SPECIAL REPORT OF RESEARCH

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College of Earth and Mineral Sciences
The Pennsylvania State University

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

by

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STATEMENT OF TRANSMITTAL

Special Report SR-65 transmitted herewith has been prepared by the Coal Research Section of the College of Earth and Mineral Sciences Experiement Station. Each of the Special Reports presents results obtained in connection with one of the research projects supported by the Department of Mines and Mineral Industries of the Commonwealth of Pennsylvania or a technical discussion of related research. The following is a list of Special Research Reports issued to date:

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SR-27	A Preliminary Investigation into the Application of Coal Petrography in the Blending of Anthracite and Bituminous Coals for the Production of Metallurgical Coke	May 1, 1961
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SR-31	Mineral Matter Removal from Anthracite by High Temperature Chlorination	March 26, 1962
SR-32	The Effect of Crusher Type on the Liberation of Sulfur in Bituminous Coal	April 29, 1962
SR-33	Investigation of the Circular Concentrator - Flotation Circle System for Cleaning Fine Coal	September 10, 1962

SR-34	Reactions of Coal with Atomic Species	September 24, 1962
SR-35	The Preparation Characteristics of the Bituminous Coal Reserves in Pennsylvania with Special Emphasis on Sulfur Reduction	October 31, 1962
SR-36	A Study of the Burning Velocity of Laminar Coal Dust Flames	November 5, 1962
SR-37	Molecular Sieve Material From Anthracite	November 16, 1962
SR-38	Studies of Anthracite Coals at High Pressures and Temperatures	April 29, 1963
SR-39	Coal Flotation of Low-Grade Pennsylvania Anthracite Silts	May 13, 1963
SR-40	Changes in the Physical Properties of Anthracite Upon Heat Treatment	July 10, 1963
SR-41	Some Aspects of the Chemistry of Sulfur in Relation to Its Presence in Coal	August 20, 1963
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SR-57	The Evaluation of Anthracite Refuse as a Highway Construction Material	July 30, 1966
SR-58	An Investigation of the Cleaning of Bituminous Coal Refuse Fines by an Experimental Hydrocyclone	August 15, 1966
SR-59	Chlorination and Activation of Pennsylvania Anthracites	October 24, 1966
SR-60	Development and Testing of an Injection Well for the Subsurface Disposal of Acid Mine Water	February 1, 1967
SR-61	Investigations of the Cyclone Washing of Fine Coal in Water	December 12, 1966
SR-62	Linear Programming Short Course	May 1, 1967

SR-63	Planning Belt Conveyor Networks Using Computer Simulation	May 15, 1967
SR-64	The Economic Importance of the Coal Industry to Pennsylvania	August 1, 1967

William Spackman, Director
Coal Research Section

SUMMATION OF RESULTS

Alkalinity and acidity were the two water quality parameters investigated in order to evaluate the effect of acid mine drainage on the ground water regimen of a strip mined area of the Bituminous coal field of Pennsylvania. The alkalinity was related to the occurrence of calcium carbonate. The acid potential of a rock was related to the occurrence of pyrite by three leaching tests which were also used to evaluate the effects of rock type, iron bacteria and alkalinity on acid production. Rock and water samples were collected from an area underlain by Lower and Middle Kittanning formations (Allegheny group of the Pennsylvanian) and from a second study area underlain by Upper Kittanning and Lower Freeport formations (Allegheny group). Because the former area produced acid mine drainage and the latter did not, analyses of the rock and water samples were compared to determine the compositional variations responsible for divergent water qualities. To facilitate comparisons of various chemical components, extremely acid and alkaline water samples were collected from other mines to establish quality extremes. The hydrology of the two study areas was approximated from measurements and observations made on domestic wells in one area.

It was found that the ranges of total sulfur contents (used to estimate the pyritic sulfur content) of the acid and non-acid areas were similar and could not explain the different water qualities produced. The leaching tests showed acid generation to be partly dependent upon the sulfur content of a sample and to be greatly influenced by the crystallinity of the pyrite, the presence of iron bacteria and calcium carbonate. Ground waters in an acid mine drainage area, although not

containing potential free acidity, had low pHs; thus may support iron bacteria which will catalyze the acid forming reactions. The alkalinity of these waters was low and could not neutralize much acid. On the other hand, ground waters in a non-acid mine drainage area had high pHs which may not harbor the iron bacteria; consequently acid production will be low and may be effectively neutralized by the available alkalinity. Precautions should be taken to prevent the refuse of an infected mine from being placed in a sterile mine (in regard to the iron bacteria) thereby innoculating the mine with these bacteria. In one study area the almost complete lack of sulfate ion in the alkaline mine drainages suggests that the pyrite present is inert and acid mine drainage is not produced.

The overall permeability of the rocks in the study area is very low. The general hydrologic setting is essentially composed of alternating aquifers and aquitards layered in accord with the cyclicity which is characteristic of the rocks in the area and may cause the ground waters to have a predominant lateral flow. It is suggested that the strata near the coal seams, probably the underclays, are the major aquitards in the area and may, under certain conditions, confine acid waters to surface water sources.

To test the proposed hypotheses and to determine the metamorphism of acid mine drainage in the ground water reservoir an extensive and highly specialized water monitoring system must be installed.

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INTRODUCTION

A. Background of the Acid Mine Drainage Problem

Since opening the first coal mine in Pennsylvania in 1761, coal mining has become one of the main industries in the state. As the coal is mined, the iron disulfides, occurring either as marcasite or pyrite in the unmined coal and in the undisturbed strata associated with the coal, are exposed to the atmosphere and are readily decomposed. During this decomposition, compounds are formed by a complex series of chemical reactions. These compounds can be easily dissolved in water to produce acid and associated hydrous iron complexes. The acidity adversely affects the aquatic life of streams receiving this acid water, and where significant volumes of acid are released, the domestic and industrial use of this water is possible only with costly chemical treatment. The recreational use of this acid water is nil (Klingensmith, 1965, p. 1).

Klingensmith (1965) estimates about 2300 miles of Pennsylvanian streams have been adversely affected by acid mine drainage, derived from both deep and shallow mines. He points out that there are two dissimilar acid mine drainage problems within Pennsylvania owing to the different hydro-geologic environments of the Anthracite and Bituminous coal fields.

In the Anthracite area, located in the north-eastern portion of Pennsylvania, most of the coal strata are intensely folded and plunge many coal seams underground to great depths. Consequently, mines as

deep as 2000 feet have been dug to extract coal. These deep mines are located beneath the water table and are continuously flooded by ground water which must be pumped to the surface during the mining operation. The pollution of surface streams occurs during the mining phase when acid water, formed at depth, is pumped to the surface. In a way, the pollution of surface streams can be controlled by controlling the pumping rate. During dry periods, the acid water can be impounded and released during heavy rains when it can be diluted. At the cessation of mining and after the equipment is withdrawn from the mine shaft, pumping ceases and water is allowed to flood the shaft which eventually drains to the surface by a complex drainage network. Occasionally, mine water drainage tunnels are extended to the surface or gravity overflows are created which allow the extensively mined areas to drain.

Due to the plunge of the strata, the mines are concentrated under a small land area and consequently, a relatively small number of water discharge points have been established to drain extensive mining operations.

However, in the Bituminous area of the western part of Pennsylvania, the coal strata are essentially flat lying with broad structures having dips which rarely exceed 10°. Anomalous structures, such as paleogeologic slump structures, and disconformities, may be present locally (Williams et al, 1965), but these are small in scale by comparison to those structures in the Anthracite region. In this area, the coal seams are mined either through horizontal or gently inclined mine shafts or drifts, if the coal seam is thick enough to be entered by man and

equipment; or strip mined, if the overburden is thin enough to be removed economically. Because of this latter consideration, many of the strip mines in the Bituminous area are located in the uplands where the overburden is thinnest. This has a profound affect on the water quality in the area as the acid mine water can drain naturally into the adjacent streams or infiltrate into soil and bedrock and then percolate through the underlying strata to the ground water regimen.

Unlike the deep mines in the Anthracite area, the strip mines in the Bituminous region, because of the low dips of the coals and near surface occurrence of usable coals, disturb vast areas. As a consequence, numerous widely spaced discharge points result. Hence, pollution by acid mine drainage is widespread in the Bituminous coal field.

B. Definition of Acid Water

A water containing mine drainage is considered acid in this study if the potential free acidity exceeds the alkalinity. The potential free acidity is determined by boiling the sample for two minutes, cooling to room temperature and titrating the sample with a 0.0248N sodium hydroxide solution to pH 7.0; the alkalinity is determined by titrating the raw sample with a 0.01639N sulfuric acid solution to pH 4.5 (Rainwater and Thatcher, 1960).

Acid mine drainage pollution is defined in this study as any water sample whose potential free acidity exceeds the alkalinity and whose sulfate content (as $SO_4^{=}$) exceeds 250 mg/l (milligrams per liter).

It is recognized that other components of acid mine drainage such as iron, manganese, aluminum and others, also constitute a pollution potential, however, these were not studied as their occurrence was extremely variable and difficult to interpret from a geological standpoint and will require specific research beyond the objectives of this investigation.

C. Problem Origin and Development

1. Origin of Study

In the voluminous literature concerned with acid mine drainage abundant data are published showing the various effects of acid waters on surface water quality. Reports dealing with the acid problem commonly center about pollution of streams and rivers and except where ground water pollution has obviously taken place these studies neglect the effect of acid mine drainage on the ground water resources. Chemical interactions may occur in the ground water regimen which can adversely or propituously affect the quality and must be evaluated in appraising the ground water resources of an area. It is possible that an area afflicted with extensive acid polluted surface water supplies, may contain an abundant potable water supply in the ground water reservoir and may serve as a suitable supply to a community or the sole source of supply for widely scattered domestic users.

The two most important chemical parameters affecting water quality, as concerned in this study, are the alkalinity, as generated by

calcium carbonate, and the acidity, as generated by the decomposition of the iron disulfides. These parameters are strongly influenced by, and related to, the chemical composition of the rocks in contact with the water. Therefore, the water quality will be influenced by the type of strata present in that area. These strata also play an important role in determining how the acid pollutant will pass through the ground water regimen by interacting chemically with the infiltrating fluids. Hence, a study of water quality should include an investigation relating the occurrence of acidity and alkalinity to the various rock types found in the area.

While the mechanisms for the generation of alkalinity from calcium carbonate are rather well known, the mechanisms of acid generation under varying field conditions and the factors influencing acid production are not fully understood. For this reason an evaluation of factors responsible for the production of acid mine drainage is a first requisite to gain an understanding of the mechanism of acid formation. If the mechanism were ascertained under varying conditions, then the interactions of acid-producing materials with water of non-acid origin could be properly evaluated and the resulting water quality predicted.

2. Problem Evolvement

In the fall of 1963, a study was undertaken to determine the effect of acid mine drainage on the quality of ground water in a strip mined bituminous area. A study of water quality in the Bituminous area has a distinct advantage over a similar study made in the Anthracite area because certain extraneous factors may be eliminated.

First, the complexities imposed on the hydrology by the strongly folded strata of the Anthracite region are eliminated. Water samples from the Bituminous area can be obtained easily through shallow wells which penetrate distinct sampling horizons instead of deep shafts which are commonly flooded, interconnected and inaccessible. Second, a water sample obtained from a deep shaft in the Anthracite area may represent a mixture of varying water qualities, that may be stratified according to density differences. For these reasons, these samples will not be representative of the water quality of an aquifer located at the sampling interval. For obvious reasons, rock samples can be obtained more easily and readily from strip mines than from abandoned deep mines.

These considerations led the writer to restrict this study to the strip mined Bituminous area where the influences of the above mentioned complexities are eliminated from measurements made on basic parameters. This was considered desirable because the geochemical-hydrogeologic system is complex enough even under the simplest field setting. Hereafter, unless specifically mentioned, all discussions refer exclusively to the strip mined areas of the Bituminous coal field of Pennsylvania.

In the summer of 1964 an area in the vicinity of Mercer, Pennsylvania, was chosen for a study relating ground water quality to the geology. The considerations leading to selecting this site were (1) availability of geologic maps and (2) rather detailed hydrologic information for that particular area published in a report by Poth (1963). Poth's study was to provide a hydrogeologic framework for the study.

However, after spending three days in the area, the writer could not locate surface waters contaminated by acid mine drainage. Data obtained later at the Acid Mine Drainage Section of the Pennsylvania Department of Health in Harrisburg, Pennsylvania, corroborated the observations and conclusion that the area lacked severe acid mine drainage pollution. From stream quality maps of the state, it was apparent that acid mine drainage problems seemed to be restricted to some areas while absent in others. With further investigation it became apparent that the paucity of acid mine drainage was identified with areas abounding with calcareous materials in the bedrock strata and the overburden, while the occurrence of acid mine drainage was associated with those areas where calcareous materials were absent.

The ability of calcareous materials to neutralize acid waters is documented in a number of case histories. The outstanding one concerns a portion of Slippery Rock Creek in western Pennsylvania where prior to 1958 a limestone plant discharged a highly alkaline waste water into the creek. In 1958 the limestone plant ceased operations and at the same time the Department of Health began an extensive stream survey of the watershed to determine the impact of the cessation of the alkaline discharge. In July, 1964, a large fish kill occurred in the creek. Data gathered by the survey showed that the absence of the lime slurry previously discharged by the limestone plant permitted a body of acid water, flushed out by an unusually heavy rainfall, to travel the length of the creek unneutralized (Lyon, 1965).

In a regional survey of surface water quality in Appalachia, Biesecker and George, (1966, p. 11) found acid mine drainage problems to be less severe in areas having a high concentration of alkaline waters. Where calcareous materials are present some alkalinity should be generated in the region by waters coming in contact with the calcium carbonate. Since the neutralizing capacity of the calcium carbonate-bicarbonate system is low under natural conditions, the amount of acidity generated in the area must also be low enough to be offset by the natural alkalinity.

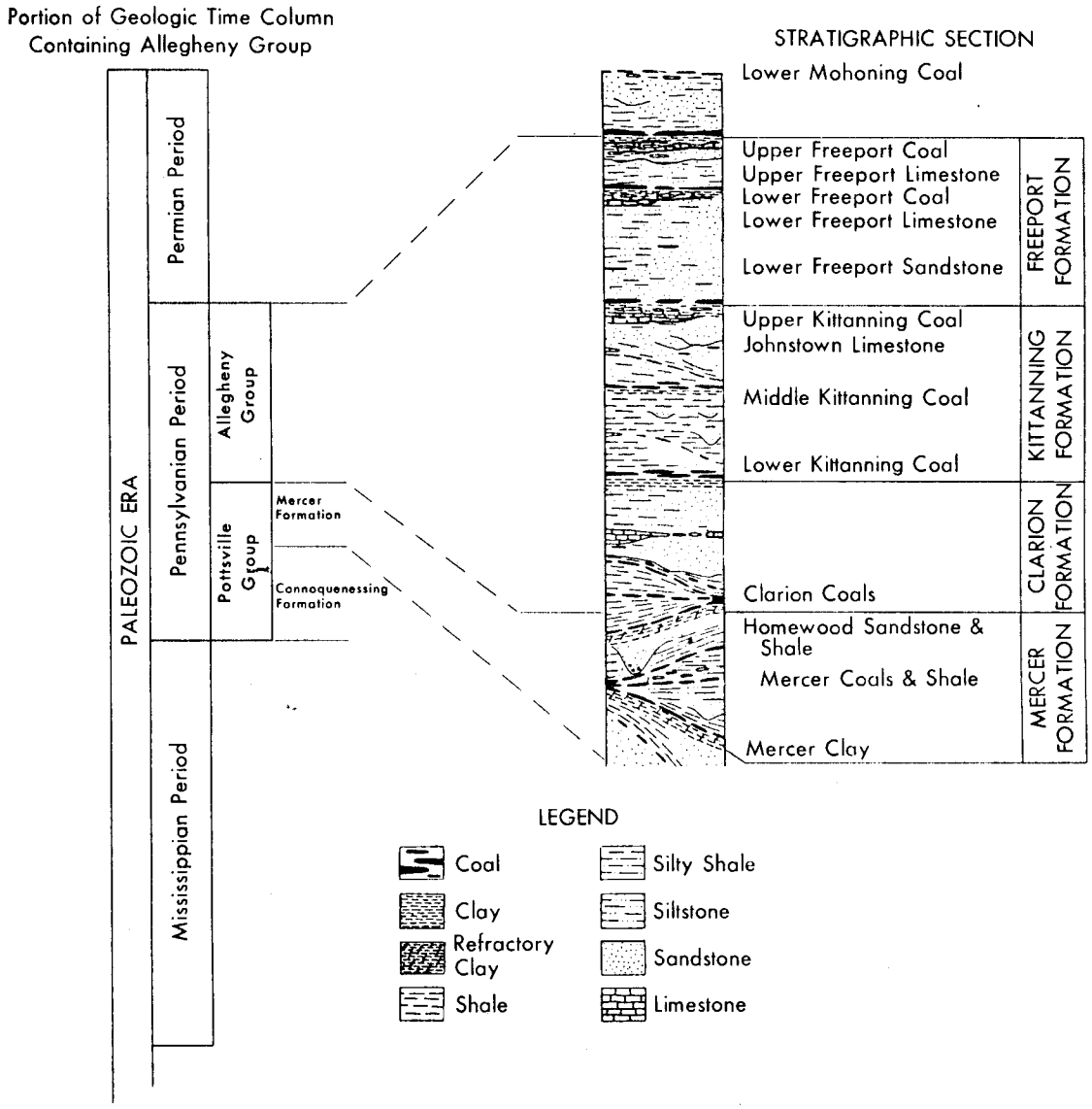
The amount of acidity produced is dependent in part upon the amount of iron disulfide available for decomposition. The greater the amount of pyrite present the greater the acid potential. If the acidity produced does not exceed the natural alkalinity, assuming the presence of calcium carbonate, then the waters will be non-acid. Should the acidity exceed the natural buffering capacity, the waters will be acid. The threshold value beyond which the water will be acid is fixed by the natural alkalinity found in an area and the amount of acid produced. While the former is more or less determined by the solubility of calcium carbonate and hence can be viewed as a constant (in the sense of a maximum value); the latter is dependent upon the amount of pyrite and marcasite. In a general way then, the areas of high sulfur will be the areas of greater acid potential.

A clarification concerning the use of the word "sulfur" is in order. For the time being the word "sulfur" can be used to indicate the gross value of the sulfur content of the sample, bearing in mind

that the majority of this value is composed by pyrite and/or marcasite. Differentiation of the two crystal cases is difficult; hence, iron disulfide will be referred to collectively as pyrite. Unless a specific comparison is made, in which case the text will convey the meaning, pyrite will be used in this report to mean iron disulfide, regardless of its form. It will be shown later that the method used in analyzing the "sulfur" content of a sample gives a value for total sulfur, that is, all forms of sulfur as organic, pyritic and sulfate sulfur, are ignited and analyzed simultaneously. Of these, pyritic sulfur is the form responsible for producing acid mine drainage. Although the analysis gives "total sulfur", it is a good estimator of the "pyritic sulfur" of the sample. This will be discussed in greater detail in a later section of this report.

3. Geological Control of the Occurrence of Acid Mine Drainage

The occurrence of sulfurous materials in the stratigraphic section of western Pennsylvania has been outlined in a general way by Williams (1960) and Williams and Keith (1963). Williams (1960) documented a transgression of paleoenvironments, based on fossil evidence, in the Allegheny group of the Pennsylvanian age rocks (Figure 1). In the basal portion of the Allegheny of western Pennsylvania, the rocks contain fossils indigenous to a marine-brackish water paleoenvironment. In the upper portion of the Group, the rocks show evidence of having been deposited in a continental-fresh-water paleoenvironment. In a vertical succession the lower "marine" rocks, in general, grade upward into the upper "continental" rocks. Additional work by Ferm and



STRATIGRAPHIC NOMENCLATURE AND GENERALIZED SECTION OF THE ALLEGHENY GROUP IN WESTERN PENNSYLVANIA
(Williams, 1960)

Figure 1

Williams (1960) has shown that the basal "brackish" rocks also exhibit a lateral transgression, becoming more "marine" in the western portion of Pennsylvania.

The rocks established as having been deposited in a marine paleoenvironment in the Pennsylvanian (age) commonly contain bitumens which are preserved only under reducing conditions, whereas the rocks of continental origin show evidence of being oxidized. Because the formation and deposition of iron disulfide is favored by reducing environments, the lithologies of the basal portion of the Allegheny group in the eastern portion of the Bituminous coal field should be higher in sulfur (as pyrite) than the rocks in the top portion of the group. Further, the sulfur content in the basal section should increase as the paleoenvironment becomes progressively more marine toward the western part of the Bituminous area.

Mansfield and Spackman (1965) traced the variations in the petrography and composition of the Lower Kittanning, Lower Clarion and Upper Freeport seams across the Bituminous coal field of Pennsylvania. They found this relation to hold ture. With the exception of the Freeport coal, whose anomalous trend was attributed to chance, the coals became more sulfurous as the environment of deposition became more marine.

Williams and Keith (1963) have statistically related the distribution of sulfur in coals to the occurrence of marine roof rocks. By comparing the Lower Kittanning coal to the Upper Freeport coal, they showed that the coals capped by marine roof rocks had a greater sulfur content than the coals capped by continental roof rocks.

As pointed out previously, the amount of acid mine drainage and the quality of water produced in an area ultimately depends upon the interaction of the quantity of acid produced through the chemical oxidation of the iron disulphides, and the availability of a neutralizing medium, commonly in the form of calcium carbonate. This phenomenon permits the following generalizations to be made: (1) mines in the Bituminous coal field extracting coals from strata of a marine paleoenvironment, in the absence of calcium carbonate should create severe acid mine drainage, whereas, under the same conditions, (2) mines extracting coals from strata of a continental-fresh-water paleoenvironment should present less severe acid mine drainage problems. (3) Mines extracting coals from a non-marine paleoenvironment in the presence of calcium carbonate may produce non-acid waters.

These generalizations apply to areas where the strata are assumed to be conformable and continuous throughout the mine. Exceptions may be present, whereby the conformable relations are disrupted by faults, by the slump structures previously mentioned (Williams et al, 1965), or as in the north-western part of Pennsylvania, where glacial channels have been cut into the coal seams and subsequently filled with glacial till. In the latter case, the glacial till in this area being highly calcareous presents a calcium carbonate rich stratum directly in contact with a high sulfur "marine" coal. Exceptions also can be created when a mining operation strips more than one coal and exposes strata of varying paleoenvironments.

The fact that some strip mines produce acid waters while others do not is of considerable importance to this study. By locating strip mines that produce waters of varying qualities, in essence, locates the combinations of rocks responsible for those water characteristics. Hence, by comparing water qualities and rock types of "acid" strip mines with "non-acid" strip mines an insight to the occurrence of acid mine drainage can be gained.

Accordingly the objectives of the study were expanded to include a comparison of two areas of strip mining; one area underlain by rocks of the "marine-brakish water" Lower and Middle Kittanning formations, while the other area underlain by the "fresh water" Freeport strata. The former is expected to produce acidic water, while the latter is expected to produce non-acid water.

4. Objectives of the Study

The objectives of this study were:

a. To determine what compositional variations exist between the strata of an acid and non-acid strip mine.

b. To determine the acid potential of rocks with varying sulfur content.

c. To evaluate the various factors affecting the production of acid mine drainage.

d. To determine the water quality characteristics of areas of varying rock types.

e. To ascertain what interactions take place in the field between acid mine drainage and natural waters.

The aforementioned objectives were restricted to the strip mines mining coal from the Allegheny group in the Bituminous coal field of Pennsylvania.

D. Mechanics of Acid Formation

The following sections are a brief summary of salient articles in the field of acid mine drainage research. It is intended to familiarize the reader with the theories and mechanics of acid formation and the attempts toward alleviating the problem. It is not a comprehensive summary of all the research and work in the field. For reference pertaining to an excellent basic study of the problem the reader is referred to Temple and Koehler (1954); for an excellent literature review (207 articles) to Lorenz (1962); and for research potentialities to Hanna et al (1963).

1. Oxidation of Pyrite

Acid mine drainage commonly has a pH in the range of 2, contains an acidity ranging form 4 to 20 mg/l (as H^+), has an abundance of iron, usually 50-500 mg/l as ferrous iron, and a high sulfate content, in the range of 500-10,000 mg/l (as $SO_4^=$). These data were obtained from Braley (1954, p. 138) and Temple and Koehler (1954, p. 7). Varying amounts of aluminum, calcium and magnesium are also present and originate from the chemical breakdown of rocks containing these elements in the presence of acid.

A mechanism explaining the formation of acid mine drainage must account for these ionic species and concentrations through plausible chemical reactions. The solubility of pyrite in water is so low (at pH of 2 it is 1.48×10^{-2}) that the high range of concentrations of sulfate cannot be explained by simple dissolution (C.S. Clark, 1965).

It has been generally acknowledged that the chemical oxidation of pyrite in the presence of water and air to a soluble hydrated iron sulfate, and the subsequent dissolution and hydrolysis of the oxidized form in water, is responsible for the generation of acid and the concentration of iron and sulfate found in acid waters. The reaction in its simplest form can be represented by equation (1),

$$FeS_2 + 3\text{-}1/2\ O_2 + H_2O = FeSO_4 + H_2SO_4 \qquad (1)$$

The iron sulfate, in turn, can hydrolize as in equation (2),

$$FeSO_4 + 2\ HOH \rightleftharpoons Fe(OH)_2 + SO_4^{=} + 2H^{+} \qquad (2)$$

Yellow and white crusts or coatings commonly appear along certain horizons on the exposed surfaces of the rocks and coal in mines. These minerals have been identified as melanterite (white crystals of ferrous sulfate), copiapite (yellow crystals of ferric sulfate), halotrichite (white crystals of iron or magnesium aluminum sulfate) and alunogenite (white crystals of aluminum sulfate), (Lorenz, 1962, p. 7). These minerals contain varying amounts of water in the hydrated form which varies with the mode of formation. If aboundant calcium carbonate is present in solution, minor amounts of gypsum (hydrated calcium sulfate) or anydrite (calcium sulfate) may be present. The hydrated iron sulfates are the minerals which react in accordance with equation (2).

The ferrous iron generated in the reactions described by equation (2) can be oxidized to the ferric state with the generation of additional acidity, as in equation (3),

$$Fe(OH)_2 + HOH \rightleftharpoons Fe(OH)_3 + H^+ \quad (3)$$

Stumm and Lee (1961) estimate that, "fifty percent of the acidity in acid mine drainage arises from the oxygenation of ferrous iron; the remainder arises from the oxygenation of sulfide or polysulfide." The ferrous and ferric hydroxides associated with equations (2) and (3) impart the red color that is characteristic of acid mine drainage. The precipitated iron hydroxide is the popular "yellowboy" often observed in streams.

2. Factors Affecting Pyrite Oxidation

a. Oxygen. Kinetic experiments have been developed which establish the rate of iron disulfide oxidation as a function of the amount of oxygen present. A recent study by C.S. Clark (1965) in which the oxidation rate of pyrite was determined with respect to various concentrations of dissolved oxygen, established that, "the dissolved oxygen concentration is rate controlling in pyrite oxidation with an order of about two-thirds."

From data collected in two field investigations of acid mine waters in the Anthracite area, Barnes, Stuart and Fisher (1964) and Barnes and F.E. Clarke (1964) postulated a reaction for the oxidation of pyrite under anaerobic conditions using water as the oxidizing agent. The reaction suggested was,

$$FeS_2 + 8\ HOH = Fe^{++} + 2SO_4^{=} + 7\ H_2 \quad (4)$$

which would require the reduction of water in order to oxidize the pyrite. The liberation of free hydrogen in the reaction casts doubt that such a reaction takes place. However, the workers suggest that the hydrogen combines with the available carbon in the coal seams to form methane which is abundant in both shallow and deep mines.

C.S. Clark (1965, p. 13), however, calculated the limits of the partial pressure of hydrogen gas required for equation (4) to react spontaneously. For a decrease in the Gibbs Free Energy function, which is required for the equation to react, the partial pressure of hydrogen must be less than 10^{-10} atmosphere. The partial pressure of hydrogen gas in the earth's atmosphere is about 10^{-4} atmospheres, and it is Clark's conclusion that, "the pressure of hydrogen near pyrite oxidizing in a mine is about one million times greater than the maximum it could be if the reduction of water is to be able to oxidize pyrite."

b. Temperature. A study of the kinetics of sulfide to sulfate reactions by Morth and Smith (1966) tested among other factors, the dependency of the rate of oxidation on temperature. The experiment utilized a Warburg Respirometer to measure oxygen uptake rates. It demonstrated that at a constant relative humidity the oxidation rate of pyrite nearly doubled for a 10° C. temperature rise.

c. Mode of the Iron Disulfide. The crystallography, the size of the particles and the purity of the mineral, all have an affect on the stability of the mineral. The crystallography of the disulfide, whether it occurs as marcasite (orthorhombic) or pyrite (isometric-pyritohedral), plays a very important role in its reactivity. Marcasite,

incidentally, alters to pyrite with time. Braley (1954a) showed that marcasite reacted 10 times more rapidly than yellow pyrite, while black amorphous pyrite reacted 80 times faster than the yellow pyrite.

The size of the mineral particles is also very important. It has been shown that the oxidation rate of pyrite increases as the particle size decreases (Clark, 1965, p. 28). As the size of the crystal gets smaller, the surface area to volume ratio increases. This causes an increase in the surface energy to bonding energy ratio. At a critical size, the surface energy will exceed the bonding energy and the grain will readily decompose. Usually this size is in the micron range and the iron disulfide grains are not readily discernible with the naked eye. Rocks which appear to be pyrite free, but actually contain these finely diseminated pyrite particles, will gradually become coated with crusts of white and yellow hydrated iron sulfates upon exposure to the atmosphere.

A close look at the occurrence of pyrite reveals the variability of form. Gray et al (1963) and Neavel (1966), although using different classification systems, recognize various modes of occurrence of pyrite. Two main groups are noted, the megascopic and the microscopic forms. Gray et al, arbitrarily establish 100 microns as the dividing size. Aside from the size differences, Neavel also classifies according to form. The following is a brief description of his classification scheme.

Euhedral- any pyrite occurrence exhibiting distinctive crystal outlines, either isolated or aggregated.

Dendritic- occurrences which give the appearance of branching growth.

Cleat Class- tabular occurrence oriented vertically, normal to bedding.

Bleb Class- this is the "catch all" class for the generally spherical particles.

Layer Class- generally coarse grained and have a long form parallel to bedding.

This classification will be used in this report with two additions; pyrite coatings on joints in coals will be included in the cleat class, and large nodules (greater than 10 cms) occurring in layers of coal are included in the layer class.

During the study determining the oxidation rates of pyrite, Temple and Koehler (1954, p. 24) noted that some sulfur balls were extremely reactive, readily becoming soft and flaky, while others remained inert and hard. Spectrographic analyses showed that sulfur balls which remained inert contained more calcium and magnesium than the sulfur balls which were oxidizing. Washing the inert sulfur balls with dilute hydrochloric acid caused them to oxidize and produce acid. The conclusion drawn was that the calcium and magnesium present prevented the sulfur balls from oxidizing. Similar conclusions have been drawn by other investigators (Lorenz and Tarpley, 1963).

d. Bacteria. As early as 1919, Powell and Parr (in Temple and Koehler, 1954, p. 17) stated that, "the (sulfur oxidation) reaction seems to be hastened by the presence of bacteria or some catalytic agent." Later workers investigating the oxidation rates of sterilized versus unsterilized samples, proved that the presence of certain iron bacteria

did indeed act as catalysts in the formation of acid mine drainage.

Three bacteria have been isolated and identified; *Thiobacillus thiooxidans*, a sulfur-oxidizing bacterium; *Thiobacillus ferrooxidans*, a bacterium which oxidizes ferrous iron (Temple and Koehler, 1954, p. 17) and *Ferrobacillus ferrooxidans*, another sulfur oxidizing bacterium (Silverman and Lundgren, 1959, in Hanna et al, 1963, p. 282). These bacteria prefer an environment having a pH range of 2.8-3.2.

An example of a catalytic effect of these bacteria is found in Temple and Koehler's work (1954, p. 20) where two leaching units containing sulfur balls differed in that only one was innoculated with *Thiobacillus ferrooxidans*. After 109 days, the inncoulated sample produced a total acidity of 12,500 ppm (as $CaCO_3$), while the other produced nearly half that amount, 6,400 ppm (as $CaCO_3$).

E. Treatment and Methods of Controlling Acid Mine Drainage

1. Neutralization

Many methods of treatment have been advanced in attempting to alleviate the acid mine drainage problem. Foremost involves the neutralization of the acid water and many schemes and techniques have been devised for this purpose utilizing lime or limestone as the neutralizing medium (Lorenz, 1962, pp. 10-11). The disadvantages of neutralization are the increase in the hardness of the treated water, the problem of disposing of the sludge of iron hydroxides and calcium sulfate that is produced, the armoring effect of the iron hydroxide on the surface of

the limestone rendering it inert, and the cost (it is estimated that one pound of limestone is required to neutralize one pound of sulfuric acid). As a result, neutralization of acid mine drainage is generally restricted to those cases where neutralization is absolutely necessary, for example, a municipality whose source of water supply is a stream that is occasionally acid or a mining operation that is required by law to discharge a neutral effluent into a stream.

2. Mine Sealing

The sealing of underground mines from the atmosphere has been attempted with varying success. The technique involves sealing the mine shaft with an air tight seal which permits the water to flow freely but retards air circulation. The technique is based on the theory that oxygen is required for the oxidation of pyrite and the formation of acid producing materials. The seal prevents the ingress of oxygen as the mine atmosphere is depleted of oxygen through sulfide oxidation. Eventually, the partial pressure of oxygen in the mine is sufficiently reduced to prevent further oxidation from taking place.

Various investigations appraising the effectiveness of mine sealing give conflicting data and the method is still in controversy (Lorenz, 1962, pp. 11-14). A most recent study undertaken by the Bureau of Mines and the Coal Industry Advisory Committee to the Ohio River Valley Water Sanitation Commission (ORANSCO) will attempt to accurately evaluate the effectiveness of mine sealing by a detailed survey of water qualities before and after the sealing of a mine near Kittanning, Pennsylvania, (Moebs, 1966).

3. Burial of Acid Producing Material and Backfilling

In the absence of oxygen the oxidation of the pyritic material is reduced or prevented. By segregating the acid producing materials from the host rock, and burying these materials with clay or impervious material at the base of the backfill, the reacting sulfides are sealed from the atmosphere and isolated from water. If this segregation and burial is done correctly, the mine can be backfilled with the prevention of acid mine drainage.

