the overlying strata. These breaks extended not only up through the Sewickley coal, offsetting it, but also on up to land surface. As a consequence three mines in the Sewickley coal had to be abandoned. Slaughter reports (Slaughter and Darling, 1962, p. 130) that apparently during low-flow periods, the tunnel is capable of diverting nearly all the flow of the upper one-third of the watershed of Georges Creek, presumably through the fractures extending up from the Pittsburgh workings. This judgment is based in part upon observations of flow of Georges Creek on October 3, 1957, when flow at Borden Shaft, 2.6 miles north of Midland, was estimated to be 1.5 cfs (cubic feet per second) and decreased to 0.0 cfs at Ocean, 0.9 mile north of Midland. These observations are supported by measurements made on September 24, 1964, when flow decreased from 0.55 to 0.34 cfs over the same reach of stream.

Concepts of Ground-Water Flow Systems

Very little is known about the nature and configuration of the ground-water flow system in the coal basins of Maryland as it occurred prior to underground mining. Some insight into the probable nature of the system may be gained from published results of investigations in western Pennsylvania (Carswell and Bennett, 1963; Poth, 1963) where the boundary conditions for the flow system in the bedrock are quite similar. The upper boundary of the flow system is the land surface which is similar in topography and relief to unglaciated parts of western Pennsylvania. The lower boundary is the interface between fresh, circulating ground water and saline, relatively stagnant water at depth. It has been encountered in only one well in the coal basins of Maryland at a depth between 800 and 1,500 feet in the valley of North Branch Potomac River

(Slaughter and Darling, 1962). The lower boundary in Maryland is believed by the authors to be similar to the lower boundary in Pennsylvania in general nature and configuration. The lithology of the coal measures in Maryland is very similar to the lithology in western Pennsylvania, and therefore the internal boundaries in the flow system should be very similar.

In Mercer, Lawrence, and Butler Counties, Pennsylvania, the land surface has been dissected into discrete hills a few square miles in area, and as a result the shallow part of the ground-water flow system is subdivided into discrete "hydrologic islands." Precipitation enters the upper, middle part of each hill, moves vertically down through the clay confining layers and sandstone aquifers, moves horizontally through the fractured sandstones at several levels, and is discharged from several of these aquifers into the valleys around the margin of the hill. Some of the infiltrating precipitation moves vertically deeper into the underlying sandstones to recharge the deep part of the ground-water flow system, moves longer distances horizontally under the "hydrologic islands" and the small uplands streams, and after upward vertical movement is discharged to major streams that comprise base level in the region. Water rises in wells above the top of the aquifer in which it encountered during drilling, indicating artesian conditions. Water levels in wells in the same aquifer stand at a higher elevation under hills than under valleys, indicating recharge under the hills as would be expected under water-table conditions. Because data were insufficient for the preparation of potentiometric maps, this concept of the ground-water flow system under natural conditions prior to any extensive underground mining is based upon observations of internal flow and water levels in individual wells in Pennsylvania. Water-quality data substantiate this concept of the system. The ground-water flow system under natural conditions is probably very similar in Maryland, modified only in net direction of lateral flow by the steeper dip of the strata away from the margins of the Maryland coal basins.

During the initial development of a large, underground, drift-entry coal mine the ground-water flow system in the immediate vicinity of the mine is radically altered. Prior to removal of coal from the rooms and panels, the main heading and lateral headings act as line sinks for ground-water discharge, short-circuiting the flow paths from point of infiltration of precipitation to point of ground-water discharge. Proportionately large quantities of the total flow of ground water from the mine are derived from storage as the water pressure decreases in adjacent aquifers above and below the headings.

During continued development of the drift-entry mine, the ground-water flow system tends to establish a new equilibrium between inflow and outflow under the new and constantly changing boundary conditions. As headings are advanced, the coal is removed from rooms and panels over a very large area compared to the thickness of the coal. A mine in relatively horizontal strata then acts more as a plane sink or underdrain rather than a line sink, accepting all of the downward flow of ground water from above. Proportionately less water is removed from storage, and all but the edges of the workings come to act more as a conduit for steady-state transmission of ground water. Because of the increase of velocity of flow in the open mine workings, recharge to the deep part of the ground-water flow system is virtually cut off in the vicinity of the mine.

During final mining operations pillars are removed from the panels as mining retreats toward the main portal, and the roof of the mine is allowed to fracture and collapse. The secondary faults and fractures associated with the roof failure extend up through the overlying strata and result in more efficient capture of any lateral ground-water flow that might have occurred in either an overlying aquifer or an upper mining level. Removal of water from storage in an overlying aquifer provides more available storage space for recharge. Therefore it is possible that less storm-water runoff may result from a given amount of precipitation. In addition some ground water may be diverted to the mine before reaching a local stream. Therefore it is possible that the base flow of a stream may correspondingly be reduced locally. Where fractures extend up to the land surface, water already in the stream may be diverted into the underground flow system. The latter situation appears to be the case where Georges Creek traverses mine workings drained by Hoffman Drainage Tunnel. During this investigation at no place in the Georges Creek basin were the abandoned mine workings in the Sewickley coal found to have a discharge to the surface that is independent of the drainage system in the underlying workings in the Pittsburgh coal. It is probable that the bore holes that were originally drilled to drain the workings in the Sewickley coal have collapsed and these workings are presently drained by the extensive fractures and faults which extend up from the Pittsburgh workings and which necessitated abandonment of three mines in the Sewickley coal.

The composition of mine drainage is the output of a complex hydrogeochemical system where several solute-to-mineral equilibria are not attained. The composition is therefore partly determined by

water flow rates as well as chemical reaction rates. The time available for chemical reaction between ground water or mine drainage and the minerals in the fractured zone of strata overlying an abandoned mine in horizontal strata can be estimated given reasonable assumptions. The time is directly proportional to the distance, or thickness of the zone, and inversely proportional to the velocity of vertical flow in the zone. The basic equation for computing time is:

$$T = \frac{D}{V} \qquad (1)$$

where:

T = time to travel a known distance (the thickness), in days

D = distance between top and bottom of the zone, in feet

V = mean velocity between top and bottom of zone, in feet per day

Assuming that the rock in the roof of the mine is completely saturated and that the rock as a whole is hydraulically homogeneous in the zone of saturation, then the velocity of flow in the zone is proportional to the hydraulic conductivity (K) of the fractured materials, their effective porosity (p) and the hydraulic gradient (i). The basic equation for computing velocity is:

$$V = \frac{Ki}{p} \qquad (2)$$

where:

V = mean velocity of a particle of fluid, in feet per day

K = hydraulic conductivity, in feet per day

i = hydraulic gradient, or change in pressure, expressed in feet of water per foot of corresponding distance travelled

p = effective porosity, expressed as a decimal fraction

For vertical flow in a saturated, homogeneous zone the hydraulic gradient may be taken as unity, and equation (2) reduces to:

$$V = \frac{K}{p} \qquad (3)$$

The hydraulic conductivity (K) may be calculated from the following modified form of the Darcy equation:

$$Q = K\ i\ A \qquad (4)$$

where:

Q = discharge of the mine, in cubic feet per day

K = hydraulic conductivity, in feet per day

i = hydraulic gradient, here taken as unity, in feet per foot

A = area of the mine roof, in square feet

The discharge (Q) and the area (A) of the mine at site 11 which has the median discharge of those measured (figure 3) and which is in a recharge area of the flow system may be used to obtain a rough estimate of the hydraulic conductivity (K) of fractured roof materials over abandoned mines, thus:
Given:

Q = 5.3×10^{-2} cubic feet per second = 4.6×10^{3} cubic feet per day

A = 4.2×10^{-1} square miles = 1.2×10^{7} square feet

i = 1 foot per foot

Then substituting into equation (4):

$4.6 \times 10^{3} = K\ (1)\ 1.2 \times 10^{7}$ or $K = 3.8 \times 10^{-4}$ feet per day

Using this median estimate of hydraulic conductivity and a reasonable estimate of the effective porosity of the fractured zone, a rough estimate may be made of the mean vertical velocity of a fluid particle in the zone, thus:
Given:

$K = 3.8 \times 10^{-4}$ feet per day

$p = 1 \times 10^{-2}$ to 1×10^{-3}

Then substituting into equation (3):

$$V = \frac{3.8 \times 10^{-4}}{1 \times 10^{-2} \text{ to } 1 \times 10^{-3}} \quad \text{or}$$

$$V = 0.4 \text{ to } 0.04 \text{ foot per day}$$

Average velocity for surface streams in western Maryland is about 1 foot per second (90,000 feet per day) or between 200,000 and 2 million times faster than the 0.4 to 0.04 foot per day vertical ground-water flow. It may be concluded from equation (1) that for comparable distances the time available for chemical reaction in the ground-water flow system is 5 to 6 orders of magnitude greater than in streams.

This difference between time of travel in the ground-water system compared to surface streams is of particular significance to the effectiveness of some processes of acid neutralization under oxidizing conditions in the two systems. When carbonate rocks either occur in the streambed or are added to a stream containing mine drainage rich in iron as well as acid, insoluble ferric hydroxide tends to precipitate on the reacting carbonate mineral surfaces. This insoluble coating tends to reduce the rate of acid-base reaction logarithmically with time, and for all practical purposes the reaction is regarded as having stopped. Because the time for chemical reaction is 5 to 6 orders of magnitude greater in the ground-water system, however, the quantity of acid neutralized may be 5 to 6 times greater than in streams over comparable distances and over comparable surface area of reacting mineral. Thus, in an oxidizing environment, for practical purposes the acid-base reaction in the ground-water system may not be regarded as having stopped once the insoluble , yet permeable, ferric hydroxide coating is formed.

Summary

The coal measures of western Maryland are in shallow, synclinal basins lacking complex structure. Underground mining, however, has resulted in secondary faults and fractures which have significantly modified the vertical permeability of overlying strata. The strata consist of a repeating sequence of sandstone, siltstone, and shale that displays two lithologic aspects, either few lithologic types or a variety in lithologic types, the latter being characterized by marine shales and red beds. The most abundant minerals in the coal measures are quartz, micas and clays, and carbonates. The geochemistry of mine drainage, although involved with all minerals susceptible to attack by strong acids, is dominated by reaction of carbonates with the acid produced during oxidation of pyrite, a less abundant accessory mineral.

The hills within the basins contain many self-draining mines with drift entries. Only three large mines (at sites 13, 16, 17, and 18) were worked from both shaft and slope entries which required either pumping or tunneling to keep them dry. The drift-entry mines at sites 1, 3, 4, 5, 6, 10, 11, 14, and 15 are sufficiently isolated hydraulically that discharge and chemical data from these mines may be used as a control group for interpreting the discharge and water chemistry at the nine remaining mines which have more complex mining and hydrologic settings. The mine at site 7 is positioned stratigraphically below and structurally down dip from a larger mine at site 8. Similarly the mine at site 9 is below and down dip from larger mines in the same hill. The relationship between the discharge and area of the mine workings (figure 3) indicates that the upper mines may be losing water to the lower mines at 7 and 9 by drainage through the intervening rock strata. The history of mining and drainage of mines at sites 16 and 17 reveals that workings in the Sewickley coal are losing water to lower workings in the Pittsburgh coal by drainage through the intervening rock strata.

The boundary conditions for the ground-water flow system in the coal basins of Maryland prior to underground mining are similar to the conditions in western Pennsylvania. Precipitation enters the upper part of each hill, moves down through confining layers and aquifers, moves horizontally through the fractured sandstone aquifers at several levels, and is discharged into the valleys around the margin of the hill. The headings of a new drift-entry coal mine act as line sinks, short-circuiting the ground-water flow from point of infiltration to point of natural discharge. As coal is removed over a very large area compared to the thickness of the coal, the mine acts more as a plane sink or under-

drain. Fractures associated with roof failure result in more efficient capture of any lateral ground-water flow that might have occurred in either an overlying aquifer or an upper mining level. The time of travel for a particle of water in vertical ground-water in the fractured strata overlying an abandoned mine is five to six orders of magnitude longer than travel time in a surface stream over a comparable distance. Time available for chemical reaction between mine drainage as ground water and minerals in the fractured strata compared to time for reaction between mine drainage as streamflow and minerals in the streambed is correspondingly five to six orders of magnitude greater.

GEOCHEMISTRY OF MINE DRAINAGE

The chemical formation and neutralization of acid water in underground coal mines of western Maryland is primarily controlled by solution of gases and mineral matter and by subsequent reaction of the dissolved chemical species with more mineral matter both in and adjacent to the mine workings. Mine drainage as an aqueous solution begins with the chemical evolution of fresh ground water unaffected by mine drainage. The initial products of pyrite oxidation are then dissolved in and react with this fresh ground water. The resulting acid water reacts with minerals in the mine rock on contact, increasing the number of dissolved chemical species and reducing the acidity by acid-base reaction with carbonate minerals. At any time before discharge to the surface, the acid water may be diluted by mixing with fresh ground water or with even less mineralized surface water.

Fresh Ground Water

Infiltration precipitation dissolves gaseous carbon dioxide which is released by organic decay to the pore spaces in soil and rock above the water table. The dissolved carbon dioxide reacts in water to produce carbonic acid.

$$CO_2(aq) + H_2O(1) \rightleftarrows H_2CO_3(aq). \qquad (1)$$

The H_2CO_3 dissociates to bicarbonate

$$H_2CO_3(aq) \rightleftarrows H^+ + HCO_3^- \qquad (2)$$

and to carbonate

$$HCO_3^- \rightleftarrows H^+ + CO_3^{-2} \qquad (3)$$

In waters having a pH less than 6.3, the H_2CO_3 species of carbon dioxide predominates. At pH values between 6.3 and 10.2, the HCO_3^- is dominant.

As the water moves down to the water table and then within the zone of saturation, it comes in contact with carbonate minerals of which calcite is the most reactive. The hydrogen ion reacts with the calcite to produce calcium and bicarbonate ions

$$CaCO_3(s) + H^+ \rightleftarrows Ca^{+2} + HCO_3^-. \qquad (4)$$

At a slower rate the hydrogen ion also reacts with dolomite to produce magnesium as well as calcium and bicarbonate ions

$$CaMg(CO_3)_2 + 2H^+ \rightleftarrows Ca^{+2} + Mg^{+2} + 2HCO_3^- \qquad (5)$$

By removing hydrogen ions from solution, reactions (4) and (5) increase the pH and reduce the acidity of the ground water.

The hydrolysis reaction in equation (4) proceeds to the right until calcium and bicarbonate are in equilibrium with calcite. Within the range in concentration of CO_2 commonly occurring in soil (0.003 to 0.03 atmosphere partial pressure), the sequence of reactions in equations (1) through (4) should obtain equilibrium with calcite at concentrations for calcium between 45 and 100 mg/l and for bicarbonate between 140 and 300 mg/l (Hem, 1970). In the absence of highly soluble minerals other than calcite and in the absence of clays with adsorbed sodium ions, calcium remains the dominant anion in fresh ground water.

The resulting composition is typical of the chemical composition of water from wells unaffected by mine drainage in the coal basins of western Maryland (appendix II, table 3). In six samples of water, the dissolved solids concentration ranges from 35 to 305 mg/l , having a median of 170 mg/l . Calcium ranges from 6.0 to 75 mg/l , having a median of 42 mg/l or 70 percent of the equivalents of cations. Magnesium, the next most abundant cation, ranges from 2.3 to 15 mg/l , having a median of 7.9 mg/l or 20 percent of the equivalents of cations. Bicarbonate, which is the only

significant source of alkalinity in the fresh ground water, ranges from 27 to 292 mg/l , having a median of 182 mg/l or 80 percent of the equivalents of anions.

As indicated by figure 2 and the remarks column in table 3, all the wells are open to one or more coal seams; however, the iron concentration does not exceed 0.80 mg/l and the sulfate does not exceed 45 mg/l . The median value for sulfate is only 16 mg/l or 9 percent of the equivalents of anions. This small concentration of sulfate probably is derived either from precipitation or from chemical weathering of pyrite under natural conditions. In no sample is the pH less than 6.7. Although pH of the six samples was measured in the laboratory and, therefore, may be in error by several tenths of one pH unit, the reported pH indicates that water from wells All-Ac 50, Bc 24, and Ca 8 are supersaturated with respect to calcite. Similarly, water from wells All-Cb 1 and Gar-Ad 1 and Ae 8 are undersaturated with respect to calcite.

Chloride concentrations in water from wells that are 500 feet or less in depth range from 0.6 to 33 mg/l , having a median of 7.5 mg/l. Concentrations exceeding about 5 mg/l probably are derived from winter salting of nearby roads or from septic wastes seeping through the ground at shallow depth. Water entering well All-Da 7 between depths of 1521 feet and 2379 feet contains 9,550 mg/l of chloride and 16,000 mg/l dissolved soli The wells that are 500 feet or less in depth have not intercepted this zone of saline water.

Mine Drainage

Assuming natural conditions and an oxidizing environment, a simplified expression of the stepwise reaction that ultimately produces ferric hydroxide, acid, and sulfate from pyrite is:

$$FeS_2(s) + 7/2O_2(aq) + H_2O = Fe^{+2} + 2SO_4^{-2} + 2H^+ \quad (6)$$

$$Fe^{+2} + 1/4O_2(aq) + 5/2H_2O = Fe(OH)_3(s) + 2H^+ \quad (7)$$

In the presence of both calcite and dissolved oxygen, equation (7) may take the form of the neutralization - oxidation reaction:

$$Fe^{+2}+1/4O_2(aq)+5/2H_2O+CaCO_3(s)=Fe(OH)_3(s) +Ca^{+2}+H_2CO_3(aq). \quad (8)$$

Equations (7) and (8) assume oxidizing conditions throughout the reaction sequence. Following reaction (6), it is possible that the mine drainage might enter a reducing environment. This situation might be particularly true of drainage moving from an upper mining level to a lower mining level through the intervening rock strata. Assuming a reducing environment is present, the ferrous iron produced in reaction (6) might be removed from the aqueous system in the form of siderite ($FeCO_3$). In this case, neither equation (7) nor equation (8) would apply, and oxidation of 1 mole of pyrite would produce only 2 moles of hydrogen ion.