4. Application of Inhibitors

Just as the burial of the acid producing materials by an impervious layer to prevent the oxidation of these materials retards acid production, the coating of the pyritic materials with an inert chemical serves the same purpose. Investigations have been limited because of the difficulty involved in applying the chemical inhibitor in field operations (Lorenz, 1963, pp. 19-21). Preliminary studies with chromates and phosphates by Braley, showed that these chemicals acted as neutralizers rather than inhibitors. The impracticability of applying the inhibitor to every reacting surface discouraged further investigations. Further, the inability of marcasite and pyrite to form solid solutions at ambient temperatures necessitates strong concentrations of the proposed inhibitor (Barnes and Romberger, 1967, p. 12). Dilution by natural water flow precludes effective application.

Some research has been performed in the use of bactericides to prevent the bacteria from catalyzing the oxidation of the disulfides. Temple and Koehler, (1954, p. 17) located an area on the roof of a drift

mine that was producing acid. They scraped away the acid area until the rock surface was neutral and observed the formation of acid. It was established that, "the sulfur bacteria develop concurrently with acid formation." They once again scraped the area clean and sprayed the area with a solution of acriflavine. For six days of spraying the surface remained neutral. Acid appeared, however, when the spraying was stopped. The ability of the bacteria to recover after prolonged applications of bactericides suggests that this method is not feasible.

5. Hydrologic Isolation of the Mine

If water is prevented from contacting the acid producing materials, the soluble acid sulfates generated within the mine operations will be contained therein. The installation of diversion ditches, to divert surface water flows away from the mine pits and maintain them as dry as possible, is part of the procedures recommended for the prevention of acid waters (Brant and Moulten, 1960).

Dutcher et al (1967, p. 3) suggest dewatering deep mines in advance of mining thereby preventing acid mine drainage formation during mining.

6. Dilution

If the acid waters generated within the mine can be impounded and released during periods of high stream flow, the dilution of the acid by the streams can bring the acidity and chemical concentrations within the recommended limits. If alkaline streams are available, neutralization can be afforded by the mixing of the two. Barnes and Romberger (1967) have shown that significant reductions in acidities

can take place by mixing acid water with waters having as little as 50 mg/l HCO_3^-. Included in their work are nomographs which will predict the resulting pH from mixing of waters having a known initial pH and the dilution.

METHOD OF STUDY AND DATA PROCUREMENT

A. Introduction

The approach to achieving the objectives previously outlined was divided into three phases. The first phase entailed mapping the distribution of various formations in the two areas and collecting rock samples representative of the two extremes of paleoenvironments. The rocks were analyzed for total sulfur content. Based on these values, a number of rock samples were selected for leaching studies to relate the acid potential of the rock to the total sulfur content. The leaching study established the acid potential of a rock in terms of its sulfur content. Consequently, the areas from which the rocks were collected could be assigned a "rank" of probable expected acidities. The rank is based on the total sulfur analyses of all rocks collected from than area.

In the second phase of the study, water samples were collected and analyzed for ions indicative of certain chemical reactions. Commonly the water samples of mine pools and highwall bleeds were obtained at the same time the rock samples were collected. This was done to preclude the loss of the sampling point when the mine was backfilled. Water samples from streams, springs and mine shaft drainages, in and about mine workings were also collected for the same reason.

Homes in the areas were canvassed and the residents querried to determine which private sources of water supply could be sampled and to obtain information concerning the supply. From water samples obtained

from domestic wells, springs and streams in the immediately adjacent virgin areas, a background of chemical quality was established against which a comparison of water analyses obtained from the mined areas could be made to appraise quality changes.

The hydrologic and well construction data obtained through the interviews and field measurements of water table elevations, were used to construct water table maps and to gain an understanding of the general hydrologic setting of the areas.

The third phase, which will be completed in the future, concerns a field evaluation of concepts derived from the analysis of data gathered in laboratory experiments described in the present report. The field evaluation will be achieved by the tracing and sampling of water, from infiltration points to discharge points in strip mined areas, as it passes through the various rock types and noting the quality changes. The information obtained from the first phase of the study can be used to predict the effect of the various components of the rocks on water quality and what quality variations may be expected by mixing waters of different composition. The information gathered in the second phase of the study will be used as a guide to the selection of specific sites within the study areas where additional sampling points, as monitoring wells, will be installed. The installation of drill holes to specified depths will be spaced according to a determined pattern by which various segments of the ground water flow system can be intercepted and sampled. By this scheme the water can be sampled as it transgresses various rock types and the resulting water quality changes ascertained. The wells

will also serve as additional control for accurately defining the hydrology of the areas by their use in standard pumping test and in establishing potential distributions to construct flow nets. It is hoped that the hydrologic concepts developed in these areas can be extended to other areas in the Carboniferous of Pennsylvania where the basic hydrology is not yet known but believed to be similar.

It will be during this final phase that the effect of acid mine drainage on the ground water resources of a strip mined area will be studied and evaluated.

B. Site Selection

As previously mentioned, the two areas of study were to be geologically representative of the extremes of paleogeologic conditions which may be found throughout the Allegheny coal seams of Pennsylvania; to wit, an area underlain predominantly by rocks deposited in a continental (oxidizing) environment and an area underlain mostly by rocks deposited in a marine (reducing) environment were selected.

As additional requirements, the areas had to have many homes with private water wells by which the ground water could be sampled and the depth of the water table measured.

Further, the areas had to be in part actively mined to provide fresh rock sampling exposures and to present conditions whereby acid mine drainage could form and yet contain virgin areas from which background water samples could be obtained.

With the advice of Prof. E.G. Williams of the Department of Geology and Geophysics, The Pennsylvania State University, two areas of study that met these requirements were selected to the north and to the south of Clearfield, Pennsylvania (see Plates I and II).

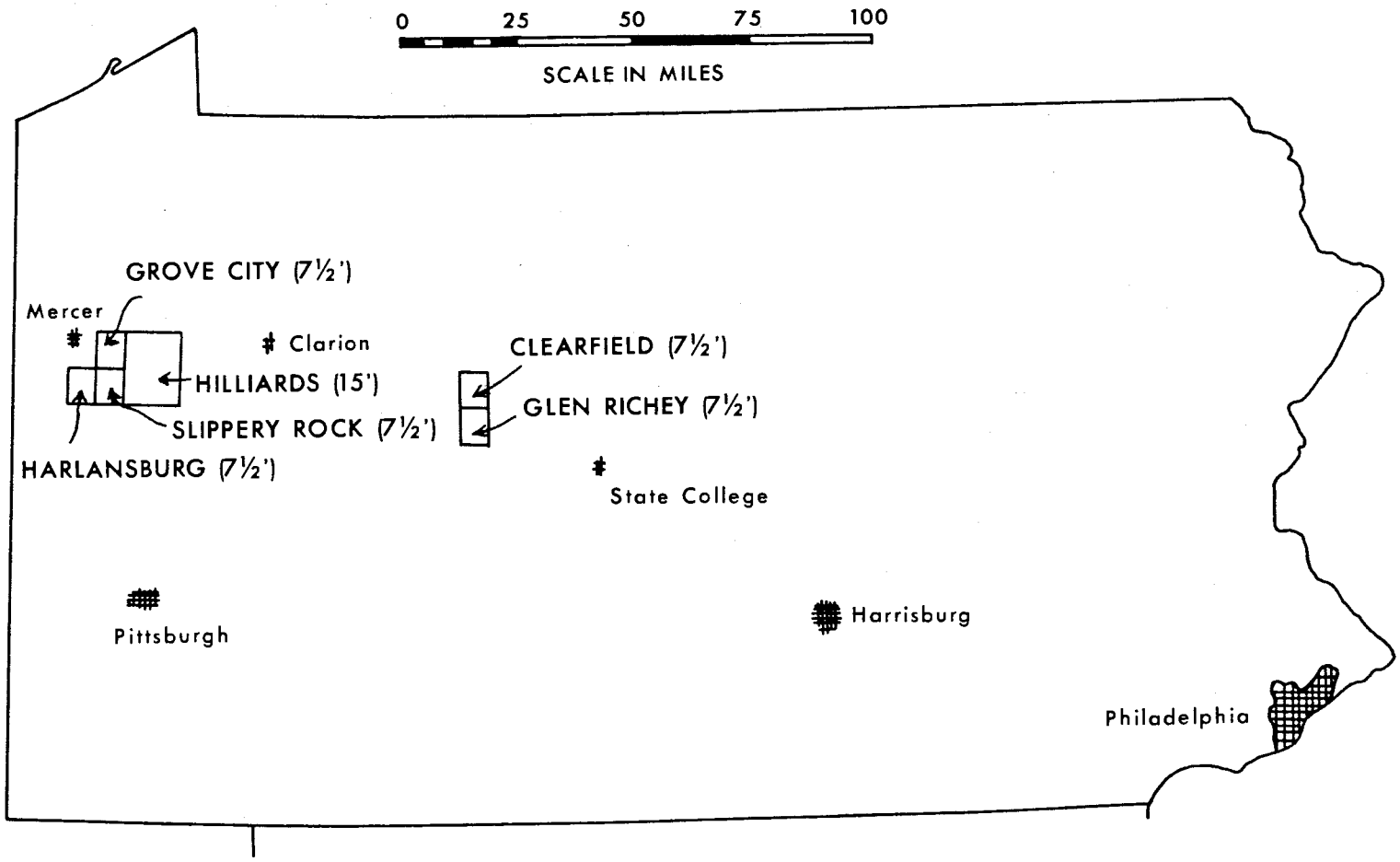
The area north of Clearfield, hereafter referred to as "the Clearfield area" is located on the Clearfield 7-1/2 minute Quadrangle, enclosed by streams and underlain almost entirely by Kittanning (marine to transitional) coal seams (see Plate I and Figure 2). It was expected that this area should create acid mine drainage when strip mined. Stream quality maps at the office of the Sanitary Water Board in Harrisburg, Pennsylvania, show a source of acid mine drainage located in the central portion of the mined area selected for study.

The area south of Clearfield, Pennsylvania, hereafter referred to as "the Glen Richey area," is located on the Glen Richey 7-1/2 minute Quadrangle, bounded by streams and almost entirely underlain by Freeport (continental) coal seams (see Plate II and Figure 2). This area should not produce severe acid mine waters and as the stream quality maps mentioned above showed, this area is free of acid mine drainage.

C. Data Collection

1. Geology

The geology of the two areas was compiled from geologic information made available through the courtesy of Dr. Arthur A. Socolow, State Geologist of the Bureau of Topographic and Geologic Survey of Pennsylvania; and from Prof. Eugene G. Williams who has compiled numerous



INDEX MAP SHOWING THE LOCATIONS OF QUADRANGLES USED IN THE STUDY

Figure 2

stratigraphic sections and correlations in the lower Carboniferous seams of the Clearfield Basin of Pennsylvania. During the course of the field work, additional rock sections exposed in road cuts, such as the newly constructed Interstate 80 which transects the Clearfield area and newly opened mines, were described, measured and incorporated within the geologic framework. The geologic data are represented by the two geologic maps shown in Plates I and II.

2. Stratigraphy

The stratigraphy of the Allegheny group is summarized in the following excerpt from the "Guidebook for Field Trips, Pittsburgh Meeting, 1959," published by the U.S. Geological Survey:

"The Allegheny group averages 280 feet in thickness. It consists of six mappable coals or coal zones separated by variable and locally cyclic sequences of shale, siltstone, sandstone, limestone and clay. Fine-grained sandstones, siltstones and shales are the predominant rock types in the Allegheny, whereas coals, underclays and limestones constitute a minor part. The major coal zones and associated underclays are the most persistent beds and the sandstones are the most variable in occurrence. The Allegheny has been arbitrarily subdivided into three formations at the horizon of certain economically important coal or clay beds. The resulting formations, from bottom to top, are the Clarion, Kittanning and Freeport.

Some systematic lithologic and faunal changes, both stratigraphic and geographic, have been noted in Allegheny rocks. Marine and brackish fossils occur in concretion-bearing shales or limestones above the Lower and Upper Clarion coals, the Scrubgrass coals, and the Lower and Middle Kittanning coals. These fossils are only found north of the Conemaugh River. Allegheny sediments stratigraphically above the Kittanning formation do not contain marine fossils. In addition, no marine fossils have been found with the Kittanning formation south of the Conemaugh River.

Lower Allegheny coals tend to be more impure and irregular in occurrence than Upper Allegheny coals. Upper Allegheny underclays are calcareous, in many places containing fresh-water limestones, whereas Lower Allegheny clays are non-calcareous and generally higher in

Kaolinite. Two of the most widely mined plastic clays in the state occur below the Lower Kittanning and Lower Clarion coals.

Most of the Allegheny sandstones are fine grained, lenticular, low-rank graywackes or quartzose graywackes. Some are cross bedded with disconformable lower contacts, whereas other are planar-bedded and have gradational contacts. No major compositional changes have been observed among the Clarion, Kittanning and Freeport sandstones." (Dutcher et at, 1959, p. 71)

Most strip mines in the areas of study rarely made pits deep enough to expose more than two coals.

a. Method of Sampling. Samples of the various rock types were taken from sections in strip mine highwalls or fresh exposures representative of dissimilar paleoenvironments as designated by the geologic maps. When a mine was located in a particular area to be sampled, the exposed highwall was measured and described in a general way. These descriptions appear in Appendix B of this report. When possible, the rocks were sampled from the walls of active mines so as to obtain unweathered samples. In abandoned mines the weathered surface of the exposure was picked away until a fresh surface was exposed.

The sampling was limited only to the formations which were accessible on the highwall. In some cases, as in road cuts, and where a talus rubble sloped against a highwall, a complete section was sampled by climbing the talus slope. However, in the majority of cases the height to which samples were taken from the highwall was limited by the writer's reach.

The shales, sandstone, underclays and limestones were sampled by random grab samples, that is, a handful of rock was collected along a particular lithology at random intervals and incorporated into one

field sample. All coals were channel sampled, that is, a "V" shaped cut was made into the coal seam and incorporated into one field sample. The "V" shaped cut extended from the roof or cap rock down to the lower contact; in some cases where the highwall was partially backfilled the coal was sampled as far down as possible, but not necessarily the entire thickness. Complete samples (the rock literally lifted out of the highwall) were taken of thin (less than eight inches) riders or binders, a six inch zone above, and where possible, below the coal seam. A "rider" or "coal smut" is a thin impure coal containing abundant earthy matter. A "binder" or "parting" is a siliceous rock within the coal seam.

b. Sample Labeling. Samples were labelled according to a scheme which allows rapid identification of the horizon, mine and area from which the sample was collected. Each sample has a label which is usually composed of a series of letters followed by either one or two sets of digits.

The letters designate the area where the mine is located as follows:

CM--the Clearfield area
RM--the Glen Richey area
CL--near Clarion, Pennsylvania (only water samples were collected)
KM--the Krebs mine located on the map of the Glen Richey area (only water samples were collected)
GRC--a mine located on the 7-1/2 min. Grove City Quadrangle
BR--a mine located on the 15 min. Hilliards Quadrangle
SLR--a mine located on the 7-1/2 min. Slippery Quadrangle
HRG--a mine located on the 7-1/2 min. Harlansburg Quadrangle

For the locations of these quadrangles refer to Figure 2.

Only the RM and CM designations, where extensive sampling took place, are followed by two sets of digits. In these cases, the number immediately following the letters refers to specific mine locations as outlined on the "Water and Rock Sampling Location Maps," of the two areas (Plates III and IV). In the other cases, where only one mine was sampled in the quadrangle, no qualifying digit was required. The locations of these mines are illustrated on portions of the quadrangle pertinent to the mine location.

The last group of digits refers to the sampling interval as indicated on the "Stratigraphic Profiles" of various mines. The stratigraphic section is described and dots are placed opposite the horizon sampled. These dots are numbered in accordance with the sample number. For example, CM-6-5, indicates a sample collected from mine #6 in the Clearfield area, opposite the sampling horizon marked by the dot numbered 5 on the "Stratigraphic Profile of Mine CM-6."

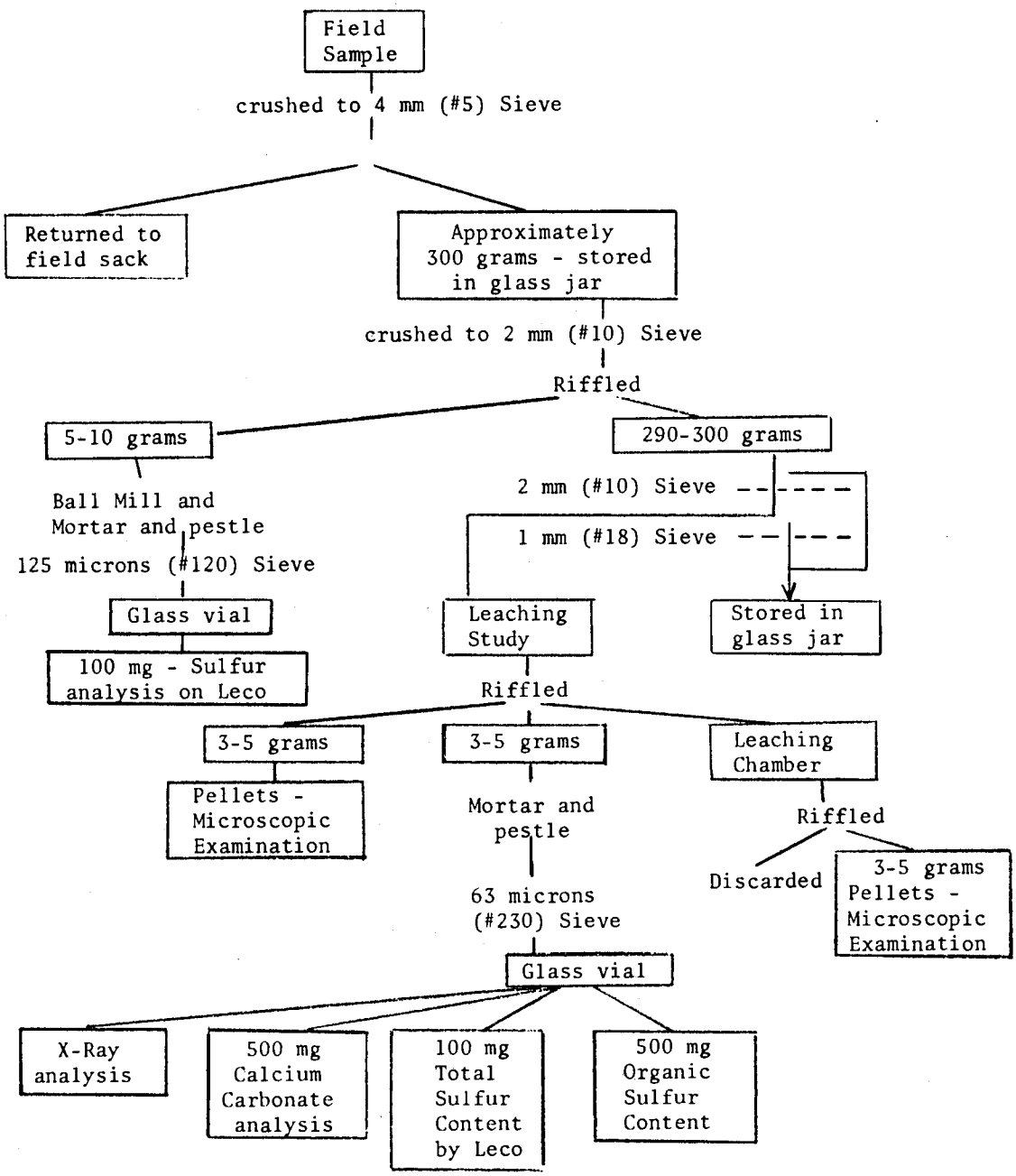
c. Sample Preparation. To insure representative analyses of field samples, the samples were split by the following technique. The field sample was crushed by a rock crusher until the sample was small enough to pass a 4 mm sieve. The crushed sample was riffled into two parts; one portion weighing approximately 300 grams was stored in a glass jar and the remainder of the sample was returned to the field sack.

The jarred sample of approximately 300 grams was crushed further to pass a 2 mm sieve and riffled into two unequal parts; a 5-10 gram portion which was placed in a glass vial and the remainder of the

sample, which was returned to the jar. The vialed sample was pulverized by a ball mill and mortar and pestle until fine enough to pass a 125 micron sieve in preparation for a total sulfur analysis. The jarred sample was retained for leaching studies. A flow sheet for the sample preparation is shown in Figure 3.

d. Sample Analysis. The rock samples were analyzed for total sulfur, organic sulfur and calcium carbonate content. A brief description of the chemical methods is given below. For the detailed procedure for a particular analysis refer to the "Chemical Methods" section of Appendix A.

(1) Total Sulfur. A Leco (Laboratory Equipment Company) automatic sulfur analyzer was available through the Anthracological Laboratory of The Pennsylvania State University for determining sulfur contents of the samples. A weighed sample, ground to 125 microns, was placed in a crucible with tin and iron accelerators and ignited in the center of an induction coil. The coil and the sample were contained in an air tight cylinder through which a continuous flow of oxygen passed over the sample and entrained the combustion gasses into an automatic titrating vessel. The titrating vessel contained a dilute solution of hydrochloric acid, and a blue iodine starch solution which was bleached by the sulfur oxides. A photometric unit sensing a lighter color automatically dispensed an iodate solution until the original color or endpoint was reached. The amount of iodate solution required to titrate the sample was read from the buret containing the solution and readily



FLOW SHEET FOR SAMPLE PREPARATION AND SAMPLE ANALYSIS

Figure 3

converted to a total sulfur value. The value is the percentage sulfur on a weight per weight basis.

The total sulfur content of a sample is the sum of organic sulfur, pyritic sulfur and sulfate sulfur. The sulfate sulfur constitutes a small portion of the total sulfur content of a sample (Fieldner and Selvig, 1951, p. 16) and is neglected. The rocks used in the leaching study had to be analyzed for the pyritic sulfur content, as it is the component of the total sulfur content that produces the acidity. The organic sulfur component is relatively inert; hence, it was necessary to know what portion of the total sulfur content was pyritic and what portion was organic sulfur.

(2) Organic-Pyritic Sulfur. The method for the determination of organic sulfur involves digesting a pulverized sample in nitric acid. The nitric acid selectively dissolves the pyritic sulfur while leaving behind the organic sulfur. After digestion, the samples are analyzed on the Leco and the percentage sulfur obtained is the organic sulfur content of the sample. Subtracting the organic sulfur value from the total sulfur value gives the pyritic sulfur concentration.

The success of this analysis depends on the proper combination of particle size, acid strength and digestion time so as to assure that all of the pyritic sulfur is dissolved while not affecting the organic sulfur. The method for the determination or organic sulfur used in this study was developed by Richard C. Neavel, formerly with the Geology Department of The Pennsylvania State University, who by experimenting with various concentrations of nitric acid, digestion periods

and sample sizes, developed an optimum combination of all three for satisfactory results (Neavel, 1966, p. 50).

A 3-5 gram portion of the sample used in leaching was riffled from the main sample and ground to pass a 63 micron sieve. This pulverized sample was analyzed for total sulfur, while a 0.5 gram portion was dried, weighed and digested in 25% nitric acid. After 48 hours, the sample was centrifuged, washed and dried and subsequently analyzed for the sulfur content.

(3) Calcium Carbonate. The occurrence of calcium carbonate in the highwall of a mine was noted during the field description of the stratigraphic section. The presence of limestone or calcareous sandstones and siltstones, as well as glacial till (commonly abounds with calcareous material) was noted and the extent of these deposits recorded. Detailed measurements were not necessary since calcium carbonate has a limited solubility in water and the saturation index is easily achieved by a minimum amount of calcium carbonate in the section. Natural ground water movements with the coal and associated strata are normally slow enough to afford effective solutioning periods.

However, in the leaching studies it was necessary to accurately determine the calcium carbonate content of the rocks used in the tests. In the leaching tests, partial neutralization could occur due to the calcareous matter in some of the rocks. This fact must be considered in the study.

The calcium carbonate content of the rocks was determined by leaching a 0.5 gram portion of the rock crushed to pass a

63 micron sieve in hydrochloric acid. The only source of calcium ions was assumed to be calcium carbonate. The sample crushed in preparation for the organic sulfur analysis was used also for the calcium carbonate analysis.

After 24 hours, the sample was filtered, washed, the effluent volume measured and an aliquot of the leachant analyzed for the calcium ion content on the Atomic Absorption Spectrophotometer. This value was adjusted to give a percentage value on a weight per weight basis.

E. Leaching Studies. The purpose of these studies was to evaluate the acid potential of rocks with varying composition using a technique described by Hanna and Brant (1962). The technique involved placing a sieved portion of the crushed rock sample into an inert chamber whereby a continuous flow of humidified air passed over the sample. Periodically the sample was flushed and the effluent analyzed for various components indicative of certain chemical reactions. The components analyzed were the acidity, pH, alkalinity, calcium and sulfate ion concentrations, whose significances are covered in detail in the section on water chemistry. By placing the sample in an oxidizing environment, and periodically flushing the sample, the field conditions of normal atmospheric oxidation of the samples with occasional flushings by rainfall were simulated.

(1) Factors Affecting the Generation of Acidity. The amount of acid that a particular sample may produce is dependent upon a number of factors; many of which were listed in the "Mechanics of Acid

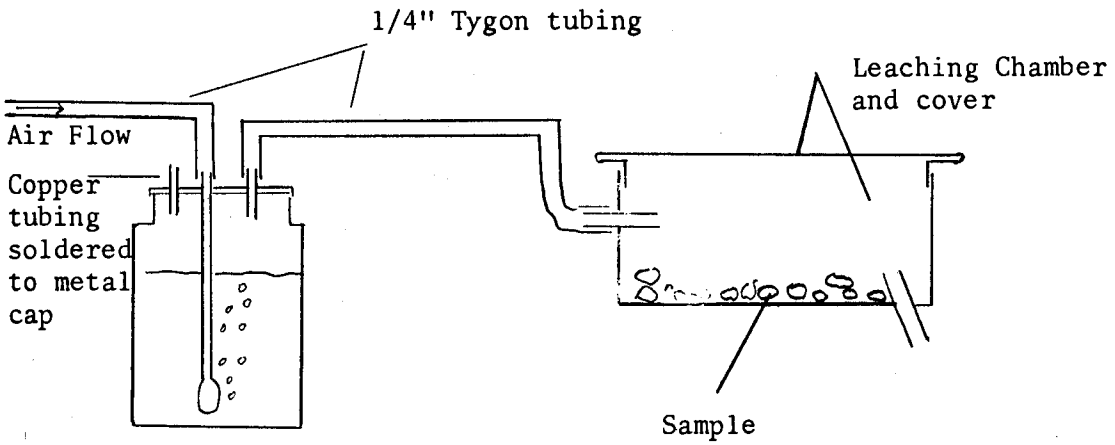
Formation" section of the Introduction. The factors pertinent to the generation of acidity in the leaching study are enumerated with discussions as to how their effects were standardized and/or controlled in the leaching experiment.

Availability of Water and Oxygen: The necessity of oxygen in the formation of oxidation products from the iron disulfides has been established by C.S. Clark, (1965). Because oxygen is depleted as the oxidation process progresses, a constant source must be provided to insure a constant oxidation rate.

Water is also necessary to, "provide a means by which the oxidation products are dissolved from the pyrite surface," (Morton and Smith, 1966, p. 85). In order to provide a constant flow of air (oxygen) without drying the samples, the air flow was bubbled through water before entering the leaching chambers.

The leaching chambers were constructed from plastic boxes by drilling two 1/4 inch holes, one hole through which air may enter the chamber and a drain hole on the opposite side of the plastic box, that also served as an air exhaust. Hard plastic tubing (one inch long by 1/4 inch in diameter) was inserted into the holes and cemented. A wide mouth glass jar with a metal cap was utilized as a humidifier. Holes were punched in the metal cap and copper tubing (one inch long by 1/4 inch in diameter) was soldered into each hole in the cap. Tygon tubing was used to connect each air intake of the leaching chamber to the outlet of the humidifier. The jar was half filled with water, and

an aerating stone was submerged and used to supply the air to the humidifier. A schematic of the leaching units and humidifier is illustrated in Figure 4.



SCHEMATIC OF THE LEACHING UNITS AND AIR SUPPLY

Figure 4

The Size of the Sample Particles: For a given volume or weight of a sample the surface area of reaction is greatly increased as the particle size becomes smaller. If the iron disulfide is finely disseminated throughout the rock, the quantity of sulfide available for reaction increases with the surface area. Hence, the reactivity of a sample is a function of size. The smaller the size, the greater the amount of acid generated. This was established by Hanna and Brant (1962).

The field sample was crushed in a jaw crusher and sieved according to the flow sheet in Figure 3. The 1-2 mm fraction

of the sample was chosen for the leaching tests for the following reasons:

(1) Particles finer than 1 mm, as noted in a preliminary leaching test, cemented together forming hard nodules which effectively sealed the enclosed particles and prevented their oxidation.

(2) The 1-2 mm fraction drained well after the sample was flushed because at this size the sample did not clog the drain spigot, did not pour off with the effluent and retained a minimum amount of water.

(3) Larger size particles would not be representative of the field sample. The sample size that could be placed in the leaching chamber was limited to 350 grams and yet had to be representative of the field sample. Grinding a sample to finer and finer size particles in effect, homogenizes the sample, yet there is a lower limit beyond which the sample violates the conditions of (1) and (2) above. It was felt that the 1-2 mm size was a good compromise.

The samples were carefully weighed to the tenth gram before being placed in the leaching chamber. The volume of each sample was measured simultaneously with the initial rinsing by rinsing the sample in a graduated cylinder and noting the volume of water displaced. To facilitate comparison, all acidity values were adjusted to a common base of "acid yield per 100 grams" by multiplying the acidity values by 100/weight of sample.

Amount of Iron Disulfide Present: Obviously the greater the amount of disulfide present in the sample, all other things being equal, the greater the acid potential of the sample.

As this was one of the factors being tested, additional efforts were made to insure the accurate determination of the total sulfur content, percentage of organic and pyritic sulfur and the amount of calcium carbonate. This was done by taking the 1-2 mm fraction of the sample which was to be used for the leaching test and riffling a 3-5 gram portion to be chemically analyzed. In this way, segregation of material, which may have occurred during the field granding stage, was eliminated and the analyses were representative of the leached samples and not the field samples. The 3-5 gram portion was pulverized in a ball mill to pass a 230 mesh screen (63 microns) and portions withdrawn according to the specific analysis.

State of the Iron Disulfides: The size of the iron disulfide cyrstals or particles affects the stability of the mineral. Large well formed crystals having a high bonding energy are more stable than finely grained particles whose sizes are such that the surface energy of reaction exceeds the bonding energy and readily break down.

Iron disulfide may occur either as marcasite or pyrite, marcasite, a polymorph, is more reactive than pyrite and readily decomposes.

The reaction rate is also affected by impurities present. Temple and Koehler (1954, p. 24) noted that some sulfur balls collected in West Virginia readily decomposed while others remained hard and inert. Finely crushing the inert sulfur balls (effectively increasing the surface area) had no effect on oxidizing the sample. Spectrographic analyses showed that the inert sulfur balls contained more calcium and

magnesium than the sulfur balls which were reacting. Significantly, washing the inert sulfur ball; and presumably removing the calcium and magnesium, caused the sulfur ball to break down with the consequent formation of acid.

Time Between Flushings: The iron disulfide which is insoluble (C.S. Clark, 1965, p. 3) must be converted to soluble hydrous iron sulfate before it can hydrolize in water to produce acid. Though the ferrous salts are readily soluble, the oxidation of the disulfide to the sulfate state requires a long period of time (measured in days). Hence, the acidity produced by a sample varies with the amount of ferrous sulfate produced that is available for hydrolysis. The longer the interval between flushing, the greater the opportunity for conversion of iron disulfide to ferrous sulfate by oxidation. The oxidation of the disulfide will not continue indefinitely. Morth and Smith (1966), state that a build up of reactive products at the reactive sites of the pyrite will eventually cause the oxidation process to stop. The reactive products formed at the sites are commonly copiapite, a yellow hydrate ferric-ferrous sulfate, and strakeyite, a white tetrahydrate of ferrous sulfate (Hanna et al, 1963, p. 276).

The samples used in the leaching study were flushed twice a week by completely soaking the sample with 100 ml of aerated distilled water. The sample was stirred, and the effluent drained through the spigot in the wall of the leaching chamber. The effluent was filtered through a plastic screen which trapped all particles greater than 0.5 mm to be returned to the chamber. The fines that filtered

through were discarded. All samples were flushed within a one hour time interval.

Temperature : Many investigators have shown the oxidation rates to be dependent upon temperature. Morth and Smith (1966, p. 91) have plotted oxygen uptakes, as measured in a Warburg Respirometer, against various temperatures and percentage relative saturations and demonstrated a dependence of oxygen uptake upon both. At a constant percentage relative saturation the oxygen uptake rate increased with temperature increase, indicating a greater oxidation rate of the material.

A constant temperature room large enough to contain all the leaching units of the experiment was not available. Because the temperature of all units would be the same as the room temperature, any variation in temperature would have an equal effect on all samples.

Bacteria: It has been shown by many investigators that bacterial action can enhance the production of acid from coal strata by increasing the oxidation rate. The various bacteria that can affect the reaction were listed in the introduction to this report. It was assumed that the samples collected in the field were not contaminated by these bacteria. It is argued that the samples were collected from fresh surfaces, by picking away the weathered rock, and as such, were not exposed to the bacteria. Most of the bacteria are found either in mine pools or soils, and seldom penetrate into the rock layers.

The samples used in the leaching study were not sterilized. All samples were air dried during storage reducing the chances of bacterial contamination. During one part of the experiment, however,

the effect of bacteria upon the production of acid was tested by innoculating selected samples with bacteria found in acid mine drainage pools.

(2) Expression of Results. The objective of the leaching study was to compare the acid production of rocks of various sulfur contents. In order to compare the samples, adjustments of acidities produced were made to a common base. The curves presented in the following section represent cumulative milligrams of hydrogen ion produced per 100 grams of sample after a given period of time. The values were calculated according to the following prodecure:

1- 100 ml of aerated distilled water were added to the sample in the leaching chamber.

2- The sample was stirred while immersed in the water and drained through a spigot into a plastic screen which filtered the sample from the leachate. The trapped sample was returned to the leaching chamber.

3- The volume of the leachate was measured in a graduated cylinder and recorded.

4- Acidity determinations were made on 25 ml of the leachate.

5- The total weight of hydrogen ions obtained from the flushing was obtained by multiplying the weight of hydrogen ions obtained in (4) by volume of leachate/25.

6- The concentration of hydrogen ions obtained in (5) represents the yield of acidity for a particular weight of sample. To be able to compare the samples, the acidity values were adjusted to

read mg of hydrogen/100 grams of sample by multiplying the value obtained in (5) by 100/ weight of sample leached.

3. Hydrology

The hydrology of the two areas was approximated by canvassing the homes in the areas and obtaining information from the residents concerning their water supply. Water level measurements were made in their wells where possible. From these water level measurements, and elevations of springs and creeks, water table maps were drawn for the areas.