From equation (6) it may be concluded that each time one mole of pyrite is oxidized, two moles of sulfate are formed. Principles of chemical kinetics dictate that the mass of pyrite that is oxidized in unit time is proportional to the total mass of exposed and oxidizable pyrite in the mine assuming all other factors are constant. The mass of sulfate that is formed in unit time, therefore, is also proportional to the total mass of exposed and oxidizable pyrite in the mine. The concentration of pyrite in the mine is equal to the mass of exposed pyrite divided by the volume of disturbed coal and waste rock remaining in the mine. The volume of disturbed coal and waste, however, is dominantly a function of the area of mine workings. This last relationship assumes that there is relatively small variability in the thickness and recovery of workable coals in comparison with variability in area of mine workings. On the other hand, the concentration of sulfate in mine drainage is equal to the total mass of sulfate that is formed in unit time divided by the discharge or volume of flow of drainage for the same unit time. As indicated in figure 3, the discharge is a function of area of mine workings; as noted above, the volume of disturbed coal and waste is also a function of the area of mine workings. Therefore, the concentration of sulfate in mine drainage should be directly proportional to the concentration of pyrite in the mine.

This conclusion relating sulfate to pyrite should be valid provided several fundamental assumptions are satisfied. These assumptions are: (1) There is no significant source of sulfate other than pyrite oxidation; (2) no significant quantities of sulfate are removed from drainage by sulfate reduction in the presence of sulfate-reducing bacteria with an adequate organic food supply; (3) no significant quantities of sulfate are removed by precipitation from drainage supersaturated with respect to gypsum; (4) sufficient gaseous and dissolved oxygen is available and sufficient time has elapsed since initiation of the stepwise reaction sequence such that the rate of pyrite oxidation is relatively the same for

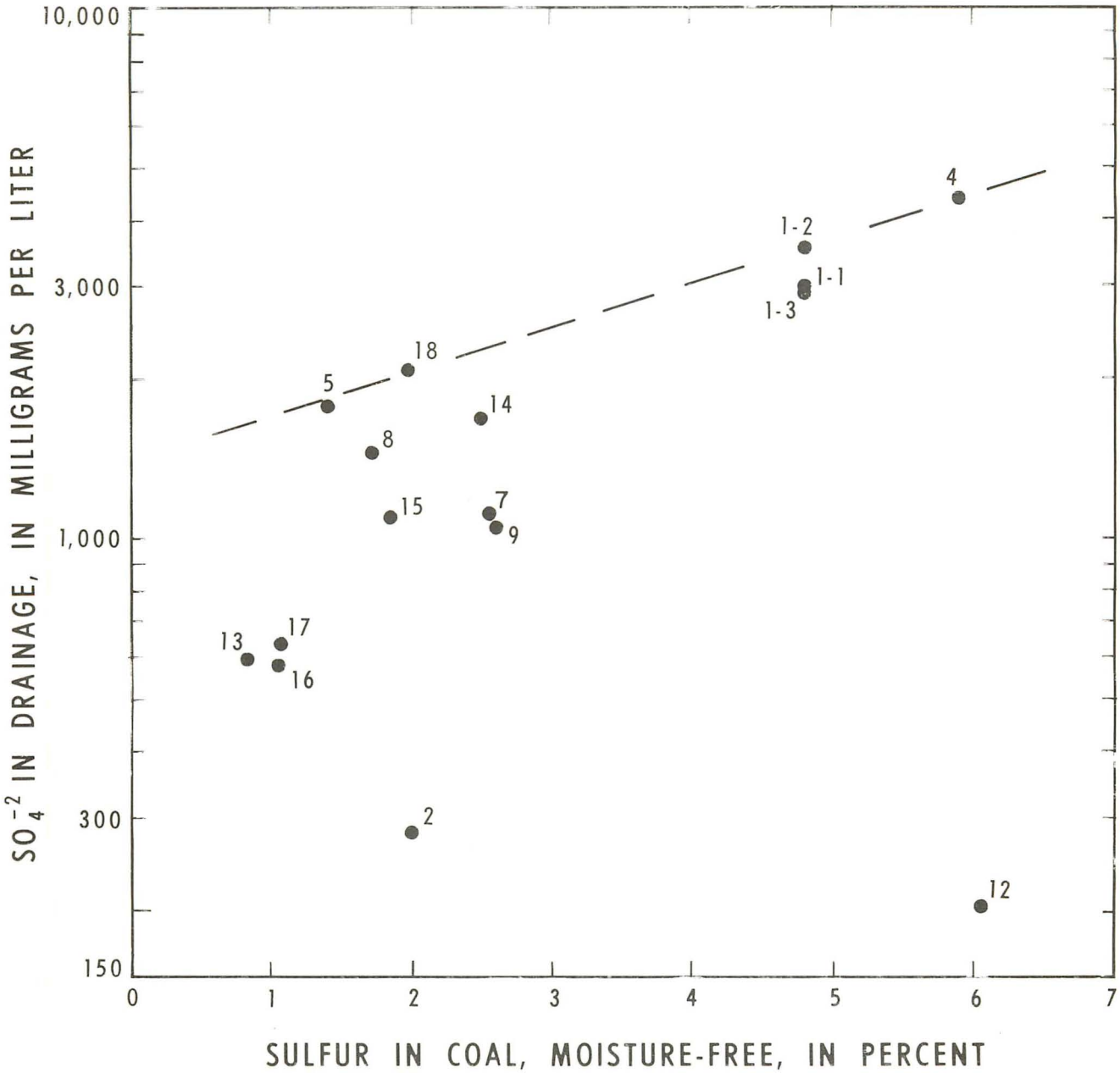

Figure 4.—Graph showing relation of sulfate concentration in drainage to sulfur concentration in coal.

all mines considered; and (5) the drainage area determining the discharge of the mine is no more than the area of mine workings. Data collected in this investigation indicate that for several mines, assumptions (4) and (5) may be the most difficult to satisfy in western Maryland.

In addition, it should be noted that not all pyrite in coal and associated waste remaining in the mine is equally reactive or oxidizable (Caruccio and Parizek, 1967; Caruccio, 1970) nor is pyrite the only form of sulfur in coal. As concentrations of sulfur in coal exceed one percent, however, it appears that readily oxidizable pyrite constitutes an increasingly dominant portion of the total pyrite, and the total pyrite constitutes an increasingly dominant portion of the total sulfur in coal. As a result of this latter relationship, it may be inferred that if the previous assumptions are satisfied then the concentration of sulfate in drainage should be proportional to the concentration of sulfur in coal.

Figure 4 shows the relationship between sulfate in drainage and sulfur in coal for drainage corresponding to available analyses of coal (Abernethy and Ode, 1952; Cooper and Abernethy, 1949;

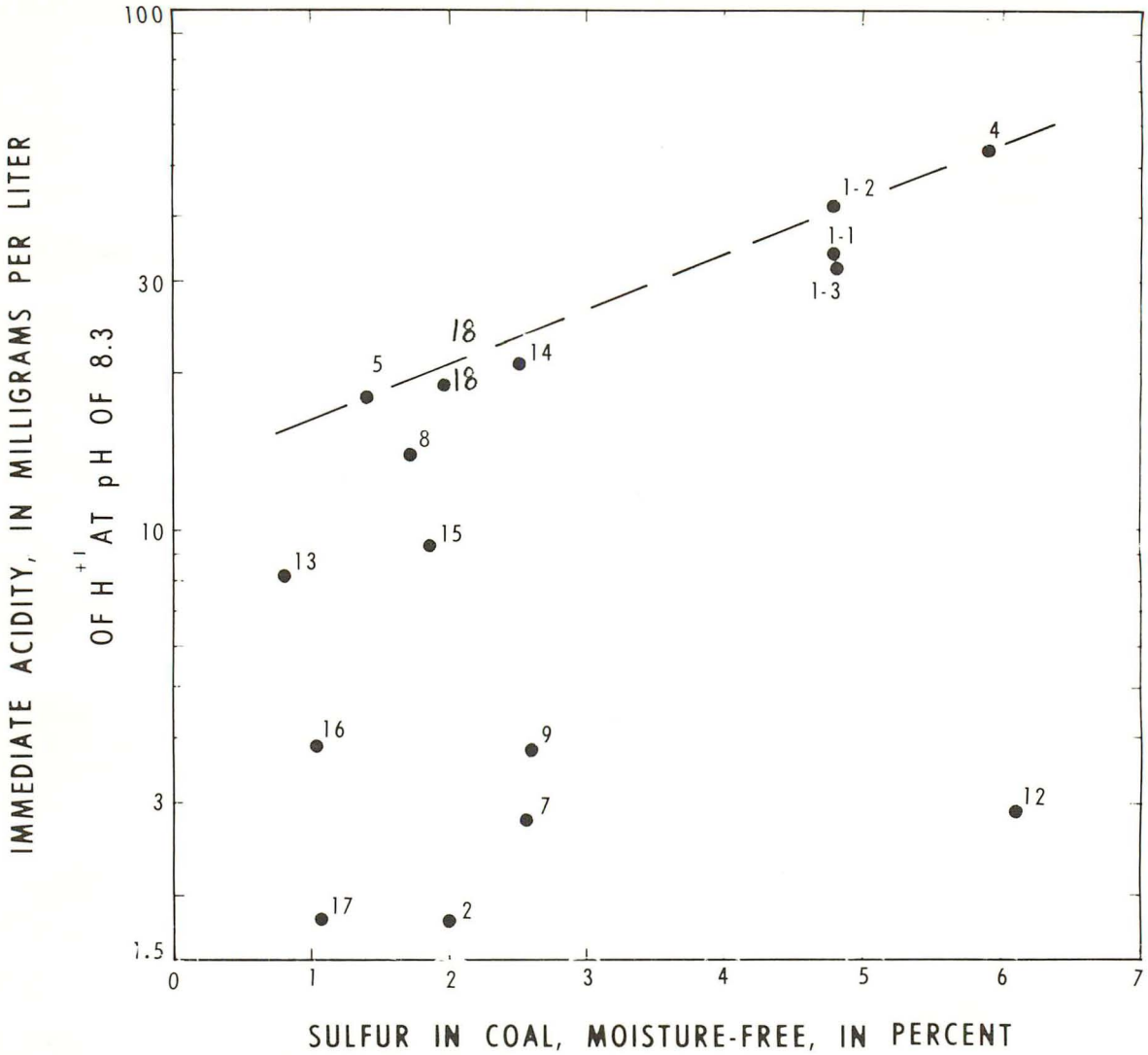

Figure 5.—Graph showing relation of immediate acidity of drainage to sulfur concentration in coal.

Swartz and Fieldner, 1922). In spite of all the assumptions that need to be satisfied, at least a limiting sulfate concentration can be estimated for a given sulfur concentration in coal. Departures from the upper limit of sulfate concentration apparently are related primarily to assumptions (4) and (5). As an example, mines at sites 4 and 18 were the only active mines that were sampled. Gaseous oxygen is abundantly available as a result of the forced-air ventilation system that is required for mining. These two mines were the youngest that were sampled. Perhaps sufficient time had not elapsed since initiation of the reaction sequence, and therefore oxidation rates at these two mines significantly exceeds oxidation rates at the remaining mines. It should be noted that sites 4 and 18 define the upper limit of sulfate concentration. In addition, the hydrogeologic setting of mines at sites 2, 12, 13 and 16 indicates that these mines are receiving drainage either from adjacent strip mines or from overlying streams, and therefore the drainage area determining the discharge may significantly exceed the area of mine workings. The relationship between the measured sulfate concentration in drainage at sites 2, 12, 13 and 16 and the limiting sulfate concentration for a given concentration of sulfur in coal is the relationship that would be expected if dilution with relatively sulfate-free water were taking place. Some of the deepest pooling occurs in the mine at site 13. This may decrease the availability of oxygen for pyrite oxidation in this mine.

From equations (6) and (7) in the stepwise reaction in the oxidation of pyrite it may be concluded that oxidation of one mole of pyrite ultimately produces four moles of hydrogen ion, assuming oxidizing conditions throughout the reaction sequence followed by hydrolysis of metal ions, particularly iron and aluminum. The immediate acidity is a measure of the concentration of solutes capable of reacting with hydroxyl ion at the time of sampling. It includes both free hydrogen ions and hydrolyzable metal ions. Following the line of reasoning and assumptions used to infer a relationship between sulfate in drainage and sulfur in coal, the immediate acidity of drainage also should be proportional to the sulfur in coal. This conclusion should be valid provided an additional fundamental assumption is satisfied: (6) no neutralization has taken place in the underground environment.

Figure 5 shows the relationship between immediate acidity of drainage and corresponding sulfur in coal. In spite of all the assumptions, at least a limiting immediate acidity can be estimated for a given sulfur concentration in coal. Conclusions from figure 4 concerning sites 4 and 18 also apply to figure 5. In relation to site 2, the immediate acidity at sites 12 and 13 is significantly greater than might be predicted from the relative position of sites 12 and 13 to site 2 in the plot of sulfate versus sulfur in coal. Also, relative to the other mines, the immediate acidity at site 13 has not been significantly reduced by dilution. The relative increase in departure of sites 7, 9, and 17 from the limiting concentration in figure 5 over departure in figure 4 implies that neutralization may be taking place without significant dilution.

The relationships in figure 4 and 5 suggest that a predictive model of mine drainage composition might be developed starting with the composition of the coal and associated waste rock. The most significant conclusion from these figures, however, is that there may be a process of neutralization in the underground environment that is not a result of dilution of drainage with mildly alkaline water. Examination of additional constituents in mine drainage in relation to constituents in fresh ground water, the usual diluting medium, will reveal the nature and prevalence of this process.

According to equation (6), oxidation of 1 millimole of pyrite produces:

55.9	mg (milligrams)	Fe^{+2}
2.02	mg	H^{+}
192.	mg	SO_4^{-2}

Similarly, using the sulfate concentration at site 18 (appendix II, table 5), as an example (figure 6), oxidation of 10.88 millimoles of pyrite produces:

608.	mg or 21.8 meq (milliequivalents)	Fe^{+2}
22.0	mg or 21.8 meq	H^{+}
2090.	mg or 43.5 meq	SO_4^{-2},

where 2090 mg/l of sulfate was measured. Using the average bicarbonate concentration of fresh ground water as an example (appendix II, table 3) and neglecting any species comprising less than 10 percent of either cations or anions results in the following average-composition, fresh ground water:

44.	mg/l or 2.2 meq/l (milliequivalents per liter)	Ca^{+2}
9.7	mg/l or 0.8 meq/l	Mg^{+2}
180.	mg/l or 3.0 meq/l	HCO_3^{-}

Dissolving the initial oxidation products of 10.88 millimoles of pyrite assumed for site 18 in 1 liter of average-composition, fresh ground water produces:

44.	mg/l or 2.2 meq/l	Ca^{+2}
9.7	mg/l or 0.8 meq/l	Mg^{+2}
608.	mg/l or 21.8 meq/l	Fe^{+2}
19.0	mg/l or 18.8 meq/l	H^{+}
0.0	mg/l or 0.0 meq/l	HCO_3^{-}
2090.	mg/l or 43.5 meq/l	SO_4^{-2}

where hydrogen ion concentration is lowered and bicarbonate eliminated by reversal of equilibrium reactions (1) and (2). Diluting the above with another liter of average-composition, fresh ground water produces 2 liters of drainage having the following composition:

44.	mg/l or 2.2 meq/l	Ca^{+2}
9.7	mg/l or 0.8 meq/l	Mg^{+2}
304	mg/l or 10.9 meq/l	Fe^{+2}
8.0	mg/l or 7.9 meq/l	H^{+}
0.0	mg/l or 0.0 meq/l	HCO_3^{-}
1045	mg/l or 21.8 meq/l	SO_4^{-2}

It should now be obvious that further dilution of drainage with average-composition, fresh ground water will in no way raise the concentration of calcium and magnesium in excess of 3.0 meq/l while neutralizing the acid and lowering the concentration of iron and sulfate. In fact, dilution cannot explain the occurrence of calcium and magnesium in mine drainage in concentrations much higher than 5.0 meq/l, or 75 mg/l of calcium and 15 mg/l of magnesium, the maximum concentrations reported for fresh ground water (appendix II, table 3).

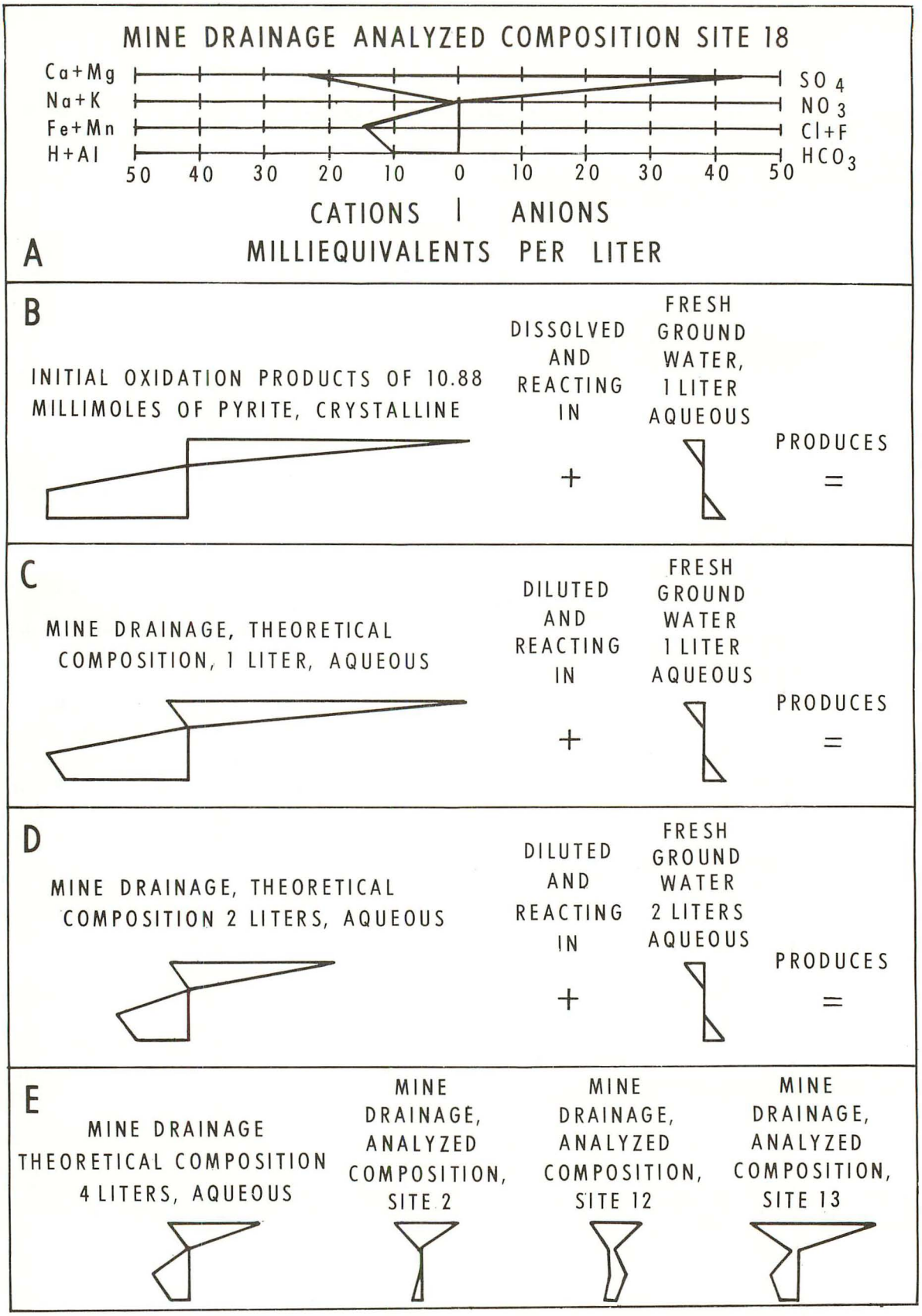

Figure 6.—Theoretical composition of mine drainage resulting from dilution with fresh ground water compared to composition as analyzed. A, explanation. B thru D, dilution sequence. E, comparison with composition as analyzed for three sites.