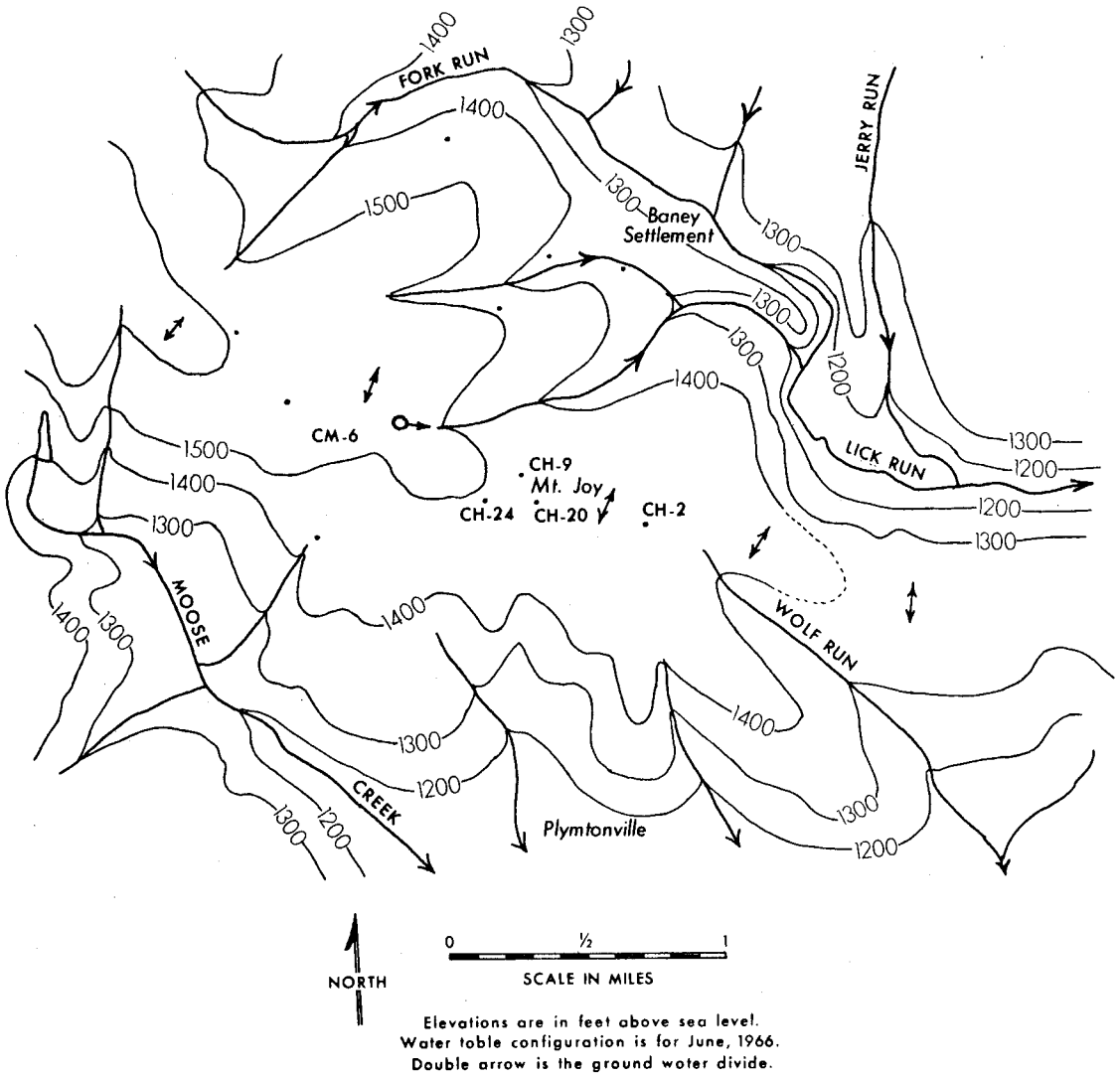
A water table map shows the elevation and configuration of the water table at any point. Lines drawn perpendicular to the water table contours, called "flow lines", show the probable direction of ground water movement and can be used to determine the approximate source and avenue of movement of a water sample.

The elevation of the water table was obtained by various means. The most common was by measuring the depth to water in a well using an electric dropline or a steel tape. An electric dropline is a device attached to an electric cable which is lowered into a well and registers water contact by a meter reading. In the majority of cases, the water table was shallow enough to be measured by a six foot steel ruler. The distance to the water, subtracted from the land surface elevation at the point of measurement, is the elevation of the water table above sea level. The elevations of land were picked off the 7-1/2 minute topographic maps by interpolating the elevation from the contour lines at a 20-foot interval. The water table elevations were plotted, and

using the elevations of streams and springs as additional control, the data were contoured to produce the water table maps (Figures 5 and 6).

During the canvassing of homes, the residents were querried about the source of their supply as to whether it was a spring, deep drilled well or shallow dug well. The depth of their well would indicate the formations penetrated. The length of casing would show which formations are being bypassed and indicate the aquifer horizon. The number of people serviced by the supply and amount of water used per day would indicate well capacity; and knowing if the well goes dry with extensive pumping, gives an indication of the drawdown. To infer the origin or discharge points of the supply, the residents were asked if any noticeable affects were felt from the drought, blasting, road construction or mining. Upon completion of the inquiry, permission was usually obtained to collect a water sample and to make a water table measurement. If the well was accessible, the sample was collected by bailing, otherwise it was collected from the household spigot. A detailed section on water sampling will follow.

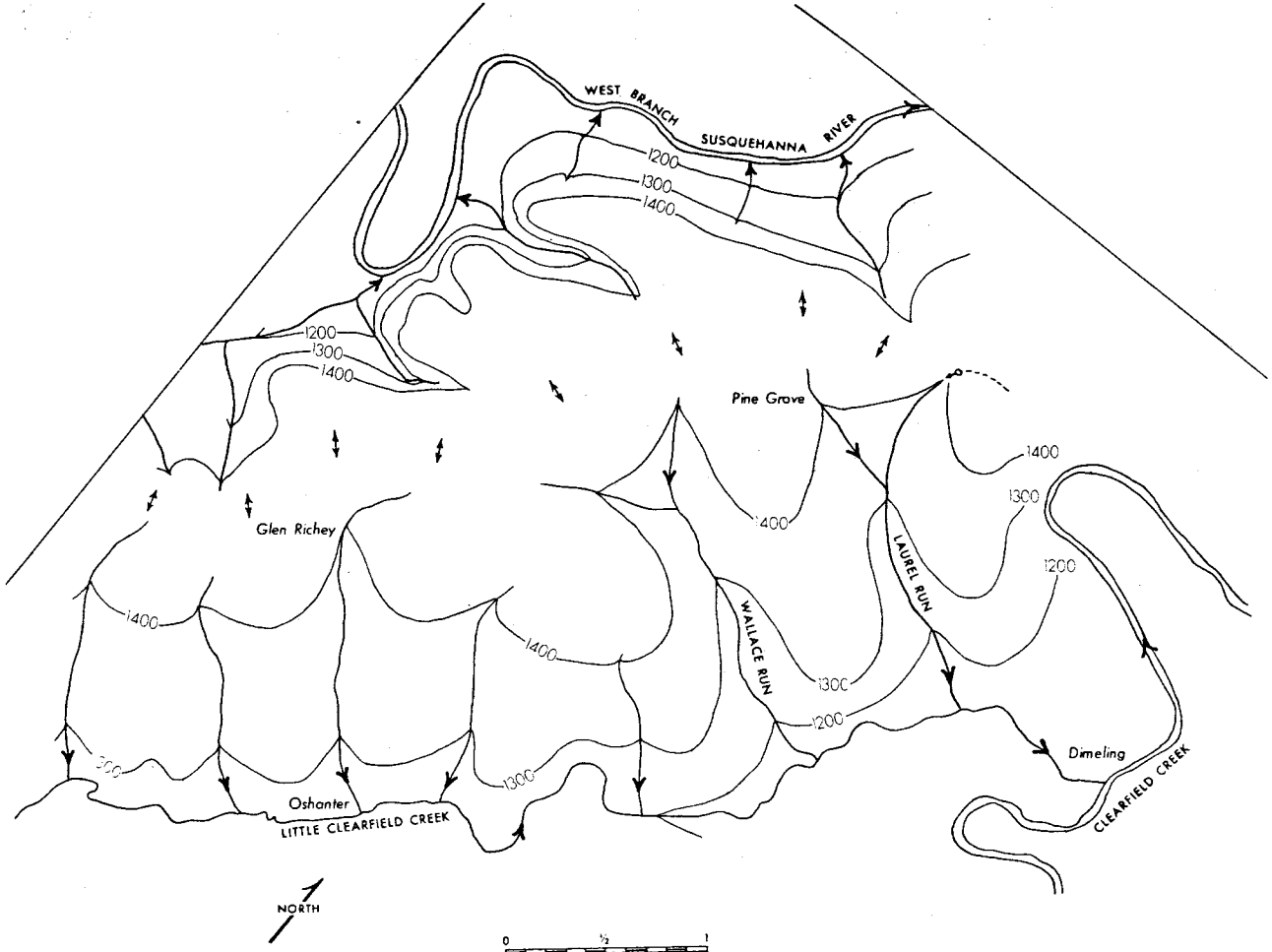
As the hydrologic control points, in this case, private wells, were limited and not properly spaced to perform an effective pumping test to evaluate the aquifer's hydraulic characteristics, the writer relied heavily upon the information conveyed by the people whose wells were sampled.



Elevations are in feet above sea level.
Water table configuration is for June, 1966.
Double arrow is the ground water divide.

WATER TABLE MAP OF THE CLEARFIELD STUDY AREA

Figure 5



Elevations are in feet above sea level.
Double arrow is the ground water divide.

WATER TABLE MAP OF THE GLEN RICHEY STUDY AREA

Figure 6

D. Water Chemistry

1. Purpose

A major concern in this study was the rock-water quality interactions, in particular, the effect of the aquifer composition on the water quality. In the leaching study, the composition of the rock was known and the quality of the effluent determined. Conversely, the analyses of the water samples collected in the field had to be related to rock compositions. If the reactions, of concern in this study, could be identified by certain chemical parameters, then these reactions would be known to occur by establishing the presence of these chemical parameters in the water sample. These reactions, in turn, could be related to the rock strata which can be characterized as affecting the water quality in a particular manner. In so doing, water qualities can be associated with rock types.

The oxidation of iron disulfide to soluble ferrous sulfate and the subsequent hydrolysis in water is the source of ferrous, ferric, sulfate ions, and acidity which are characteristic of acid mine drainage. The acid waters are capable of dissolving other minerals with the introduction of the other ions commonly found in acid mine waters. Other ions include aluminum, calcium, magnesium, manganese, sodium, potassium, silicon, carbonate, chloride and silicate (Braley, 1954, p. 137 and 1966, p. 3).

Only a few of all the ions present in acid mine drainage or ground waters were of importance in this study. These were the ions

that could be specifically related to a chemical reaction of interest. The reactions affecting water quality, as concerned in this study, were the formation of acidity and alkalinity, with the consequence of neutralization should the two mix. With a few reasonable assumptions these reactions could be identified by the presence of certain ions in a water sample. These components are discussed below in regard to their origin and significance, and method of measurement. They are alkalinity, acidity, calcium, sulfate, pH, specific resistance and temperature. The information concerning the source of these components is compiled mainly from Rainwater and Thatcher (1960), Hem (1959) and Sawyer (1960).

2. Components Measured

a. Alkalinity (HCO_3^-) and Calcium (Ca^{++}). These components are discussed together because of their interdependent relation in natural waters.

Alkalinity is defined as, "the capacity of a water containing a compound with or without hydrolysis, for neutralizing strong acid to pH 4.5," (Rainwater and Thatcher, 1960, p. 93).

The "total alkalinity" of water is a function of the carbonate, bicarbonate and hydroxide content. Contribution to alkalinity by hydroxides is rare in nature. Carbonate and bicarbonate are the predominant components of natural alkalinity and result from the action of carbon dioxide dissolved in water (carbonic acid) upon basic materials in the strata (principally calcium carbonate). Mason (1962, p. 158) states, "the pH of many terrestrial waters is controlled by the buffer

system $CaCO_2$-CO_2-H_2O; a saturated solution of carbon dioxide at its partial pressure in the atmosphere has a pH of 5.2, and a solution of calcite in air-saturated water has a pH near 8."

Carbonate forms chiefly by the solutioning of carbon dioxide in water in the absence of calcium carbonate according to equation (5).

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^= \quad (5)$$

Under normal temperature and a pCO_2 (partial pressure of carbon dioxide) of $10^{-3.5}$ atm., which approximates the pCO_2 of the atmosphere, the pH of the water is about 5.7; while a pCO_2 of one atmosphere will depress the pH of the solution to about 3.95 (Schmalz, 1967).

However, in the presence of calcium carbonate the predominant ion formed is bicarbonate in accord with equation (6).

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{++} + 2HCO_3^- \quad (6)$$

Under normal pCO_2 (about $10^{-3.5}$ atm.) the equilibrium pH of this reaction is about 8.4. It is apparent from equation (6) that the bicarbonate alkalinity and the calcium ion content are related. However, this relation is not as simple as it appears. A buffered system usually exists between the concentrations of carbon dioxide, calcium ion, bicarbonate ion, carbonate ion and pH. Within broad limits the following generalizations apply.

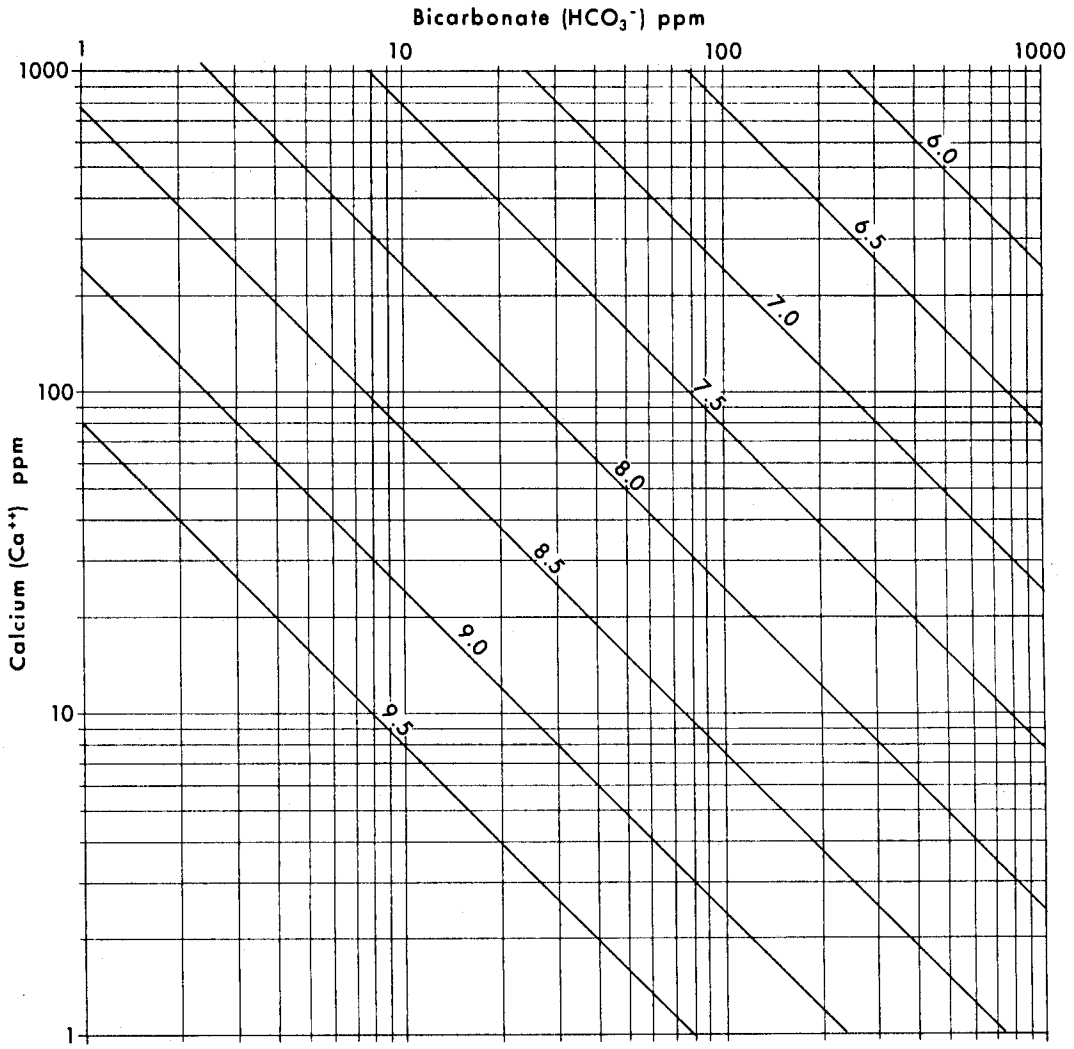
In the presence of a high pCO_2 (about one atmosphere) and in the absence of calcium carbonate, the pH of the water will be slightly acidic (pH about 4), and the water will not contain calcium ions nor alkalinity. At a pCO_2 found in the atmosphere ($10^{-3.5}$ atm.) and in the presence of calcium carbonate the pH of the water will be about 8.4 and

will contain a moderate amount of bicarbonate alkalinity (about 75 mg/l) and some calcium ion. As the pCO_2 approaches one atmosphere and in the presence of calcium carbonate, the pH of the water approaches 6.0 with increasing amounts of bicarbonate alkalinity and the calcium content approaching saturation, decreases. The plots of equilibrium pH in relation to calcium and bicarbonate activities in contact with calcite are shown in Figure 7.

The significance of alkalinity measurements is obvious. By determining the alkalinity of ground waters in an area, the neutralizing capacity and threshold values are established which limit the amount of acidity that can be produced in that area without adversely affecting the water quality. Calcium determinations were made to establish if neutralization took place and to approximate what the alkalinity would have been, in accordance with equation (6) and Figure 7. The assumption was made that the only source of calcium ions was calcium carbonate.

Two methods of measurement were used in the determination of calcium ion content of the water samples; a complexometric method using EDTA and a spectrophotometric method. Results from both methods compared favorably.

In the complexometric method a murexide indicator turns dark purple in the absence of calcium, but with calcium forms a pink colored complex (Rainwater and Thatcher, 1960, p. 128). By using murexide as an indicator, the sample can be titrated with a standard solution of disodium EDTA to a sharp endpoint.



EQUILIBRIUM pH IN RELATION TO CALCIUM AND BICARBONATE ACTIVITIES IN SOLUTIONS IN CONTACT WITH CALCITE - TOTAL PRESSURE IS 1 ATM @ 25°C.
(Hem, 1961, p. 22)

Figure 7

Unfortunately, EDTA also combines with other heavy metals, notably iron. Satisfactory results were obtained in analyzing natural and unpolluted waters by complexing or reducing the small amounts of metals with sodium cyanide or hydroxylamine hydrochloride. Acid mine drainage, however, presented a problem because of its high iron content.

In the analysis of acid mine drainage the complexometric method was modified to eliminate this source of interference. The pH of the sample was raised to about 8 and the ferrous iron converted to ferric iron by the addition of sodium hypochlorite. At pH 8 the concentration of dissolved iron is less than 1 ppm (Hem, 1961, p. 24) and falls within the concentration of iron permitted in the complexometric method which can be removed by the cyanide. The sample with the precipitated iron was filtered, washed and the filtrate treated with complexing and reducing agents before titrated with the EDTA (see Appendix A for details).

A few tests were made to determine if the calcium coprecipitated with the iron because if it did, it would remain in the filtered portion. A solution containing 12 grams/liter of ferrous sulfate was prepared and mixed with a solution of calcium chloride that contained 48 mg/l of calcium (as Ca^{++}). The samples were made basic, filtered, washed and the filtrate analyzed by the EDTA method outlined above. The poorest trials gave 46.8 mg/l in one case and 45.6 mg/l in another. This represented a 5% error in calcium determination and was considered acceptable in this study.

In the spectrophotometric method, the Perkin-Elmer Atomic Absorption Spectrometer was used to determine the calcium ion content. This equipment was available for use through the Mineral Constitution Laboratory of The Pennsylvania State University. The sample to be analyzed was aspirated into an acetylene flame and vaporized. The atoms in the vapor were irradiated by a monochromatic light beam generated by a calcium-zinc hollow cathode lamp. The spectrum emitted by the calcium-zinc lamp was absorbed only by the atoms of calcium or zinc, hence interference by other atoms was eliminated and made this method preferable for calcium determinations in acid mine waters. As a precaution against anionic interference, a hydrochloric lanthanum oxide solution was added to the sample. The presence of the calcium ions reduced the intensity of the transmitted light that was noted by a photodetector and registered on an automatic output recorder in graphical form. A standard curve was made by running a series of standards through the machine from which absorptions of unknowns can be translated into the calcium content. An analysis could be done in about 15 seconds (Kahn and Slavin, 1962).

Calcium contents are reported in milligrams of Ca^{++} per liter (mg/l).

In the determination of sample alkalinities, the sample was titrated with a 0.01639 N sulfuric acid solution (where 1 ml $\simeq$ 1 mg/l HCO_3^-) using a magnetic stirrer and a pH meter to determine the end-points. The volume of titrant required to depress the pH to 8.2 was a measure of the carbonate alkalinity, and the additional quantity

required to lower the pH to 4.5 represented the bicarbonate alkalinity (Rainwater and Thatcher, 1960).

All field samples collected had initial pH's less than 8.4 hence all alkalinities consisted of bicarbonate alkalinities. To preclude erroneous alkalinity determinations due to chemical deterioration with age, all alkalinity titrations were done within six hours of the collection of samples.

Alkalinities are reported in milligrams of HCO_3^- per liter (mg/l).

b. Acidity (H^+) and Sulfate ($SO_4^=$). Just as an interdependent relation exists between the alkalinity and the calcium content, a similar relationship exists between the acidity and the sulfate content in acid mine drainage. The acidity in acid mine drainage is assumed to develop principally from the hydrolysis of the oxidation products of pyrite. It is recognized that other divalent metals, notably aluminum, can contribute to the formation of acidity in some mining locales. However, literature reviews suggested that acidity due to other than pyrite oxidation products is negligible. Further, divalent metals, other than the iron occurring in the sulfide form, occur in an inert form and must be "chemically activated" to produce acid. For example, aluminum may occur in an inert silicate structure, but it is only after coming in contact with an acidic sulfate solution that the aluminum converts to alunogenite (aluminum sulfate) and becomes a potential acid source.

The oxidation of pyrite can be written,

$$FeS_2 + H_2O + 7\ O = FeSO_4 + H_2SO_4 \qquad (7)$$

The ferrous sulfate may be oxidized further to ferric sulfate and dissolved in water as in equation (8).

$$Fe_2(SO_4)_3 \rightleftharpoons Fe^{+++} + 3SO_4^{=} \quad (8)$$

The iron can hydrolyze as in equation (9)

$$Fe^{+++} + H_2O \rightleftharpoons Fe(OH)_3 + 3H^{+} \quad (9)$$

to form acidity and the iron hydroxides.

Thus it can be seen that the sulfate content is generally related to the acidity. The relationship is not linear because although the sulfate and iron arise from a common source, the acidity generated is a function of the oxidation state of the iron. However, a particular range of acidity values, determined by the oxidation state of the iron, can be correlated with the sulfate content of samples.

Because the acidity generated is a function of the oxidation state of the iron, it may be possible to have a sample whose acidity content increases with time as the iron is gradually oxidized. An acid discharge of a certain pH emanating from a mine may contain abundant ferrous iron in solution which will oxidize to the ferric state, become red and further depress the pH, as the water travels away from its source. The sulfate content, however, remains constant assuming no significant dilution has taken place.

The significance of sulfate measurements is obvious. The sulfate content is the tracer of acid mine drainage and can be used to approximate what the acidity must have been before neutralization took place. This is done by analyzing the sulfate and acidity content of acid mine drainage from various sources, and plotting concentrations of

sulfate against acidity. An assumption is made that all of the sulfate in the sample arises from the oxidation of pyrite. From the plot of various acid mine drainage compositions, a range of acidity can be interpolated for a particular value of sulfate concentration. This expected range of acidity is compared to the titratable acidity of a sample suspected of being neutralized.

Precipitation of the sulfate ion is possible in the presence of high calcium waters. A water sample originally acid may be neutralized by calcium-bicarbonate rich waters, but because of sulfate precipitation it will contain a low sulfate content. An incorrect conclusion can be reached, namely, the sample never was affected by acid mine drainage. Calculations using sulfate and calcium concentrations of water samples analyzed in this study and solubility products for gypsum and anhydrite indicate that levels of sulfate concentration indicative of acid mine drainage contamination are possible even though precipitation takes place. Hence, neutralization reactions can still be interpreted in spite of calcium sulfate precipitation.

Quantitative determinations of sulfate ion were made by adding barium chloranilate reagent which, in a buffered sample (pH 4.63), reacted with the sulfate ion to produce a wine red color. The intensity of the color developed according to the concentration of the sulfate present. The intensity was measured by a Photovolt Model 401 Colorimeter and compared to a standard curve which gave the concentration of the sulfate ion.

Sulfate concentrations are expreseed as milligrams of $SO_4^=$ per liter (mg/l) of solution.

The method of measuring acidity presented a problem, not because of analytical technique, but because of theoretical considerations concerning the definition of acidity. Rainwater and Thatcher state, "the acidic properties are attributable to the presence of mineral acids, uncombined dissolved gases, organic acids, and salts of strong acids and weak gases. Hydrolyzable salts of iron and aluminum of mine and industrial origin are common sources of acidity." (1960, p. 87).

From the foregoing paragraph it becomes apparent that the types of acidity pertinent to the study must be individually considered and analyzed. Since bicarbonate alkalinity theoretically can be in solution down to pH of 4.5, it was chosen as the endpoint for bicarbonate/alkalinity titrations. Therefore, a water sample should not be acid unless its pH was below 4.5. Many workers, in determining acidities, commonly titrate a water sample with a standard alkali solution to two endpoints, one at pH 4.5 which is defined as the "mineral acidity", and a second endpoint at pH 8.2, referred to as the carbon dioxide acidity (Sawyer, 1960, p. 212).

Titrating a sample to these endpoints is meaningful if all the acidity is in the "free acid" form, that is, existing as sulfuric acid. However, if the acidity is in major part due to hydrolysis, which in fact is the case in acid mine drainage, then the acidity determined

depends largely on the rate of hydrolysis and the oxidation state of the metal (Hem, 1959, p. 99).

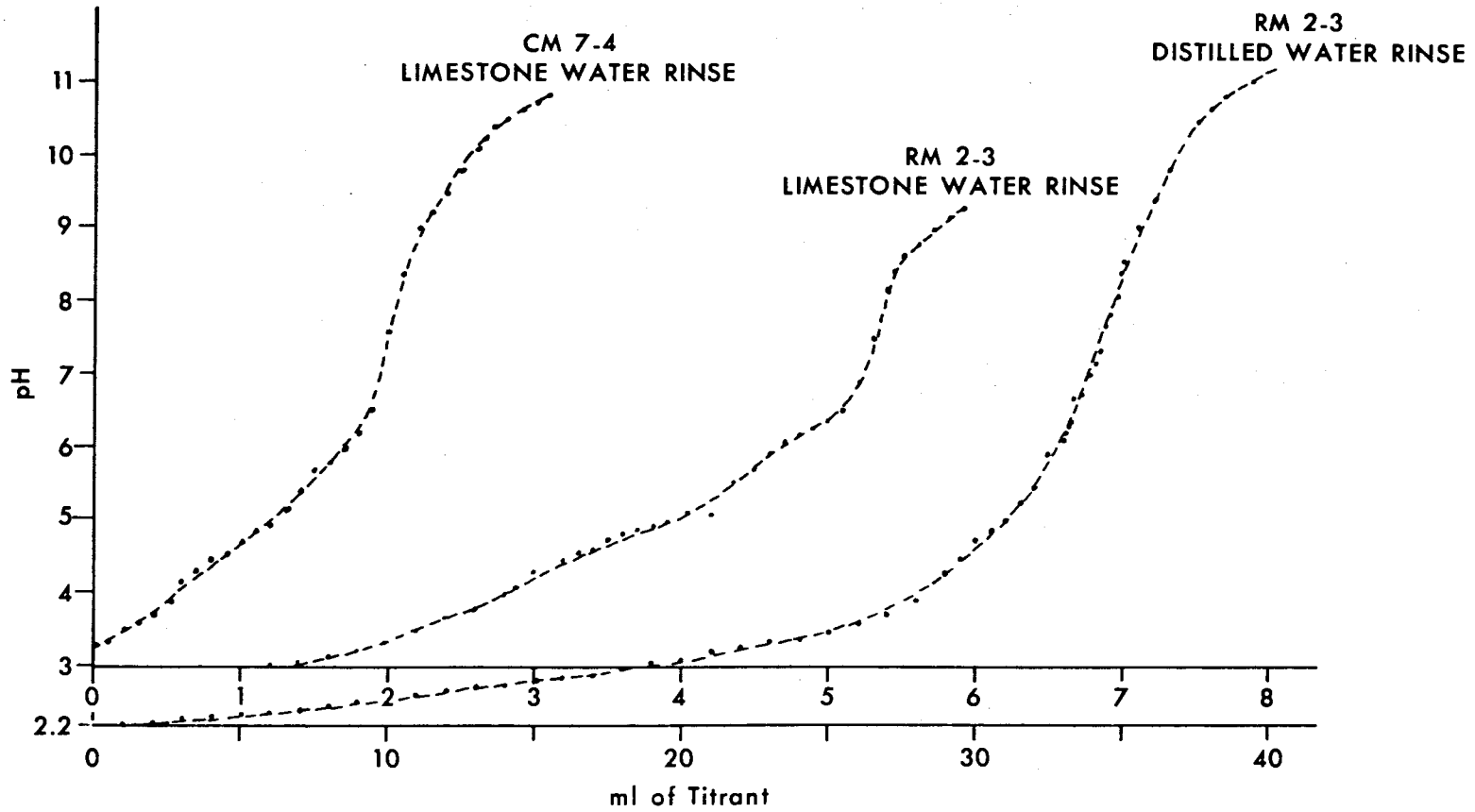
To get a true picture of the total amount of acidity present in a sample, which is the amount that nature will contend with, hydrolysis and the oxidation of the metals must be driven to completion before the sample is titrated. This is accomplished by boiling the sample for two minutes before titration. In so doing, however, the dissolved carbon dioxide is driven off with the loss of carbon dioxide acidity, whereupon titration with a standard alkali gives the acidity due only to iron hydrolysis and free sulfuric acid which is precisely the parameter of interest.

Generally, the endpoint is taken as 8.2 (phenolphthalein) and is somewhat arbitrary. A more logical endpoint to use as neutrality is pH 7 (Hem, 1959, p. 99). Titration curves were determined for three samples showing varying degrees of acidities. In all cases an inflection point (which determines the endpoint of a titration) occurred near pH 7 (Figure 8) and suggests that pH 7 is a proper endpoint.

Acidities were determined by boiling a sample for two minutes and cooling to room temperature before titrating with a standard alkali solution to pH 7 as measured by a pH meter in lieu of a chemical indicator. The result is known as "potential free acidity" and is expressed as milligrams of H^+ per liter (mg/l) of solution.

c. pH. The pH of a solution is the measure of the hydrogen ion concentration and is expressed by the relation

$$pH = \text{Log } 1/H^+ \tag{10}$$



ml of Titrant Top Scale Applies to Curves CM 7-4 and RM 2-3 (LMS)

Bottom Scale Applies to Curve RM 2-3 (DW)

TITRATION CURVES FOR THREE SAMPLES OF VARYING ACIDITIES

Figure 8

where H^+ is the concentration of hydrogen ions in moles/liter.

As such, the concentration of hydrogen ions can be expressed as a number.

While many workers consider pH and acidity synonymous and homologous, a sharp distinction is made in this study between the two. It was shown that the potential free acidity is the capacity of a water containing non-volatile compounds for neutralizing a base to pH 7; although a pH endpoint is used to define acidity, the reader is reminded that this pH endpoint represents an inflection in the titration curve. The potential free acidity does not include the component due to dissolved carbon dioxide in the form of carbonic acid.

The pH, on the other hand, represents the concentration of the hydrogen ions in a solution at the instant of measurement and represents the state of the environment. A field water sample saturated with carbon dioxide may have an acidic pH, but a zero potential free acidity.

Although the pH effectively indicates the state of the environment, two considerations prohibit its use as an "acidity" measurement. First, it was shown that the acidity of a sample varied with the oxidation state of the metal in solution. For this reason it would be possible for two samples to have the same pH but widely different potential free acidities, if one sample contained the cation in the reduced state while the other contained the cation in the oxidized state. Secondly, Temple and Koehler state, "the sulfates of iron have a buffering action which is most pronounced between pH 2 and 4, so that

large increases in ferrous sulfate in this pH range produce only a small drop in pH." (1954, p. 6).

With the above, the pH measurement may seem to be a meaningless parameter, being essentially replaced by the potential free acidity. However, the pH, although not quantitatively estimating the acidity, does indeed measure the state of the environment and is a critical factor in this study.

The iron bacteria, which catalyze the oxidation reactions, thrive in an acidic environment. A water sample may have no free acidity, but due to a high dissolved carbon dioxide content, it may have a low pH which is conducive to bacterial existence.

All pH measurements were made in the field with a Photovolt Model 126 Portable pH Meter, using a Photovolt Combination Electrode (catalog number 1208). The meter was standardized against either a pH 4.6 or pH 7.0 buffer depending upon the range of field measurements.

The same meter, using Beckman electrodes, was used in the laboratory to measure titration endpoints. In determining acidities the meter was standardized against a pH 7 buffer, and in the determination of alkalinities, against a pH 4.6 buffer.

d. Specific Resistance. Electrolytic conductivity (specific conductance) is a measure of the ability of a solution to transmit an electrical current, and is defined as the reciprocal of the resistance in ohms of a one centimeter cube of the liquid at a specified temperature. The conductivity is measured in mhos (the reciprocal of ohms).

The specific conductance that could be measured by a Solu-Bridge Model RB-Q4, Conductivity Meter was limited to 1000 micromhos, which is the range of most waters in the eastern United States. In the beginning of the study, however, it was found that acid mine drainage values exceeded the limit and were beyond the range of the Solu-Bridge Meter. Attempts to extend the range of the meter by varying the cell constant were not successful. The problem was solved by measuring the resistivity instead of the conductivity.

An Industrial Instruments Model RC-7P Conductivity Bridge with a range of 0.2 to 2,500,000 ohms was used to measure resistivity. It covered the range of resistivity of all water samples encountered in the study including acid mine drainage. To obtain the specific resistance, the measured resistance is divided by the cell constant, which in all cases was unity. Thus, all resistances reported are specific resistances and expressed in ohms/1 cm^3 of solution.

The ionic strength in a large way determines the electrical properties of the solution and as such can be used as an indicator, in rather wide limits, of the dissolved solids content.

Table 1 - Examples of Specific Resistance Values for Solutions of Various Ionic Strengths

Solution	Specific Resistance (ohms/cm^3)
30% sulfuric acid	1
Sea Water	about 40
0.05% salt water	1000
Raw water	
Excellent quality	about 35,000
Distilled water	1,000,000

Specific resistance measurements were used in two ways. First, specific resistance values were compared to various ranges of sulfate and acidity concentrations. Having established a general relationship, water quality analyses could be determined confidentally by confirming ionic strengths obtained through quantitative measurements with resistivity measurements. Secondly, resistivity measurements could be used to rapidly reconnoiter an area for water quality expectations. By making field determinations of specific resistances and relating these values to values of previous analyses water characteristics could be inferred. Sources of strong ionic concentrations, indicative of acid mine drainage contamination could be mapped without detailed chemical analyses.

Specific resistance of water samples were measured in the laboratory by the Model RD-7P Conductivity Bridge.

e. Temperature. Water sample temperatures were required for pH and resistivity measurements as they were partially temperature dependent and had to be adjusted accordingly. Temperature readings were also used to indicate the depth of circulation of the water discharges. Generally, the deeper the circulation the colder the water temperature. It was found that in the summer ground water temperatures in the areas averaged about 10° C., streams about 15° C., and pools of stagnant water from 17° to 26° C. Thus temperature measurements indicated in a general way whether a pool was mostly stagnant water or a spring and whether a stream was mostly surface runoff of ground water bleed.

The temperature was measured by submerging a thermometer and recording the temperature to the 0.5° C. unit.

3. Method of Collecting Water Samples

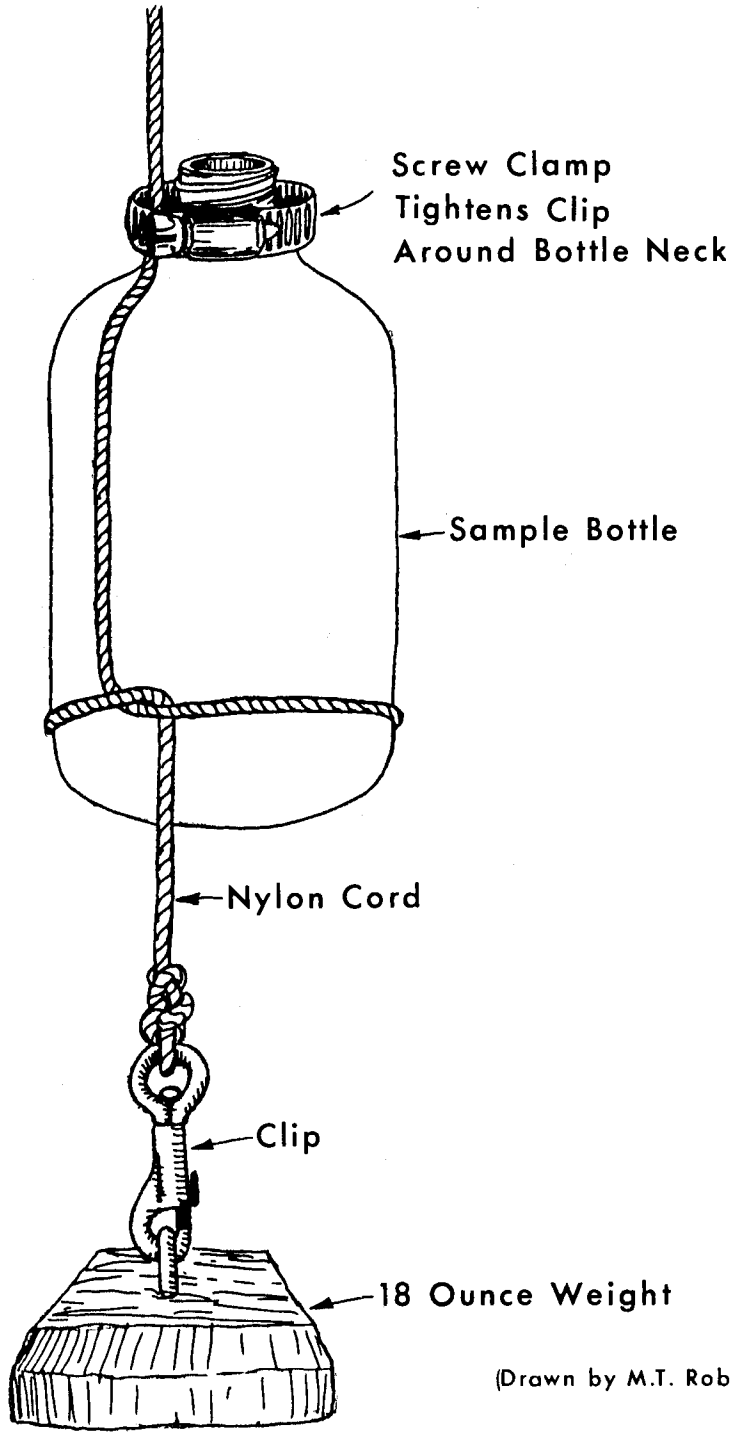
Water samples were collected from homes, springs, streams and mine pools in 16 ounce screw cap plastic bottles. In all cases the bottle was filled to the top to eliminate the air space and screwed tightly and remained sealed until the contents were to be analyzed.

In homes where the pump or well was inaccessible, water samples were taken from the household spigots, in which cases pH measurements were eliminated. Household pressurized water systems radically affect the dissolved gases content and the pH.

In deep wells or shallow dug wells, where the casing diameter was more than six inches, a plastic bottle was lowered by a nylon cord into the well and water was sampled directly. A lead weight was tied to the units to submerge the bottle and to keep the bottle upright (Figure 9). In mine pools, the identical arrangement was cast into the center of the pool and gradually pulled ashore as the bottle was filling to assure a uniform sample. In streams and springs, and mine bleeds, the plastic bottle was immersed and held in the flowing water by metal tongs until filled.

Water samples were labelled by a code similar to that used to label the rock samples and contains letters and a number. The letters designate the area and source from which the water sample was collected as follows:

C--the Clearfield study area



METHOD OF SUBMERGING 16 OUNCE SAMPLE BOTTLE IN UPRIGHT POSITION

Figure 9

R--the Glen Richey study area
CL--near Clarion, Pennsylvania
GR--a strip mine near Grove City, Pennsylvania
HR--a strip mine near Haarlansburg, Pennsylvania
SL--a strip mine near Slippery Rock, Pennsylvania
K--the Krebs mine

The following letters indicate the source sampled and are joined to the letters above:

H--private water supply from a home
T--stream
M--mine drainage or a pool in a mine

For example, CH indicates a water sample obtained from a home in the Clearfield study area, RT indicates a stream sample in the Glen Richey area, etc.

The number following the letters locates the exact sampling point by a corresponding number on a map showing the locations of water sampling points (Plates III and IV).

DATA AND INTERPRETATIONS

Interdependent relations were found to exist between the factors investigated. To attempt to discuss all the factors and the pertinent data in an integrated discussion encompassing all the interactions will involve too many divergencies from the main theme. Instead, the factors will be discussed separately. After the individual cause and effects of each factor have been established, the factors will be related to each other as they were noted to occur in the field and laboratory experiments.

The four major subdivisions in this chapter are- Stratigraphic Data, Aqueous Geochemical Data, Areal Characteristics Related to Water Quality Parameters and Hydrologic Data. The first three subdivisions are intimately related but discussed separately for clarity.

The section on Stratigraphic Data is concerned mainly with distribution of sulfur in strata of the various formations. The data are presented on stratigraphic profiles of various mine highwalls and roadcuts and show lithologic variations, sampling intervals and percentage sulfur of rocks taken from the sampling intervals. These stratigraphic profiles are located in Appendix B of this report. The sulfur values of the Clearfield and Glen Richey areas are analyzed statistically to determine the source of variation and to compare the gross sulfur content between the areas. Selected samples were used in leaching tests to relate the acid potential of a rock to its sulfur content. Other factors affecting acid production, such as grain size, bacteria, etc., also were considered in

these tests. These results are discussed in the Stratigraphic Section instead of the Geochemical Section because they depend on the rock characteristics.

The section on Aqueous Geochemical Data deals mainly with the chemical quality of water samples collected from various areas. The quality parameters are discussed and interpreted. A need is established for extending water sampling to other areas in order to obtain quality extremes to facilitate comparisons of water qualities. Distinctive water quality groups are differentiated and associated with various areas.

The section on Areal Characteristics Related to Water Quality Parameters, associates the geology with the chemical quality of water found in these areas and includes a discussion of factors present in the areas that give rise to acid and non-acid waters.

The last section of Hydrologic Data elucidates the ground water flow systems existing in the areas and shows the need for adequate well control in order to properly evaluate the aquifer characteristics.

A. Stratigraphic Data and Interpretations

1. Preliminary Determination of Experimental Error and Variance in Total Sulfur Determinations

a. Purpose. As a prelude to the determination of sulfur distribution within the section, it was deemed necessary to evaluate the range of variation attributed to experimental error. The questions to be answered were what sulfur variation existed within the strata which

would affect sampling; what variation in sulfur content could be attributed to inaccuracies in riffling; and what was the precision of the Leco Automatic Titrator?

Accordingly, unweathered samples were sampled selectively from the highwall of a recently opened mine in the Glen Richey area. In mine RM-6, the Lower Freeport and the overlying shale and sandstone were exposed (see Figure 37). Three sampling stations were paced approximately 75 feet apart. At each station, the coal and six inches above the coal were channel sampled, and grab samples were taken from a two foot interval in the overlying shale. Three samples were obtained at each sampling station. By analyzing the sulfur contents of the three samples from the same lithology obtained 75 feet apart, the lateral variation in sulfur content could be ascertained for the control areas.

To test the variation introduced by riffling, three 5-10 gram portions were riffled from each field sample after crushing the sample to pass a 2 mm screen. Each 5-10 gram portion was pulverized in a ball mill to pass a 125 micron sieve. And, each pulverized portion was analyzed three times for total sulfur content. Hence, each field sample was riffled three times, and each riffle was analyzed thrice, giving a total of nine sulfur determinations for each field sample. The results are listed in Table 2.

b. Interpretation of Results. Throughout this discussion the sample group will be modified by a subscript denoting the riffle number.

(1) Precision of the Leco Automatic Titrator. Trends in variation are apparent from the data presented in Table 2. However, the

Table 2 - Sulfur Percentages Used in the Analysis of Variance

Sample Group	First Riffle	Second Riffle	Third Riffle
RM-6A (6" above coal)	0.94	1.20	1.00
	0.98	1.19	0.98
	0.96	1.21	1.00
RM-6B (6" above coal)	0.54	0.56	0.55
	0.52	0.56	0.59
	0.58	0.55	0.57
RM-6C (6" above coal)	1.63	1.27	1.22
	1.63	1.31	1.14
	1.64	1.24	1.12
RM-6E (shale)	0.79	0.54	0.78
	0.83	0.59	0.78
	0.80	0.60	0.79
RM-6K (shale)	0.83	0.48	0.64
	0.84	0.46	0.64
	0.79	0.43	0.63
RM-6H (shale)	0.69	0.55	0.63
	0.71	0.56	0.63
	0.71	0.53	0.64
RM-6F (coal)	1.88	2.09	1.12
	1.79	2.03	1.19
	1.65	1.93	1.10
RM-6G (coal)	1.51	2.96	1.93
	1.56	3.12	1.72
	1.64	3.26	1.83
RM-6I (coal)	2.02	1.17	1.49
	1.99	1.27	1.54
	2.07	1.14	1.63

Samples RM-6A, RM-6B and RM-6C represent samples of rock six inches above the coal taken 75 feet apart. RM-6E, RM-6K and RM-6H represent samples of shale taken from a two fool interval above the coal 75 feet apart. RM-6F, RM-6G and RM-6I are channel samples of the Lower Freeport Coal taken 75 feet apart.

data were statistically analyzed by a One Factor Analysis of Variance (1FAOV) testing the variations within the riffles against the variations between the riffles for each sample group. The data were assumed to have a normal distribution. With the exception of RM-6B, all groups had significant differences at the $F_{0.05}$ level.

Because the between and within variances of RM-6B were not significant, the data for RM-6B were used to calculate a mean, variance and standard deviation to be used to estimate the precision of the Leco Titration unit. The mean is 0.5577, the variance is 0.000438 and the standard deviation is 0.0219. Applying Bessel's correction, to obtain the best estimator of the standard deviation ($\hat{\sigma}$) the value becomes 0.0295. Moroney (1951, p. 62) states that 95% of the area of a normal distribution lies less than two standard deviations from the mean, hence, 0.0590, rounding to 0.06, is the precision of the Leco Automatic Titrator used in this report. In other words, any measurement on the Leco will be within plus or minus 0.06 of the grand mean 95 times out of 100. Where the sulfur content exceeds 4%, the precision of the Leco is 0.12, since the scale was expanded by a factor of two.

Although the precision of the Leco is 0.06, results are still reported to the hundredths of a percent rather than rounding off to the nearest tenth of a percent. This is done to leave the "rounding off" of the values up to the reader using whatever method he chooses.

(2) Variation Due to Riffling. The 1FAOV showed that a signigicant difference existed between riffles of each sample group

with the exception of RM-6B. This is interpreted to mean that a significant error was introduced by the riffler under certain conditions. It is necessary to explore the conditions whereby a riffling error is introduced as it is pertinent to the study.

The total sulfur values shown on the stratigraphic profiles of mines and roadcuts in Appendix B were obtained from analyses using the Leco instrument. These values represent the total of two components, organic suflur and pyritic sulfur. It was established by Neavel (1966) and Reidenouer et al (1967) that an increase in total sulfur content reflects directly and proportionately an increase in pyritic sulfur. They showed that throughout a vertical section of coal, the percentage of organic sulfur generally varied at a lesser rate than did the other two components. Hence, increases in total sulfur values represented increases in pyritic sulfur values, whereas the organic sulfur was more or less "background" reading. Thus the variations in this discussion are directly concerned with the variations in pyritic sulfur content.

As shown previously, the modes of occurrence of pyrite have variable forms as well as variable sizes which radically affect the percentage sulfur values. This effect manifests itself as the error introduced in the field collection of samples and in riffling the samples in preparation for the analyses. Two examples will serve as an illustration.

If a rock contains microscopic pyrite less than 10 microns in size and is finely disseminated throughout the rock, there

is in essence one population. The sample can be viewed as a rock homogeneous in regard to its sulfur content. The probability that one riffle has the same sulfur content as another is great. Field collection of this rock type presents no problem as the stratum is homogeneous and can be adequately sampled by one sample.

On the other hand, a coal stratum may contain megascopic nodules, grains, layers of pyrite of variable thickness and coatings along joints, in addition to the finely disseminated grains. This coal can be considered as a mixture of two sulfur populations, the first being the finely disseminated grains, the other being the megascopic nodules and coatings external to the coal. Due to the variability of concentration of the megascopic grains in the coal seam the percentage of sulfur of any one channel sample of the coal reflects a ratio of the microscopic grains to the megascopic grains. Since this ratio varies laterally, the sulfur content of samples taken from various spatial sites will also vary accordingly.

These megascopic grains also affect the accuracy of the riffler. In preparing the samples for sulfur analyses, all samples, regardless of their megascopic pyrite content were crushed to pass a 2 mm sieve and riffled. Large grains of pyrite (which in themselves may weigh about one gram) became separated from the sample and became segregated from the coal because of their relatively finer size and greater density. These particles were noted to accumulate in clusters and to concentrate in zones. To accommodate the 2 mm size of the sample a large riffle was used. The rows were about 1 cm wide. Although

this size effectively split the coal, it allowed entire clusters of pyrite grains to pass through. Consequently, the pyrite concentration was weighted to one side of the riffle.

The writer suggests that to properly riffle a sample containing megascopic grains of pyrite, the sample should be crushed and sieved on a series of screens. Each sieved fraction must be riffled by an appropriately sized riffle corresponding to that size fraction. When all fractions have been riffled, the riffled segments are combined into one sample. The error due to riffling was avoided in leaching experiments by selecting a nearly uniform size of particle. Hence, sulfur measurements made on the samples used in the leaching study are considered accurate.

(3) Lateral Variability of Total Sulfur in the Strata.

To test the variability of sulfur content in the field, each sample group within a rock type had to be compared to the other sample groups within the same stratum. With the exception of RM-6B, a significant variation existed "within" each group and prevented a one factor AOV from being run "between" the groups.

This difficulty was circumvented by treating each riffle of similar lithologies as one factor. Thus, within each lithology there were nine factors. A one factor AOV on nine factors within each lithology showed, predictively, that significant variations existed between factors. Groups within each lithology could still be compared by partitioning the variance to each group used in a comparison. For example, RM-6A_1, RM-6A_2, RM-6A_3 were compared to RM-6B_1, RM-6B_2, Rm-6B_3

and RM-6C_1, RM-6C_2, RM-6C_3. The partitioning was achieved by the method of orthogonal comparisons (Steel and Torrie, 1960). Comparisons between each group could now be made even though a signigicant difference existed within each group.

In all cases, except in comparing RM-6F against RM-6I where the F calculated was 4.2583 and the $F_{(3,24)}$ at the 0.05 level was 4.2597, the groups were significantly different. Therefore, at Mine RM-6, there is a significant variation of total sulfur content along the strata and this variation is assumed to exist in other strip mines.

Reidenouer et al (1967) show that a significant lateral variation of pyrite does indeed occur; the loci of pyrite deposition being a function of the paleotopography. Consequently, the pyrite content in the present study probably reflects the paleotopography and the sample pyrite content varies according to the particular location from which the sample was taken.

c. Summary. Before a comparison could be made between the sulfur content of the study areas, the sources of variation due to sampling, riffling and analyzing had to be ascertained. It was found that the precision of the Leco Automatic Sulfur Titrator was 0.06 on sulfur values less than 4%, and 0.12 on sulfur values greater than 4%. However, significant variations in sulfur content were introduced by riffling samples and by sampling the strata using the method outlined for this study. Hence, direct comparisons of total sulfur contents cannot be made between the two areas of study based on sulfur values obtained from one sampling station at an arbitrary location in a strip mine.

2. Distribution of Total Sulfur

The stratigraphic profiles of various mines in Appendix B show the rock types, sampling locations and percentage sulfur of the rocks collected from the sampling interval. In general, zones of high sulfur content tend to occur about the coal seams.

The two areas of study cannot be compared in regard to their total sulfur contents. Significant variations, due to radical sulfur distributions in the strata and due to riffling error, occur within the sample groups which prevent accurate comparisons from being made.

Instead of a direct comparison of gross sulfur contents, with the intention of demonstrating one area to contain more sulfur than the other, a comparison of ranges of sulfur contents will reveal the similitude of total sulfur concentrations. The similitude can be used to deduce whether or not the total sulfur contents of the areas could account for the differences observed in water quality.

Table 3 shows the total sulfur contents of the areas of study plotted according to the spatial distribution of the rock samples as they were noted to occur in the field. Within each mine column, a total sulfur value appears at the lithologic horizon that was sampled in that mine. Each sulfur value is represented by a line scaled in proportion to the total sulfur value in the center column for visual comparison. These lines show significant overlaps to suggest that the ranges of sulfur contents in the two areas are comparable. Thus, the original contention, that a difference in sulfur content between the Clearfield and Glen Richey areas accounts for acid and non-acid waters, is rejected.

Table 3 - Graphic Representation of Ranges of Total Sulfur Contents of the Clearfield and Glen Richey Areas

	Clearfield Area								Glen Richey Area								
	CM-2	CM-3	CM-4	CM-5	CM-6/7	CM-8	CM-10	Ranges of Sulfur Contents 1 2 3 4 5 6 7 8	RM-1	RM-2	RM-3	RM-4	RM-5	RM-6	RM-9	RM-15	RM-16
Shale									.05 .09								.14 1.02 1.19
Up. Fpt																	.01
Shale																	
Rider																	
Shale											.72 2.0 1.35	.11 .88	.37	1.10 .8		.22 .26	
Binder													2.19 2.29				
Lo. Fpt											2.0 .63 .60		1.15	1.8		0.8	
Shale												.43 .98				0.1	
D Rider																	
Shale	.01			.35 .14											.10		
Up. Kit	.47 .48	.05 .48 .49		.56 .56			0.48								2.46 2.00		
Shale				.10	1.17												
Coal S smut					2.00 0.64												
Sand-stone	.01						1.80 0.63										
Clay	.04																
Mid. Kt			1.73		0.42		7.0										
Rider							2.36										
Smut																	
Shale			3.09 .53		.29 .42	.21 .22											
Mid Kit		.31 .49 .69 .23	1.13														
Shale		.07 .38 .01 .24															
Lo. Kit		1.4															

All values are in sulfur percentages. Solid lines scale off values for the Glen Richey Area; dotted lines scale off values for the Clearfield area.

3. Leaching Studies

The purpose of these studies was to assign a rank of acid potential to rocks of varying sulfur contents and to evaluate the factors affecting acid generation. Since the presence and absence of acid mine drainage in the two study areas cannot be explained solely as a function of the sulfur contents, other factors must play an important role in the formation of acid mine drainage. Thus, the leaching experiments were designed, in part, to relate the acid potential of a rock to its sulfur content, and in part, to evaluate the various factors affecting the acid potential.

Three leaching studies were performed. The first was a pilot study to determine the flushing interval, the optimum grain size of the samples to be leached, and the mechanics of operation. The second study related the acid potential of a rock to its sulfur content using distilled water as the leaching medium. The third leaching study repeated the pattern of the second leaching experiment, but used water that was in contact with limestone as the leaching medium to determine how this would affect the acid generation.

a. First Leaching Study. An initial leaching test was performed using the rocks listed in Table 4. The rocks were crushed to pass a 4 mm sieve and contained a complete range of sizes smaller than 4 mm. This initial test was done to determine the ranges of acidities that can be expected, the optimum leaching interval and to ascertain what grain size would be best for the leaching study. The results are illustrated in Figure 10.

Discussion of Results. Generally, the results showed that

Table 4 - Description of Rocks Used in the First Leaching Study

Sample Number	Rock Type	Percentage Sulfur
CM-6-5	Fine grained shale	0.3
RM-6E	Shale	0.7
RM-6L	Refuse from tipple	1.94
RM-6C	6" above the coal	1.30
RM-6D	6" above the coal	3.10

the higher the sulfur content, the greater the acidity produced. All samples showed an initial surge of acid development with a subsequent slackening with time. This is attributed to an initial high acidity generated by the oxidation products that had developed prior to the first flushing with water. Thereafter the time interval was too short to allow for development of a high concentration of oxidation products, but did permit a gradual oxidation to take place with a steady increase in acidity. This is exemplified by sample RM-6L which was not flushed from the third day to the 37th day, whereas sample RM-6C was flushed periodically. The former shows a surge of acid released on the 44th day due to a high concentration of oxidation products, while the latter shows a gradual, steady acid production.

In order to maintain similar oxidation intervals, so as to compare the samples accurately, it was necessary to flush all samples at the same time in all leaching experiments hereafter.

During the course of the experiment, it was noted that the very fine particles cemented together with the larger ones in the

leaching chambers thus preventing the enclosed particles from reacting. Further, the fine grained particles poured off with the leachate giving the fluid a muddy appearance. To overcome this difficulty, all samples to be leached hereafter were sieved and the 1-2 mm fraction (passed a #10 sieve and caught by a #18 sieve) was used in the leaching chamber. This size was also noted to retain a minimum amount of liquid when the sample was drained.

b. Second Leaching Study. With the mechanics of the leaching technique gained from the first experiment, a second leaching experiment was performed intending to relate the acid potential of various rocks to their sulfur contents. To ensure accurate determinations of the sulfur content of the rock being leached, the sieved sample (the 1-2 mm fraction) to be used in the study was riffled to obtain two 3-5 gram portions. One portion was used to make pellets for microscopic examinations and the other was analyzed for total sulfur, pyritic sulfur and calcium carbonate. The samples used in the second leaching study are listed in Table 5. The results of the second leaching study are shown Figure 11.

Table 5 - Description of Rocks Used in the Second Leaching Study

Sample Number	Rock Type	Percentage Total Sulfur	Percentage Pyritic Sulfur	Percentage Calcium Carbonate
RM-3-5	Shale	1.57	1.38	0.13
RM-3-6	Binder	0.86	0.73	0.15
RM-4-1	Binder	1.09	0.76	0.37
RM-3-1	Coal "D"	1.47	1.05	0.14
CM-6-1	Shale covered with many salt crusts	0.59	0.39	0.15
CM-6-2	Shale of lower 15' Bed	1.15	0.93	0.42
CM-10-9	Coal, same location as CM-10-10	3.51	2.82	Trace
CM-10-10	Coal	7.01	5.81	Trace
CM-7-4	6" above coal smut	1.85	1.08	Trace
RM-9-2	Coal	1.75	1.25	Trace
RM-2-3	Shale, thin bedded above coal	5.42	-	Trace

Discussion of Results. From the start of the experiment until the tenth day the samples exhibited a uniform rate of acid production (Figure 11). From the tenth to the 16th day a slight increase in slope is indicated. This was due to a mechanical breakdown of the heating system in the laboratory. The room temperature was 27° C. on the tenth day, 29° C. on the 13th day and returned to normal after the 16th day; at which time the slopes of the lines again approached those prior to the elevation of temperature. Although inadvertent, these anomalously high temperatures demonstrated that acid generation is affected by temperature.

Restricting the discussion to the time before the 20th day, it is apparent that many anomalies exist. For example, coal sample

CM-10-9 (2.82% pyritic sulfur) yielded less acid than coal sample RM-9-2 (1.25% pyritic sulfur). Similar anomalies can be found with the shales. The most obvious explanation for the anomalous acidities was the difference in weatherability of the various samples attributed to the mode of pyrite occurrence. Although the sulfur analyses determined percentage pyritic sulfur, no attempt was made to differentiate marcasite from pyrite, or for that matter, to determine the presence of troilite or pyrrhotite (both are forms of FeS). In an attempt to explain the high acidities associated with relatively low sulfur values, a mineralogic study was done to determine the state of the iron disulfide in the leached samples.

The easiest and most obvious method for identifying the mineralogic state of the iron disulfide was the X-ray diffraction method. The sample was ground and a powder smear could be made on a glass slide which could be easily X-rayed with an iron tube. The apprehension of converting marcasite to pyrite by grinding has been shown to be untrue by Izard and Clemency (1967) who state, "that the polymorphic inversion of marcasite to pyrite by grinding is non-existent." Therefore, all that was needed for identification was a powder smear of the sample.

Unfortunately, the high organic matter of the samples impeded and masked good diffraction patterns. Many attempts were made to separate the pyritic material from the host rock by heavy liquid separation methods, but these were not successful.

Identification of marcasite and pyrite was possible with the aid of Steve Scott of the Department of Geochemistry and Mineralogy

of The Pennsylvania State University, who used a technique that takes advantage of the fact that marcasite rotates planes of light, whereas pyrite does not. Polished pellets were made by binding the sample of rock with a plastic cement in a cylindrical form, cutting the cured plastic with a diamond saw and polishing the end on a series of polishing wheels. These polished pellets were viewed through a calcite analyzer with an oil immersion lense of an "ore microscope". Upon rotating the stage marcasite became extinct, but pyrite did not.

In all pellets, the form of the iron disulfide was pyrite. Marcasite was not detected; thus, the anomalous acidities of the leaching study cannot be explained by the crystallographic state of the iron disulfide.

The pellets that were used to differentiate marcasite from pyrite were again examined and photographed to determine what difference in grain size existed. This study gave positive results.

On the 31st day, samples CM-7-4 and CM-10-9 gave almost identical acidities. Yet CM-7-4 contained 1.08% pyritic sulfur while CM-10-9 contained 2.82%, more than twice the amount. The calcium carbonate contents show only traces and cannot be used to explain the differences. To assure a valid comparison, CM-10-9, a coal, should be compared to another coal. There are two approaches, either to accept the argument that CM-7-4, although located six inches above a coal smut, contained abundant carbonaceous matter enough so that it was coal-like and could be compared to a coal, or to compare CM-10-9 with the coal sample RM-9-2. This latter coal contained 1.25% pyritic sulfur, yet

produced more acid than CM-10-9. Again, the trace amounts of calcium carbonate cannot be used to explain the differences in acidities. The explanation lies in the distribution of grain size. Figure 12 shows photomicrographs of the samples under discussion.

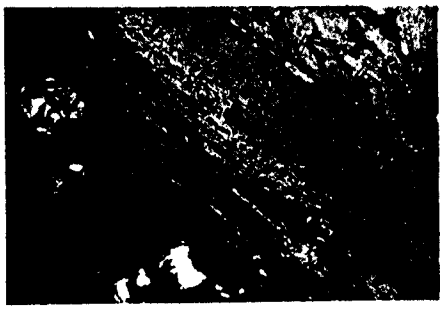
It is readily apparent that significant variations in grain size exist that account for the different acidities.

At the base of the graph it is noticed that binders RM-3-6 (0.73% pyritic sulfur) and RM-4-1 (0.76% pyritic sulfur) show no acid generation in spite of the fact that CM-6-1 (0.39% pyritic sulfur) and CM-6-2 (0.93% pyritic sulfur) generated noticeable acidities. Photomicrographs of pellets of the samples, Figures 13 and 14, show the grains of pyrite to be all of approximately the same size, and may even be finer grained in the non-acid producing samples. Hence, the explanation used previously, that different acidities can be related to different grains sizes, does not apply. The effect of calcium carbonate cannot be properly evaluated; however, the writer feels the calcium carbonate content of CM-6-2 (0.42%) is on par with that of RM-4-1 (0.37%) and that of CM-6-1 (0.15%) is equal to that of RM-3-6 (0.15%) and hence did not markedly influence leaching results.

The alternative consideration is the rock type, which when grouped, suggests that the shales, all things being equal, generate more acid than the binders. This is probably due to the difference in permeabilities. The binders effectively seal the pyrite grains from the oxidizing environment, but the permeability of the shale, even though very low, is sufficient to permit oxidation of the enclosed



100μ
CM-10-9



100μ
CM-10-9



100μ
CM-7-4



100μ
CM-7-4



100μ
RM-9-2



100μ
RM-9-2

PHOTOMICROGRAPHS OF SAMPLES
CM-7-4, CM-10-9 AND RM-9-2

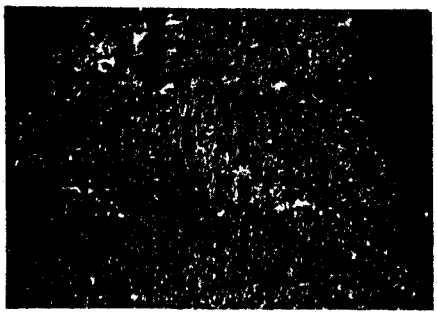
Figure 12



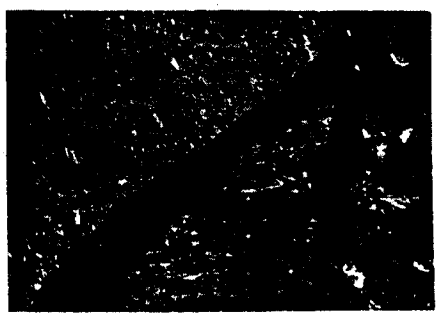
100μ
RM-3-6



100μ
RM-3-6



100μ
RM-4-1



100μ
RM-4-1



100μ
RM-4-1



100μ
CM-6-1

PHOTOMICROGRAPHS OF SAMPLES
RM-3-6, RM-4-1 AND CM-6-1

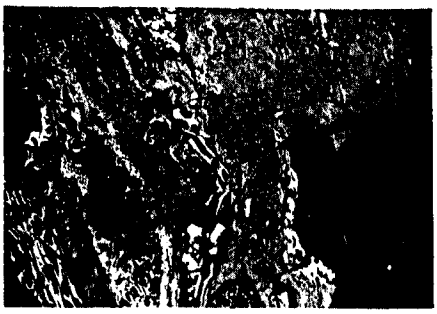
Figure 13



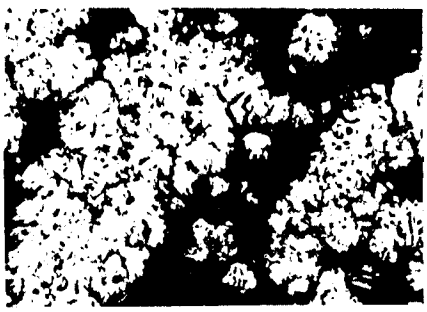
100μ
CM-6-2



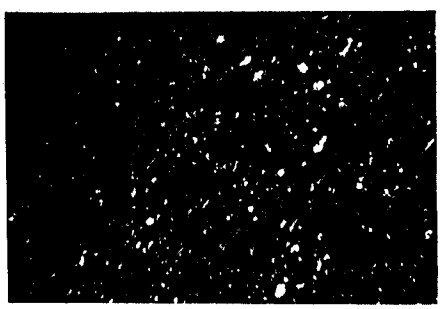
100μ
RM-3-1



100μ
RM-3-1



100μ
RM-3-5



100μ
RM-3-5



100μ
RM-3-5

PHOTOMICROGRAPHS OF SAMPLES
CM-6-2, RM-3-1 AND RM-3-5

Figure 14

pyrite. However, by this argument, coal RM-3-1 (1.05% pyritic sulfur) and shale RM-3-5 (1.38% pyritic sulfur) because of a relatively high permeability should be generating more acid than what is recorded. The grain size distribution noted in photomicrographs of these samples (Figure 14) resolves the apparent conflict.

Of academic interest are the peculiar patterns seen in some of the pyrite grains in photomicrographs of samples RM-4-1 (Figure 13) and RM-3-1 (Figure 14). White arrows direct the reader's attention to the grains in discussion. These two photographs were enlarged and are shown in Figure 15. Here again, white arrows direct the reader's attention to the peculiar patterns. The writer offers no explanation as to their origin or their identity.

Twenty days after the trends of acid generation were established, the effect of bacteria on acid generation was tested. Specifically the bacteria used are the type found in acid mine drainage pools and in this dicussion are taken to mean the *Thiobacillii* and the *Ferrobacilli*. On the 20th day three drops of acid mine drainage (sample #CL-1) were added to RM-2-3, RM-3-1 and RM-3-5. The assumption made was that the bacteria were present in the samples of acid water collected. This seemed justified based on abundant reference in the literature stating the ubiquity of these bacteria in mine waters. Indirect evidence establishing the bacteria as present in these samples is discussed later.