Theoretical dilution of drainage that has a limiting sulfate concentration, site 18, with average-composition fresh ground water results in a composition that is not typical of drainage actually sampled (appendix II, table 5). In 21 samples of mine drainage, the dissolved solids concentration ranges from 342 to 6,830 mg/l , having a median of 1720 mg/l or one order of magnitude higher than in fresh ground water. Calcium ranges from 40 to 399 mg/l , having a median of 240 mg/1 or 3.2 times higher than the maximum reported in fresh ground water. Magnesium ranges from 12 mg/l to 281 mg/l , having a median of 72 mg/l or 4.8 times higher than the maximum in fresh ground water. Theoretical concentrations of calcium and magnesium resulting from dilution obviously are much too low to be typical of the real world. Iron ranges from 0.55 to 748 mg/l , having a median of 42 mg/l or nearly one order of magnitude lower than theoretical concentrations resulting from one-time dilution. Sulfate ranges from 205 to 4410 mg/l , having a median of 1,100 mg/l which is approximately equivalent to the theoretical concentration resulting from one-time dilution and which is 99 percent of the equivalents of anions.

Based entirely upon concentrations of calcium and magnesium, the composition of water from only sites 2, 12, and 14 come close to fitting the theoretical example of dilution (figure 6). The overall composition of water from site 13, however, is the closest fit because the concentration of iron in water from sites 2 and 12 is substantially lower than the theoretical concentration. This difference in concentration of iron may be explained by the fact that the dissolved oxygen in water from sites 2 and 12 was considerably higher than 1 mg/l (appendix II, table 4). As a result the redox potential (Hem, 1970) was high enough to permit oxidation of ferrous iron to ferric iron followed by precipitation of ferric hydroxide according to equation (7).

The occurrence of calcium and magnesium in concentrations much higher than 5.0 meq/l at the remaining 15 sites possibly could be explained as the result of one of three processes: (1) solid-liquid reaction involving calcium and magnesium minerals and hydrogen ion in mine drainage; (2) evaporation resulting in concentration of the calcium and magnesium available in diluting ground water; and (3) sorption-desorption reaction involving exchange of hydrogen ion in solution for adsorbed calcium and magnesium in a solid exchange medium.

Synthetic, organic, cation exchangers, commonly in the form of a specially treated resin, are used in water treatment plants when sodium and potassium as well as calcium and magnesium must be removed from the water. The ions that are removed by the hydrogen cation exchanges are replaced by hydrogen ion in solution and the pH is correspondingly lowered:

$$H_2R+\left\{\begin{matrix} Ca^{+2} \\ Mg^{+2} \\ 2Na^{+} \\ 2K^{+} \end{matrix}\right. = \left.\begin{matrix} Ca \\ Mg \\ Na_2 \\ K_2 \end{matrix}\right\} R+2H^{+}$$

The reaction is reversed and the resin is regenerated by adding strong sulfuric acid, and therefore a process exists for putting calcium and magnesium into solution while raising the pH. However, if natural hydrogen cation exchanges occur in the underground coal mine environment and play a significant role, it is to be expected that a comparable increase of sodium and potassium ions in solution should accompany an increase in calcium and magnesium ions. Comparison of data in table 5 with table 3 (appendix II) reveals that concentrations of sodium and potassium in mine drainage on the average are identical with concentrations in fresh ground water. Under these conditions the hypothesis of a process of natural hydrogen ion exchange would appear untenable.

Evaporation or any other non-selective process of raising the concentration of calcium and magnesium above the 5.0 meq/l maximum concentration reported in fresh ground water would require a corresponding rise in the concentration of all other ions in fresh ground water. On the average, mine drainage contains concentrations of calcium that are 3.2 times higher than maximum in fresh ground water and magnesium that are 4.8 times higher than maximum, yet concentrations of the stable, mobile ions of sodium, potassium, and chloride are practically identical with fresh ground water. To explain the change in concentration by a process of evaporation or any other non-selective process would also appear to be untenable.

Calcium and magnesium are introduced into fresh ground water by the reaction of hydrogen ion with calcite and with dolomite according to equations (4) and (5). This process might also explain the increase in concentration of calcium and magnesium in mine drainage where the large source of hydrogen ion lies in less readily reversible reactions (6) and (7) rather than in equilibrium reactions (1) and (2). A steady supply of hydrogen ion removes bicarbonate from the system by reversing equilibrium reactions (1) and (2). According to equation (1), the partial pressure of carbon dioxide in the mine drainage increases, and gaseous carbon dioxide (termed "black damp" by the western Maryland miners) is evolved to the air in abandoned

drift-entry mines and is lost to the atmosphere. As bicarbonate is removed from the aqueous system, equilibrium reactions (4) and (5) are driven to the right, and concentrations of calcium and magnesium become much higher than what they would be for a simple calcium, magnesium, and bicarbonate system in equilibrium with calcite. Any common, calcium and magnesium-bearing minerals other than carbonates or sulfates on reaction would leave a unique anion as a tracer to indicate the source of the calcium and magnesium. Gypsum is the only likely source of calcium other than calcite. As indicated in the discussion of the mineralogy of the coal measures, however, the occurrence of gypsum in western Maryland is too uncommon to be significant.

It may be concluded that among the three possible processes, solid-liquid reaction between calcite, dolomite, and hydrogen ion appears to be the most tenable hypothesis for explaining the occurrence of calcium and magnesium in drainage from 15 out of 18 sites in concentrations exceeding 5.0 meq/1. The most significant result of this conclusion is that neutralization must be taking place in the underground environment by reaction of hydrogen ion from pyrite oxidation with crystalline calcite and dolomite and with the bicarbonate product.

Under oxidizing conditions, the insoluble ferric hydroxide produced in reaction (8) has been observed by previous investigators to coat the reactive surfaces of carbonate minerals when they are added to mine drainage that has a high concentration of iron. In spite of the large adsorptive properties of this coating it has been regarded as relatively impermeable such that it initially inhibits and finally stops reactions (4) and (5). As pointed out in the discussion of vertical flow velocities and time of travel in the ground-water flow system, this conclusion, which was based upon observations in the laboratory and in surface streams, may not be valid when applied to processes of neutralization in the underground environment.

Under reducing conditions, it is possible that the ferrous iron formed in reaction (6) may combine with some of the bicarbonate or carbonate formed in reactions (3), (4), and (5). No coatings are formed. Neutralization may be accomplished by removing ferrous iron directly from the system as crystalline siderite without producing any hydrogen ion through hydrolysis of ferric iron. Calcium and magnesium remain in solution replacing ferrous iron.

A measure of mine drainage neutralization that is geochemically meaningful should indicate the decrease in gross acidity rather than indicate simply the pH or acidity at time of sampling. A neutral solution by definition is a solution in which the hydrogen ion activity is equal to the hydroxyl ion activity, and therefore the pH is 7.0. The pH of a water that has low pH and low concentrations of hydrolyzable metal ions and dissolved solids is a good measure of the acidity of the water and indicates the amount of alkalinity needed to decrease the hydrogen ion activity (raise the pH) to neutrality. The pH of acid mine drainage, however, is a very poor measure of the acidity of the water and does not indicate tha amount of alkalinity needed to decrease the hydrogen ion activity to neutrality. It is a poor measure because hydrolyzable metal ions, particularly iron and aluminum, commonly comprise the major part of the acidity. These ions buffer acid drainage by producing additional hydrogen ions when they hydrolyze at values of pH between 3.0 and 5.0 (See equation (7) . In addition neither the pH nor the acidity indicate the amount of neutralization that may have taken place prior to sampling.

The measure of mine drainage neutralization used in this report, the neutralization ratio, takes into account the progress of the neutralization process and is defined on the basis of the relation of an estimate of gross acidity to gross alkalinity. Equations (6) and (7) establish a stoichiometric relation between pyrite, sulfate, and hydrogen ion where one mole of sulfate ultimately corresponds to two moles of hydrogen ion assuming oxidizing conditions throughout the reaction sequence followed by hydrolysis of metal ions. The equivalents of sulfate in drainage are therefore a direct measure of the gross acidity which is here defined as the potential acidity prior to any neutralization. The hydrogeologic setting of mines in western Maryland allows this relationship to be applied to interpretation of the composition of mine drainage with a fair degree of confidence. Neutralization takes place as a result of the introduction of chemical species that contribute to alkalinity of the water. In natural waters these species are ions of carbonate, bicarbonate, and orthophosphate. If all or part of these ions are not present in the water at time of sampling because all or part have been removed by chemical reaction, a measure of those removed as well as those remaining in solution may be obtained by summing an equivalent of stable cations with which they are most likely associated in solution. Thus the sum of equivalents of calcium, magnesium, sodium, and potassium minus the sum of equivalents of the anions chloride, fluoride, and nitrate is a direct measure of the gross alkalinity which is here defined as the alkalinity removed plus the alkalinity remaining. Dividing the equivalents of gross alkalinity by equivalents of gross acidity gives a ratio of alkalinity to acidity that describes the

Table 2.—Comparison of degree of neutralization of drainage at 18 sites by means of neutralization ratio

Site Number	$\frac{(Ca^{+2} + Mg^{+2} + Na^{+} + K^{+}) - (Cl^{-} + F^{-} + NO^{-}_{3})\ meq/l}{SO^{-2}_{4}\ meq/l}$	Neutralization Percent
7	1.23	123
10	1.22	122
3-1	1.11	111
3-2	1.10	110
16	1.04	104
17	1.02	102
9	.87	87
11	.76	76
6	.72	72
2	.69	69
15	.69	69
5	.58	58
18	.55	55
13	.55	55
8	.55	55
14	.52	52
4	.47	47
12	.45	45
1-1	.44	44
1-3	.42	42
1-2	.40	40

degree of completeness of the neutralization process and which is here defined as the neutralization ratio. The ratio is unity when the gross alkalinity produced during formation and neutralization of mine drainage is equal to the gross acidity produced during formation of mine drainage. Accurate determination of the ratio requires an analysis containing all major chemical species in which equivalents of cations balance equivalents of anions.

By means of the neutralization ratio, table 2 compares the degree of neutralization that has taken place in the underground environment prior to sampling at each of 18 sites. The table indicates that for all sites sampled, an amount of gross alkalinity has been formed during neutralization sufficient to neutralize between 40 and 123 percent of the gross acidity formed by pyrite oxidation. Site 12 where both water chemistry and the hydrogeologic setting indicate that the most dilution has taken place has experienced by coincidence only 45 percent neutralization or next to the least for all sites. Sites where greater than 80 percent neutralization has taken place were found during this investigation only in the Castleman and Georges Creek coal basins. Among these, sites 7, 9, 16, and 17 in the Georges Creek coal basin are where the hydrogeologic setting indicates that they are receiving mine drainage from other mines above by flow through the intervening rock strata.

Figure 7 shows the relationship between gross alkalinity and gross acidity upon which the neutralization ratio is based. Comparison of figure 7 with table 5 (appendix II) reveals that drainage with a neutralization ratio less than 1.00 plots to the right of the line of unity and contains considerable concentrations of aluminum, iron, and hydrogen ion but no free bicarbonate. Drainage with a neutralization ratio greater than 1.00 plots to the left of the line of unity and contains little if any aluminum, iron, and hydrogen ion but may contain consider-

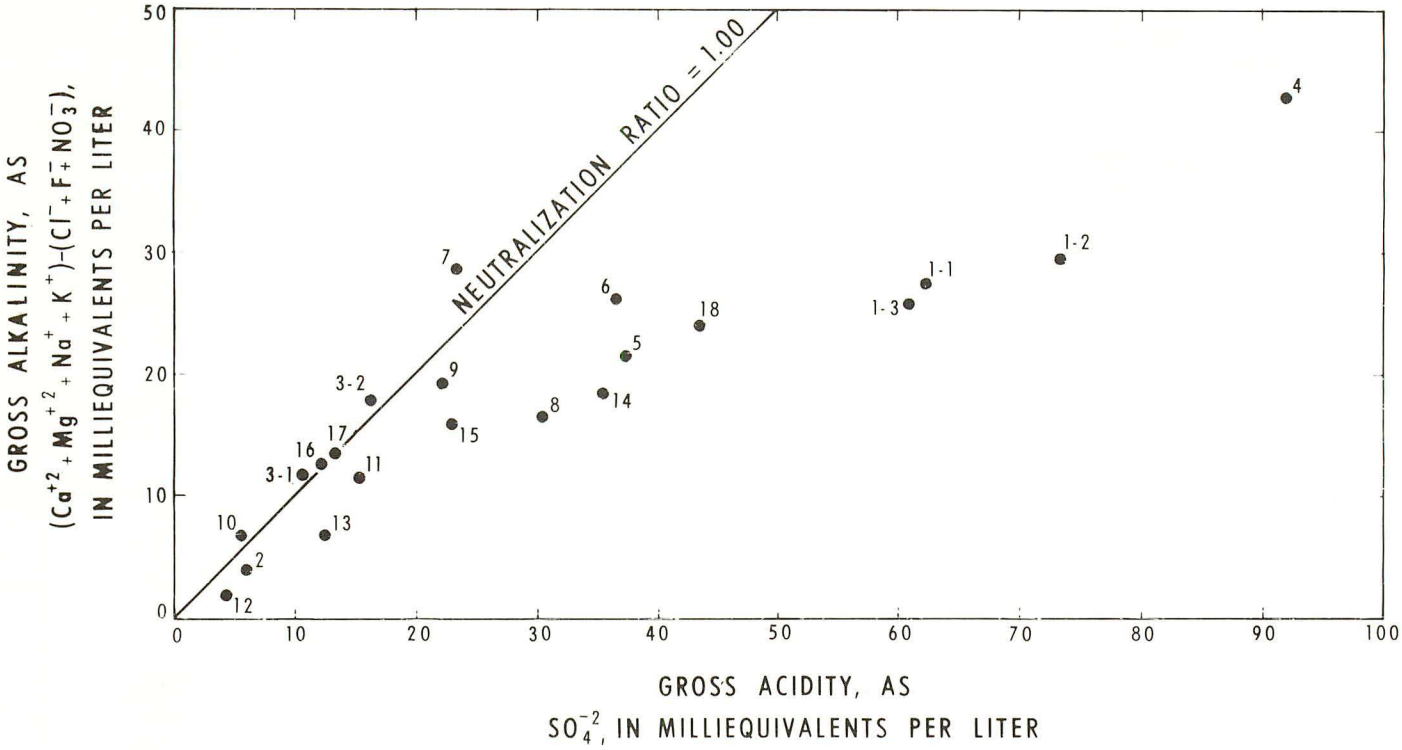

Figure 7.—Graph showing relation of gross alkalinity produced during neutralization to gross acidity produced during acid generation at 18 sites.

able concentrations of bicarbonate. When bicarbonate as well as aluminum, iron, and hydrogen ion occur simultaneously, the water composition is unstable. Under these conditions as in the case of site 9, any alkalinity measured in the field is usually lost prior to analysis in the laboratory. Drainage with a neutralization ratio equal to 1.00 plots on the line of unity and contains little if any bicarbonate or aluminum, iron, and hydrogen ion.

Under these conditions as in the case of site 17, the water composition is approximately a pure calcium magnesium sulfate.

The above relationships tend to substantiate the hypothesized process of mine drainage neutralization by solid-liquid reaction. Iron and hydrogen ion originally associated with sulfate are progressively replaced in solution by calcium and magnesium originally associated with crystalline carbonate. Cations of calcium, magnesium, iron, and hydrogen remain balanced by an equivalent concentration of sulfate. The drainage composition that ultimately results is a nearly pure calcium magnesium sulfate. The process then continues until the drainage comes into equilibrium with calcite by the appearance of equilibrium concentrations of bicarbonate.

Minor constituents (appendix II, table 6) in general are controlled by the same chemical processes that control the concentration of the major constituents just discussed. As an example table 7 (appendix II) shows what happens to the minor constituents when drainage from site 4, the most acid and the most mineralized, is neutralized in the laboratory with sodium hydroxide rather than crystalline calcium carbonate. The hydrolyzable metals such as chromium, cobalt, copper, nickel, and zinc are removed from solution and like aluminum appear in the precipitate. Strontium on the other hand is not removed with neutralization and because of its common association with calcium, may actually increase in concentration when the neutralization agent is calcite or dolomite. Some minor constituents, like the major constituents sodium, potassium, and chloride, should be relatively stable in coal-mine-drainage environments but less is known about their behavior. Some minor constituents are controlled by several little-understood processes that are independent of the stratigraphic and geologic environment where they first became a part of mine drainage.

Summary

In the coal basins of western Maryland, fresh ground water unaffected by mine drainage is typically a calcium magnesium bicarbonate water containing an average of 180 mg/l of bicarbonate. In general this composition is a result of the reaction of calcite with acid from dissolved carbon dioxide derived from the soil. Water from six wells that are 500 feet or less in depth contains less than 40 mg/l of chloride.

Provided many fundamental assumptions are satisfied, the concentration of sulfate in mine drainage and the acidity of the water should be proportional to the concentration of sulfur in the coal. Although these assumptions are only partly satisfied in western Maryland, a maximum sulfate concentration and acidity can be estimated for a given sulfur concentration. The relationship of the measured concentrations to the maximum concentrations indicates that neutralization may be taking place in the underground environment by a process other than dilution.

Theoretical dilution of mine drainage with average-composition, fresh ground water cannot account for the high concentrations of calcium and magnesium measured in drainage from 15 out of 18 mines. Solid-liquid reaction between calcite, dolomite, and hydrogen ion appears to be the most tenable hypothesis to explain these high concentrations. As a consequence, neutralization must be taking place in the underground environment by reaction of hydrogen ion from pyrite oxidation with crystalline calcite and dolomite.

The neutralization ratio indicates that an amount of gross alkalinity has been formed at each mine during neutralization in the underground environment sufficient to neutralize between 40 and 123 percent of the gross acidity formed during pyrite oxidation. The most nearly neutralized drainage sampled in the Georges Creek basin issues from mines where the hydrogeologic setting indicates that these mines are receiving mine drainage from other mines above by flow through the intervening rock strata.

The relationship between gross alkalinity and gross acidity divides the analyses of mine drainage into two incompatible compositions. Water with a neutralization ratio less than 1.00 is a calcium magnesium sulfate type with supplemental aluminum, iron, and hydrogen. Water with a neutralization ratio greater than 1.00 is a calcium magnesium sulfate type with supplemental bicarbonate.

In general, the concentration of minor constituents in mine drainage are controlled primarily by the same chemical processes controlling the concentration of major constituents. Geochemical interpretation of minor constituents, however, is more difficult as a result of the problems introduced by attempting to measure trace amounts of elements in iron-rich waters and problems introduced by occurrence of additional chemical processes unrelated to the stratigraphy.

HYPOTHESIS OF HYDROGEOCHEMICAL SYSTEM

Simultaneous consideration of the hydrogeologic setting of underground mines in western Maryland and the geochemistry of mine drainage leads to the hypothesis of a hydrogeochemical system for formation and natural neutralization of acid coal-mine drainage.

Figure 8 is a schematic diagram showing the basic components in the hypothesized hydrogeochemical system. At the extreme left of the generalized geologic section, fresh ground water enters the underground mine after passing relatively unaltered through two coal seams where they have not been mined. The composition of fresh ground water is exemplified by the analysis of water from well All-Cb 1 which is a calcium magnesium bicarbonate water with only 141 mg/l of dissolved solids. In the mine the fresh ground water dissolves the iron and acid sulfates resulting from pyrite oxidation, loses its small bicarbonate alkalinity in neutralizing some of the acid, and becomes a strongly acid, iron sulfate solution. The acid in this mine water attacks minerals in the fallen roof rock and in the heaved underclay in the mine floor. Aluminum and silica are released from the clays and calcium, magnesium, and bicarbonate from the carbonates as well as large concentrations of minor elements. The bicarbonate produced by reaction of hydrogen ion with carbonate minerals reacts with additional hydrogen ions producing carbonic acid which dissociates to water and carbon dioxide which in turn is lost to the mine atmosphere, further reducing the acidity of the water. As the hydrogen ion activity decreases with neutralization (pH increases) the composition of the mine water is altered further by the removal of ferric iron, aluminum, and some minor metal ions when they hydrolize, precipitate from solution, and are replaced in solution by equivalent concentrations of hydrogen ion. The composition of the mine water that drains from the underground

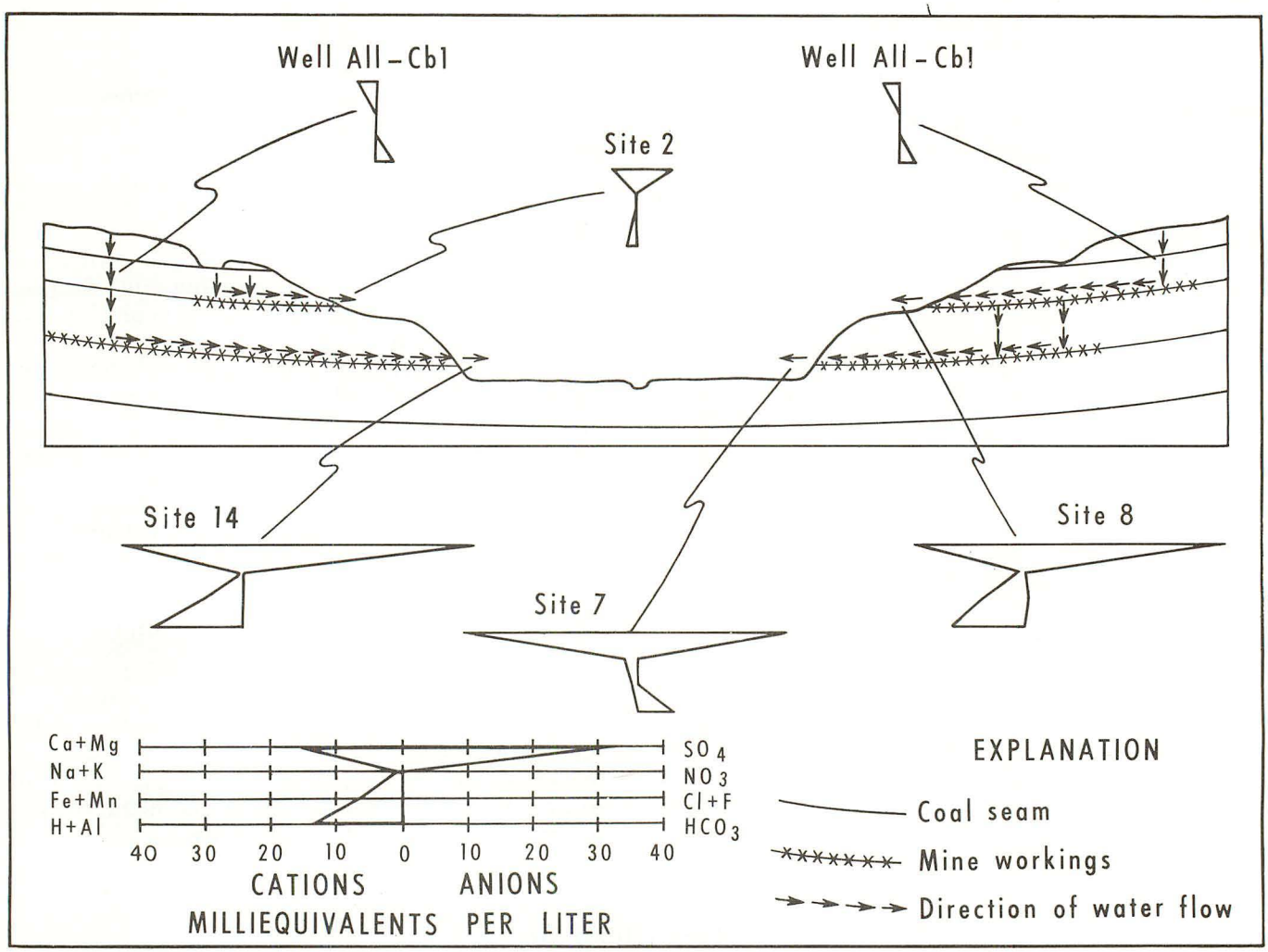

Figure 8.—Geologic section with pattern diagrams showing differences in water composition resulting from differences in path of ground-water flow.

mine indicates that it has been affected not only by processes of acid generation but also by processes of acid neutralization. The composition of this mine drainage is exemplified by the sample analyzed from site 14 which is a calcium magnesium sulfate water with considerable iron, aluminum, and hydrogen ion. The neutralization ratio, however, indicates that 52 percent of the gross acidity already has been neutralized in the underground environment.

In the center left of the generalized geologic section in figure 8, fresh ground water enters the underground mine, dissolves the reaction products of pyrite oxidation, and undergoes the same processes of neutralization that produced the water composition at site 14. The mine water is diluted, however, with water infiltrating from either a natural stream or a strip mine that has a drainage area significantly larger and separate from the area of the underground mine. The composition of this mine drainage is exemplified by the analysis for site 2 which is very similar to the analysis for site 14 except that the concentration of dissolved solids as well as the concentration of calcium and magnesium indicate that considerable dilution has taken place. The mine water drains from the mine with 69 percent of the gross acidity already neutralized.

At the extreme right of the generalized geologic section in figure 8, fresh ground water enters the upper mine, dissolves the reaction products of pyrite oxidation, and is partly neutralized. Some of the mine water drains from the mouth of the upper mine. The composition of this mine drainage is exemplified by the analysis for site 8 which is practically identical to the analysis for site 14. The

mine water leaves the mine with 55 percent of the acidity already neutralized.

In the center right of the generalized geologic section in figure 8, that part of the half-neutralized mine water that does not drain from the mouth of the upper mine moves down to the lower mine. As discussed in the section of this report dealing with the stratigraphy of the coal measures, pyrite is primarily associated with coal and with beds immediately above and below a coal. Coal beds comprise a very small part of the total thickness of the coal measures, and correspondingly beds with a large pyrite concentration form a relatively small part of the same total thickness. For this reason, it is probable that processes of neutralization dominate over processes of acid generation as mine water moves down to the lower mine. The reaction products of pyrite oxidation in the lower mine therefore are dissolved in highly neutralized mine drainage as well as in fresh ground water. Under these hypothesized conditions the composition of the mine water that drains from the lower mine is exemplified by the analysis for site 7 which is very similar to the analysis for site 14 except that the presence of bicarbonate indicates that considerably more neutralization has taken place. The neutralization ratio indicates that an amount of gross alkalinity has been produced during neutralization aufficient to neutralize 123 percent of the gross acidity produced during acid generation.

SUMMARY AND CONCLUSIONS

The coal-mine drainage problem is a result of acceleration of some of the natural geochemical processes of weathering when beds containing pyrite are selectively disturbed by mining. Based upon sulfate loads, the problem is most severe in Maryland in the North Branch Potomac River Basin. This investigation into the relation between drainage composition and the associated coal-measure stratigraphy is based upon measurement of water discharge and complete analysis of water samples collected at the surface discharge point of 18 underground mines in eight coal seams. The mines and sampling points were carefully selected using maps of the underground workings and criteria that conformed to the experiment design. Methods of sampling, sample treatment, field analysis, and laboratory analysis were selected within the scope of the investigation to maximize the chances of obtaining a complete and representative analysis of waters that are known to be unstable and difficult to analyze. Previous water investigations in Maryland include reconnaissance studies of water quality in the State, inventories of sources of mine drainage, and studies of either concentrations or loads of selected mine-drainage constituents at selected sites. Previous geologic investigations in connection with appraisal of coal resources provide reconnaissance studies of the coal-measure stratigraphy in all Maryland coal basins and provide detailed studies of the lower half of the coal measures in three out of five coal basins.

The three, shallow structural troughs containing the coal measures have relatively simple, nearly horizontal structure which directs ground-water flow and dictates mining practice. In different parts of the stratigraphic section and in different coal basins, there are subtle differences in the relative abundance of sandstone, siltstone, shale, coal, argillaceous limestone, red beds, and their associated mineral suites. Hills within the coal basins contain many self-draining, drift-entry mines. Mines samples at sites 1, 3, 4, 5, 6, 10, 11, 14, and 15 are sufficiently isolated hydraulically that data from these drift-entry mines may be used to interpret the discharge and composition of water from the remaining nine mines. The mines at sites 2, 12, and 13 are gaining water either from adjacent strip mines or from streams. The relationship of discharge to area of mine workings and the history of mining indicate that mines at sites 7, 9, 16, and 17 are gaining water from other mine workings above by interflow through the intervening rock strata. During final mining operations, coal pillars are removed, and fractures associated with roof failure result in more efficient capture of any lateral ground-water flow that might still occur in either an adjacent overlying aquifer or an upper mining level. Hydraulic analysis of data from 18 mines indicates that the time for reaction of acid and crystalline calcite in the fractured roof rock in the underground environment is five to six orders of magnitude greater on the average than time for reaction in surface streams.

Fresh ground water unaffected by mine drainage is typically a calcium magnesium bicarbonate water containing an average of 3.0 meq/l (180 mg/l) of bicarbonate ion. Dilution of concentrated mine drainage with this water can account for the concentrations of calcium and magnesium observed in drainage from only three out of 18 mines. Concentrations of calcium and magnesium in drainage from the remaining 15 mines exceed 5.0 meq/l, and solid-liquid reaction between calcite, dolomite, and hydrogen ion appears to be the most tenable

hypothesis for explaining these concentrations. As a consequence, neutralization must be taking place by this same solid-liquid reaction process. The neutralization ratio, an ion ratio that uses the more stable ionic species to measure neutralization, indicates that on the average 70 percent of the acidity has been neutralized prior to discharge at the land surface. This hypothesis both for explaining large concentrations of calcium and magnesium and for explaining the process of neutralization is substantiated by the fact that the most neutralized mine drainage is associated with interflow between mining levels through the intervening rock strata.

The proposed hypothesis of the hydrogeochemical system for formation and neutralization of acid coal-mine drainage describes the generalized paths of ground-water flow associated with three related water compositions. These related compositions are a result of: (1) partial neutralization of acid mine water within the mine workings, (2) substantial dilution in addition to partial neutralization, and (3) complete neutralization within the strata between mining levels and within the mine workings.

Most previous investigations into the mine drainage problem in Maryland have been inventories of pollution which provide data useful in the location and design of artificial waste-water treatment plants. The conclusion reached from this investigation is that one answer to the problem might result from acceleration of those natural geochemical processes of weathering that lead to natural neutralization as a result of selectively utilizing those beds in the stratigraphic section which do not contain abundant pyrite. This possibility is supported by the fact that, in the case of mines at sites 7, 9, 16, and 17 fracturing and the consequent disruption of the natural ground-water flow system has unintentionally resulted in natural beneficial treatment of the mine water. Testing of the proposed hypothesis of the hydrogeochemical system may lead to new methods for intentionally using the natural underground environment in place of or in conjunction with mine-mouth water treatment plants.

Three additional conclusions drawn from this investigation may assist in planning future investigations. First, because of the relative simplicity of the hydrogeologic setting compared to the anthracite coal region of Pennsylvania, the bituminous coal fields of western Maryland comprise a suitable outdoor laboratory for basic research in the geochemistry of mine drainage. Second, careful comparison of the volume of discharge with the area of mine workings may reveal the existence of extraneous sources of water that might significantly affect the composition of the drainage. Third, complete chemical analysis both of unaffected ground water and of mine drainage for all major dissolved species may reveal the principal processes governing the water composition and the general path of ground-water flow.

FUTURE INVESTIGATIONS

Future investigation of the acid coal-mine drainage problem could be conducted in two stages -- the first stage directed to testing the hypothesized hydrogeochemical system, the second to testing the feasibility of using neutralization-producing rock strata in place in the ground.

To test the proposed hypothesis, a search could be made for solid products of neutralization reactions precipitating in the pore spaces in the strata between two mining levels. A large part of the precipitate should be the same solids as those in sludge resulting from artificial neutralization by mine waste-water treatment plants. These include ferric oxy-hydroxide hydrates, aluminum hydroxides, and minor metal hydroxides. In addition, ferrous carbonate may occur in place of ferric hydroxide as a result of the possible presence of reducing conditions. To predict the occurence of additional solids, the dissolved oxygen concentrations reported in table 4 may be used to compute the redox potential of the mine drainage sampled. Data on redox potential in addition to the water analyses may be used in an available computer program to predict the possible occurrence of all minerals that would be in equilibrium with the mine waters, assuming that equilibrium conditions prevail. The solid products of neutralization should tend to plug the pore spaces and to reduce the permeability of the fractured strata overlying the lower mine. As a consequence, a larger cross sectional area is needed if flow is to remain the same, and it is probable that the products of neutralization are spread more evenly over a larger area with time. As a result, the older the lower mine, the more widespread should be the neutralization products in the intervening rock strata.

Rock cores, water samples, and hydraulic data from several test holes drilled into the strata between mines at sites 7 and 8 should provide sufficient neutralization process in the hypothesized system. In lieu of core drillings, some additional information on the composition of the mine water

entering the roof of the lower mine might be gained by careful water sampling inside an active mine that is gaining flow from other mine workings above. A suitable water-borne tracer could provide positive evidence of interflow between mining levels if some of the tracer is recovered; however, if none is recovered, this test would be inconclusive.

A test of the feasibility of using neutralization-producing strata could be divided into three subinvestigations: 1) a test-drilling program for simultaneous collection and later analysis of specific geochemical, geologic, and hydrologic data; 2) an investigation of the feasibility of initiating controlled roof breaks; and 3) and investigation of the feasibility of conducting all underground mining on more than one level.

The test-drilling program could be designed to collect representative rock cores of the entire stratigraphic thickness in areas proposed for future underground mining. In the laboratory, percolation-extraction tests on the cores would determine not only the acid-producing potential of the strata, but also the neutralization capacity of the strata. A standardized solution simulating mine drainage can be developed for these tests. Part of the cores may be used to work out the details of the stratigraphy and to estimate coal reserves in the southern half of the Upper Potomac coal basin, in the Upper and Lower Youghiogheny coal basins, and in the upper half of the coal measures in the Georges Creek coal basin. It is difficult to define clearly the effect of differences in the relative abundance of lithologic types and mineral suites upon the composition of either fresh ground water or mine drainage using stratigraphic and hydrologic data currently available. For this reason a detailed study of the distribution of the minerals that are involved in mine drainage geochemistry, ideally, would be made in conjunction with the stratigraphic study. At the time of drilling, water samples could be collected, along with data on water pressure, temperature, and flow in the borehole as drilling progresses. These data would aid in detecting confining layers, general direction of water flow, and the possible presence of osmotic membrane effects of clays. Geophysical logs could be used both to identify zones of great conductivity, which may be associated with acid formation or neutralization, and to select zones for sampling water.

An investigation of controlled roof breaks could be directed to the control of the geometry and extent of the fracture system in the roof rock resulting from a roof break. It would be necessary to have control over the fracture system in a variety of rock competence and bedding thickness. If the fracturing could be programmed, then secondary permeability could be increased in strata between mining levels, resulting in either initiation of or increase in interflow and neutralization between mining levels. An investigation of multilevel mining could be directed to evaluating the feasibility of mining economically marginal coal reserves, where natural mine-water treatment would be one of the benefits of mining.

The ultimate objective of future investigations would be to demonstrate that an active underground mine could produce neutralized drainage as well as coal without artificial treatment, either during production or after the mine is abandoned.