The effect of adding three drops of CL-1 and, presumably, the introduction of bacteria into the leaching chambers is obvious from



50μ

RM-4-1



50μ

RM-3-1

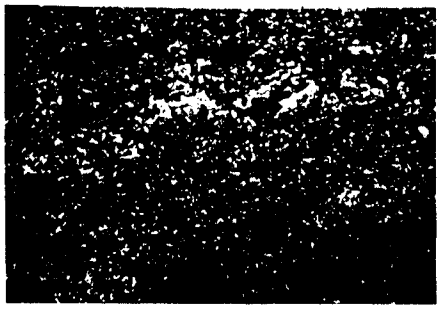
ENLARGEMENTS OF PHOTOMICROGRAPHS
OF SAMPLES RM-4-1 AND RM-3-1

Figure 15

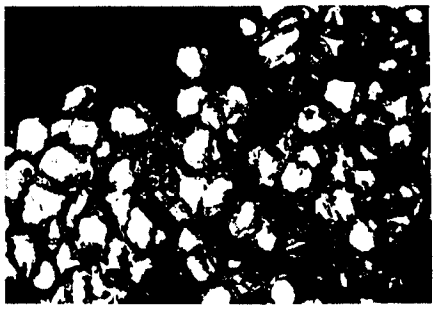
the dramatic surge of acid generation for sample RM-2-3. However, RM-3-1 and RM-3-5 were not affected. Perhaps the presence of calcium carbonate in the sample or the larger grain size had a nullifying affect (Figures 14 and 16). An attempt to evaluate the effect of calcium carbonate was done in the third leaching study and will be covered in detail in that discussion.

The effect that the bacteria had on the leachate quality is extremely significant. Prior to the addition of the bacteria, the acidity generated by RM-2-3 ranged from 3.65 - 5.00 mg/l and released sulfate concentrations on the order of 2000 mg/l. After the addition of the bacteria, the acidity concentration in the leachate soared to about 19 mg/l and on one day actually yielded 74.9 mg/l acidity (based on leaching 29 grams of sample with 100 ml of water). Sulfate concentrations were up around 34,000 mg/l. Thus, a water quality that could easily have been neutralized by waters in a glaciated terrain (this will be covered in more detail in the following section), became so extremely acid by the addition of bacteria that under natural conditions it would constitute a major pollution problem.

On the 31st day three drops of CL-1 were added to sample CM-10-10. After an inexplicable delay, an increased acid generation was again noticed. Here, too, the leachate quality was radically affected. Before the addition of the bacteria it had an acidity that ranged from 4.7 to 7.2 mg/l and sulfate contents that averaged about 2500 mg/l. After the bacteria affected the oxidation rate, the acidity



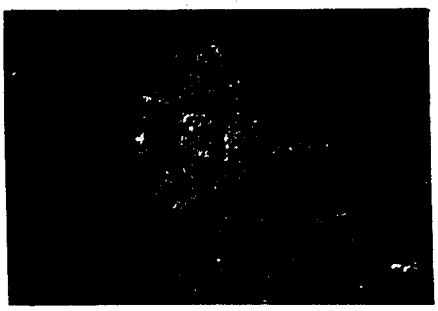
100μ
RM-2-3



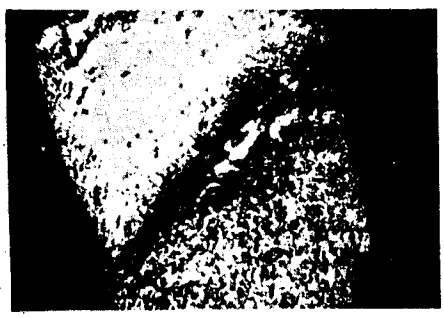
100μ
CM-10-10



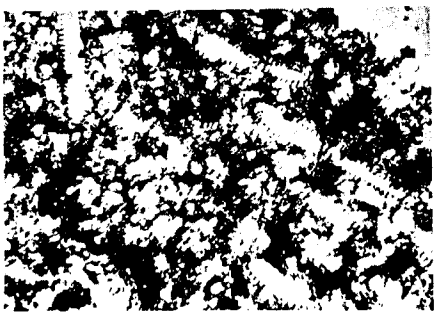
100μ
CM-10-10



100μ
GRC-2



100μ
GRC-2



100μ
Nodule from Mine GRC

PHOTOMICROGRAPHS OF SAMPLES RM-2-3, CM-10-10, GRC-2 AND A NODULE FROM MINE GRC EXHIBITING UNUSUAL PATTERNS

Figure 16

increased to about 25 mg/l and the sulfate content averaged about 17,000 mg/l, (based on leaching 55 grams of sample with 100 ml of water).

An attempt was made to decrease the bacteria's effectiveness by leaching sample CM-10-10 with highly alkaline waters. The intention being to create an alkaline environment which was hostile to the bacteria's existence. On the 61st day waters with an alkalinity of 1500 mg/l (as HCO_3^-) were used to rinse sample CM-10-10. The only effect this had was to partially neutralize the acid waters. After the initial highly alkaline rinse, subsequent rinse waters had alkalinities of 350 mg/l (similar in magnitude to the alkalinities of ground waters in a heavily glaciated area). In effect, these alkaline waters did not inhibit the bacterial action as was noted by the return to the high acid output on the 66th day.

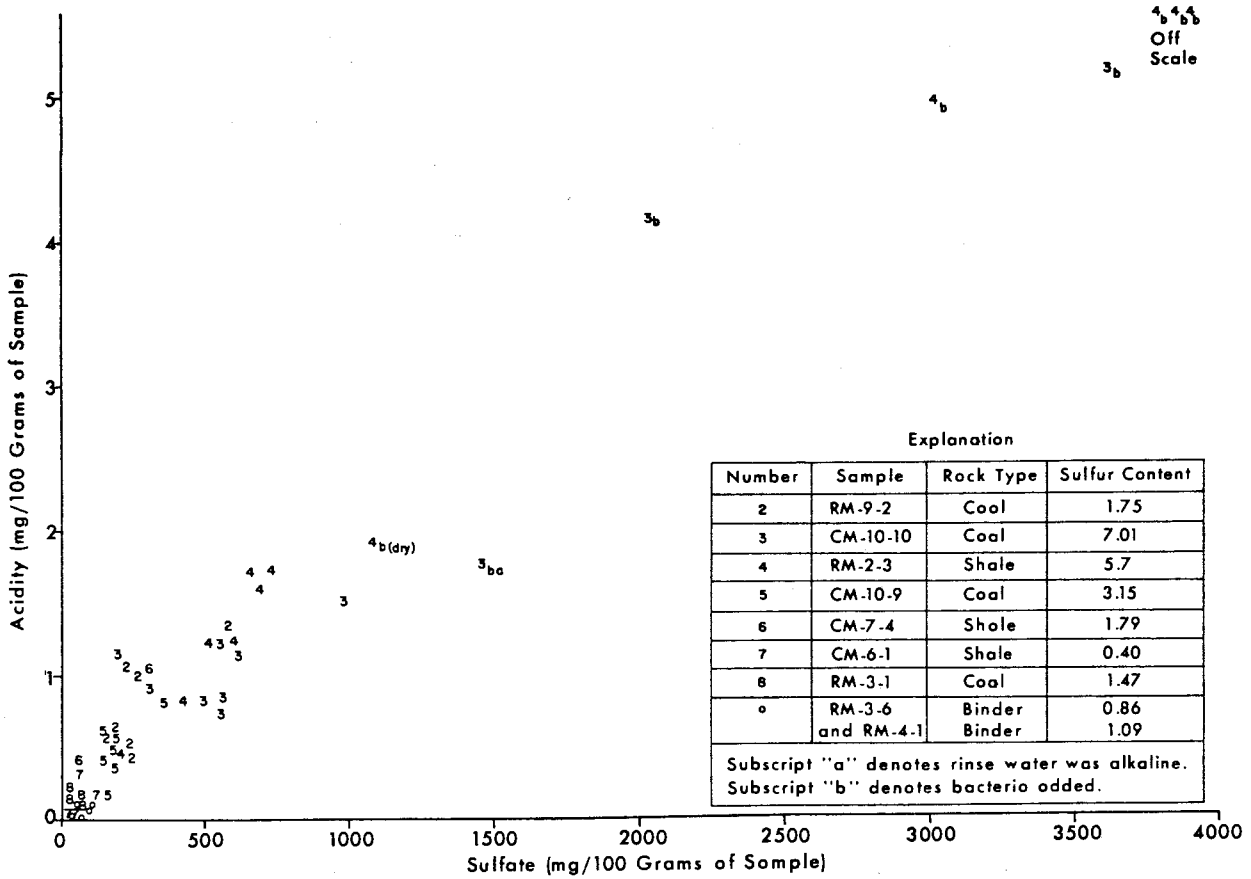
Leachate from the samples containing the bacteria commonly had a deep red color and stained the glassware with iron. Effluents from the other samples commonly were clear or slightly milky and turned deep red when the sample was heated. This suggests that the bacteria do indeed, oxidize their environmental components, thereby releasing additional acidity.

The humidity played an important role in the generation of acid. On the 53rd day sample RM-2-3's air supply was not humidified for the following three days. The affect is noted by the obvious reduction in acid production. Upon humidifying the air supply on the 56th day the acid production returned to the original level.

In Figure 17 all rock samples used in the leaching study are plotted according to the sulfate and acidity yields for each flushing interval. All values in the plot are adjusted to a common base for valid comparisons. There is a tendency for all values of acidities generated by binders to cluster about the lower part of the axis, that is, the low values. This further confirms the contention that binders produce less acid than coal and shales. A linear trend is apparent and expresses the relationship described previously of the sulfate ion to the acidity. The effect of bacteria is readily apparent. All values with a "B" subscript are values obtained from samples that were innoculated with bacteria. It is obvious that bacteria exert more than an incidental affect on the production of acid.

c. Third Leaching Study. The third leaching study was designed to determine how the acid potential of the rocks would be affected by flushing the samples with a water containing calcium ions and alkalinity. This phase of the experiment was prompted, in part, by observations reported by Temple and Koehler (1954) who noted a lack of oxidation of iron disulfide containing calcium and magnesium, and in part, on field observations made by the writer who noted that acid mine drainage was absent in areas abounding with calcium carbonate. The experiment was an attempt to determine if neutralization was the dominant mechanism or if the presence of calcium carbonate inhibited the oxidation of pyrite.

For this test, samples of rocks indigenous to an area high in calcium carbonate content (GRC-2) were included in the leaching



PLOT OF ACIDITY (mg H^+) VERSUS SULFATE CONCENTRATIONS (mg $SO_4^=$) FOR ROCK TYPES USED IN SECOND LEACHING EXPERIMENT

Figure 17

study. The samples used in the third leaching study are listed in Table 6.

Table 6 - Description of Rocks Used in the Third Leaching Study

Sample Number	Rock Type	Percentage Total Sulfur
CM-6-1	Shale	0.51
CM-7-4	6" above coal smut	1.85
CM-10-10	Coal	7.01
RM-2-3	Shale	5.42
RM-9-2	Coal	1.75
GRC-2	6" above coal	3.89

The water used to flush the samples was prepared by filling a gallon jar containing limestone chips (Vanport limestone) with distilled water and bubbling air through the water. The pCO_2 was that found in the atmosphere ($10^{-3.5}$ atm.). The water remained in contact with the limestone for at least three days before a flushing period. Prior to leaching, enough water was poured off to leach all the samples in addition to providing a sample for analysis. This was done to standardize the water used in leaching all the samples. The alkalinity of the water varied from 68.5 to 78 mg/l (as HCO_3^-) and the calcium content varied from 19.5 to 24 mg/l (as Ca^{++}). The pH ranged from 7.6 to 8.2.

Based on the supposition that calcium carbonate inhibits the formation of acid mine drainage, it was anticipated that the rocks from the calcium carbonate rich areas would yield high calcium ion contents at the start of the experiment with a gradual decrease until depleted. This would coincide with a gradual development of acidity

becoming more pronounced as the calcium carbonate in the sample was depleted. To test this hypothesis, GRC-2 was riffled into two parts; one part was leached with distilled water and the other rinsed with limestone water. Hereafter, for the sake of this discussion, the water used in the third leaching experiment that was in contact with limestone chips at a pCO_2 of $10^{-3.5}$ atmospheres is referred to as "limestone water."

The possibility existed that acidity would be produced and neutralized, in which case neutralization would be mistakedly interpreted as an inhibition of acid generation. To ascertain if neutralization took place, the pH and the calcium and alkalinity content of the limestone water was determined before and after the leaching process. This was in addition to the acidity and sulfate determinations made on the effluent. By determining the amount of alkalinity used the degree of neutralization would be indicated.

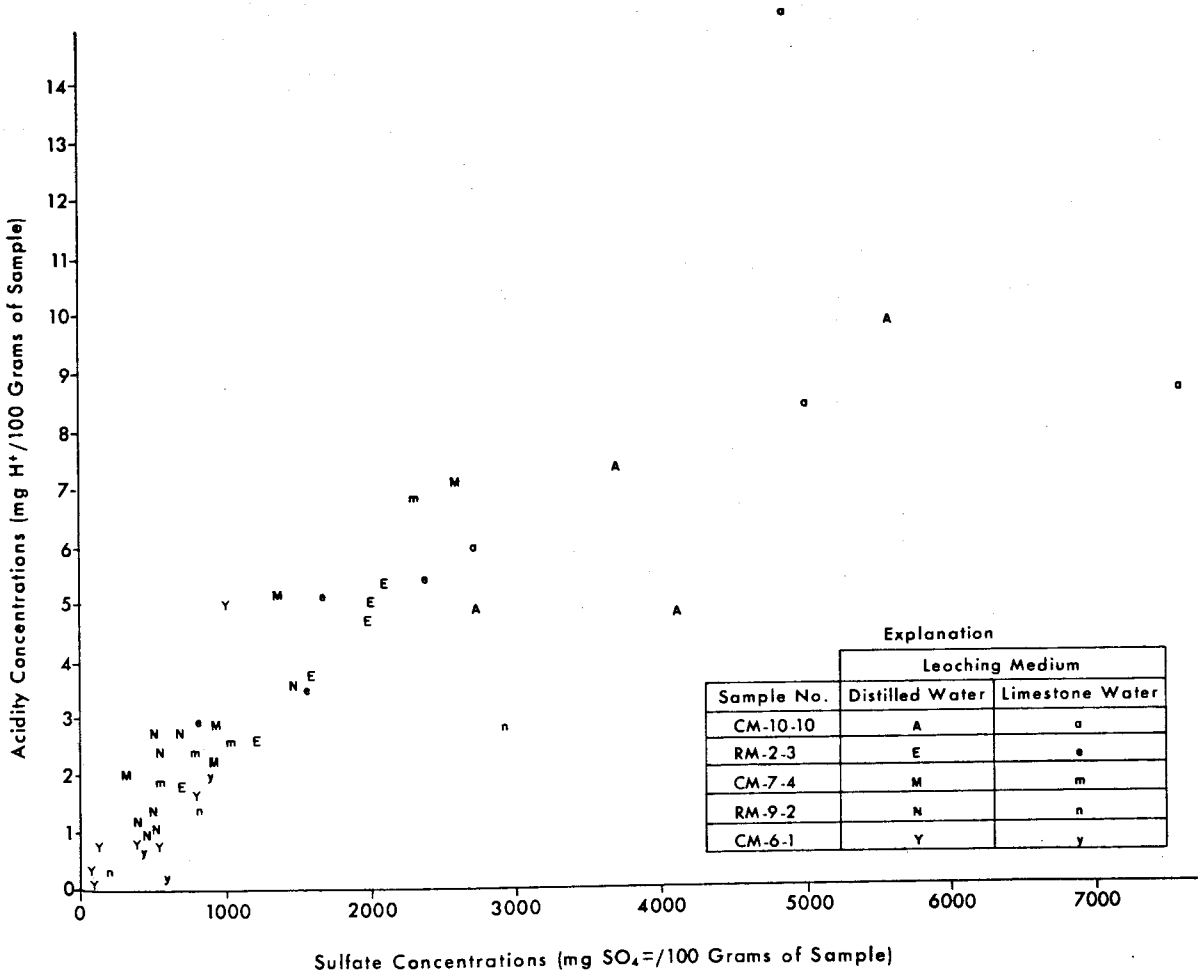
In the event neutralization occurred, with the formation of a calcium sulfate precipitate, a decrease in the sulfate content would occur. In this case, a low sulfate content due to precipitation may be mistakedly interpreted as an inhibition of acid production. To avoid this mistake, the calcium ion was measured before and after the leaching process. Since the precipitate required calcium cation, a measurement of calcium ion before and after leaching would relate how much calcium was removed from solution and hence, how much sulfate was precipitated.

At the start of this test all rock samples were rinsed (with the exception of sample GRC-2 used with distilled water) in limestone water. The results of this experiment are shown in Figure 18.

Discussion of Results. In general the limestone water used in the third leaching study did not appear to affect the generation of acidity. This is apparent from the trends in acid generation seen in Figure 18, and is further demonstrated by Figure 19. Figure 19 is a replicate of Figure 17 and includes plots of sulfate and acidity values obtained from the third leaching experiment.

If neutralization took place in the third leaching study, the plots from this experiment should cluster in a high sulfate, low acidity range in Figure 19. If acid waters were not created (indicating an inhibitory action), then the points should cluster in a low sulfate, low acid range. Instead, the points from the second and third leaching studies intermingle at all ranges. This suggests that water flowing over limestone under a partial pressure of carbon dioxide found in the atmosphere does not develop enough alkalinity to affect acid mine drainage reactions. Notice in Figure 18 that sample GRC-2 rinsed with distilled water gave identical acidities as sample GRC-2 rinsed with limestone water.

When it became apparent during the first three weeks of the third leaching study that the calcium ion content of the water had no affect on the acid mine drainage mechanism, a test was included to determine what affect alkalinity would have on the reaction. Aside from the obvious neutralizing capacity, this was an attempt to determine if an



PLOT OF SULFATE VERSUS ACIDITY CONCENTRATIONS OF LEACHATES OF THE SECOND AND THIRD LEACHING EXPERIMENT

Figure 19

inhibitory affect could be ascribed to the highly alkaline waters. On the 16th day samples CM-10-10 and CM-7-4 were rinsed with highly alkaline waters. These alkaline waters had a bicarbonate concentration of 1500 mg/l. After a preliminary high alkaline rinse, the samples were subsequently rinsed with limestone water that contained a solution of sodium bicarbonate that increased the alkalinity to 350 mg/l.

With the addition of alkalinity, a notable reduction in the sulfate content of the effluents of samples CM-10-10 and CM-7-4 resulted. The calcium ion concentration of the water used in the leaching was less than that of the leachate which precludes the possibility of calcium sulfate precipitation. The diminution of acidity with an attendent reduction in sulfate suggests that alkaline waters can inhibit acid generation in moderate acid producing materials and decrease the acid generation in strong acid producing materials.

On the 28th day samples GRC-2 (both samples), CM-7-4, CM-10-10 and RM-9-2 gave anomalously high acidities. The leachates had the characteristic red color noted in previous experiments to be associated with bacterial oxidation. Samples of the effluent were examined for bacteria by Bill Eberhardt of the Department of Civil Engineering of The Pennsylvania State University who noted bacteria to be present, but pointed out that many strains of bacteria aside from the *Thiobacillus* and *Ferrobacillus* could exist at a low pH. Attempts to stain the bacteria for positive identification were not successful; although the bacteria had the shape and size of *Ferrobacillus* and *Thiobacillus*.

The writer strongly suspects that bacterial contamination had occurred as suggested by the leachate appearance and anomalously high acidities.

RM-2-3, however, was intentionally innoculated with bacteria on the 16th day to determine what affect calcium ion had on bacterial catalysis. The trend of acid production for RM-2-3 which shows a marked increase in acidity content on the 16th day demonstrates that calcium ion in the waters has no affect on impeding bacterial action. On the 21st day an attempt was made to destroy the bacteria by rinsing the sample with a highly alkaline solution (distilled water containing 1500 mg/l bicarbonate), thereafter rinsing the sample with distilled water containing 350 mg/l bicarbonate, to test what affect alkalinity without the calcium ion had on acid generation. The graph and leachate analyses show that the alkalinity initially impeded bacterial action, but decreased in effectiveness as time went on. On the 28th day, limestone water was used instead of distilled water, in conjunction with the alkalinity (350 mg/l), with no noticeable affect.

d. Summary of Results From All Three Leaching Tests. In an attempt to assign a rank of acid potential to rocks of varying sulfur content, three leaching tests were performed. The first test was a pilot study to determine the mechanics of operation and optimum flushing intervals, sample size and granularity. It showed a necessity for flushing all samples at the same time to maintain similar oxidation periods in order to make valid comparisons of acid potentials. This first experiment also demonstrated that fine particles cemented together

and impeded the oxidation of the enclosed particles. The 1-2 mm fraction of sieved samples was chosen as the optimum size that was representative of the field sample, retained a minimum of water when drained and yet did not cement together or pour off with the effluent.

The second leaching test was intended to relate the acid potential of various rocks to their sulfur contents. The samples used in this study were analyzed for pyritic sulfur, total sulfur and calcium carbonate content. Portions of the sample were molded in plastic pellets and used for microscopic examination. The second leaching experiment demonstrated acid generation to increase with temperature. Anomalously high acidities existed, where some samples yielded more acid than samples having a higher pyritic sulfur content. As the mode of iron disulfide in all samples was pyrite, marcasite was not responsible for the high acidities. The calcium carbonate content seemed insignificant. The variation in acid generation was closely related to the variation in grain size as the photomicrographs of the samples showed. Hence, acid generation cannot be ascribed only to the pyritic sulfur content, but must consider the grain size as well. The amount of acid produced increased with finer pyrite grain size.

Permeabilities apparently are important as evidenced by the fact that binders produced much less acid than coals and shales all other things apparently being the same.

Bacteria, assumed to be present in samples of acid mine drainage, were added to some samples. Rocks with finer grained pyrite were affected more radically than the coarse grained pyrite, while rocks

containing (0.13 to 0.42 percent) calcium carbonate apparently were unaffected. Attempts to permanently decrease the bacteria's effectiveness by rinsing the samples with alkaline water were not successful.

The third leaching study was designed to determine if water in contact with limestone had any affect on acid generation. The rinse water was analyzed for alkalinity and calcium content, and the leachate, in addition to these two, was analyzed for acidity and sulfate. This was done to determine if neutralization took place or if the oxidation reaction was impeded. The third leaching study showed water in contact with limestone to have no affect on acid generation. However, high alkaline waters, when used to rinse the samples, impeded acid production and temporarily inhibited bacterial reactions. It was suspected that several samples were inadvertently contaminated by the acid bacteria causing anomalously high acidities and demonstrating the ineffectiveness of water in contact with limestone to impede bacterial contamination.

B. Aqueous Geochemistry

Water samples were collected and analyzed from streams, domestic wells, seepages from mine shafts and mine pools in the Clearfield and Glen Richey areas. Although not evident at first, water qualities differed for the two areas. Comparison of the water qualities initially was difficult because of an uncertainty in what concentrations and types of ionic species should be ascribed to a particular aquifer of

given composition. In order to more readily discern the water quality variations thought to exist, water sampling was extended to areas known to contain very alkaline and very acid waters for end member comparisons. Alkaline water samples were collected from strip mines in the area of Mercer, Pennsylvania. Highly acid mine drainages were collected from the Krebs mine (Plate IV) and a strip mine southwest of Clarion, Pennsylvania. After the extremes of water quality were established, the subtle variations of the water characteristics of the Clearfield and Glen Richey areas became obvious. Thereafter, water compositions could be grouped according to generalized water characteristics associated with certain geologic terrains.

The following discussion will first demonstrate the apparent semblance of water qualities of the Glen Richey and Clearfield areas and relate how analyses of water samples from other areas exhibiting quality extremes bore out the differences that actually existed. This is followed by a discussion of the groups of water qualities found in each area with emphasis on the characteristics relevant to this study. The examples used may be biased by the writer's experiences and impressions of what is taking place chemically in the field. Because water qualities are transitional in nature, no precise division can be used to separate quality groups from each other. Further, because of mine drainage pollution some samples may not be representative of the geologic environment. For these reasons the writer may use examples which he believed are exemplary of the point in discussion. This approach, although idealistic, will illustrate the various chemical components in the

discussion and treat them as entities. After these chemical components have been identified and defined, they can be segregated from samples which are transitive in nature or comprised as mixtures of the components.

In the following tables, only the data pertinent to the discussion are listed. For additional information concerning the date, location of sample, etc., refer to Appendix C.

1. Water Qualities from the Clearfield Area

a. Ground water. The samples of ground water obtained from the virgin areas (water not influenced by mining) of the Clearfield area had compositions listed in Table 7.

Table 7 - Analyses of Ground Water from the Unmined Portions of the Clearfield Study Area, Pennsylvania

Sample	Source	Temp °C	pH	Specific Resistance (ohms)	HCO_3^-	H^+	$SO_4^=$	Ca^{++}
					(all expressed in mg/l)			
CH-12	Dug Well	11	5.3	25,000	5	0	0	0
CH-14	Dug Well	10.5	5.44	24,000	6	0	0	0
CH-16	Spring	9	4.85	28,000	6	0	0	0
CH-17	Dug Well	10	5.60	27,000	5	0	0	0

Of interest is the acidic pH, in spite of the fact that the samples contain no potential free acidity. The alkalinity is very low and for all practical purposes has no neutralizing capacity. The complete lack of calcium, sulfate and hydrogen ions is corroborated by the extremely high specific resistance. The value of the resistance is so high, indicating an extremely low dissolved solids content, as to classify the water as "excellent quality raw water" (Table 1; Industrial Instruments, 1965).

Samples of ground waters obtained from areas in and about the strip mines had chemical compositions listed in Table 8.

Table 8 - Analyses of Ground Water in and about the Strip Mined Areas of the Clearfield Area, Pennsylvania

Shallow Wells (less than 12 feet deep)

Sample	Temp. °C	pH	Specific Resistance (ohms)	HCO_3^- (all expressed in mg/l)	H^+	$SO_4^=$	Ca^{++}	Relation to 1480' A.S.L.
CH-5A	10	5.30	17,000	4	0	14	2	Level
CH-18	9	4.80	4,300	3	0.08	72	0	Above
CH-20	14	6.20	8,000	21	0	23	6	Above
CH-22	11	5.48	6,700	8	0	33	7	Above
Deep Wells (deeper than 12 feet)								
CH-4A	-	6.70	5,800	84	0	0	10	Below
CH-6	15	6.75	4,500	100	0	17	5	Below
CH-15	18	5.60	5,600	12	0	27	0	Above
CH-21	14	6.50	6,000	38	0	23	11	Level
CH-23	13	7.00	5,200	50	0	33	11	Below
CH-24	14	6.50	2,000	32	0	53	38	Level
CH-9A (Deep)	-	6.95	3,400	170	0	0	2	Below
CH-9B (Dug)	10	5.20	3,400	4	0	85	12	Above

The analyses show ranges in all components that seemingly overlap and vary too much to be isolated for grouping purposes. For example, the alkalinities vary from 3 to 100 mg/l and the calcium ion content varies from 0-38 mg/l. These extreme values were expected to occur between areas and not within one area.

This apparent dilemma in the variability of water qualities was resolved by water samples collected from CH-9. At this site, a deep well and a shallow well were sampled. The deep well had 25 feet

of casing that effectively sealed off the upper strata penetrated by the shallow well; thereby making it possible to compare waters of shallow and deep circulations.

The data suggest that calcareous material must be present at depth in the area from which the water samples were collected. This is the only plausible explanation for the high alkalinity observed in the deep well and the absence or low alkalinity noted in the shallow well. The lack of a high calcium ion concentration that should accompany a high alkalinity at the observed pH (see Figure 7) is explained by a natural cation exchange process occurring within the ground water regimen. Such exchange processes can and do occur in nature (Foster, 1950). This is further supported by the low specific resistance that indicates an abundance of ions other than those analyzed.

The Stratigraphic Profile of Roadcut CM-5 (Figure 28) shows the Johnstown limestone to be present at a depth of 24 feet. The elevation of the top of the limestone is 1480 feet above sea level. Assuming for practical purposes a horizontal dip for all strata in the area, then the extrapolation of the top of the limestone bed or a calcareous horizon into the area of CH-9 would intercept the deep well CH-9A, but not the shallow well CH-9B. Further, since the deep well is cased 25 feet into the strata, it will obtain waters of deep circulation which would be affected by the limestone or at least a calcareous horizon stratigraphically equivalent with the Johnstown limestone. The shallow well on the other hand will draw water only from the shallow

horizons, which was not in contact with the calcareous strata. This is suggested by the sulfate content of the water samples, which in turn, implies that a significant lateral component of flow must be taking precedent over a vertical component. This is based on the following argument. The source of sulfate for CH-9B is a strip mine located topographically higher than the elevation of the well (Plate III). The water table map (Figure 5) indicates that ground water flow should be from the strip mine to the area of the wells. If the flow line had a deep circulation pattern, then the deep well should intercept this pattern and a water sample from this well should show at least a trace of sulfate. The fact that it does not, supports the contention that the lateral permeability greatly exceeds the vertical permeability thereby causing the ground water to have a prominent lateral translation which would be intercepted by the shallow well and not the deep well. As a less attractive alternative, contaminated water has not yet reached the deeper well.

The analyses of Wells CH-9A and CH-9B are not sufficient in themselves to draw any conclusions for the area as a whole. However, they do suggest that there is present within the Clearfield area calcareous deposits capable of neutralizing dilute acid waters and that the ground water movement in the area must have a significant lateral component.

With this cognition, and assigning 1480 feet above sea level as an approximate horizon above which calcium carbonate is not present, then the origin of the water qualities in Table 8 can be understood.

The premise is, wells drawing water above the 1480 foot elevation should be less alkaline than wells drawing water below this horizon. However, one more consideration must be interjected. Since the highwall of mine CM-6 contains calcareous material, then calcium ion must begin to appear at higher elevations. The alkalinity will not appear because of the acid conditions existing at the mine. Calcium ion may, therefore, appear in some of the shallow wells. This may happen if the calcium ion is released in the higher elevations, moves predominantly laterally in the zone of the bedrock aquifer until it intercepts the regolith aquifer. The regolith is the layer of incoherent rock material, whatever its origin, that rests on the bedrock, and as such will permit water to follow the topography and be intercepted by the shallow wells. The sulfate ion, for the same reason, should be found most abundantly in the shallow wells; except where the deep wells are not cased and permit vertical leakage.

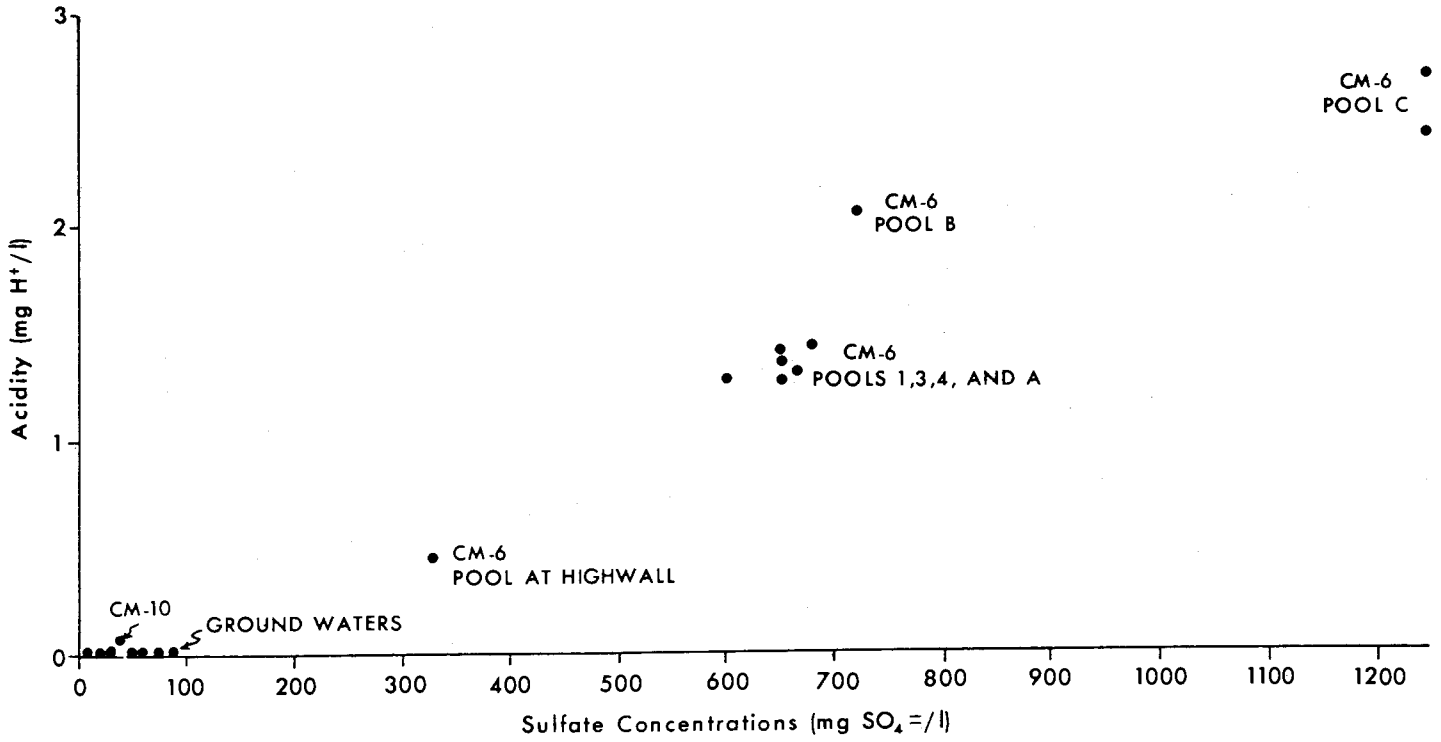
The wells above, below and on level with the 1480 foot elevation are shown in Table 8 in the appropriate column. There is general agreement to the aforementioned hypothesis.

b. Mine Drainages. The magnitude of the alkalinity found in ground waters should cause the strip mines in the Clearfield area to discharge a moderately acid mine drainage. Analyses of the mine drainages from strip mines CM-6 and CM-10 in Table 9 showed this to be the case. For exact locations of pools in mine CM-6 see Figure 20.

Table 9 - Selected Analyses of Acid Mine Drainages from Mines CM-6 and CM-10 in the Clearfield Study Area, Pennsylvania

Sample	Source	Temp. °C	pH	Specific Resistance (ohms)	HCO_3^-	H^+	$SO_4^=$	Ca^{++}
					(all expressed in mg/l)			
CM-6	Pool by wall	22	3.8	1,800	0	0.45	330	46
CM-6	Pool #3	19	3.50	1,100	0	1.4	665	76
CM-6	Pool B	16.5	3.5	1,040	0	2.1	720	76
CM-6	Pool C	15	3.65	580	0	2.70	1270	153
CM-10	Pool	15.5	4.1	8,400	0	0.15	40	5

Generally the acidities were lower than some of the acidity values of acid mine drainage reported in the literature. Acidity values common to acid mine drainage are about 20 mg/l with some values being as high as 50 mg/l (as H^+). Of concern was the high calcium content of many of the samples. The analyses of the ground waters had shown that alkalinity was generated at depth in the area and although alkalinity was not indicated in the shallow waters, calcium carbonate deposits were noted in the highwall of the mine that could potentially create alkaline waters and in part neutralize the acidity. To determine if this was the case the sulfate concentrations were plotted against the acidity values for all samples collected in the Clearfield area. As Figure 21 shows, a quasi-linear trend is apparent similar to the one obtained from the plot of the sulfate and acidity concentrations of the effluents from the leaching studies. If neutralization was taking place, the points should plot in the high sulfate low acidity range. The absence of points in this region indicates that if neutralization were taking place it was not significantly reducing the acidity of the mine drainages from these mines.