SELECTED REFERENCES

ABERNETHY, R. F., and ODE, W. H., *1952, Chemical analyses of coal cores* in *Toenges, A. L., and others, 1952, Castleman basin, Garrett County, Maryland: U. S. Bur. Mines Bull. 507, table 13, pp. 100-112.*

AMSDEN, T. W., *1953, Geologic map of Garrett County: Maryland Dept. Geology, Mines and Water Resources.*

AMSDEN, T. W., OVERBECK, R. M., and MARTIN, R. O., *1954, Geology and water resources of Garrett County: Maryland Dept. Geology, Mines and Water Resources Bull 13, 349 p.*

ANDERSON, P. W., *1970, Occurrence and distribution of trace elements in New Jersey streams: New Jersey Dept. Environmental Protection Waste Resources Circ. 24, 24 p.*

BAKER, W. A., *1922, Methods of mining employed in the coal mines of Maryland* in *Swartz, C. K., and Baker, W. A., 1922, Second report on the coals of Maryland: Maryland Geol. Survey, V. 11, Pt.1, pp. 135-288.*

BARNES, IVAN, and CLARKE, R. E., *1964, Geochemistry of ground water in mine drainage problems: U. S. Geol. Survey Prof. Paper 473-A, 6 p.*

BARNES, IVAN, STUART, W. T., and FISHER, D. W., *1964, field investigation of mine waters in the northern anthracite field, Pennsylvania: U. S. Geol. Survey Prof. Paper 473-B, 8 p.*

BARNETT, P. R., and MALLORY, E. C., JR., *1971, Determination of minor elements in water by emission spectroscopy: U. S. Geol. Survey Techniques Manual, Book 5, Sec. A, Chapter A2, 31 p.*

BERRYHILL, H. L. JR., and DE WITT, W. JR., *1955, Revised correlation of Koontz coal and Pennsylvania - Permian boundary in Georges Creek basin, Allegany County, Maryland: Am. Assoc. Petroleum Geolgists Bull., V. 39, No. 10, pp. 2087-2090.*

BERRYHILL, H. L. JR., and others, *1956, Geologic map of Allegany County: Maryland Dept. Geology, Mines and Water Resources.*

BIESECKER, J. E., and GEORGE, J. R., *1966, Stream quality in Appalachia as related to coal-drainage, 1965: U. S. Geol Survey Circ. 526, 27 p.*

BITUMINOUS COAL RESEARCH, INC., *1969, Supplement to mine drainage abstracts, a bibliography: Pennsylvania Coal Research Board, Dept. Mines and Mineral Industries, Harrisburg, Pa.*

BROWN, EUGENE, SKOUGSTAD, M. W., and FISHMAN, M. J., *1970, Methods of collection and analysis of water samples for dissolved minerals and gases: U. S. Geol. Survey Techniques Manual, Book 5, Sec. A, Chapter A1, 160 p.*

BUCKLEY, H. B., *1968, Forty-sixth annual report of the Maryland Bureau of Mines: Maryland Bur. Mines, Westernport, Md., 33 p.*

CARSWELL, L. D., and BENNETT, G. D., *1963, Geology and hydrology of the Neshannock quadrangle, Mercer and Lawrence Counties, Pennsylvania: Pennsylvania Geol. Survey, 4th. Ser., Bull. W-15, 90 p.*

CARUCCIO, F. T., *1968, An evaluation of factors affecting acid mine drainage production and the ground water interactions in selected areas of western Pennsylvania* in *Papers of Second Symposium on Coal Mine Drainage Research: Bituminous Coal Research, Inc., Monroeville, Pa., pp. 107-149.*

---------, *1970, The quantification of reactive pyrite by grain size* in *Papers of Third Symposium on Coal Mine Drainage Research: Bituminous Coal Research, Inc., Monroeville, Pa. pp. 123-131.*

CARUCCIO, R. T., and PARIZEK, R. R., *1967, An evaluation of factors influencing acid mine drainage production from various strata of the Allegheny Group and the ground water interactions in selected areas of western Pennsylvania: Pennsylvania Coal Research Board Spec. Research Rept. SR-65, 175 p.*

CLARK, W. B., and others, *1905, Report on the coals of Maryland: Maryland Geol. Survey, V. 5, Pt. 4. pp. 219-651.*

CLARK, W. B., and MATHEWS, E. B., *1909, Maryland mineral industries, 1896-1907: Maryland Geol. Survey, V. 8, Pt. 2, Plate 10, 11, pp. 164,172.*

COLLIER, C. R., and others, *1964, Influences of strip mining on the hydrologic environment of parts of Beaver Creek basin, Kentucky, 1955-59: U. S. Geol. Survey Prof. Paper 427-B, pp. B1-B85.*

COOPER, H. M., and ABERNETHY, R. F., *1949, Chemical analyses of coal cores* in *Toenges, A. L. and others, 1949, Investigation of lower coal beds in Georges Creek and north part of Upper Potomac Basins, Allegany and Garrett Counties, Md.: U. S. Bur. Mines Tech. Paper 725, Table 2, pp. 101-115.*

CORBETT, R. G., and GROWITZ, D. J., *1967, Composition of water discharged from bituminous coal mines in northern West Virginia: Economic Geology, V. 62, pp. 848-851.*

DAVIES, W. E., *1968, Engineering geology in Mineral resources of the Appalachian region: U. S. Geol. Survey Prof. Paper 580, pp. 91-93.*

DURUM, W. H., HEM, J. D., and HEIDEL, S. G., *1971, Reconnaissance of selected minor elements in surface waters of the United States, October 1970: U. S. Geol. Survey Circ. 643, 49 p.*

EMRICH, G. H., *1966, Test for evaluating the quality of mine drainage characteristics of coal seams* in *Pennsylvania Dept. Health, 1966, Mine drainage manual, 2d ed. Div. Sanitary Engr. Pub. 12, pp. V-6 to V-14.*

EMRICH, G. H., and THOMPSON, D. R., *1968, Some characteristics of drainage from deep bituminous mines in western Pennsylvania* in *Papers of Second Symposium on Coal Mine Drainage Research: Bituminous Coal Research, Inc., Monroeville, Pa., pp. 190-222.*

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION , *1969, Stream pollution by coal mine drainage in Appalachia: FWPCA, Ohio Basin Region, Cincinnati, Ohio, 261 p.*

GIBSON, F. H., and SELVIG, W. A., *1944, Rare and uncommon chemical elements in coal: U. S. Bur. Mines Tech. Paper 669, 23 p.*

GIEZYŃSKI, A., *1970, Combating the hazard of caving in mine workings* in *Central Mining Institute Annual Report, 1969: Ministry of Mining and Power, GIG, Katowice, Poland, 1970.*

HEADLEE, A. J. W., and HUNTER, R. G., *1951, Germanium in coals of West Virginia: West Virginia Geol. and Economic Survey Rept. Inv. 8, 15 p.*

HEIDEL, S. G., and FRENIER, W. W., *1965, Chemical quality of water and trace elements in the Patuxent River basin: Maryland Geol. Survey Rept. Inv. 1, 40 p.*

HEINE, W. N., and GIOVANNITTI, E. F., *1970, Treatment of mine drainage by industry in Pennsylvania: Am. Soc. Civil Engineers Proc., Jour. Sanitary Eng. Div., V. 96, No. SA3, Paper 7362, pp. 743-755.*

HEM, J. D., *1970, Study and interpretation of the chemical characteristics of natural water, 2d ed.: U. S. Geol. Survey Water-Supply Paper 1473, 363 p.*

HENNEN, R. V., REGER, D. B., and PRICE, W. A., *1914, Preston County: West Virginia Geol. Survey County Report.*

HOPKINS, T. C., JR., *1966a, Western Maryland mine drainage survey, 1962-1965: Water Quality Investigation Div., Maryland Dept. Water Resources, V. 1, Pt. 1-5, 259 p.*

---------, *1966b, Western Maryland mine drainage survey, 1962-1965: Water Quality Investigation Div., Maryland Dept. Water Resources, V. 2, Pt. 6, 251 p.*

---------*1966c, Western Maryland mine drainage survey, 1962-1965: Water Quality Investigation Div., Maryland Dept. Water Resources, V. 3, Pt. 7, 203 p.*

HURLBUT, C. S., Editor, *1952, Dana's manual of mineralogy, 16th edition: John Wiley & Sons, Inc., New York, 1956, 530 p.*

LORENZ, W. C., and STEPHAN, R. W., *1967, Factors that affect the formation of coal mine drainage pollution in Appalachia* in *U. S. Army Corps Engineers and U. S. Dept. Interior, 1969, The incidence and formation of mine drainage pollution, Appendix C (V. 18), Attachment C* in *Report for development of water resources of Appalachia: Office of Appalachian Studies, Corps of Engineers, Cincinnati, Ohio, pp. C-C-1 to C-C-17.*

MASON, BRIAN, *1952, Principles of geochemistry: John Wiley & Sons, Inc., New York, N. Y., 276 p.*

MIHOK, E. A., *1969, Catalytic oxidation of ferrous iron in acid mine water by activated carbon: U. S. Bur. Mines Rept. Inv. 7337, 7 p.*

MUSSER, J. J., *1963, Description of physical environment and of strip-mining operations in parts of Beaver Creek basin, Kentucky: U. S. Geol. Survey Prof. Paper 427-A, 25 p.*

PARIZEK, R. R., and TARR, E. G., *1972, Mine drainage pollution prevention and abatement using hydrogeological and geochemical systems* in *Papers of Fourth Symposium on Coal Mine Drainage Research: Bituminous Coal Research, Inc., Monroeville, Pa., pp. 56-82.*

PARKER, H. N., and others, *1907, The Potomac River basin: U. S. Geol. Survey Water-Supply Paper 192, 364 p.*

PENNSYLVANIA DEPT. HEALTH, *1966, Factors involved in estimating quality and quantity of mine drainage* in *Pennsylvania Dept. Health, 1966, Mine drainage manual, 2d ed.: Div. Sanitary Engr. Pub. 12, pp. V-1 to V-5.*

POTH, C. W., *1963, Geology and hydrology of the Mercer quadrangle, Mercer, Lawrence, and Butler Counties, Pennsylvania: Pennsylvania Geol. Survey, 4th Ser., Bull. W-16, 149 p.*

POTTER, P. E., SHIMP, N. F., and WITTERS, J., *1963, Trace elements in marine and fresh-water argillaceous sediments: Geochim. et Cosmochim. Acta, V. 27, pp. 669-694.*

POUGH, F. H., *1953, A field guide to rocks and minerals: Boston, Mass., Houghton Mifflin Co., 333 p.*

RANKAMA, K. and SAHAMA, T. G., *1950, Geochemistry: University of Chicago Press, Chicago, Ill., 912 p.*

RAINWATER, F. H., and THATCHER, L. L., *1960, Methods for collection and analysis of water samples: U. S. Geol. Survey Water-Supply Paper 1454, 301 p.*

RANDOLPH, B. S., and MARTIN, G. C., *1905, Map of the Georges Creek coal basin showing the location of mining properties and the areal extent of the Pittsburg ("Big Vein") and lower coals, map* in *Clark, W. B., and others, 1905, Report on the coals of Maryland: Maryland Geol. Survey, V. 5, Pt. 4, Plate 32, p. 386.*

REGER, D. B., PRICE, W. A., and TUCKER, R. C., *1923, Tucker County: West Virginia Geol. Survey County Report.*

REGER, D. B., and TUCKER, R. C., *1924, Mineral and Grant counties: West Virginia Geol. Survey County Report, 866 p.*

RUBELMANN, R. J., *1963, Interim report no. 1 on the western Maryland pH survey: Water Quality Survey and Study Section, Maryland Water Pollution Control Commission Interim Report, Annapolis, Md., 29 p.*

SANDELL, E. B., *1959, Colorimetric determination of traces of metals, Third Edition: Interscience Publishers, New York, p. 31.*

SINGER, P. C., and STUMM, WERNER, *1970, Acid mine drainage - the rate-determining step: Science, V. 167, pp. 1121-1123.*

SKOUGSTAD, M. W., and SCARBRO, G. F., JR., *1968, Water sample filtration unit: Environmental Sci. Technology, V. 2, pp. 298-301.*

SLAUGHTER, T. H., and DARLING, J. M., *1962, The water resources of Allegany and Washington Counties: Maryland Dept. Geol., Mines and Water Resources Bull. 24, 408 p.*

STEPHAN, R. W., and LORENZ, W. C., *1967, A review of current research on coal mine drainage in Appalachia* in *U. S. Army Corps Engineers and U. S. Dept. Interior, 1969, The incidence and formation of mine drainage pollution, Appendix C (V. 18), Attachment B* in *Report for development of water resources of Appalachia: Office of Appalachian Studies, Corps of Engineers, Cincinnati, Ohio, p. C-B-1 to C-B-26.*

STOCKTON, N. A., *1905, The coal mines of Maryland* in *Clark, W. B., and others, 1905, Report on the coals of Maryland: Maryland Geol. Survey, V. 5, Pt. 4, pp. 219-651.*

SWARTZ, C. K., and FIELDNER, A. C., *1922, Table of analyses (Composition and fuel value of the coals of Maryland)* in *Swartz, C. K., and Baker, W. A., 1922, Second report on the coals of Maryland: Maryland Geol. Survey, V. 11, Pt. 1, in pocket.*

SWARTZ, C. K., MARTIN, G. C., and SISLER, J. D., *1922, Areal distribution and lines of outcrop of the coals of the Georges Creek and Upper Potomac basins, map* in *Swartz, C. K., and Baker, W. A., 1922, Second report on the coals of Maryland: Maryland Geol. Survey, V. 11, Pt. 1, Pl. 5, p. 288.*

THOMAS, J. D., *1966, Chemical quality reconnaissance of water of Maryland streams: Maryland Geol. Survey Rept. Inv. 5, 61 p.*

TOENGES, A. L., TURNBULL, L. A., and WILLIAMS, LLOYD, *1949, Investigation of field and estimated reserves, Pt. 1,* of *Investigation of lower coal beds in Georges Creek and north part of Upper Potomac Basins, Allegany and Garrett Counties, Md.: U. S. Bur. Mines Tech. Paper 725, 142 p.*

---------, *1952, Coal deposits Castleman Basin, Garrett County, Maryland: U. S. Bur. Mines Bull. 507, 112 p.*

U. S. ARMY CORPS ENGINEERS and DEPT. INTERIOR, *1969, The incidence and formation of mine drainage pollution Appendix C (V. 18)* in *Report for development of water resources of Appalachia: Office of Appalachian Studies, Corps of Engineers, Cincinnati, Ohio, 398 p.*

WAAGE, K. M., *1949, Stratigraphy of Georges Creek coal basin Pt. 4* of *Investigation* in *Toenges, A. L. and others, 1949, Investigation of lower coal beds in Georges Creek and north part of Upper Potomac Basins, Allegany and Garrett Counties, Md.: U. S. Bur. Mines Tech. Paper 725, pp. 19-28.*

---------, *1950, Refractory clays of the Maryland coal measures: Maryland Dept. Geology, Mines and Water Resources Bull. 9, 182 p.*

---------, *1952, Stratigraphy of Castleman coal basin* in *Toenges, A. L., and others, 1952, Castleman basin, Garrett County, Maryland: U. S. Bur. Mines Bull. 507, Pt. 4, pp. 20-26.*

WALKER, P. N., *1971, Flow characteristics of Maryland streams: Maryland Geol. Survey Rept. Inv. 16, 160 p.*

APPENDIX I

MAPS OF

UNDERGROUND MINE WORKINGS

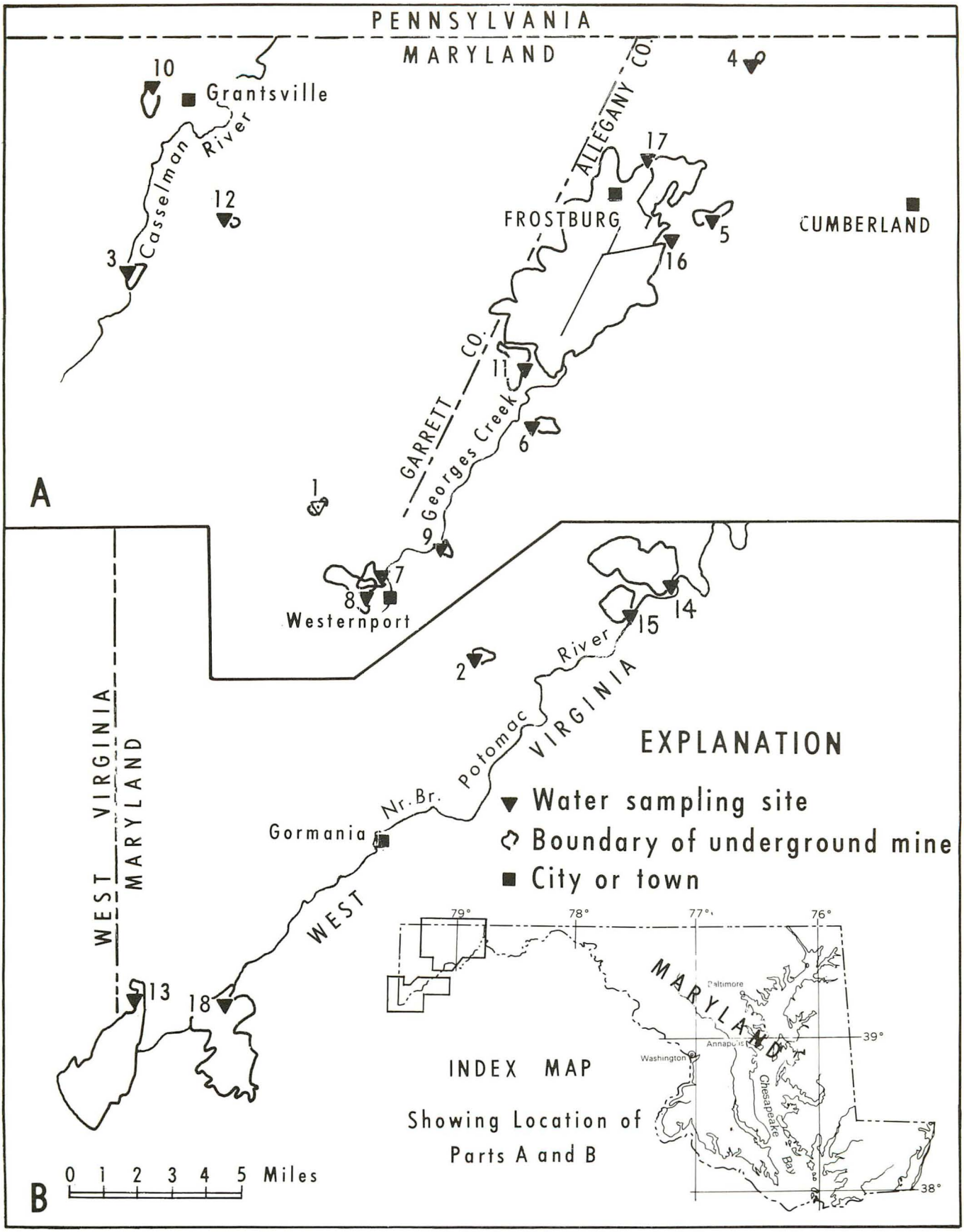

Figure 9.—Distribution of the selected underground mines and 18 water sampling sites in three coal basins. A, Castleman and Georges Creek basins. B, Upper Potomac basin.

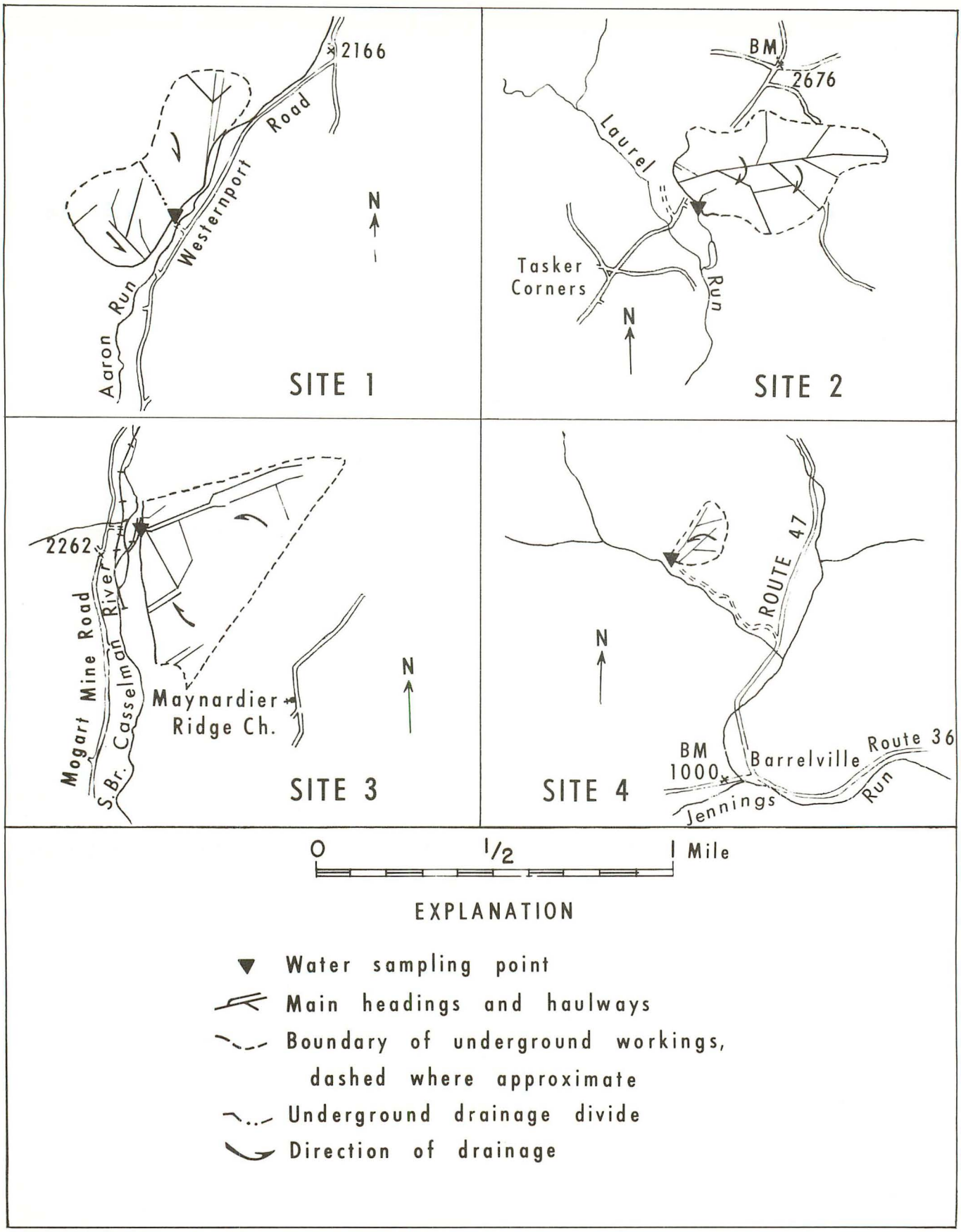

Figure 10.—Maps of the location and extent of underground mine working showing inferred direction of water flow. Sites 1 through 4.

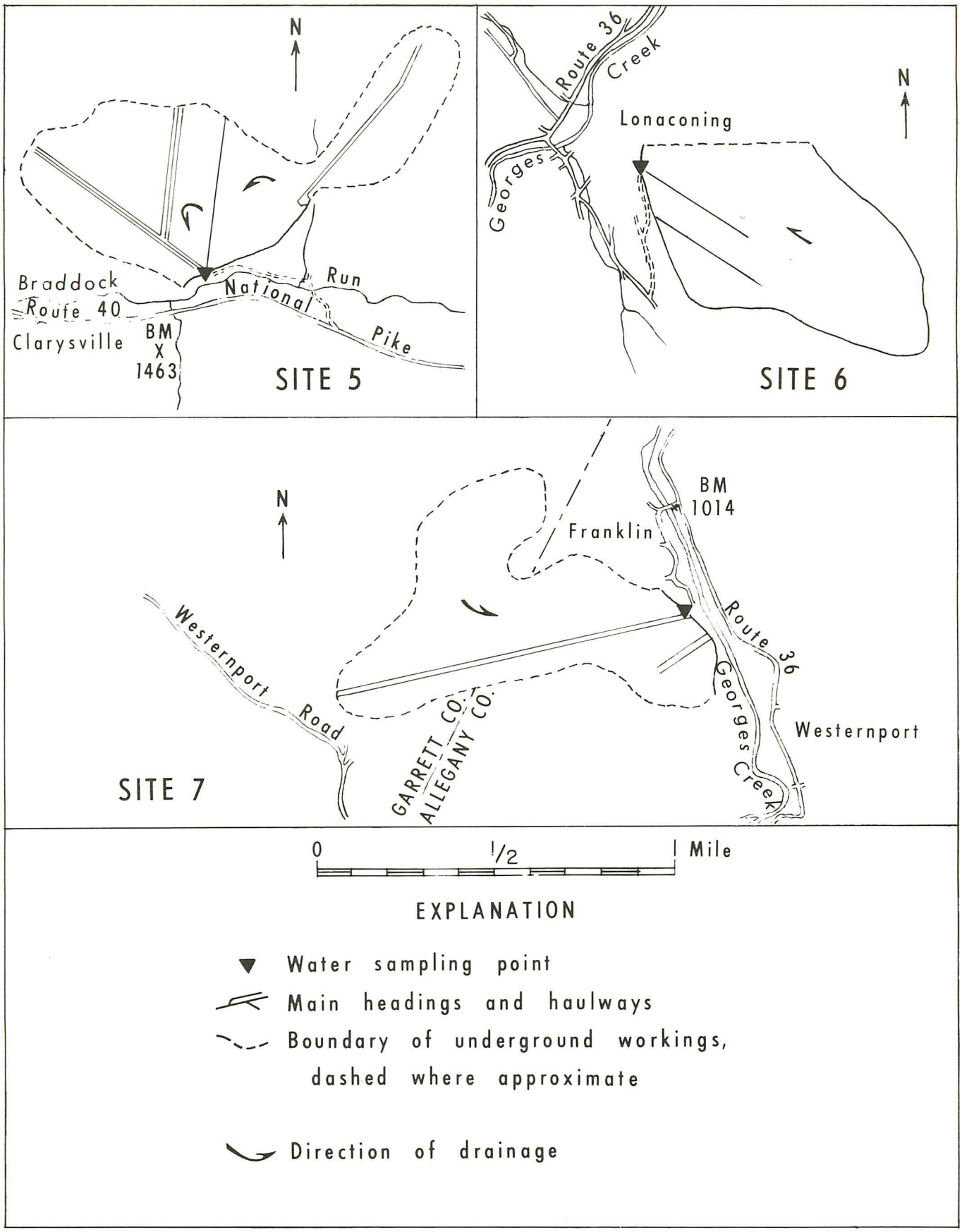

Figure 11.—Maps of the location and extent of underground mine workings showing inferred direction of water flow. Sites 5 through 7.

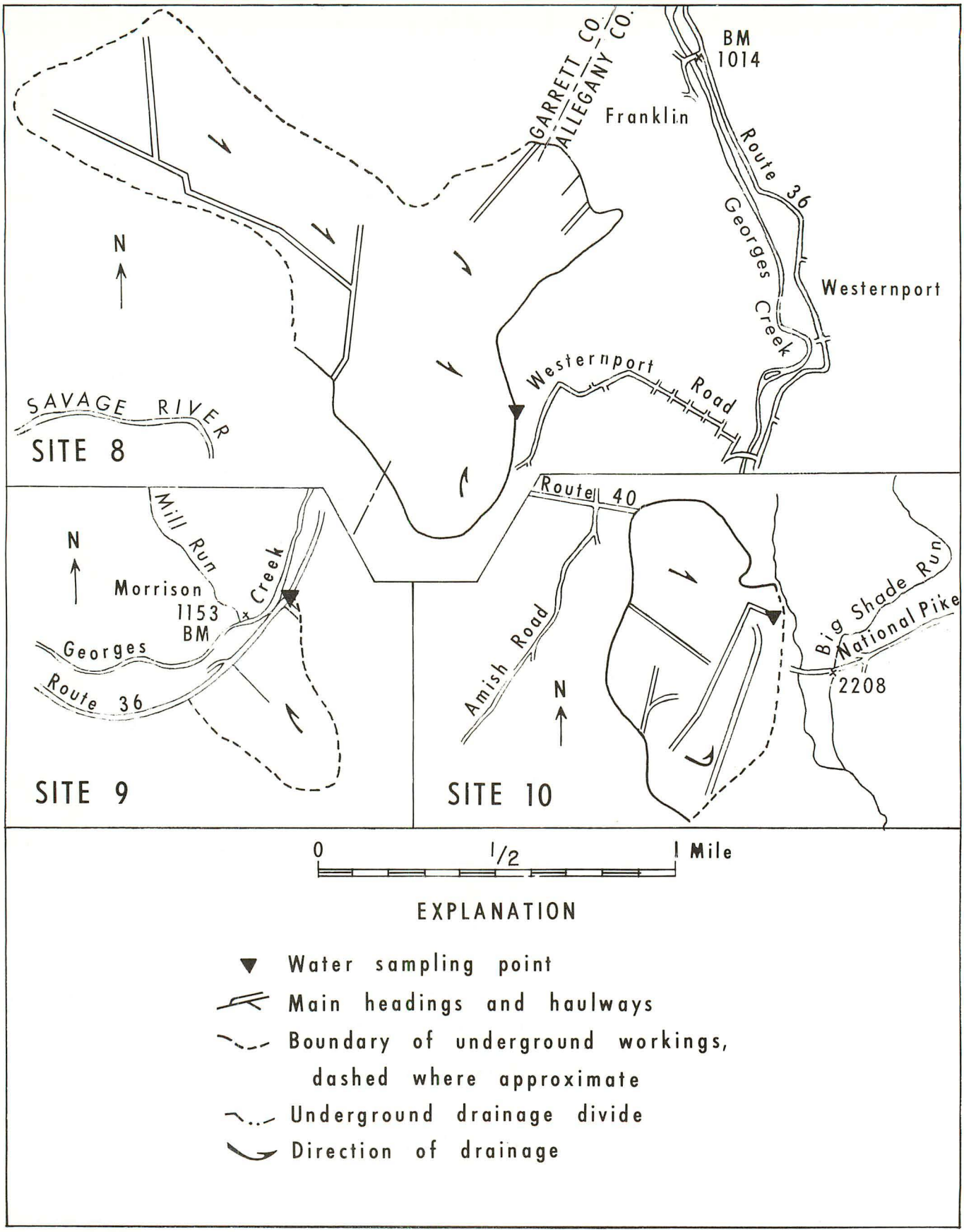

Figure 12.—Maps of the location and extent of underground mine workings showing inferred direction of water flow. Sites 8 through 10.

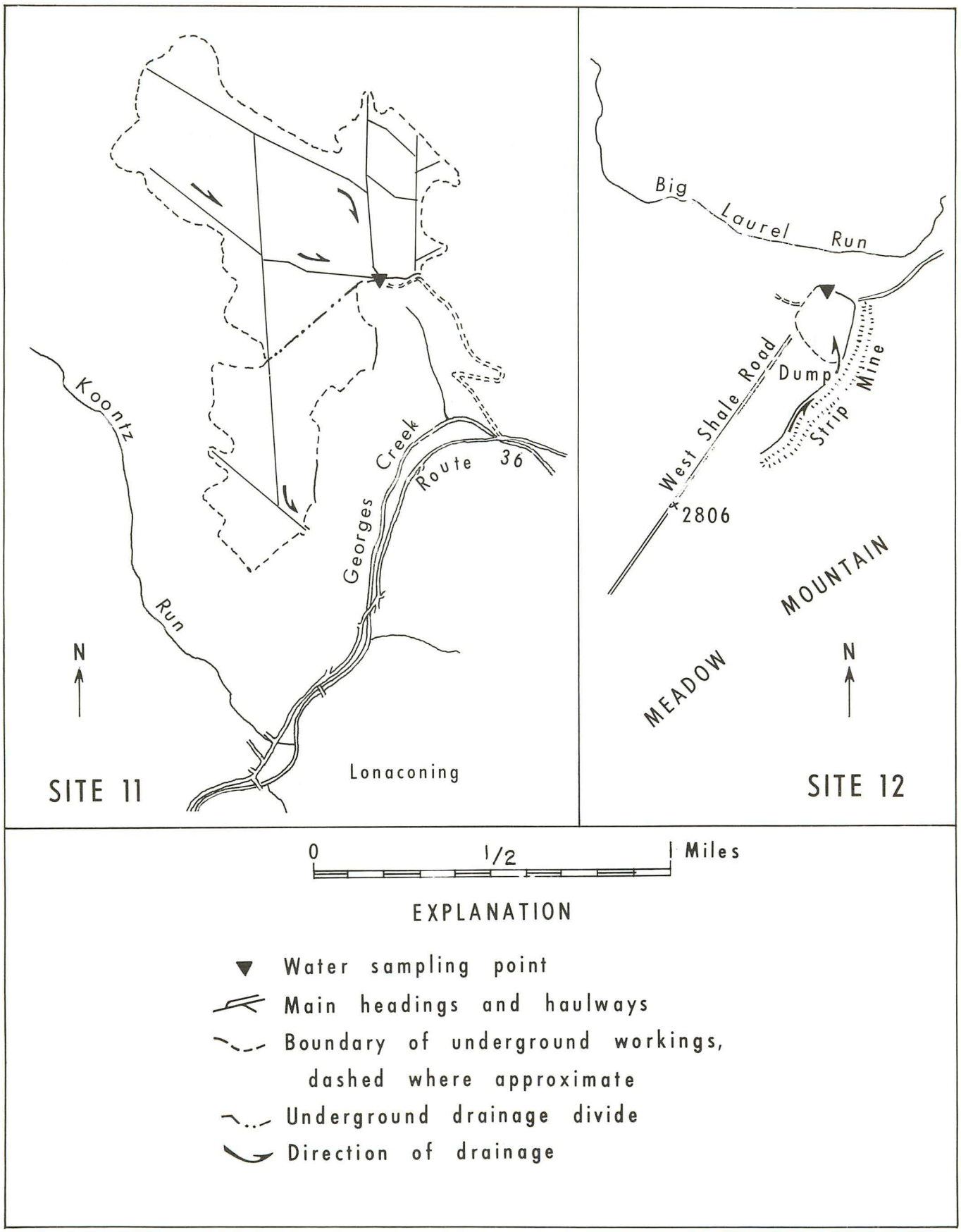

Figure 13.—Maps of the location and extent of underground mine workings showing inferred direction of water flow. Sites 11 and 12.

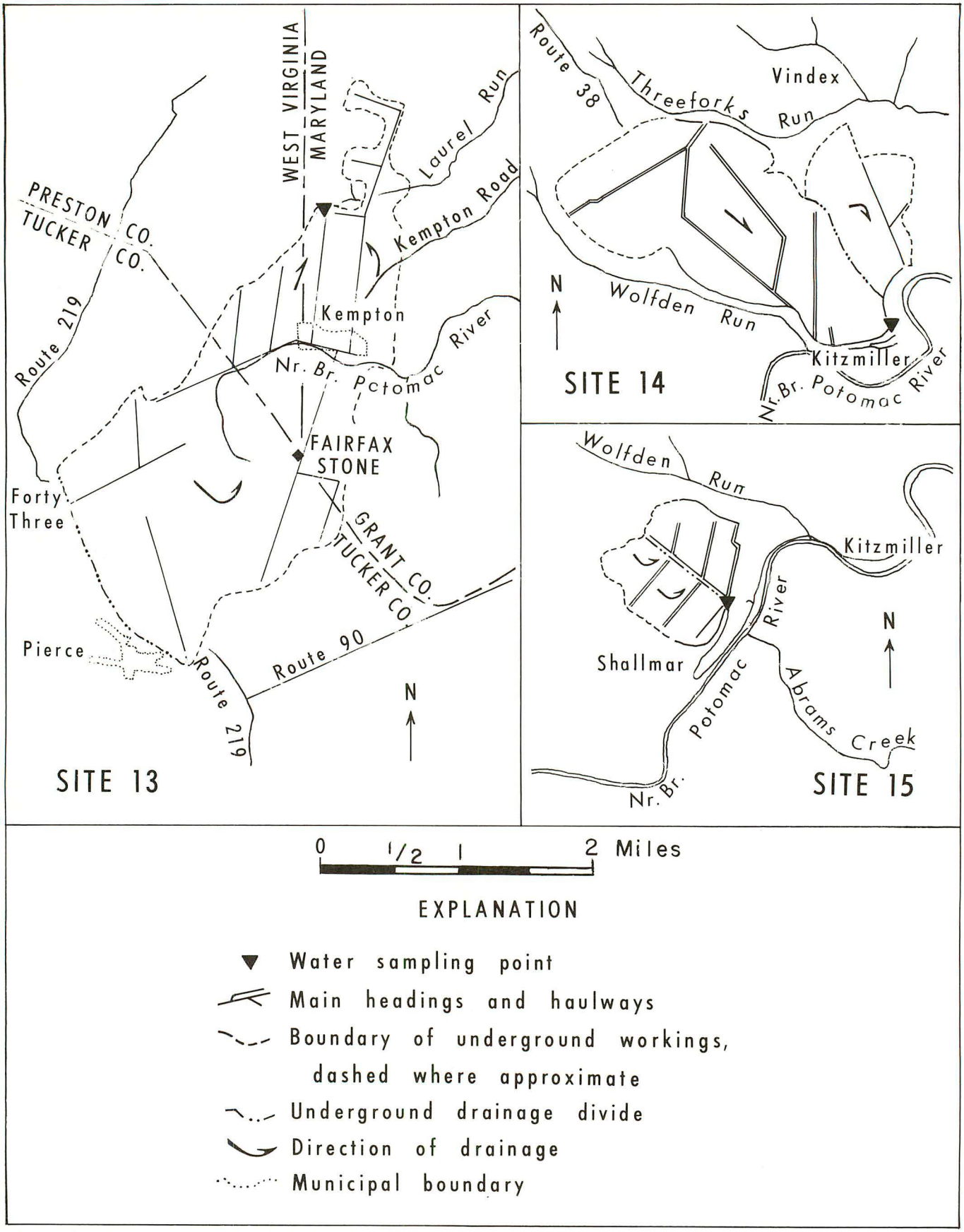

Figure 14.—Maps of the location and extent of underground mine workings showing inferred direction of water flow. Sites 13 through 15.