PLOT OF SULFATE CONCENTRATIONS VERSUS ACIDITIES OF ALL WATER SAMPLES COLLECTED FROM THE CLEARFIELD AREA, PENNSYLVANIA

Figure 21

2. Water Qualities of the Glen Richey Area

To further evaluate the anomalously low acidities of the Clearfield area a comparison was made with mine drainages and ground waters from the Glen Richey area. Since the areas had comparable ranges in sulfur concentrations, it was of particular interest to note what apparent differences existed in water qualities.

All drainages from mines sampled in the Glen Richey area were non-acid. Selected analyses are represented in Table 10.

Table 10 - Selected analyses of Mine Drainages and Ground Waters of the Glen Richey Area, Pennsylvania

Sample	Source	Temp. °C	pH	Specific Resistance (ohms)	HCO_3^-	H^+	$SO_4^=$	Ca^{++}
					(all expressed in mg/l)			
Ground Waters								
RM-7	Ground water	13.5	8.3	2,800	75	0	0	50
RM-5B	Ground water	8.5	6.55	8,600	9	0	0	14
RM-5D	Spring	10	7.0	11,000	27	0	less 10	12
Mine Drainages								
RM-1	Shaft drainage	-	7.9	4,500	71	0	0	33
RM-5	Air Shaft Drainage	8	7.25	7,000	25	0	28	19
RM-7	Shaft/Strip Drainage	11.5	7.5	1,950	123	0	0	66
RM-17	Pool in New Mine	-	7.80	4,700	36	0	0	30

A comparison of mine drainages from the Glen Richey and the Clearfield areas shows obvious differences. Mine drainages from the Clearfield area, although not highly acidic, contain measurable acidities;

those from the Glen Richey area have none. Further, the sulfate contents of the two areas are radically different. In the mine drainages from the Clearfield area, the sulfate concentrations plotted against the acidities demonstrate a trend similar to the one exhibited by the leachates of the leaching study; even though the acidity values are lower than those reported in the literature. Hence by this relationship, of low sulfate to low acidity, the mine drainage of the Clearfield area stems from the mild production of acid in this area coupled with the possibility of neutralization. The latter possibility is suggested by the high calcium ion concentration of some drainages from CM-6 and the presence of calcareous material in the highwall of mines CM-6 and CM-7.

However, the lack of sulfate anion in the mine drainages of the strip mines and deep mines, old and new, of the Glen Richey area is perplexing. Aside from the overlap of total sulfur contents of the two areas determined from the detailed samples previously discussed in this report, extensive pyrite coatings on coals were noted in the Glen Richey strip mines. Yet, sulfate, except for trace amounts, is mostly absent. With the exception of the pHs, the mine bleeds of the Glen Richey area are comparable to the ground waters (shallow and deep) of the Clearfield area.

Thus the facility to readily compare and interpret water compositions of the two areas was shown to be non-existant. It became apparent that the original intention of choosing two areas with extremes of paleoenvironments to obtain water qualities of varying compositions

was not readily met in the areas chosen for study. The Clearfield area, although underlain mostly by Lower-Middle Kittanning strata, yielded waters representative of a transitional paleoenvironment and not those of a marine paleoenvironment. This is not to mean that strata of a marine paleoenvironment were not present in the Clearfield area, rather conditions were such that high acid waters were not produced.

There was a further complication in that the mine drainages of the Glen Richey area resembled too closely the ground waters of the Clearfield area. The lack of obvious quality differences prevents comparisons from being made and hinders the interpretation of geochemical interactions.

To obtain the "end members" or quality extremes, extremely acid and alkaline waters were collected and analyzed to establish what variations and concentrations of ionic species could be expected. Once these extremes were established, the behavior of water quality parameters representative of these extremes became apparent. Henceforth, it was possible to identify the presence of alkalinity or acidity, in samples transitional in nature or comprised of a mixture of various components.

3. Acid Mine Drainages From Strip Mines

a. Krebs Mine. The Krebs mine is located approximately two miles due east of the northern portion of the Glen Richey area (Plate IV). The major coal seam mined is the Lower Clarion and has a total sulfur content ranging from 0.56 to 12.4 (Reidenouer et al, 1967). Water samples from this mine had compositions represented in Table 11.

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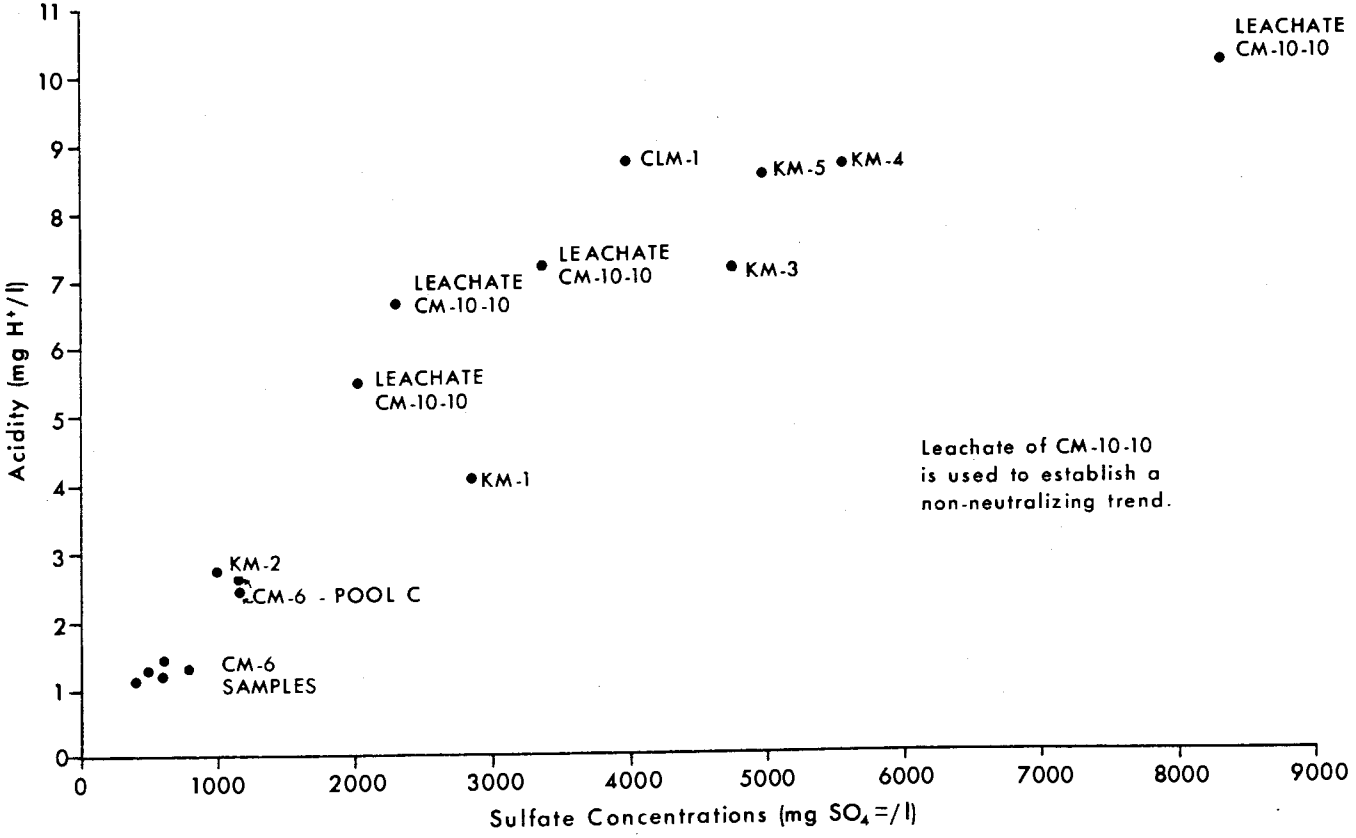
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Table 11 - Selected Analyses of Acid Mine Drainage Collected from the Krebs Mine, Pennsylvania

Sample	Source	Temp. °C	pH	Specific Resistance (ohms)	HCO_3^-	H^+	$SO_4^=$	Ca^{++}
					(all expressed in mg/l)			
KM-1	SE Highwall	12	3.15	480	0	4.05	2860	108
KM-3	West wall	13	4.15	300	0	7.1	4800	360
KM-4	East wall	17	3.95	360	0	8.65	5660	198
KM-5	Stream from mine	-	2.80	325	0	8.5	5000	265

Note that KM-1, although having a lower pH, has a lower potential free acidity concentration than KM-3; showing that pH readings alone to determine acidities can be misleading. The sulfate and acidity concentrations plotted in Figure 22 now extend the graph into a region more typical of acid mine drainage concentrations reported in the literature. Still KM-3 has an abnormally high calcium ion content that is probably not representative of neutralization. This is based on Figure 22 which is a plot of all mine drainages sampled in this study and high acid leachate values. The plots of leachate CM-10-10 obtained from the leaching study, more or less establish the trend of the graph in the upper ranges. In this leachate, neutralization was definitely non-existant because calcium carbonate was not present in the sample used in the leaching study. Since the analyses of all high calcium containing KM samples plot in line with this trend established by CM-10-10, rather than falling below it, the calcium cation must arise from other than the calcium-bicarbonate system.



PLOT OF SULFATE CONCENTRATIONS VERSUS ACIDITIES OF ACID MINE DRAINAGES

Figure 22

The calcium and sulfate ion concentrations for samples KM-3 and KM-4 exceed the maximum theoretical concentrations limited by the solubility products of anhydrite and gypsum with unit activities. The products of the concentrations of calcium and sulfate ions for KM-3 and KM-4, in moles/liter, are $4.5X10^{-4}$ and $2.92X10^{-4}$, respectively. The solubility product for anhydrite is $6.1X10^{-5}$ (Lange, 1961, p. 1088); and for gypsum as $CaSO_4 \cdot 2H_2O$ is $2.0X10^{-5}$ as calculated from equation (11) and using a Free Energy of Formation of -430.14 KCal/gFW (S. P. Clark, 1966, p. 449).

The equation used is,

$$dF = -RT \ln K \qquad (11)$$

where dF is the change in the Free Energy of Formation; R is the Gas constant and T is the temperature in degrees Kelvin.

The data show that the calcium and sulfate concentrations far exceed the solubility products and that, despite this, precipitation does not occur. This is best explained by the activity coefficients not being unity as it was assumed in the calculations. The extremely low resistance suggests that the samples do contain a strong ionic concentration which must reduce the activity coefficients considerably to permit the observed concentrations of calcium and sulfate ions to remain in solution without precipitating.

Further, these analyses suggest that the calcium cation, hitherto connoted with a neutralizing medium, may in some circumstances, such as in the case of the KM samples, assume an apparently passive role. As such, the source of the calcium cation may arise from the dissolution

of calcium carbonate by the acid waters. In this case the bicarbonate anion is not formed.

b. Mine CL-1. A strip mine southwest of Clarion, Pennsylvania mining the Clarion coal was also sampled (Figure 23). Samples were taken from the mine pool and had a pH of 2.35, acidity of 8.7 mg/l, a sulfate concentration of 4000 mg/l and a calcium ion content of 350 mg/l. This sample is also plotted in Figure 22 and falls in trend with the other samples of acid mine drainage. The product of the calcium and sulfate ion concentrations at unit activity also exceeds the solubility product discussed above. The product of these values is $3.64X\ 10^{-4}$. Here too the activities must be reduced considerably to accommodate the excessive ionic concentrations.

In summary, the analyses of the mine drainages collected from the Krebs mine and mine CL-1, succinctly revealed a relation between the sulfate concentrations and acidities which can be used to estimate original acidities in samples. The data also show that under certain circumstances the calcium ion could not be related to a neutralizing mechanism. The concentrations of calcium and sulfate ion exceed the maximum concentrations calculated from solubility products of gypsum and anhydrite at 10° C. This is explained by the activities not equal to unity and corresponds to a strong ionic concentration. This is substantiated by the low specific resistance values exhibited by the samples.

4. Water Qualities of the Mercer Area

With the extreme of water quality (relative to this study)



PORTION OF CLARION QUADRANGLE (15')
SHOWING THE LOCATION OF MINE CL-1

Figure 23

established in the acid range, it was desirous to determine the characteristics of a highly alkaline ground water and how it would affect acid mine drainage. It was recalled that in the initial phase of this study (summer, 1965) the area near Mercer, Pennsylvania was relatively free of acid mine drainage. It was here that water samples were collected to establish the extremes of water quality in the alkaline range.

Strip mines in this area mine the Lower Clarion coal which in this region is about 30 inches thick and contains numerous nodular bands of pyrite along the top of the seam. Further, the joints in the coal are extensively coated by tabular grains of pyrite. The strata above the coal include the Vanport limestone, which may attain a thickness of 20 feet. Extensive glacial deposits are present and often glacial channels about 25 feet deep, filled with glacial material, are exposed in the highwall.

Five strip mines were visited; rock samples were collected from four of the mines and water samples from three of them. The analyses of the water samples are represented in Table 12.

Table 12 - Selected Water Analyses of the Mercer Area, Pennsylvania

Sample	Source	Temp. °C	pH	HCO_3^-	H^+	$SO_4^=$	Ca^{++}
				(all expressed in mg/l)			
GRM-1	Highwall bleed	10.5	7.65	112	0	125	50
GRM-3	Pool	-	7.45	170	0	100	68
HRM-2	Pool in mine	10.5	7.1	240	0	60	81
SLM-1	Pool in mine	12	7.05	224	0	140	98
SLM-2	Pool in mine	11	6.45	152	0	740	117
SLM-3	Pool in talus	10.8	6.35	382	0	150	290
SLM-4	Pool in talus	10.8	6.6	388	0	140	300

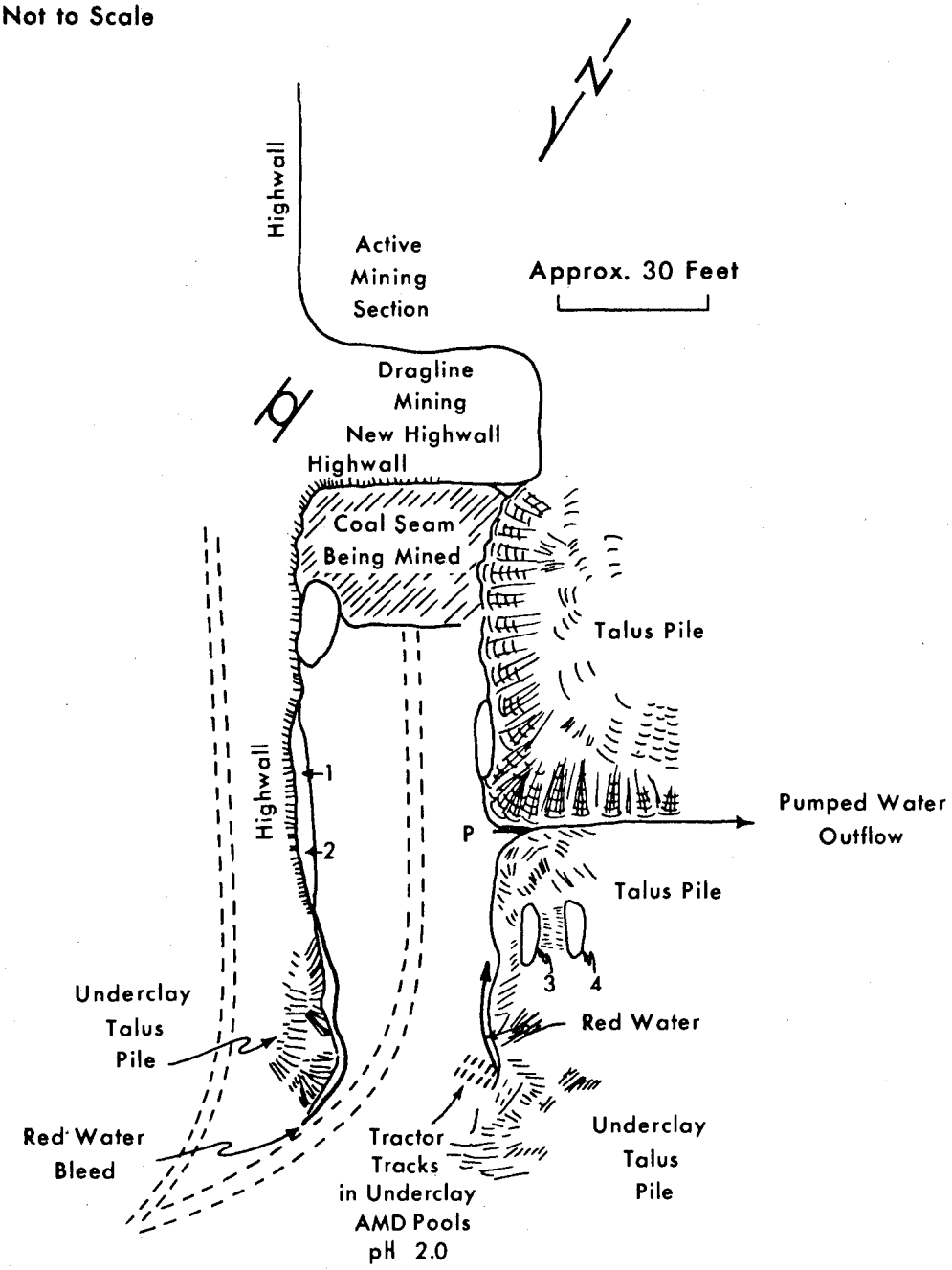
Water sample GRM-1 represents a ground water bleed from a clay zone at the base of the Vanport limestone in the highwall of the mine. The high sulfate results from the high sulfurous refuse piled on the land surface above the highwall. This was the only sample of ground water obtained in the area. However, numerous analyses of ground water in the area by Poth (1963) corroborate the trends of water qualities which will be discussed.

Of interest is the extensive alkalinity generated by the strata in this area. Samples SLM-3 and SLM-4 were collected from a spring emanating from a talus pile. The alkalinity of these samples is capable of neutralizing about 6 mg/l of acidity; this assumes a mole to mole reaction and neglects the dilution factor. Thus, there exists in this area a considerable neutralizing capacity.

The sulfate concentrations measured in this study suggest that neutralization is taking place. On Figure 24 it is noted that small pools of water in the tractor tracks were acidic. Yet, the major pools

1 Water Sampling Point

Not to Scale



PLAN VIEW OF MINE SLR-1
SHOWING WATER SAMPLING POINTS

Figure 24

by the highwall contained no acidity. Sample SLM-2 is used as evidence that neutralization is taking place. From Figure 21 the acidity concentration for a sulfate content of 740 mg/l should be in excess of 1.5 mg/l. The relatively lower alkalinity of sample SLM-2 coupled with a high sulfate content established the neutralization mechanism. The source of sulfate concentration of this magnitude can only be associated with acid mine drainage.

With the exception of SLM-2, the activities of the calcium and bicarbonate concentrations and pH of the water samples in Table 12 show general agreement to the equilibrium relations illustrated in Figure 7.

5. Summary of Aqueous Geochemical Data

The shallow ground waters in the virgin portions of the Clearfield area contain very little dissolved solids and practically no alkalinity. The pHs of the samples were acidic ranging from 4.85 to 5.6. Although acidic, the samples had no potential free acidity showing that the low pH values were due to the dissolved carbon dioxide content.

The ground waters in and about the strip mines of the Clearfield area had lower specific resistance values than those in the virgin areas indicating a greater dissolved solids content; hence showing that more chemical activity was taking place in these areas. The shallow wells had higher sulfate contents and less alkalinity than the deeper wells. Where calcareous material was present, the ground waters had noticeable amounts of alkalinity. Although the alkalinity is genetically related to the calcium carbonate-bicarbonate reaction, it cannot be

correlated with the calcium ion content. This may be due to a natural ion-exchange mechanism; possibly exchanging sodium for calcium.

A shallow flow system, hydraulically essentially separate from the deeper flow system, must be present in the area in order to transmit the sulfate ion from the mines and only affect the shallow wells. Samples from deep wells cased below this horizon show only traces of sulfate ion. This furthur suggests that the ground water reservoir of this area must be horizontally stratified.

The mine drainages from this area were not as acidic as some "common" acid mine drainages reported in the literature. Because some calcium carbonate was noted to be present in the highwall of the strip mine, it was suspected that partial neutralization was taking place. However, a plot of sulfate versus acidity showed this not to be true. The alternate explanation is that the Clearfield area, although producing acid mine drainage, produces a comparatively mildly acidic mine drainage.

In an attempt to place these lower acidities in their proper prospective a comparison was made of mine drainages from the Clearfield and Glen Richey areas. However, it was found that these drainages had very little in common. The drainages of the Glen Richey area had practically no sulfate, contained varying degrees of alkalinity and no acidity, and with the exception of the pHs, resembled the ground waters of the Clearfield area.

It became apparent that the areas chosen did not yield drainages anticipated to be characteristic of strata representative of extremes

of paleoenvironments. In order to better evaluate the water characteristics, extremes of water quality were sought outside of the initial areas of study. Highly acidic and very alkaline waters demonstrated ionic compositions of such diverse characteristics that comparisons, and hence, interpretations were facilitated.

The highly acidic waters also showed a sulfate-acidity relationship similar to the one derived from the plot of the lechates of the leaching study. These samples also showed the calcium ion to act in a passive role; possibly derived from acid waters dissolving the calcium carbonate in an acidic environment thereby releasing calcium ions without releasing the bicarbonate anion.

The alkaline waters of the Mercer area showed a remarkable capacity to neutralize acidity and examples of natural neutralization were discovered.

C. Areal Characteristics Related to Water Quality Parameters

The following sections will relate all the preceeding data in an integrated and comprehensive manner. The geology will be discussed with reference to stratigraphic profiles of the areas, the total sulfur analyses and the geologic maps. In turn, the data obtained from the leaching studies will be used to evaluate the various factors affecting acid mine drainage production, such as bacteria, total sulfur contents, grain size of the pyrite and alkalinity, to predict the quality of water expected from certain geologic environments. The analyses of

water sampled in the areas will either confirm the prediction or contradict the expected quality. If the predictions of water quality, as determined by the geology and results of the leaching studies, are not substantiated by water quality analyses, then secondary interactions very likely occurring in the field are offered as explanations.

1. Areas of High Acid Mine Draniage

The Krebs mine and mine CL-1 both mine the Lower Clarion coal which is representative of a coal from strata of a marine paleoenvironment. The total sulfur contents for the Krebs mine used in this report were obtained from data found in the work by Reidenouer et al, (1967). In their work only the coal was sampled. The total sulfur contents had a mean of 2.24%, but a standard deviation of 10.23 showing an extreme variability in sulfur content.

At mine CL-1 only water samples were collected. This mine was used to establish an extreme of water quality; hence rocks were not collected at this site.

As the water quality analyses showed, these mines yield highly acidic waters. The correspondingly high sulfate concentrations suggest that the pyrite present in the strata readily decomposes through oxidation to hydrous ferrous sulfates, which in turn, hydrolyze to produce the acidity and the high sulfate content. However, the presence of high calcium concentrations implies that neutralization may be taking place. As Figure 22 shows, however, the water analyses are on trend with other sulfate-acidity analyses of acid mine drainage; concluding that if neutralization is taking place, it is not significantly abating

the acidity. To account for the high calcium contents with no apparent neutralization, it is postulated that at these mines the generation of acidity hydraulically antecedes the calcareous materials and that the calcium carbonate is readily dissolved by the acidic waters. In this geochemical environment, bicarbonate ion is not generated; the carbonate ion released from the calcareous material is converted to carbonic acid.

The ionic strength of these drainages is very high as shown by the low specific resistances. At these ionic strengths the activities of the components are reduced considerably, thereby enabling high concentrations of calcium and sulfate ions to co-exist without precipitating.

2. Areas of Acid Abatement Through Neutralization

In the strip mines of the Mercer area the Lower Clarion coal is representative of coal from strata associated with a marine paleoenvironment. The coal was noted to be extremely pyritiferrous, capped in places by one to three inch thick nodular bands of pyrite. Many of the vertical joints in the coal were coated by megascopic crystals of pyrite. The stratigraphic profiles of the mines in this area show the magnitude of the total sulfur contents measured in these sections (see Appendix B).

In this area most of the upper coals and associated strata of the Allegheny group are missing. The coals and strata of the lower portion of the group are directly overlain in many places by thick glacial deposits. These glacial deposits are calcareous and composed mainly of sand and gravel with many rock fragments of mixed composition.

These calcareous deposits comprising the glacial drift are in addition to the Vanport limestone found in situ, which may attain a thickness of 20 feet.

Although the coal representative of a marine paleoenvironment and demonstrated to be highly sulfurous, produces extremely acidic waters, calcareous glacial deposits by generating extremely alkaline waters offset the acid potential of these mines.

Pyrite nodules and the pyrite joint coatings collected from the Mercer area were placed in a leaching chamber to determine if these specimens would readily decompose to produce acid waters. Within two weeks the nodules began to expand and part as pages of a book. Water was noted to condense between the partings and tested "extremely acid" with hydronium paper. The nodules became coated with white crystals which also gave "extremely acid" indications when wetted with water.

The pyrite coatings on the joints, however, remained inert. They also produced acid, but gave "slightly acid" readings when tested with hydronium paper.

One possible explanation for the difference in weatherability is that the nodules are composed of marcasite, and being the pseudomorph would more readily decompose than the joint coatings composed of pyrite. Newhouse (1927) identifies "marcasite...to be the chief form of iron disulfide present as stratigraphic bands in coal beds." To investigate this contention further, 16 X-ray diffraction patterns were made of various pyrite nodules and cleat coatings to determine the crystallographic state of the iron disulfide.

The results of these X-ray analyses contradict the findings reported by Newhouse (1927). It was found that in the four mines sampled in the Mercer area the banded nodules found in the Clarion coal were composed exclusively of pyrite, while the cleat coatings were predominantly marcasite, with measurable amounts of pyrite and ironous disulfide (a form of marcasite). No troilite or pyrrhotite (both forms of FeS) was found. Hence, the purported stability of iron disulfide as pyrite and the instability of the disulfide as marcasite was not substantiated by this study.

Regardless of the reason, the pyrite nodules in the coals of the Mercer area readily decompose to produce acid mine drainage. In addition to the decomposition noticed in the laboratory, high sulfate contents in some waters collected from the mine floor (Table 12) can only be explained by the decomposition of the pyrite in the strata of the mine.

The highly calcareous deposits found in the area impart an exceptionally high alkalinity to the ground water (Table 12). Consequently, although acid mine drainage is formed in the area, the highly alkaline waters effectively offset the acidity generated. To determine the amount of acidity that can be neutralized by these alkaline waters requires the conversion of the weight of bicarbonate ion to the equivalent weight required to neutralize a unit weight of acidity. The conversion of mg/l of bicarbonate to me/l (milli-equivalents per liter) is done by dividing the bicarbonate concentration by 61.02. By these calculations it was found that the ground waters in the Mercer area are

capable of neutralizing acid waters containing about 4 mg/l acidity. Samples SLM-3 and SLM-4 by the same conversion can neutralize acidities in excess of 6 mg/l. If ground waters similar in quality to those found in the Mercer area were to be present in the Clearfield area, all mine drainages produced at Clearfield would be neutralized and rendered alkaline.

3. The Clearfield Study Area

This area is representative of a medium between the very acid areas and the alkaline areas. The total sulfur contents are not exceptionally high. The values used in Table 3 have a mean of 0.81 and a standard deviation of 1.22. The strata are representative of a brackish water paleoenvironment and contain calcareous materials above the coal.

These calcareous materials do produce some alkalinity. Although not high, certainly not approaching the values of the Mercer area, the alkalinity can neutralize minor amounts of acidity. Water sample CH-9A had the highest alkalinity observed in the Clearfield area and potentially could neutralize about 3 mg/l of acidity. However, most of the waters coming in contact with the calcium carbonate developed only enough alkalinity to effectively neutralize about 0.5 to 1 mg/l acidity. This suggests that the calcareous deposits are not ubiquitous and that locally developed alkalinity is diluted by non-alkaline waters.

It is difficult to determine exactly how much acid is being produced in the strip mines of the Clearfield area. The samples of

acid mine drainage collected from this area represent waters that conceivably were alkaline before encountering the acidic environment. Hence, it may be possible that partial neutralization took place. If this is the case, the acidity that was measured is lower than what it may have been originally. However, the low sulfate contents do not support this hypothesis. Assuming the most favorable conditions for calcium sulfate precipitation by assuming unit activities and using the highest calcium ion concentration found in the ground water samples (50 mg/l), the sulfate content calculated from the solubility product, could be as high as 2500 mg/l before precipitation occurs. Yet all the sulfate concentrations of the acid mine drainages from mines in the Clearfield study area are well below this. Even assuming a dilution factor of 2X, the sulfate concentrations no-where approach the concentrations noted in mines KM and CL. The conclusion is that no great quantities or concentrations of acid mine drainage are produced in the Clearfield area. This low acid productivity, coupled with minor amounts of alkalinity generated classifies the Clearfield area as a moderate acid producer.

4. The Glen Richey Study Area

This is by far the most interesting of all the areas investigated. The strata are predominantly "continental" at the hill tops, and become increasingly "marine" with topographic and stratigraphic depth. This explains the more acid-like qualities of the lower reaches of streams in the Glen Richey area where they encounter "marine" strata.

Most of the total sulfur contents were measured in uplands in the Freeport seams. At mine RM-9, the Upper Kittanning seam was measured and these data are included in this discussion. However, the data of RM-2 are omitted, for although this mine is located in the Glen Richey area, it is topographically low and mined the Clarion coal seam.

The ranges of sulfur contents of this area and the Clearfield area overlap significantly. The mean of the data used in Table 3 is 0.91 and the standard deviation is 0.24. Aside from these values, which are not being used as comparison values but as indications of the degree of sulfur present, numerous total sulfur contents of the Lower Freeport and Upper Kittanning coals sampled in Clearfield County are available from the Bureau of Mines. The values for 1966 which represent analyses of samples taken from about a thousand tons of coal, vary from 0.7 to 2.7, with a mean of 1.76 and a standard deviation of 0.71 (Aresco and Janus, 1967). Sulfur analyses were obtained from this publication and from personal laboratory determinations. Statistical calculations were done in this study. Not only did the sulfur analyses of coals sampled in the present study show a high sulfur content, but data from the Bureau of Mines substantiate the fact that the coals of the Glen Richey area have abundant sulfur. Abundant pyrite coatings were noted on the coal cleats in many mines of the Glen Richey area.

In spite of the abundance of sulfur, no acid mine drainage is produced in the Glen Richey area. Water samples were collected from strip mines and deep mines and all showed no acidity. The alkalinity generated is sufficient in most cases to neutralize about 2 mg/l acidity.

Because the total sulfur contents of the Clearfield and Glen Richey overlap, the mine drainages of the two areas should be similar in composition. Lack of acidity in the Glen Richey area may be attributed to neutralization. If this were true, drainages should show high sulfate contents. What is remarkable is the almost complete absence of sulfate anion in the mine drainages of the Glen Richey area. The previous arguments in regard to the precipitation of calcium sulfate again apply. In the Glen Richey area, sulfate contents in excess of 2000 mg/l can be in solution, yet there is only a trace.

The specific resistances of the RM waters tend to be higher than those of the CM drainages demonstrating further the low ionic concentrations.

Assuming that the sulfur contents measured are representative of pyritic sulfur (field observations showed this to be true, in part, for the cleat coatings) and that they have a complete range of sizes. Further, that these concentrations are distributed in a random fashion such that the mines from which the water samples were collected contained these concentrations of sulfur, then the conclusion reached is that mines in the uplands of the Glen Richey area do not generate acid mine drainage. This is in spite of the fact that the magnitude of the sulfur concentrations is on par with those mines where significant quantities of acid mine drainage are produced.

5. Conclusions Regarding the Occurrence of Acid Mine Drainage

The most critical factor determining the presence or absence of acid mine drainage is calcium carbonate. Alkaline waters can be

generated through this medium which will effectively abate the acidity. However, in order for an effective alkalinity concentration to develop other conditions must be met. Foremost is the availability of carbon dioxide which must be put into solution as carbonic acid before contacting the calcium carbonate. Laboratory experimentation has shown that under the pCO_2 (partial pressure of carbon dioxide) found in the atmosphere, ineffective quantities of alkalinity (about 70 mg/l) are put into solution. In order that high quantities of bicarbonate be formed, the water must come in contact with high pCO_2s before contacting the calcium carbonate. High pCO_2s are found in the soil air where organic decay may raise the pCO_2 in excess of 100 times that of the atmosphere (Hem, 1960, p. 35). At these pressures, concentrations of bicarbonate increase to about 450 mg/l (Foster, 1950, p. 36); effectively increasing the neutralizing capacity by a factor of seven. Calcium carbonate alone will not offset any acidity generated. A soil cover is extremely important in developing alkalinity and as such plays an important role in preventing acid mine drainage. This calcium carbonate-bicarbonate system must be antecedent to the acidic environment to be effective.

As well as providing alkalinity for neutralization, calcium carbonate serves also to render the ground waters alkaline. This is supported by analyses of water samples taken from the virgin areas of the Clearfield study area, where in the absence of calcium carbonate, the samples had acidic pHs though no potential free acidities. Ground waters in the presence of calcium carbonate, however, showed very high

pHs. The fact that the ground water has an acidic or basic pH has diversified and important affects on the occurrence of bacteria and the stability of pyrite.

It was shown through the leaching studies that bacteria found in acid mine drainage dramatically increase the generation of acid mine drainage by catalyzing the oxidation of pyrite. Bass-Becking et al (1960, p. 254) have shown that pyrite under normal oxidizing conditions in distilled water gave a pH of 3.1 and a concomitant Eh rise that persistently ended at +650 mv. Higher Ehs were observed to occur, "only in the presence of organisms-iron bacteria which can give rise to Eh +860 mv and pH lower than 2.0." Bass-Becking et al (1960, p. 272) show that the iron bacteria, which include *Thiobacillus ferrooxydans* and *Ferrobacillus ferrooxydans*, are found in a range of pH environments extending from 2.0 to 8.9, and a range of Ehs from +850 to +60 mv. This may explain why once the bacteria were introduced in the leaching chambers, they persisted despite efforts to eliminate them with alkaline waters. Although these bacteria are found in a wide range of environments, their optimum growing environment is confined to a limited pH range.