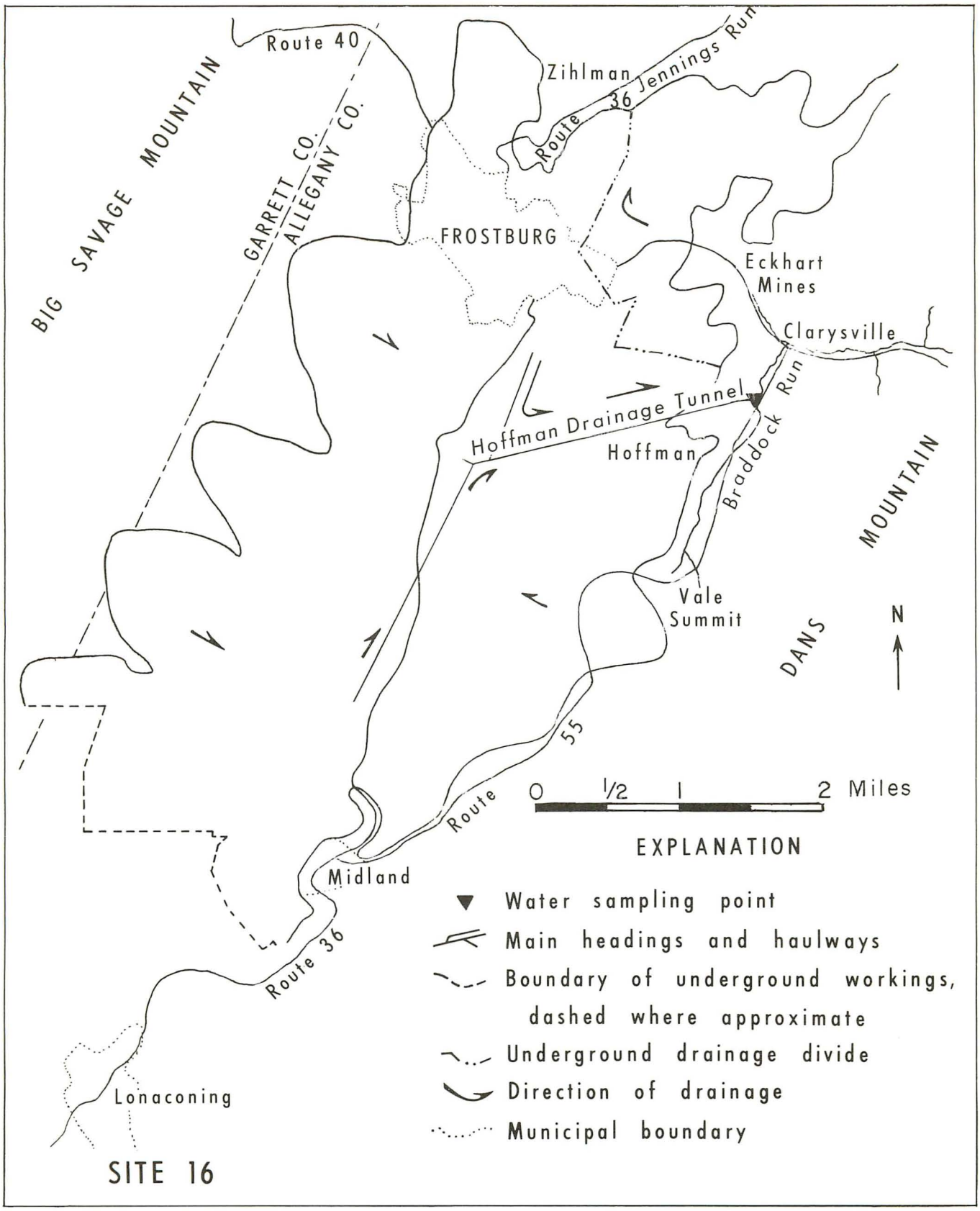

Figure 15.—Map of the location and extent of underground mine workings showing inferred direction of water flow. Site 16.

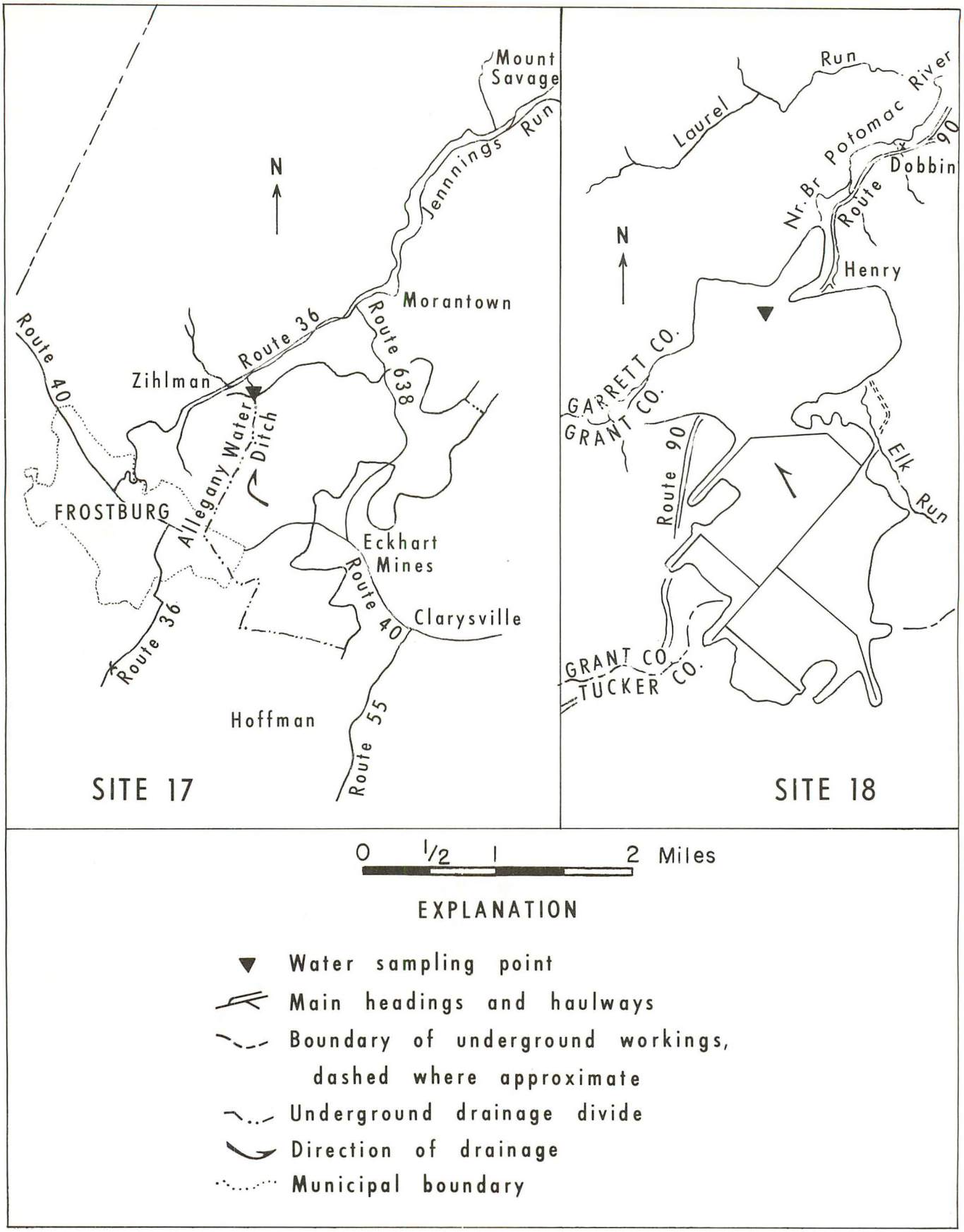

Figure 16.—Maps of the location and extent of underground mine workings showing inferred direction of water flow. Site 17 and 18.

APPENDIX II
TABLES OF
CHEMICAL ANALYSES

Table 3.—Chemical analyses of water from wells unaffected by mine drainage (milligrams per liter except as indicated)

Well number	Date of collection	Water-bearing formation	Depth of well (feet)	Silica (SiO_2)	Aluminum (Al)	Iron (Fe)	Manganese (Mn)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Copper (Cu)	Zinc (Zn)	Sulfate (SO_4)	Bicarbonate (HCO_3)	Chloride (Cl)	Fluoride (F)	Nitrate (NO_3)
All-Ac 50[a]	May 1, 1950	Conemaugh	107	--	--	--	--	42	7.9	63		--	--	16	292	7.5	0.1	9.8
Bc 24	Nov. 14, 1957	Conemaugh	88	6.1	.0	.59	.05	60	15	3.3	3.9	.00	.58	22	237	2	.2	.7
Ca 8	May 10, 1957	Conemaugh	45	7.8	.0	.18	.12	75	7.4	9.3	2.0	.00	.00	45	182	33	.1	.3
Cb 1	March 6, 1951	Conemaugh	500	7.8	.0	.64	.03	34	7.4	3.4	2.8	--	--	8.8	141	1.1	.1	4.2
Gar-Ad 1[b]	March 6, 1951	Allegheny and Pottsville	300	5.4	.1	.80	.34	6.0	2.3	0.8	.8	--	--	4.5	27	0.6	.1	.3
Ae 8	March 7, 1951	Conemaugh	85	6.6	1.1	.27	.04	30	8.2	3.4	1.1	--	--	10	87	27	.1	4.6
Maximum			500	7.8	1.0	.80	.34	75	15	9.3	3.9	.00	.58	45	292	33	.2	9.8
Minimum			45	5.4	.0	.18	.03	6.0	2.3	.8	0.8	.00	.00	4.5	27	0.6	.1	.3
Median			107	6.6	.0	.59	.05	42	7.9	3.4	2.0	.00	.58	16	182	7.5	.1	4.2
All-Da 7[c]	--	Pocono	2,379	--	--	2.9	--	--	--	--	--	--	--	70	--	9,550	--	--

Well number	Total phosphate (PO_4)	Dissolved solids	Hardness as $CaCO_3$		Specific conductance (micromhos at 25° C)	pH (units)	Remarks
			Total	Noncarbonate			
All-Ac 50	--	--	138	0	428	8.3	Well in valley bottom, open to strata between Lower Bakerstown and Upper Freeport coals.
Bc 24	.0	237	211	17	408	7.6	Well in mountainside stream valley, open to strata between Pittsburgh and Barton coals.
Ca 8	.0	305	218	68	463	7.6	Well in valley bottom, near axis of eastern structural trough, open to strata between Barton and Lower Bakerstown coals.
Cb 1	--	141	115	0	246	7.4	Well in mountainside stream valley, reported to yield 170 gpm from sandstones between Barton and Upper Kittanning coals; in fall, well is pumped continuously for 6 weeks.
Gar-Ad 1	--	35	24	--	54	6.8	Well on mountain slope, reported to flow 8 gpm from sandstone between Middle Kittanning coal and base of Pottsville Formation.
Ae 8	--	170	109	--	258	6.7	Well in draw, reported to yield 4 gpm from just below Harlem coal, open to strata between Barton and Lower Bakerstown coals.
Maximum	.0	305	218	68	463	8.3	
Minimum	.0	35	24	0	54	6.7	
Median	.0	170	138	0	408	7.6	
All-Da 7	--	16,100	2,460	--	--	7.0	Well in valley bottom, near axis of eastern structural trough, open to strata below coal measures between depths of 1,521 feet and 2,379 feet.

a/ Chemical analyses of water from wells in Allegany County from Slaughter and Darling, 1962, table 38.
b/ Chemical analyses of water from wells in Garrett County from Amsden, Overbeck, and Martin, 1954, table 18.
c/ Chemical analysis of water from deep test well from Slaughter and Darling, 1962, table 33.

Table 4.—Identification of sample sites and field analysis of coal-mine drainage.

Site no.	Date of collection	Site name	Site location	Latitude	Longitude	Stratigraphic designation of coal seams	Local names of coal seams	Area of draining mine workings (sq mi)	Discharge (cfs)	Air temperature (°C)
1-1	June 9, 1970	W&W Coal Co. #7 Mine (U.S.B.M.-#222)	Franklin Hill, Md.	39°31'23"	79°05'05"	Lower Bakerstown	Freeport	>0.12	0.027	26.0
1-2	July 22, 1970	do.	do.	do.	do.	do.	do.	do.	.022	19
1-3	Dec. 17, 1970	do.	do.	do.	do.	do.	do.	do.	.030	6.5
2	June 10, 1970	Murphy Coal Co. Susanne #1 Mine	Tasker Corners, Md.	39°21'53"	79°17'26"	Lower Bakerstown	Freeport	.12	.007	25
3-1	June 10, 1970	Morgart #1 Mine (U.S.B.M. #148)	Jennings, Md.	39°37'32"	79°11'27"	Lower Bakerstown	Freeport Honeycomb	.18	.01[a]	26
3-2	July 23, 1970	do.	do.	do.	do.	do.	do.	do.	.006	19
4-1	June 11, 1970	Clites Coal Co. Parker #2 Mine	Barrelville, Md.	39°42'35"	78°50'51"	Lower Bakerstown	Freeport	>.02	.003	31
4-2	Dec. 18, 1970	do.	do.	do.	do.	do.	do.	do.	.009	5
5	June 30, 1970	Sullivan #3 Mine (U.S.B.M.-#56)	Clarysville, Md.	39°38'38"	78°52'33"	Upper Kittanning	Blubaugh	.38	.024	29
6	June 30, 1970	Coromandel Coal Co. Big Vein Hill Mine	Lonaconing, Md.	39°33'53"	78°58'33"	Pittsburgh	Big Vein	.31	.019	35
7	July 1, 1970	Piedmont & George Coal Co. Wash #1 Mine (U.S.B.M. #167)	Franklin, Md.	39°29'48"	79°02'51"	Upper Freeport	Lower Kittanning Split Six	.38	.21	30
8	July 1, 1970	U.S.B.M. Mine #178	Westernport, Md.	39°29'12"	79°03'27"	Barton	Bakerstown	.34	.010	30
9	July 2, 1970	Morrison (U.S.B.M. Mine #128)	Barton, Md.	39°30'45"	79°01'18"	Lower Bakerstown	Freeport	.12	.032	27
10	July 23, 1970	Meyers Coal Co. Beachy #1 Mine (U.S.B.M. #13)	Grantsville, Md.	39°41'51"	79°10'34"	Upper Freeport	Beachy Grantsville	.30	.085	18
11	Aug. 11, 1970	Georges Creek Coal Co. Waynesburg #5	Lonaconing, Md.	39°35'09"	78°58'29"	Uniontown	Waynesburg	.42	.053	22
12	Aug. 11, 1970	Big Laurel Run Mine (U.S.B.M. #48)	New Germany, Md.	39°38'47"	79°08'05"	Middle Kittanning	Upper Kittanning	.02	.084	22
13	Aug. 25, 1970	Davis Coal & Coke Co. Mine #42	Kempton, Md.	39°13'14"	79°29'01"	Upper Freeport	Davis	>4.5	3.70	22
14	Aug. 26, 1970	Hamill #4 Mine (U.S.B.M. #274)	Kitzmiller, Md.	39°23'30"	79°11'03"	Upper Freeport	Lower Kittanning	2.1	.25	19
15	Aug. 26, 1970	Wolfden Coal Co. Mine (U.S.B.M. #281)	Shallmar, Md.	39°22'57"	79°12'19"	Upper Freeport	Lower Kittanning	.42	.092	26
16-1	Aug. 27, 1970	Hoffman Drainage Tunnel	Clarysville, Md.	39°38'17"	78°53'36"	Pittsburgh/Sewickley	Big Vein/Tyson	14.9	12.3	25
16-2	Dec. 17, 1970	do.	do.	do.	do.	do.	do.	do.	9.8	3
17	Aug. 27, 1970	Allegany Water Ditch	Zihlman, Md.	39°40'04"	78°54'35"	Pittsburgh/Sewickley	Big Vein/Tyson	2.0	.38	26
18	Dec. 16, 1970	Island Creek Coal Co. Alpine Mine	Henry, W. Va.	39°13'20"	79°25'56"	Lower Bakerstown	Thomas	3.7	4.00	1.5
19	Oct. 29, 1970	Distilled Water Blank								20