The following data were summarized from "Bergey's Manual of Determinative Bacteriology."

Thiobacillus ferrooxidans - Oxidize ferrous salts, optimum pH 2.5 to 5.8, no growth above 6.0, ferrous iron serves as a sufficient energy source with the concomitant formation of enormous quantities of

ferric iron in acid media where ferric iron is not otherwise produced in quantity. Habitat-mine waters, aerobic.

Thiobacillus thiooxidans - Optimum reaction pH 2.0 to 3.5, limited to 6.0, derives energy from the oxidation of elemental sulfur, aerobic, converts sulfur and thiosulfate to sulfuric acid. Habitat-soil.

Ferrobacillus ferrooxidans - Optimum pH is 3.5, oxidation retarded below 2.2 and above 4.6, aerobic, derives energy from the oxidation of ferrous to ferric iron. Habitat-mine drainage of bituminous coal fields.

As these data show, the bacteria prefer an acidic environment. It is conceivable that, although the bacteria are found under a wide pH range, their presence in an alkaline environment may represent short term acclimatization and that prolong exposure will eventually lead to their elimination. Alkaline ground waters may over sufficient time sterilize an area in regard to these bacteria. In these areas, the oxidation of pyrite will proceed at a normal rate and consequently produce less acid, other things being equal, than an area harboring the iron bacteria.

Not only will the alkaline waters of an area impede bacterial catalysis of pyrite, but as a consequence, would produce lower acidity that may be effectively neutralized by the alkalinity present. If the bacteria are then introduced, as may happen by the transfer of tipple refuse from a contaminated mine to a sterile mine (in regard to the iron bacteria) acid mine drainage may occur. As the leaching study showed, once the bacteria are established alkalinity would not surpress their

existence. Possibly acid micro-environments are established in capillary zones where the free flow of alkaline waters cannot be effective. Within these zones, bacterial catalysis of the acid reactions takes place enhancing acid production. This, in turn, raises the acidity above the neutralizing capacity of the hitherto alkaline waters, thereby not only creating acid waters, but also creating an acid environment that now openly supports and spreads the bacteria. This sudden creation of an acidic environment may have far reaching affects as will be shown. There may be a tendency for a mushrooming or chain reaction affect once the acid waters develop.

The second impediment of acid mine drainage formation by alkalinity is implicit in the following discussion concerned with the stability of iron disulfide. The stability and reactivity of iron disulfide has been attributed to the cyrstal form of the mineral; namely, pyrite is stable, marcasite, the pseudomorph is not. It is generally accepted that if the iron disulfide oxidizes it is marcasite, and if the mineral is stable, it is pyrite. Possibly the answer in regard to the mineral's stability may in part, be its crystallography, in part the impurities contained in the crystal structure, and in part the availability of its surface area to reaction.

Temple and Koehler (1954, p. 24) noted that some "sulfur balls" were reactive while others were not. Although they did not identify the crystallographic state of the iron disulfide, they did identify calcium and magnesium to be present in the stable nodules but not in the reactive one. Significantly, washing the sulfur ball with acid, implying

the removal of the calcium and magnesium, rendered the inert sample reactive.

In a study relating the occurrences of iron disulfides to their environments of deposition, Edwards and Baker (1951) noted that their samples of marcasite oxidized and decomposed, while samples of pyrite did not. Compositional analyses show that the marcasite had a formula of $Fe_{0.972-0.995}S_2$ with 4-12% of the sample composed of carbonaceous material. The pyrite samples had a formula of $Fe_{1.01-1.02}S_2$ and contained about 2% calcium carbonate. Could it be possible that the reactivity was controlled by the absence of an associated basic mineral?

In the present study, marcasite from the Mercer area was the stable form, while the samples of pyrite readily decomposed. Though detailed compositional analyses were not performed, these samples serve to illustrate that the stability or reactivity of iron disulfide cannot be attributed only to the crystallographic state.

References are common in the literature substantiating the fact that calcite is inhibitory to the oxidation of pyrite (C.S. Clark, 1965, p. 31). If the iron disulfide contains particles of calcium carbonate which will effectively inhibit the oxidation of the disulfide, alkaline ground waters will preserve the calcite and tend to stabilize the pyritic mineral. Acid waters would effectively dissolve the calcareous material, thereby removing the inhibitor, and cause the stable iron disulfide to oxidize. Further, it becomes obvious that once acid waters are formed, they in turn, will effectively leach out additional particles of calcium carbonate, thereby liberating more particles of iron disulfide for

oxidation. These additional oxidative particles react to produce more acid for more effective calcareous leaching. This chain reaction may start very simply at the top of a talus pile which is exposed to the atmosphere. Rainwater which is normally acidic and highly corrosive (Carrol, 1962) may effectively begin the leaching process. Once acid waters are generated, the mechanism becomes self propogating.

Another facet of pyrite stability was demonstrated in the leaching studies (the lower curves of Figure 11). All samples containing calcium that were rinsed with calcium bicarbonate water showed that as long as the alkalinity greatly exceeded the potential acidity the pyrite remained stable. This further supports the contention that alkaline waters inhibit the generation of acidity, not only by inhibiting bacterial growth, preserving the inhibitor if it is present, but also by providing an environment for stabilizing the pyrite.

The acid potential of an area cannot be determined by measuring the total sulfur contents of the strata or the pyritic sulfur content alone. Of particular importance is the determination of the grain size distribution of the pyrite which was shown to become extremely reactive as the particle size diminished. To determine the acid potential of an area, the mode of pyrite occurrence as well as the amount, are necessary determinations.

In conclusion, the writer emphasizes that the acid potential of an area is determined by the result of the interdependent relations shown to exist. Any attempt to judge the water quality of an area by measuring one factor, without recognizing its role in the interdependent

relation with other factors, will not be successful. This was shown true in this study, where sulfur contents alone, without noting the grain size distribution, were used to predict the water quality expected from an area. Cognizance of inhibitory minerals, bacteria, or alkalinity are also required.

D. Hydrology of the Clearfield Area

The discussion pertaining to the hydrology will be concerned mainly with the hydraulic characteristics of the Clearfield area. The hydrologic data are included solely to demonstrate that a particular ground water flow pattern exists in the area which cannot be properly evaluated at the present time. General concepts regarding the hydrology have been derived from the water table maps (Figures 5 and 6) and other data; however, it is emphasized that these concepts can only be tested by conventional aquifer analyses utilizing a specialized water monitoring system. The specially constructed drilled wells are not presently available.

Conclusions drawn in regard to the hydrology of the Clearfield area based on its data, are applicable in a general way to the hydrology of the Glen Richey area. This is based on the fact that there is a cyclicity of rock types which is similar in both areas. Although the rock types of the two areas are not identical, their gross characteristics should affect the hydrology in a similar manner. Field observations and hydrologic data relayed by residents of the Clearfield

area are used exclusively to characterize the hydrology of both areas. Improper spacing of wells and a lack of observation wells precluded pumping tests which might have been used to better evaluate the aquifer characteristics.

The geology strongly affects the hydrology and both must be investigated together. The geology can be described generally as consisting of cyclic sequences of shale, siltstone, sandstone, limestone and clay. These are the predominant rock types in the Allegheny. The coals, underclays and limestones constitute a minor part of the total thickness. The most persistent beds are the major coal zones and the associated underclays, whereas the most variable are the sandstones (Dutcher et al, 1959, p. 61).

To define the aquifers and aquitards of the area, the field values of permeabilities of these rocks must be known or determined. It was noted in the field that the rocks are commonly intensely fractured. These fractures provide additional avenues of water movement. The field permeability value is a measure of the rock's ability to transmit water as a function of the primary permeability, that is the permeability inherent in the rock, and the secondary permeability, that being afforded by the jointing and solutioning that occurred since the rock was deposited.

To specify that a shale will transmit less water than a sandstone based solely on permeability values reported in the literature would be temerarious. Conceivably, the shale may be intensely fractured and the sandstone not, and although the primary permeability of the

sandstone may be greater than that of the shale, the fracturing of the shale may supersede the primary permeabilities, rendering the shale as the major aquifer.

It is now apparent why field pumping tests are required to evaluate the aquifer characteristics. Through these tests it will be possible to evaluate the primary and secondary permeabilities combined since the results average out the two and reflect the transmissibilities of the aquifers. However, to be properly performed observation wells at selected locations and drilled to specified depths are required. More so in the Carboniferous terrain where the strata vary laterally and vertically within a relatively short distance. To properly evaluate the hydraulic characteristics of a rock type, the lithologic unit must be hydraulically isolated from the adjacent strata and individually tested. This requires a particular well construction, both in the pumped well and the observation well, whereby the casing is installed to the top of the stratum under investigation and the well bore is opened only to the stratum.

These particular well types are absent in the Clearfield area where wells were drilled solely for the purpose of obtaining a water supply and whose constructions were dictated by economic considerations. Since the water table in this area is usually within ten feet of the land surface, casing of the wells is not common practice in order to take advantage of the shallow water table. If casing was installed, it would not only add to the construction expense, but it would have a further affect by lowering the water level in the well bore where wells

are drilled in recharge areas. This would necessitate the installation of the pump at a greater depth and increase the pumping cost.

Although detailed hydrologic data were not available, general concepts regarding the hydrology of the Clearfield area can be inferred from the field observations and compilation of information conveyed by the residents. Two major generalizations regarding the permeability have been made. The first is that the overall permeability is very low; as witnessed by the shallow water table, low well yields, numerous sidehill springs, etc. Secondly, the lateral permeability greatly exceeds the vertical permeability causing a predominant lateral ground water movement.

The outstanding characteristic of the hydrology of the Clearfield area is the extremely shallow water table. Commonly the residents in the area stated that their source of water was a "spring," whereupon it was observed to be a dug well containing water standing to within six inches of the ground level. The deeper the hole was dug the correspondingly deeper the water level fell due to the averaging out of the potentials. Deep wells cased to lower aquifer horizons had deeper water levels that reflected the potential of the aquifer opened to the casing indicating that flow was essentially downward. The significance of the shallow water table becomes obvious when it is related to the low well yields in the area. Both are manifestations of the low permeabilities of the rocks in the area.

Low well yields averaging from 5-100 gpm (gallons per minute), are common in the area. The resident of CH-6 ran a simple pumping test on

his well to determine its yield. The well was 150 feet deep and had 20 feet of casing. The well was pumped dry in 25 minutes at a pumping rate of 750 gallons per hour of 12.5 gpm. After ten minutes, the water level recovered and again it was pumped dry in about 25 minutes. The fact that the well went dry meant that the well could not sustain a yield of 12.5 gpm. Taking this yield as the maximum and assuming that the pump was set at 125 feet and that the static water level was at 30 feet, then the specific capacity (yield/foot of drawdown) is 12.5 gpm/95 feet or 0.13 gpm/ft. However, this does not mean that this is the yield of the major aquifers in the area. In this area the cyclicity of the rock types recurs in so short a distance that a well as deep as CH-6 could probably penetrate two or three different rock types. Hence the yield observed is the average of all units penetrated. Even so, 0.13 gpm/ft. is a low specific capacity. High yielding wells commonly have specific capacities of about 40-60 gpm/ft.

The general hydrologic setting in this area is essentially composed of alternating aquifers and aquitards layered upon each other in accord with the cyclicity which is characteristic of the rocks in the area. This generalization is based upon the data and observations listed in Table 13.

Table 13 - Hydrologic Characteristics of Selected Wells in the Clearfield Area, Pennsylvania

Well Number	Peculiarity and Interpretation Derived
CH-4A and 4B	At this location there are two wells; a dug well 35' deep and a drilled well 102' deep. Blasting done in a mine in an adjacent area caused the drilled well to go dry but not the dug well. The conclusion is that the dug well is hydraulically isolated from the deep well by the presence of an aquitard somewhere between 35' and 102', which effectively provides two depths of water circulation.
CH-5A and 5B	There are two wells at this location, a dug well 12' deep and a drilled well 65' deep. The deep well has "very hard water...leaves rings in the tub, tastes good," while the dug shallow well has "soft water...no soap problems." These different water qualities at different depths can be explained either by stratified supplies or normal mineralization with deep circulation. The former explanation is preferred based on the information obtained at CH-9.
CH-9A and 9B	This location has two wells, a deep drilled well which is cased and a shallow well. This well was discussed previously in the Aqueous-Geochmistry Section and showed how the shallow well was affected by the sulfate from the mine while the deep cased well was not. This

Table 13 - Continued

Well Number	Peculiarity and Interpretation Derived
	supports the conclusion that an aquitard at depth inhibits deep downward flow.
CH-10A	Resident relates that a well for the household had to be drilled below the coal seam in order to obtain water. The tenuous conclusion is that the coal or strata immediately associated with the coal are the aquitards.
CH-11	A dug well about 15 feet away from a stream exhibits a water level that is ten feet higher than the stream surface. This shows the presence of a high hydraulic gradient (10 foot head/15 foot distance) in the area of CH-11. This high gradient supports the hypothesis that a low permeability is present in the area.

The fact that the water levels in the Clearfield area are shallow and that the well yields are low supports the hypothesis that the average permeability in the area is low. An actual permeability value cannot be obtained at the present time due to a lack of quantitative aquifer analyses. However, it is suggested that the strata associated with the coal seams, probably the underclays, are the major aquitards in the area; that is, they impede ground water flow but do not completely restrain it. The observation that deep cased wells continue to draw water, after being pumped dry and allowed to recover, shows that water

must be percolating to the lower levels, or in other words, recharge of the deep aquifers is taking place. However, the fact that the yields of these wells is very low and easily pumped dry, suggests that the recharge rate is low or that the transmissibility of the aquifer is low. This can be answered only by detailed pumping analyses. Regardless of the reason, a stratification of water quality and the common observation of contact springs along selected bedding horizons demonstrates a lateral flow, the low recharge of the deep aquifers demonstrates the presence of a small vertical component through the aquitards. The implications derived from this are discussed below.

Since strip mines commonly strip to the top of the underclay and assuming the underclay to be a major aquitard, then acid mine drainage pollution created by the stripping operation should be limited to the surface water supply. If acid mine drainage is formed in a mine underlain by an aquitard, two things may happen; first, a prominant lateral flow will essentially cause the acid waters to bypass the deeper ground water supply. The underlying condition is that the aquitard's integrity is maintained. If it is, then, secondly, should the floor area of the mine be small compared to the area of the aquitard recharging water to the underlying aquifer, the acid waters entering the aquifer will be diluted and possibly even neutralized, and will not adversely affect the potability of the ground water reservoir. All these conclusions are based on the assumptions that the aquitard in the area is the underclay, that it is not intensely fractured (which by definition is an

aquitard) and that the aquitard's integrity is maintained during the stripping operation.

In conclusion, it has been shown that, due to the cyclicity of the strata, a unique stratification of water flow exists in the Clearfield area, and is thought to exist in the Glen Richey area. This stratified flow pattern may under proper circumstances preserve the potability of the ground water supply, in an area of extensive surface acid mine drainage pollution.

In order to test the hypotheses presented above, an extensive and specialized water monitoring system is required. This system will be composed of drill holes selectively drilled and cased to particular horizons which will serve many purposes, including potential measurements, use as observation wells for pumping test analyses and for the collection of water samples to be chemically analyzed. This phase of the study is being planned as an extension of the present work.

SUMMARY, RESULTS AND RECOMMENDATIONS FOR FUTURE STUDY

A. Summary

Acid mine drainage pollution has become a major problem in Pennsylvania with approximately 2,300 miles of stream adversely affected. As coal is mined, the iron disulfides, occurring either as marcasite or pyrite in the coal and the associated strata are exposed to the atmosphere and readily oxidize to hydrous ferrous sulfates. These compounds are easily dissolved in water to produce acidity and associated hydrous iron complexes.

This study was undertaken to determine what affect acid mine drainage had on the ground water reservoir. The two parameters affecting water quality, as concerned in this study, were the alkalinity and the acidity. Because these parameters are strongly influenced by, and related to, the chemical composition of the rocks in contact with the water, the study was modified to include an investigation relating the occurrence of acidity and alkalinity to the various rock types found in the area of study.

An area of study was chosen in the bituminous region where the hydro-geologic environment is simpler than that of the anthracite area where complex folding and inaccessible mine shafts prevail. The area was near Mercer, Pennsylvania, and was chosen because of the hydro-geologic information that was available. However, field observations showed that acid

mine drainage was not prevalent in this area. Data later obtained from the files of the Acid Mine Drainage Section of the Pennsylvania Department of Health corroborated the observations and conclusion that the area lacked severe acid mine drainage pollution. Stream quality maps at the Mine Drainage Section showed that acid mine drainage problems tended to be confined to certain areas. It became apparent that the presence or absence of acid mine waters was influenced by the amount of calcium carbonate and the percentage of iron disulfide found in the area. Iron disulfide may occur as marcasite or pyrite, and are difficult to differentiate in the field. Unless specific mention is made of the two, iron disulfide in either form is hereafter collectively referred to as pyrite.

Literature surveys showed that a relation existed between the pyrite content of a rock and its total sulfur content. By measuring the total sulfur content, the pyritic sulfur content could be determined. Other works showed the sulfur content of a rock to be related to its paleoenvironment of deposition. It was shown that strata of a marine paleoenvironment were more sulfurous than strata of a continental or fresh water paleoenvironment.

Because the amount of acidity was thought to vary directly with the pyrite content, mines extracting coals associated with strata of a marine paleoenvironment should produce more acid than those mines mining coals associated with strata of a non-marine paleoenvironment. Transgression of paleoenvironments, with "marine" strata becoming increasingly more "fresh-water" toward the upper portion of the Allegheny group, were reported in the literature. Consequently, mines extracting

coals from the lower portion of the Allegheny group should be more acidic than mines extracting coals from the upper portion of the group.

Accordingly, the objectives of the study were expanded to include a comparison of two areas of strip mining; one area underlain by rocks of the "marine" Lower and Middle Kittanning, while the other underlain by the "fresh-water" Freeport strata. The former is expected to produce acidic water, while the latter is expected to produce non-acid water.

The objectives of the study were:

1. To determine what compositional variations exist between the strata of an acid and non-acid strip mine.

2. To determine the acid potential of rocks with varying sulfur content.

3. To evaluate the various factors affecting the production of acid mine drainage.

4. To determine the water quality characteristics of areas of varying rock types.

5. To ascertain what interactions take place in the field between acid mine drainage and natural waters.

The approach to achieving these objectives was divided into three phases. This division was done to incorporate prerequisite studies which the writer felt necessary for the solution of the problem. In the first phase, distributions of various formations were mapped for the two areas and rock samples were collected and analyzed for total sulfur content. Based on these values a number of rock samples were

selected for leaching studies that related the acid potential of the rock to its sulfur content. Consequently, the areas from which the rocks were collected could be assigned a "rank" of probable acidities.

In the second phase of the study, water samples were collected and analyzed for ions indicative of certain chemical reactions. These samples were collected from mine pools, highwall bleeds, streams and domestic wells. From these water samples a comparison was made between the water quality of the virgin (unaffected by mining) areas and the strip mined areas. The information obtained from the residents regarding their water supply was used to gain a general understanding of the hydrologic setting of the areas.

The third phase, which will be completed in the future, concerns field testing of concepts derived from the present study and will require the installation of drill holes of specified depths and casing lengths in a predetermined pattern to define more completely the ground water flow system for selected areas.

Two areas of study were selected to the north and south of Clearfield, Pennsylvania. The northern area, hereafter referred to as "the Clearfield area," is underlain mostly by strata of the "marine-brackish water" Kittanning formations. Strip mines in this area produce acid mine drainage. The other area, hereafter referred to as "the Glen Richey area," is underlain mostly by "fresh water" Freeport strata and contain strip mines that produce non-acid waters.

The geology of the two areas was compiled from geologic information obtained from the Bureau of Topographic and Geologic Survey of

Pennsylvania and from data provided by Prof. E.G. Williams of The Department of Geology and Geophysics, The Pennsylvania State University. Highwalls of mines from which rocks were collected were described in a general way and incorporated within the geologic framework.

To ensure representative analysis of field samples, the rocks were crushed, sieved and riffled into two portions. One portion, about 300 grams, was used for leaching studies while the other portion, of about 5-10 grams, was pulverized by a ball mill and mortar and pestle in preparation for other analyses. Samples used in the leaching study were analyzed for total sulfur, pyritic sulfur and calcium carbonate content. All other samples were analyzed for total sulfur contents only. Sulfur contents were analyzed by the Leco (Laboratory Equipment Company) automatic sulfur titrator.

The leaching studies were used to assess the acid potential of rocks having varying sulfur contents and to evaluate the various factors affecting acid mine drainage production such as pyrite granularity and purity, bacterial catalysis and alkalinity. In these studies a sieved portion of the sample was placed in an inert chamber whereby a continuous flow of humidified air passed over the sample. Periodically the sample was flushed with water and the effluent analyzed for acidity, alkalinity, calcium, sulfate concentrations and pH.

The ionic species analyzed in the leachates, mine drainages and ground waters, were not only used as quality parameters but also as indicators of certain chemical reactions of interest. The alkalinity, measured as mg of HCO_3^-/liter, establishes the limit of acidity that

can be produced in an area without adversely affecting water quality. Because alkalinity and calcium (as Ca^{++}) are genetically related, calcium ion was to be used as an indicator of the alkalinity present in cases where neutralization took place.

The acidity of a sample is a measure of the potential free acidity of the sample and includes the acidity due to complete hydrolysis and free acidity, but does not include carbonic acidity. The acidity (as mg of H^{+}/liter) is genetically related to the sulfate (as mg of $SO_4^{=}$/liter) ion. From a plot of various acid mine drainage compositions, a range of acidity can be interpolated for a particular value of sulfate concentration.

The pH of a sample was a good indicator of the environment from which the sample was collected. It was not used as a measure of the potential free acidity. The pH measurements were important because although a water sample may have no free acidity, a high carbon dioxide content may cause the sample to have an acidic pH which will support the iron bacteria known to catalyze the acid forming reactions.

The specific resistance measured in ohms/cm^3 of fluid was used to estimate the total dissolved solids of a sample. This measurement was also used to confirm ionic strengths measured by conventional wet methods and to rapidly reconnoiter an area for water quality expectations.

Temperature measurements indicated in a general way whether a pool was mostly stagnant water or a spring and whether a stream was mostly surface runoff or ground water bleed.

B. Results

Interdependent relations were found to exist between the factors investigated, namely, the grain size, percentage sulfur, bacterial catalysis, etc., and for the sake of clarity are discussed separately. After the individual cause and effects are established, the factors will be related to each other as they were noted to occur in the field and laboratory experiments. The four major subdivisions are--Stratigraphic Results, Aqueous Geochemical Results, Areal Characteristics Related to Water Quality Parameters and Hydrologic Results. The first three subdivisions are intimately related and the last section elucidates the particular water flow patterns existing in the area and the need for additional well control to properly evaluate the aquifer characteristics.

1. Stratigraphic Results

The stratigraphic profiles of mine highwalls and roadcuts show the lithologic variations, the sampling intervals and the percentage sulfur content of the rock taken at the sampling interval. In one mine the lateral variations of sulfur content along the strata were tested. The experimental error due to riffling in preparing the sample for total sulfur analyses, and the precision of the Leco instrument were also tested.

It was found that:

a. The precision of the Leco was 0.06. This means that 95 times out of a 100, a measurement made on the Leco for total sulfur

content will be 0.06 within the grand mean when the sulfur content is less than 4%. When the sulfur content is between 4% and 8%, the precision is 0.12.

b. A significant error was introduced when rocks and coals containing megascopic pyrite grains were riffled and precludes valid comparisons of sulfur contents between samples.

c. A significant lateral variation in sulfur content exists along the strata and presents a sampling problem. This also serves to further reduce the validity of comparing sulfur contents between two areas.

d. A comparison of ranges of sulfur contents can be made however, and a significant number of sulfur content ranges overlap. Therefore, the original contention, that a difference in sulfur content between the Clearfield and Glen Richey areas accounts for acid and non-acid waters, is rejected.

Three separate leaching studies were performed on a battery of samples in an attempt to relate the acid potential of a rock to its sulfur content and to evaluate the factors affecting the amount of acid generated. A total of 30 different samples were subjected to leaching. These included coal, binder and shale. The first leaching study was to determine the optimum grain size of the samples to be leached, the flushing interval and the mechanics of operation. The second study related the acid potential of a rock to its sulfur content using distilled water as the leaching medium. The third leaching study repeated the pattern of the second experiment, but used water that was in contact

with limestone at the partial pressure of carbon dioxide found in the atmosphere. This water is hereafter referred to as "limestone water."

The first leaching study showed:

a. A necessity for flushing all samples at the same time to maintain similar oxidation periods in order to make valid comparisons of acid potentials.

b. The need for uniform grain size of the samples. It was found that the 1-2 mm particles did not cement together, yet drained well with the least retention of water.

c. A general relation existed between samples of high sulfur content and high acid production.

The samples used in the second leaching study were analyzed for pyritic sulfur, total sulfur and calcium carbonate content. Portions of the sample were molded into plastic pellets and used for microscopic examination. The second leaching study demonstrated:

a. Acid generation to increase with temperature.

b. Coals containing pyrite grains measuring greater than 150 microns yielded 2-1/2 times less acid than coals containing pyrite grains measuring less than 10 microns.

c. Binders (siliceous impure coals) yielded very little acid suggesting that the permeability of a rock plays an important role in acid production.

d. The form of iron disulfides in the leaching studies was pyrite. Anomalously high acidities obtained in the leaching study cannot be attributed to marcasite.

e. Variations in acid generation were closely related to the variations in pyrite grain size as well as amount.

f. Bacteria, associated with acid mine drainage, profoundly influenced the generation of acidity, showing a greater affinity for fine grained than coarse grained pyrite, while rocks containing calcium (0.13 to 0.42 percent as calcium carbonate) were unaffected.

g. The bacteria's effectiveness was not permanently decreased by rinsing the samples with alkaline waters. Rather rates of acid production were at first decreased, probably due to neutralization, then resumed the rates prior to rinsing.

The third leaching study repeated the pattern of the second study, but used limestone water that had an alkalinity of about 65 mg/l (as HCO_3^-) and a calcium content of about 25 mg/l (as Ca^{++}). This leaching study showed:

a. Acid generation was not affected by the use of limestone water as the flushing medium. In one case samples rinsed with distilled water gave identical acidities as those rinsed with limestone water.

b. Bacterial catalysis of the acid generating reaction was not impeded by limestone water.

c. Highly alkaline water (1500 mg/l) impeded acid production and temporarily inhibited bacterial action.

d. Water in contact with limestone did not prevent bacteria from contaminating the samples.

The conclusions drawn are:

a. Acid generation is partly a function of the sulfur content of the sample and is greatly influenced by the crystallinity of the pyrite, the presence of bacteria associated with acid mine drainage and the presence of calcium carbonate.

b. Samples innoculated with bacteria remained contaminated despite efforts to permanently impede bacterial catalysis using highly alkaline waters. Hence, efforts should be made not to innoculate mines by iron bacteria by introducing debris from mines containing these bacteria.

c. Waters in contact with limestone at a partial pressure of carbon dioxide equal to $10^{-3.5}$ atmospheres do not generate sufficient alkalinity to effectively offset acid generation.

2. Aqueous Geochemical Results

Numerous water samples were collected from the Glen Richey and Clearfield areas. These included samples of ground water, streams and mine drainages (alkaline and acid). Analyses showed that the acid waters of the Clearfield area were not as acid as some typical mine waters reported in the literature. Further, alkaline waters of the Glen Richey area were not as alkaline as some waters reported in the literature. Consequently, additional water samples were collected from areas where extremely alkaline and very acid waters were known to occur.

Alkaline waters were collected from strip mines in the vicinity of Mercer, Pennsylvania, where extensive calcium carbonate deposits, in the form of the Vanport limestone and glacial till, were noted to

occur. These waters had alkalinities ranging from 180-385 mg/1.

Acid mine drainage samples were collected from the Krebs mine (located about two miles east of the Glen Richey area) and a strip mine (mine CL-1) southwest of Clarion, Pennsylvania. These acid samples had acidities ranging from 7.1 to 8.7 mg/1 and sulfate contents of about 4800 mg/1.

The water quality analyses showed:

a. The shallow ground waters in the virgin portions of the Clearfield area had acidic pHs, a very low dissolved solids content, and contained no potential free acidity.

b. The ground waters in and about the strip mines of the Clearfield area had a greater dissolved solids content than the ground waters from the unmined areas indicating chemical activity taking place.

c. In some cases in the Clearfield area water samples from shallow uncased wells had qualities divergent from the samples obtained from the deeply cased wells. This suggests that a shallow flow system is nearly hydraulically separate from a deeper flow system and that the ground water reservoir must be horizontally stratified both in regards to permeability and stratigraphy.

d. Where calcareous materials were present the ground waters had noticeable amounts of alkalinity and the pHs averaged about 8.0.

e. Although the alkalinity and calcium ion must be genetically related, the calcium ion content could not be used to estimate the alkalinity. This is probably due to a natural ion-exchange mechanism possibly exchanging sodium for calcium.

f. The mine drainages of the Clearfield area were not as acid as some drainages reported in the literature. The sulfate-acidity plot showed that the low acidity was not because of neutralization but due to a mild acid production in the area.

g. Mine drainages of the Glen Richey area had practically no sulfate, contained varying degrees of alkalinity and no acidity.

h. Mine drainages from the Krebs mine and mine CL-1 were highly acid and showed a sulfate-acidity plot similar to the one derived from the plot of the leachates.

i. Highly acid mine drainages showed the calcium ion to act in a passive role (that is, it was not indicative of high alkalinity) and may originate from acid waters dissolving the calcium carbonate in an acidic environment without the release of bicarbonate ion.

j. The alkaline waters of the Mercer area showed a remarkable capacity to neutralize acidity and examples of natural neutralization were discovered.

These data showed that the original intention of comparing two areas of extremes of paleoenvironment for the purpose of obtaining water qualities of divergent characters was not fulfilled in the Clearfield and Glen Richey areas.

3. Relation of Areal Characteristics to Water Quality Parameters

The following statements relate all the preceeding data in an integrated and comprehensive manner, by attempting to show how the occurrence of certain geological factors influence the water quality of an area. Using the stratigraphic data, i.e. the sulfur and calcium

carbonate distribution, in conjunction with the leaching studies, the water qualities of an area can be approximated. Chemical analyses of water samples, however, reveal the water qualities existing in the area. The analyses of waters sampled are not always those which would have been expected based on a detailed knowledge of the stratigraphy alone. In this case secondary interactions very likely occurring in the field are offered as explanation.

a. In the Krebs mine (Plate IV) and mine CL-1 (Figure 23) strata of the basal portion of the Allegheny group (Lower Clarion formation) produce severe acid mine drainages (about 7.5 mg/l). The total sulfur content of the coal at the Krebs mine (based on published data) had a mean of 2.24%, but a standard deviation of 10.23 showing an extreme variability in sulfur content. The high sulfate content (about 4500 mg/l) of the drainage suggests that the pyrite in the strata readily decomposes. The high calcium content, with no apparent neutralization, suggests that the generation of acidity hydraulically antecedes the calcareous materials which are readily dissolved by the acid waters. Probably the carbonate ion released is converted to carbonic acid. The ionic strengths of these drainages is very high, whereby the activities of the components are reduced considerably enabling high concentrations of calcium and sulfate ion to co-exist without precipitating.

b. In the strip mines of the Mercer area the Lower Clarion coal is mined and is representative of strata associated with a marine paleoenvironment. The coal was noted to be extremely pyritiferrous. The coal and the strata are overlain in many places by thick calcareous

glacial deposits. These deposits are in addition to the Vanport limestone found in situ which may attain a thickness of 20 feet. Although the coal is highly sulfurous, and produces acid waters, the calcareous glacial deposits and the Vanport limestone generate extremely alkaline waters which effectively offset the acidity. The alkalinity of these waters is capable of neutralizing between 4-6 mg/l acidity.

c. The Clearfield area contain strata representative of a medium between the very acid and alkaline mines. The total sulfur contents had a mean of 0.81 and a standard deviation of 1.22. The strata are representative of a brackish water paleoenvironment and contain calcareous materials above the coal. In this area a moderately acid mine drainage is produced with acidities averaging 2.5 mg/l and sulfate concentrations ranging from 600-1200 mg/l. This low acid productivity coupled with minor amounts of alkalinity produced locally classifies the rocks of the Clearfield area as moderate acid producers.

d. In the Glen Richey area the Freeport and Upper Kittanning coals are strip mined from strata representative of a fresh-water paleoenvironment. The ranges of sulfur contents of this area and the Clearfield area overlap significantly. The mean of total sulfur values for the Glen Richey area is 0.91 and the standard deviation is 0.24. These values are used to indicate the high amount of sulfur present in the area. Data obtained from a Bureau of Mines Report had a mean sulfur content of 1.76 and a standard deviation of 0.71. Further, abundant pyrite coatings were observed to coat the coal cleats. In spite of the abundance of sulfur, no acid mine drainage is produced in the Glen

Richey area. There is almost a complete lack of sulfate ion in the mine drainages collected from mine wall bleeds, springs, mine pools and talus bleeds. Calculations using solubility products show that the sulfate ion could be as high as 2000 mg/l before it would precipitate as calcium sulfate. The lack of sulfate ion can only be attributed to the stability of the iron disulfide found in this area.

e. Conclusions regarding the origin and occurrence of acid mine drainage are:

(1) The most critical factor determining the presence or absence of acid mine drainage is calcium carbonate by which alkaline waters can be produced.

(2) To generate a high alkalinity (about 450 mg/l) from calcium carbonate a high partial pressure of carbon dioxide is required and may be found in the soil atmosphere; as such a soil cover may play an important role in preventing acid mine drainage.

(3) Alkaline ground waters may over sufficient time sterilize an area in regard to the acid-iron bacteria; hence in these areas the oxidation of pyrite will proceed at a normal rate, produce less acidity, other things being equal, and may be effectively neutralized by the alkalinity present.

(4) If bacteria are introduced to an area, they may persist despite the alkaline waters and eventually render the environment acid; thereby enabling the bacteria to flourish and spread.

(5) Highly alkaline waters tend to stabilize iron disulfides by the preservation of the calcium carbonate inhibitor should it

be present. Acid waters will dissolve the inhibitor and render the iron disulfide reactive.

(6) Highly alkaline waters that persist in exceeding the potential acidity of a sample will stabilize the pyrite.

(7) The acid potential of an area cannot be determined solely by the total sulfur contents. Cognizance of inhibitory materials, bacterial presence, the granularity of the pyrite and the potential of alkalinity production is required.