Site no.	Water temperature (°C)	Dissolved oxygen (mg/l)	pH (units)	Immediate acidity as H^+ to pH 7.0 (mg/l)	Immediate acidity as H^+ to pH 8.3 (mg/l)	Alkalinity as $CaCO_3$ to pH 4.5 (mg/l)	Specific conductance at 25°C (micromhos)	Color	Appearance	Suspended matter collected on filter	Color of precipitation with neutralization	Remarks
1-1	13.0	5.9	2.5	32	34	None	4,200	Yellow	Clear	None	Yellow	Workings more extensive than shown on mine maps
1-2	12.5	7.1	3.0	39	42	do	4,200	Yellow	Clear	None	Yellow	
1-3	10.5	8.5	2.9	30	32	do	4,000	Yellow	Clear	None	Yellow	
2	8.5	7.5	2.7	1.6	1.8	do	810	None	Clear	-	-	
3-1	9.5	8.7	7.0	.0	.3	77	1,060	None	Slightly turbid	Orange	-	
3-2	9.5	9.5	7.0	.0	.7	96	1,400	None	Slightly turbid	-	Faint Yellow	
4-1	12.0	3.2	2.2	49	54	None	5,000	Yellow	Clear	Cream	-	Workings more extensive than shown on mine maps
4-2	8.0	4.4	2.8	36	39	do	4,400	Yellow	Clear	Cream	Yellow	
5	11.0	2.2	3.0	15	18	do	2,800	None	Clear	None	Green Yellow	
6	16.0	2.9	2.8	10	11	do	2,900	None	Clear	None	Yellow	
7	12.0	0.2	6.5	1.1	2.8	308	2,000	None	Clear	Yellow	Yellow	Odor - small H_2S
8	12.5	7.1	3.0	13	14	None	2,500	None	Slightly turbid	Yellow	Yellow	
9	10.0	1.8	5.4	3.1	3.8	29	1,600	None	Slightly turbid	Yellow	Yellow	
10	10.0	2.3	6.1	.8	1.3	72	800	None	Clear	Yellow	None	
11	11.0	0.8	2.9	5.5	6.0	None	1,800	None	Clear	None	Yellow	Drainage from dump and strip seeping into underground workings
12	10.5	8.3	2.8	2.7	2.9	do	880	None	Clear	None	None	
13	10.3	0.2	3.4	6.2	8.2	do	1,020	None	Clear	None	Yellow	Workings more extensive than shown on mine maps
14	12.0	6.7	2.8	19	21	do	2,450	Yellow	Clear	None	Yellow	
15	10.5	8.4	3.2	9.0	9.4	do	2,150	None	Clear	None	Yellow	
16-1	11.5	2.3	5.6	3.0	3.9	44	960	None	Clear	-	-	
16-2	11.0	3.5	5.6	2.4	3.2	42	1,100	None	Clear	-	-	
17	12.0	7.0	5.4	1.4	1.8	16	1,000	None	Slightly turbid	None	Yellow	
18	10.0	8.4	3.0	15	19	None	3,700	None	Clear	-	Green Yellow	Pooling for 3 months and pumping for 1 day prior to sampling
19	14.5	10.0	4.5	.1	.1	None	< 50	None	Clear	None	None	

a/ Estimated
> Larger than figure shown
< Less than figure shown

Table 5.—Laboratory chemical analyses for major constituents in coal-mine drainage. (milligrams per liter except as indicated)

Site No.	Date of Collection	Discharge (CFS)	Silica (SiO_2)	Aluminum (Al)	Iron (Fe)	Manganese (Mn)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Copper (Cu)	Zinc (Zn)	Sulfate (SO_4)	Bicarbonate (HCO_3)	Chloride (Cl)
1-1	June 9, 1970	0.027	49	49	470	5.2	374	110	1.0	0.5	0.78	3.1	2,990	0	1.0
1-2	July 22, 1970	.022	46	41	615	6.3	388	128	1.2	.9	.85	3.6	3,520	0	1.5
1-3	Dec. 17, 1970	.030	39	48	500	5.4	335	112	.9	.6	.80	3.0	2,930	0	1.5
2	June 10, 1970	.007	20	5.2	3.7	.74	53	17	.8	1.6	.03	.50	281	0	.4
3-1	June 10, 1970	.010	6.1	.0	.79	.56	157	46	1.9	2.2	.00	.10	505	92	.7
3-2	July 23, 1970	.006	7.7	.0	7.6	1.5	240	72	3.3	3.3	.22	.30	777	98	1.0
4	June 11, 1970	.003	62	21	748	8.0	399	281	1.9	1.2	.82	5.5	4,410	0	1.0
5	June 30, 1970	.024	49	31	280	5.3	261	93	23.	3.5	.20	1.5	1,790	0	1.0
6	June 30, 1970	.019	45	124	62	10	281	149	3.2	.4	.40	3.2	1,750	0	.2
7	July 1, 1970	.21	17	.0	15	.82	375	101	38.	7.8	.18	.08	1,120	342	3.1
8	July 1, 1970	.010	36	57	120	13	202	76	19.	1.4	.25	1.8	1,460	0	15
9	July 2, 1970	.032	11	68	42	3.1	266	66	12.	8.5	.18	.45	1,060	0	1.3
10	July 23, 1970	.085	8.2	.5	.55	.15	106	27	34.	2.2	.22	.16	269	94	74
11	Aug. 11, 1970	.053	16	8.3	22	3.4	138	56	1.1	1.4	.08	.68	732	0	.6
12	Aug. 11, 1970	.084	18	2.5	8.7	3.7	40	12	7.4	6.1	.00	1.3	205	0	53
13	Aug. 25, 1970	3.70	43	.8	85	2.5	80	32	5.6	3.5	.00	1.1	595	0	2.2
14	Aug. 26, 1970	.25	50	74	112	3.1	240	80	2.4	.2	.56	2.2	1,700	0	1.4
15	Aug. 26, 1970	.092	38	38	37	1.8	204	68	1.8	1.0	.18	1.2	1,100	0	.4
16	Aug. 27, 1970	12.3	13	.0	12	3.7	158	56	4.8	1.8	.00	.17	579	20	8.2
17	Aug. 27, 1970	.38	18	1.4	2.4	1.9	175	58	4.7	1.1	.00	.46	635	4	8.2
18	Dec. 16, 1970	4.00	39	30	320	4.8	310	100	12	1.8	.58	.90	2,090	0	2.4
Maximum			62	124	748	13	399	281	38	8.5	0.85	5.5	4,410	342	74
Minimum			6.1	0.0	0.55	0.15	40	12	0.8	0.2	0.00	0.08	205	0	0.2
Median			36	21	42	3.4	240	72	3.4	1.6	0.20	1.1	1,100	0	1.4
Distilled water blank			0	0	0.0	0.0	0	0	0	0	0.00	0.00	0	0	0

Site No.	Date of Collection	Fluoride (F)	Nitrate (NO_3)	Total Phosphate (PO_4)	Dissolved Solids (residue at 180°C)	Hardness as $CaCO_3$: Calcium, Magnesium	Hardness as $CaCO_3$: Noncarbonate	Specific conductance (micro mhos at 25°C)	pH (Units)	Potential Acidity to pH 8.3 (as H^+)	Free Acidity to pH 8.3 (as H^+)	Color (Platinum-Cobalt Units)
1-1	June 9, 1970	3.8	0.6	0.12	4,290	1,390	3,040	4,120	2.41	33	5.6	300
1-2	July 22, 1970	3.1	.8	5.1	5,020	1,500	3,710	4,180	2.53	--	7.9	high
1-3	Dec. 17, 1970	1.6	.1	3.4	4,510	1,300	4,610	--	2.55	34	--	--
2	June 10, 1970	1.2	.4	.00	392	202	287	810	2.94	1.7	1.1	1
3-1	June 10, 1970	.5	1.3	.00	812	581	507	1,030	7.40	.0	.0	2
3-2	July 23, 1970	1.0	1.2	4.7	1,320	896	818	1,410	6.90	--	.0	0
4	June 11, 1970	6.5	.1	.09	6,830	2,170	4,620	5,230	2.50	50	16.	500
5	June 30, 1970	3.8	.7	2.0	2,830	1,030	1,900	3,100	2.56	--	7.1	high
6	June 30, 1970	3.2	.4	2.1	2,640	1,320	1,930	2,900	2.83	--	4.8	8
7	July 1, 1970	1.1	.2	2.3	2,000	1,350	1,090	2,090	7.50	.0	.0	0
8	July 1, 1970	2.4	.8	1.2	2,220	817	1,550	2,700	2.68	--	7.2	0
9	July 2, 1970	1.0	.5	2.5	1,580	936	1,090	1,730	3.32	--	.9	0
10	July 23, 1970	.6	1.0	2.5	644	376	299	883	6.50	--	.0	0
11	Aug. 11, 1970	.8	.1	.05	1,160	575	688	1,700	2.78	3.7	--	--
12	Aug. 11, 1970	.4	.9	.00	342	150	316	974	2.89	2.4	--	--
13	Aug. 25, 1970	.8	.6	.18	1,000	331	599	1,690	2.61	5.3	--	--
14	Aug. 26, 1970	1.4	.2	2.0	2,660	929	1,850	2,940	2.57	18	--	--
15	Aug. 26, 1970	1.0	.4	.80	1,720	789	1,100	2,230	2.74	7.9	--	--
16	Aug. 27, 1970	1.0	.0	.00	955	625	648	1,070	6.30	--	--	--
17	Aug. 27, 1970	.9	.1	.00	1,000	676	691	1,170	5.92	--	--	--
18	Dec. 16, 1970	1.2	.1	.34	3,330	1,190	3,170	--	2.60	19	--	--
Maximum		6.5	1.3	5.1	6,830	2,170	4,620	5,230	7.50			
Minimum		0.4	0.0	0.0	342	150	287	810	2.41			
Median		1.1	0.4	0.8	1,720	896	1,090	1,730	2.78			
Distilled water blank		0	0	0.2	0	--	--	1.2	4.7			

Table 6.—Laboratory analyses for minor constituents in coal-mine drainage
(Analyses in micrograms per liter)

Site no.	Date of collection 1970	Discharge (cfs)	Aluminum (Al)	Antimony (Sb)	Arsenic (As)	Barium (Ba)	Beryllium (Be)	Bismuth (Bi)	Boron (B)	Cadmium (Cd)	Chromium (Cr)	Cobalt (Co)	Copper (Cu)	Gallium (Ga)	Germanium (Ge)	Lanthanum (La)	Lead (Pb)
1-1	June 9	.027	48,000	--	180	22	21	<65	45	<1	180	1,100	760	ND	ND	<10	3
1-2	July 22	.022	71,000	<23	390	10	16	< 1	--	<1	14	1,400	900	ND	<10	<10	5
1-3	Dec. 17	.030	30,000	< 5	310	26	42	< 0.4	90	<1	84	900	840	ND	<68	<23	<2
2	June 10	.007	5,100	--	0	17	5	< 6	8	2	<25	110	36	ND	ND	<10	4
3-1	June 10	.010	36	--	0	28	<2	<13	34	1	<25	25	25	ND	ND	<10	40
3-2	July 23	.006	25	<23	10	24	<1	< 1	50	2	< 1	65	2	ND	< 3	<10	<5
4	June 11	.003	130,000	--	40	35	18	<100	34	<1	340	1,100	820	ND	ND	<10	3
5	June 30	.024	44,000	--	0	15	13	< 45	35	<1	<25	360	100	ND	ND	<10	<2
6	June 30	.019	51,000	--	0	15	18	< 40	10	2	<25	830	320	ND	ND	55	<2
7	July 1	.210	70	--	0	21	<3	<30	50	2	<25	8	180	ND	ND	<10	<2
8	July 1	.010	63,000	--	20	12	15	<35	20	<1	80	580	210	ND	ND	45	2
9	July 2	.032	650	--	20	15	<3	<25	30	<1	<25	170	24	ND	ND	<10	<2
10	July 23	.085	20	<23	0	47	<1	< 1	35	<1	< 1	<23	1	ND	< 2	<10	7
11	Aug. 11	.053	16,000	<23	10	17	18	< 1	50	4	4	180	160	ND	< 4	12	6
12	Aug. 11	.084	7,900	<23	0	32	40	< 1	50	5	2	270	50	ND	<1	<10	<5
13	Aug. 25	3.70	18,000	<23	20	8	12	< 1	12	<1	5	130	5	ND	<3	<10	<5
14	Aug. 26	0.25	85,000	<23	10	10	16	< 1	22	<1	22	350	600	ND	<8	16	<5
15	Aug. 26	.092	46,000	<23	20	6	8	< 1	14	4	11	210	190	ND	<6	<10	<5
16	Aug. 27	12.3	500	<23	10	13	<1	< 1	14	3	3	70	<1	ND	<3	<10	<5
17	Aug. 27	.380	2,000	<23	0	12	<1	< 1	13	4	<1	75	10	ND	<3	<10	<5
18	Dec. 16	1.00	22,000	< 5	110	19	10	< 0.4	70	<1	33	280	590	ND	<50	23	<5
Maximum			130,000	--	390	47	42	--	90	5	340	1,400	900	--	--	55	40
Minimum			20	--	0	6	<1	--	8	<0.5	<1	8	< 1	--	--	<10	<2
Median			18,000	--	10	17	12	--	34		22	210	160	--	--	--	--
Distilled water blank			20	< 5	0	—	<0.4	<10	--	<1	2	2	<22	--	--	< 2	2

Site no.	Lithium (Li)	Manganese (Mn)	Mercury (Hg)	Molybdenum (Mo)	Nickel (Ni)	Rubidium (Rb)	Scandium (Sc)	Selenium (Se)	Silver (Ag)	Strontium (Sr)	Tin (Sn)	Titanium (Ti)	Vanadium (V)	Ytterbium (Yb)	Yttrium (Y)	Zinc (Zn)	Zirconium (Zr)
1-1	80	5,900	--	<3	2,400	<10	a/	20	<10	1,300	<65	<10	<65	180	150	2,600	120
1-2	100	7,400	--	2	3,300	<10	--	20	< 2	1,800	<25	<10	<25	3	28	3,800	42
1-3	90	6,800	<0.5	1	2,600	<20	--	10	< 1	1,000	<68	<10	<68	10	110	2,200	2,300
2	30	750	--	<3	210	2	ND	0	<10	75	< 6	<10	< 6	<10	<50	370	<50
3-1	25	650	--	<3	54	2	ND	0	<10	2,100	<13	<10	<13	<10	<50	60	<50
3-2	37	1,700	--	<1	110	< 3	--	0	< 0.6	4,600	< 7	<10	< 7	< 1	< 5	140	6
4	140	8,800	<1.5	<3	2,600	<15	a/	0	<10	2,200	<100	<10	<100	24	250	4,700	200
5	80	5,700	--	<3	870	6	ND	0	<10	280	<45	<10	<45	110	140	1,200	80
6	190	11,000	--	<3	1,700	<6	a/	0	<10	180	<40	<10	<40	120	170	2,600	<50
7	45	1,000	--	<3	21	7	ND	0	<10	1,500	<30	<10	<30	<10	<50	20	<50
8	110	13,000	--	<3	1,200	6	a/	0	<10	360	<35	<10	<35	180	220	1,500	<500
9	55	3,600	--	<3	310	15	ND	0	<10	1,400	<25	<10	<25	<10	<50	270	<50
10	12	160	--	<1	15	< 2	--	0	< 0.3	590	< 4	<10	< 4	< 1	< 5	20	< 5
11	41	4,300	--	<1	540	<3	--	0	< 0.5	270	< 6	<10	< 6	3	36	680	10
12	16	4,400	--	<1	380	16	--	10	< 0.2	140	< 2	<10	< 2	2	16	1,500	< 5
13	35	3,000	--	<1	590	8	--	0	< 0.4	440	< 5	<10	< 5	2	16	950	22
14	94	3,500	--	<1	1,600	<15	--	10	< 0.1	570	<15	<10	<15	6	62	2,400	20
15	76	2,000	--	<1	900	<10	--	10	< 0.7	550	< 9	<10	< 9	5	52	1,000	11
16	55	4,000	--	<1	190	< 5	--	0	< 0.4	210	< 5	<10	< 5	<1	6	1,000	6
17	57	2,100	--	<1	170	< 5	--	0	< 0.4	240	< 5	<10	< 5	<1	16	420	< 5
18	40	5,400	<0.5	1	500	<15	--	10	< 1	2,000	<50	<10	<50	4	39	1,200	2,000
Maximum	190	13,000	--	2	3,300	16	--	20	--	4,600	--	--	--	180	250	4,700	2,300
Minimum	12	160	--	<1	15	< 2	--	0	--	75	--	--	--	<1	< 5	20	< 5
Median	55	4,000	--	--	540	--	--	--	--	570	--	--	--	6	43	1,000	46
Distilled water blank	--	2	--	<0.4	5	--	--	0	<0.2	--	--	< 2	--	<0.2	<1	37	< 1

a/ Small amount

< Less than figure shown.

ND Specifically sought, not detected.

Talbe 7.—Laboratory analysis for minor constituents in coal-mine drainage before and after neutralization, Site No. 4 on June 11, 1970
(Anaylsis in micrograms per liter)

Sample Preparation	Aluminum (Al)	Barium (Ba)	Beryllium (Be)	Bismuth (Bi)	Boron (B)	Cadmium (Cd)	Chromium (Cr)	Cobalt (Co)	Copper (Cu)	Gallium (Ga)	Germanium (Ge)	Lanthanum (La)	Lead (Pb)	Lithium (Li)	Manganese (Mn)
Filtered, acidified in field	130,000	35	18	<100	34	<1	340	1,100	820	ND	ND	<10	3	140	8,800
Precipitate from neutralization in lab. to pH 7.0	160,000	--	18	ND	--	ND	190	640	950	ND	ND	ND	ND	--	960
Filtrate from neutralization in lab. to pH 7.0	30	20	<4	ND	--	ND	<5	270	7	ND	ND	ND	ND	--	9,200

Sample Preparation	Mercury (Hg)	Molybdenum (Mo)	Nickel (Ni)	Rubidium (Rb)	Scandium (Sc)	Silver (Ag)	Strontium (Sr)	Tin (Sn)	Titanium (Ti)	Vanadium (V)	Ytterbium (Yb)	Yttrium (Y)	Zinc (Zn)	Zirconium (Zr)
Filtered, acidified in field	1.5	<3	2,600	<15	Small Amount	<10	2,200	<100	<10	<100	24	250	4,700	200
Precipitate from neutralization in lab. to pH 7.0	--	ND	1,500	--	--	ND	ND	ND	ND	ND	22	230	4,100	ND
Filtrate from neutralization in lab. to pH 7.0	--	ND	410	--	--	ND	2,100	ND	ND	ND	ND	ND	800	ND

ND - Specifically sought, not detected

< - Less than figure shown

Table 8.—Laboratory chemical analyses of major constituents collected on 0.45-micron filter
(milligrams per liter)

Site no.	Date of collection	Aluminum (Al)	Calcium (Ca)	Iron (Fe)	Magnesium (Mg)	Manganese (Mn)	Sodium (Na)	Potassium (K)	Silica (SiO_2)
1	December 17, 1970	.34	.040	.005	.071	.002	.032	.028	.68
3	June 10, 1970	.30	.041	.000	.014	.002	.021	.006	.37
4	June 11, 1970	.087	.036	.001	.055	.002	.014	.013	.22
18	December 16, 1970	.35	.038	.185	.037	.001	.036	.032	.91
19	Distilled water blank	.032	.001	.004	.003	.001	.021	.003	.032

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