4. Hydrologic Results

The findings reported below were derived mainly from data obtained from the Clearfield area and will be concerned primarily with the hydraulic characteristics of this area. They are intended to demonstrate a particular flow pattern existing in the area and the need for additional well control. The general concepts concerning the hydrology of the Clearfield area are:

a. The overall permeability is very low; as witnessed by a very shallow water table, low well yields and numerous sidehill springs.

b. The general hydrologic setting in this area is essentially composed of alternating aquifers and aquitards layered upon each other in accord with the cyclicity which is characteristic of the rocks in the area.

c. It is suggested that the strata associated with the coal seams, probably the underclays, are the major aquitards in the area. If this is true, then acid mine drainage contamination may under certain circumstances be confined to surface water sources.

To properly evaluate the aquifer characteristics, to test the hypotheses above, and determine the metamorphism of mine drainage in the ground reservoir an extensive and specialized water monitoring system is required. Wells currently accessible are not properly spaced or constructed to be utilized in conventional pumping tests analyses.

C. Recommendations for Future Study

1. Determination of the Mode of Pyrite Distribution

As suggested by the overlapping sulfur contents of an acid and non-acid strip mined area, the determination of total sulfur content alone will not predict whether or not an area will be acid producing. A study should be made to determine the relation between the mode of pyrite occurrence and the production of acid mine drainage. As the leaching studies suggested, the granularity of the pyrite and the presence of calcium carbonate are factors which make the pyrite resistant to oxidation. Spectrographic analyses of various types of pyrite, ranging from inert to reactive, should be made to determine what impurity is present in the mineral that prevents it from oxidizing. If the impurity is determined, the genesis should be ascertained in an attempt to develop a method of applying the inhibitor in the field If the impurity is an inherent part of the mineral, then it should be related to a characteristic of the rock which can be used to appraise the stability of the mineral; hence may be an aid in appraising the acid potential of a rock.

2. Hydro-geochemical Evaluation of the Ground Water Regimen

As suggested by the hydrologic data of this present study, a stratification of ground water flow exists that may effectively divert acid mine drainage pollution from deep ground water reservoirs. Further, opportunities for neutralization were shown to exist. These considerations may lead to the establishment of potable ground water supplies in an area afflicted with severe surface acid mine drainage pollution. To test these hypotheses, a specialized water monitoring system should be installed to accurately evaluate the aquifer characteristics, to determine the aquitards in the area, and to sample the ground water for chemical analyses to determine the extent and effect of mine drainage pollution.

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APPENDIX A

Chemical Methods

Acidity and Alkalinity Determination

The analyses of acidity (potential free acidity) and alkalinity were in accord with the procedures outlined by Rainwater and Thatcher (1960, pages 91 and 94).

Sulfate Determinations

The analyses of sulfate were in accord with procedures outlined by Fisher Scientific Company using the Fisher Barium Chloranilate certified reagent (B-412).

The technique outlined is:

1. Add 10 ml of Acetate Buffer (4.63) to a sample contained in a 100 ml volumetric flask.

2. Dilute to mark with distilled water.

3. Add 0.3 gm of Barium Chloranilate, stopper the flask, and shake at least once a minute for 15 minutes.

4. Filter through a Whatman #42 filter paper and read the absorbance on a colorimeter.

The colorimeter used was the Photovolt Lumetron colorimeter Model 401, using a #530 filter.

Calcium Determinations

The analysis of calcium ion in unpolluted (mine drainage) waters was in accord with the procedures outlined by Rainwater and Thatcher (1960, p. 129) and modified by the addition of triethanolamine 30% solution (to eliminate the aluminum interference) before adding the murexide indicator.

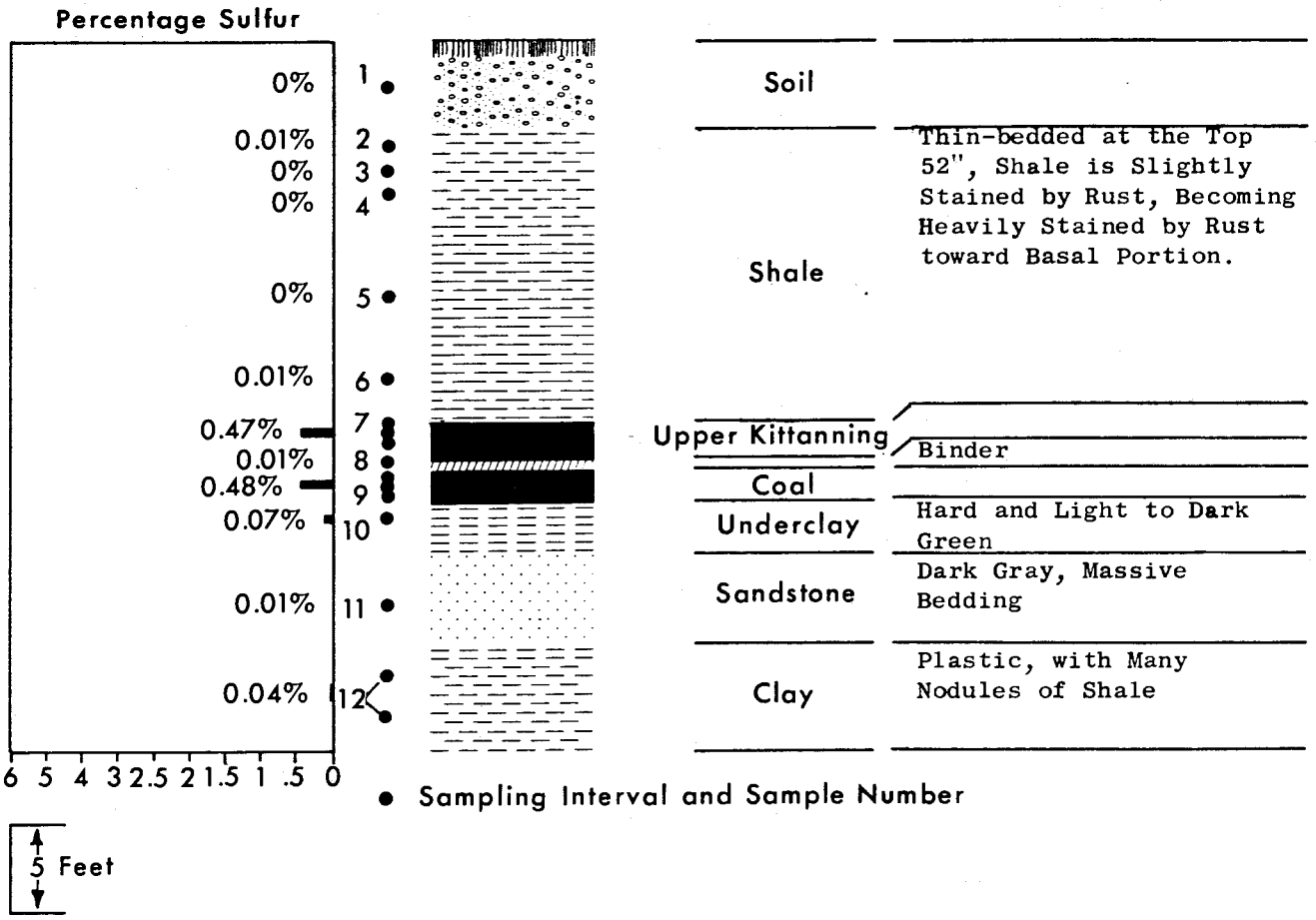
The analysis of calcium ion in acid mine drainage was done either by a wet analysis or by a method using the Atomic Absorption Spectrophotometer. The latter method, by the addition of lanthanum oxide (5% W/V) in a 25% hydrochloric acid solution as prescribed by the Methods Handbook, was preferred because of the elimination of interference by extraneous ions. The wet method is outlined as follows:

1. Pipet 25 ml of sample into a 150 ml beaker.
2. Insert stirring rod and insert into stirring assembly.
3a. Measure pH with electrodes.
3b. With stirrer running add sodium hypochlorite, N.F. 3-6% NaOCl until pH 8 is reached.
4. After precipitate has coagulated, filter through a #41 Whatman filter paper.
5. Wash filter paper twice with distilled water.
6. Add to white casserole and proceed with procedures outlined above for calcium determinations.

This method gave results within a 5% error.

APPENDIX B

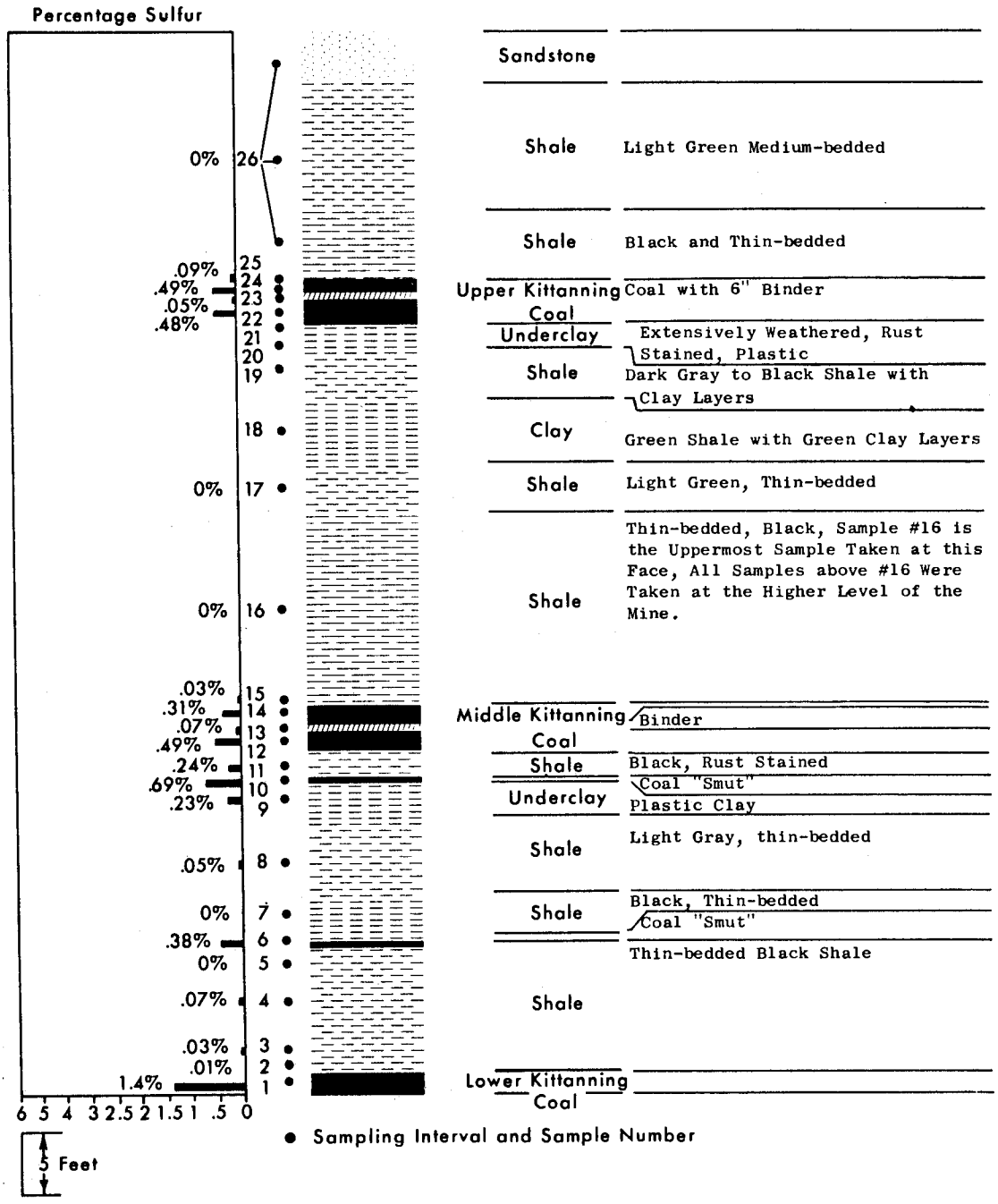
Stratigraphic Data



Samples taken from northeast bank of roadcut for Interstate 80.

STRATIGRAPHIC PROFILE OF ROADCUT CM-2

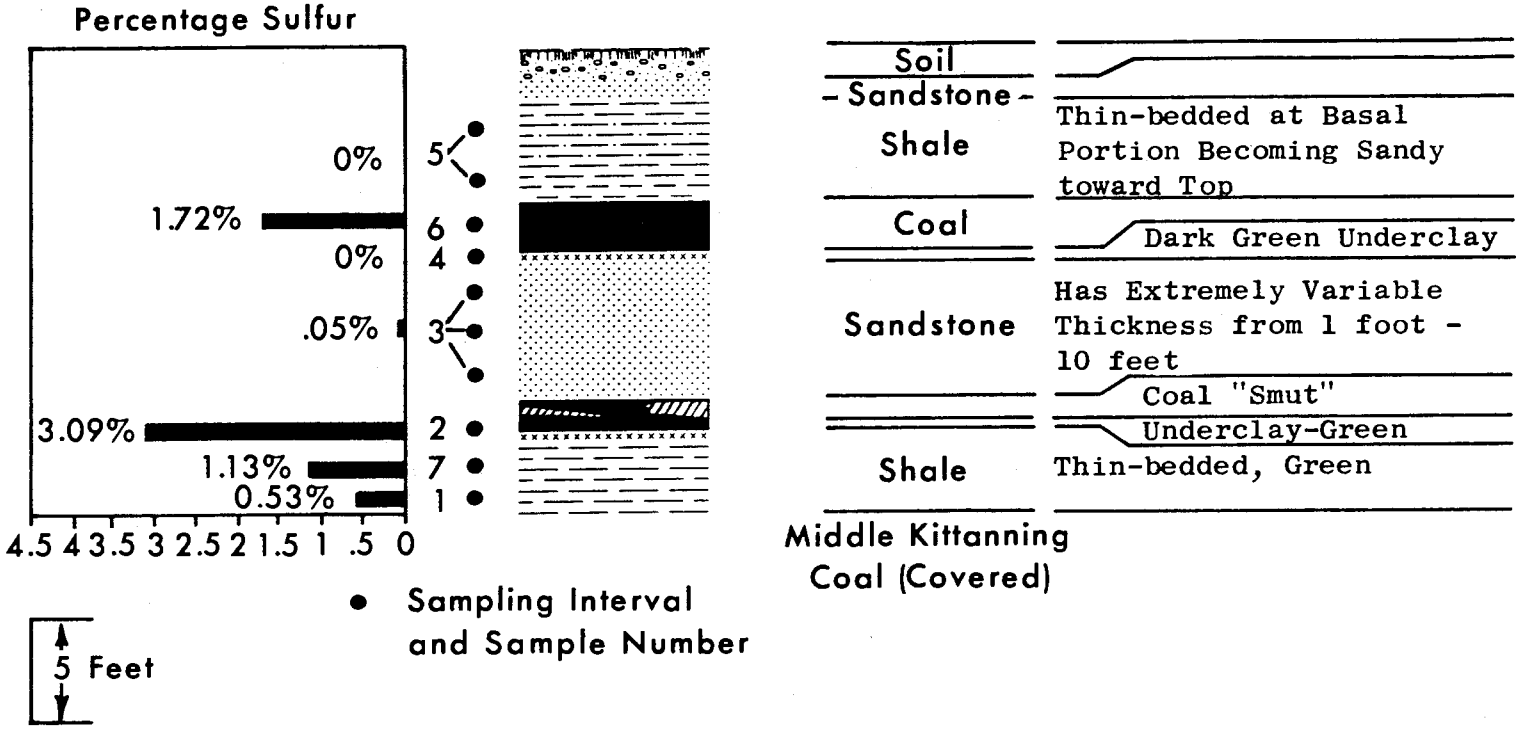
Figure 25



Mine is composed of two levels. Actively mined during the summer of 1966.

STRATIGRAPHIC PROFILE OF MINE CM-3

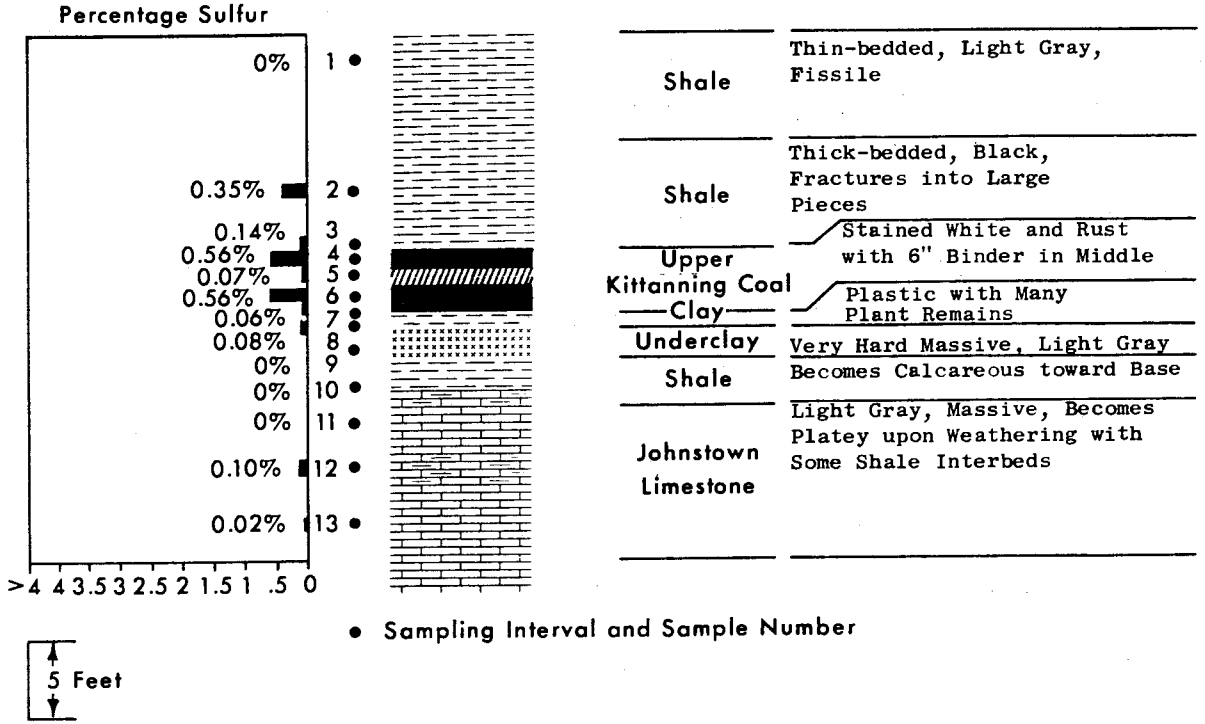
Figure 26



Mine located in back yard of CH-10 residence, is partially back filled, covering the lower coal.

STRATIGRAPHIC PROFILE OF MINE CM-4

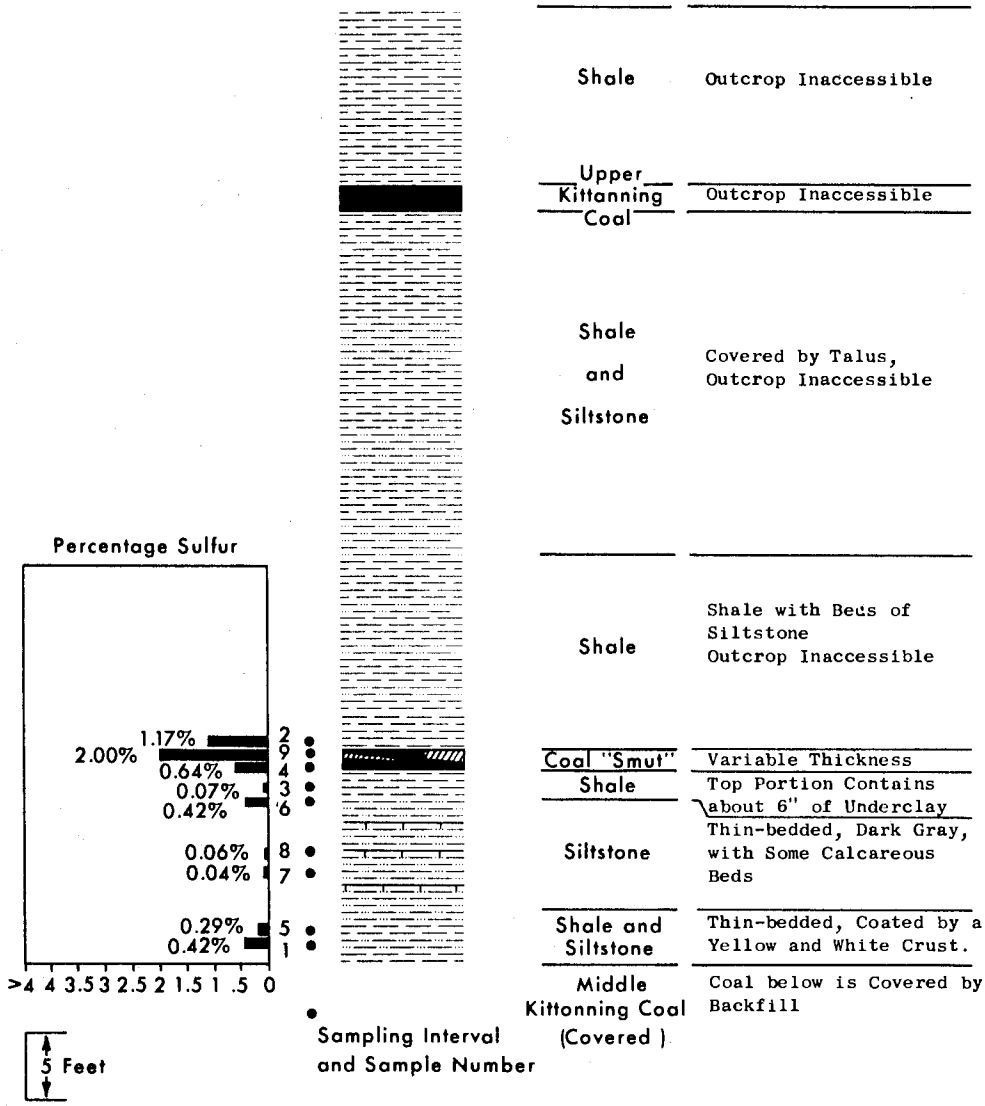
Figure 27



Located northeast of CM-2 and is a roadcut for Interstate 80.

STRATIGRAPHIC PROFILE OF ROADCUT CM-5

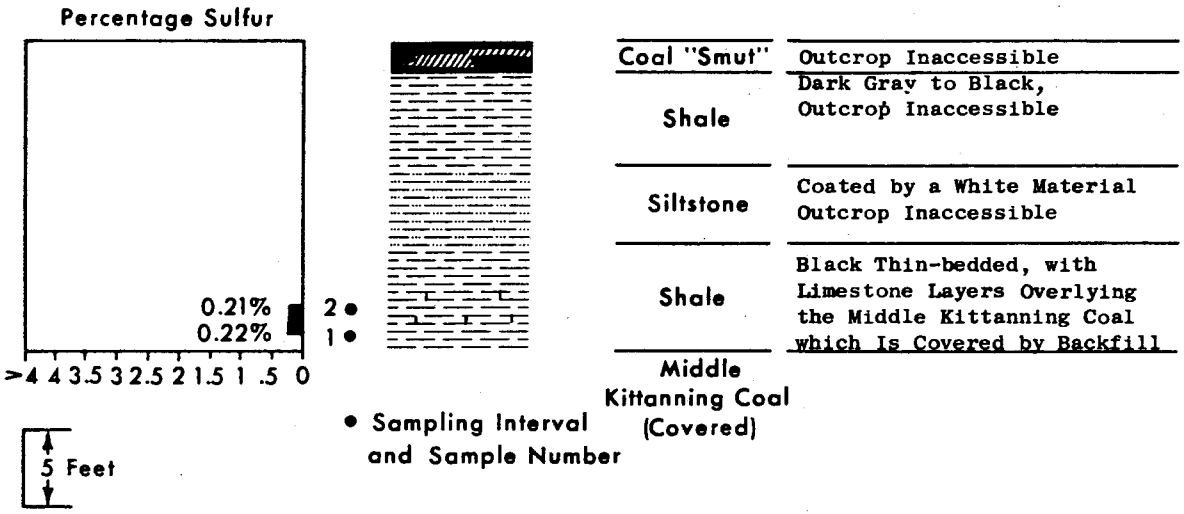
Figure 28



Part of a mine complex which has been partially back filled. Samples 1-4 were obtained from CM-6A, samples 5-6 were obtained from CM-6B, and samples 7-9 were collected from CM-7 as indicated on the southernmost highwall shown in the Plan View Map (Figure 20).

STRATIGRAPHIC PROFILE OF MINE CM-6 AND CM-7

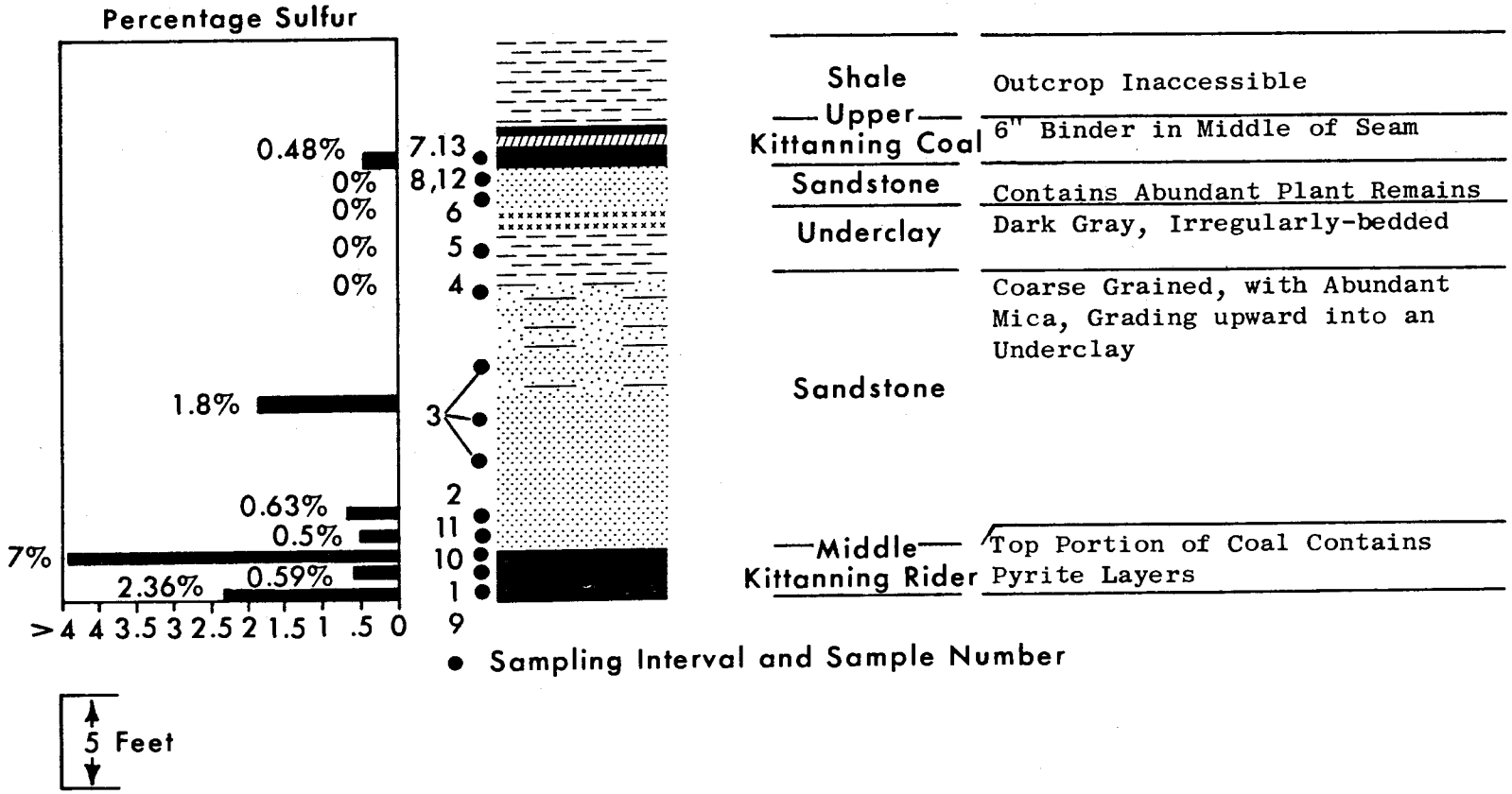
Figure 29



Mine CM-8 is located about 1/4 mile northeast of Mines CM-6 and CM-7, and about 1/8 mile south of Interstate 80. It is part of the same mine complex composed of CM-6, CM-7, CM-8 and CM-10. The mine complex has been partially back filled to cover the coal seam.

STRATIGRAPHIC PROFILE OF MINE CM-8

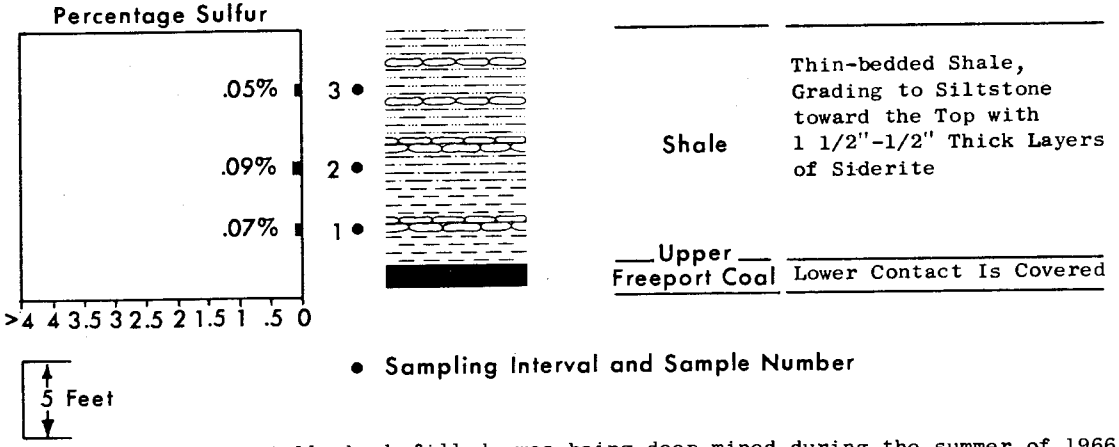
Figure 30



Mine CM-10 is located about 1/4 mile due west of mine CM-6. The section described above is part of a synclinal structure and is generalized.

STRATIGRAPHIC PROFILE OF MINE CM-10

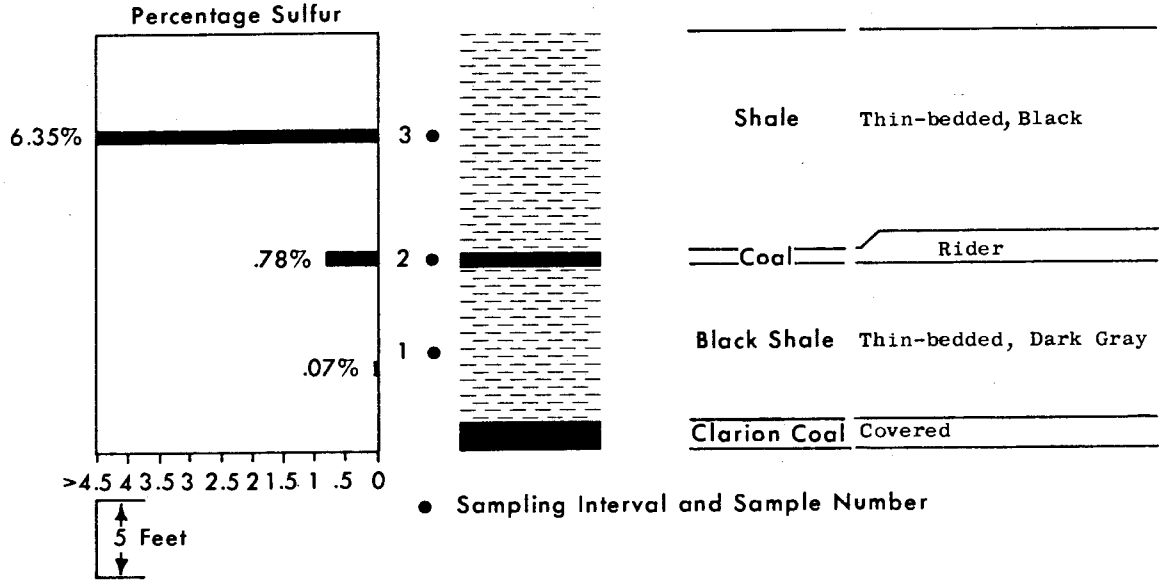
Figure 31



Strip mined and partially back filled, was being deep mined during the summer of 1966. Samples were collected from the highwall of the abandoned strip mine.

STRATIGRAPHIC PROFILE OF MINE RM-1

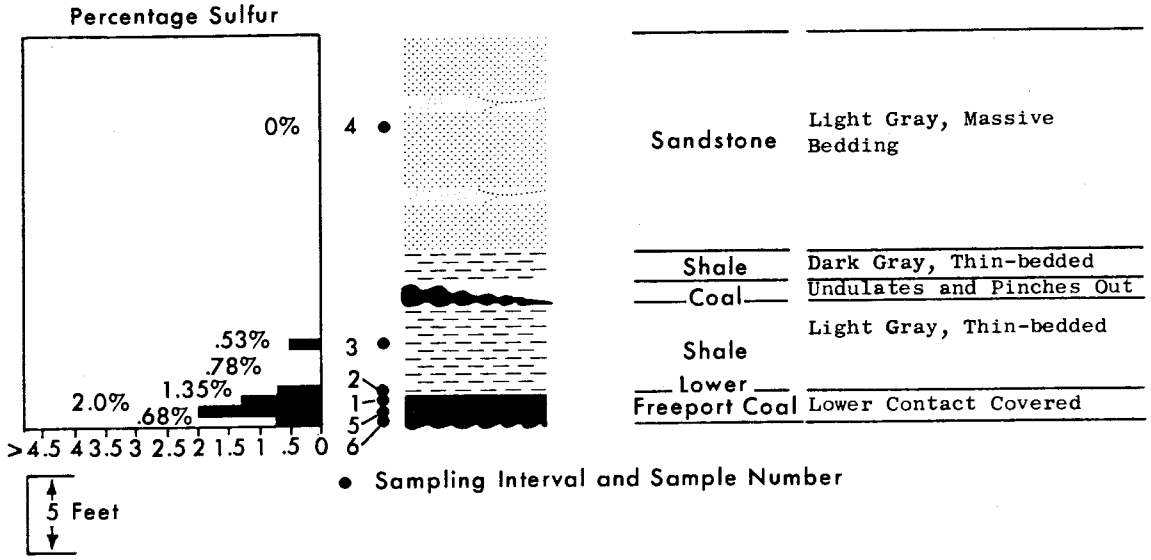
Figure 32



Although located in the Glen Richey area, the mine is topographically low and mined the Clarion seam. The mine has been partially back filled covering the coal seam.

STRATIGRAPHIC PROFILE OF MINE RM-2

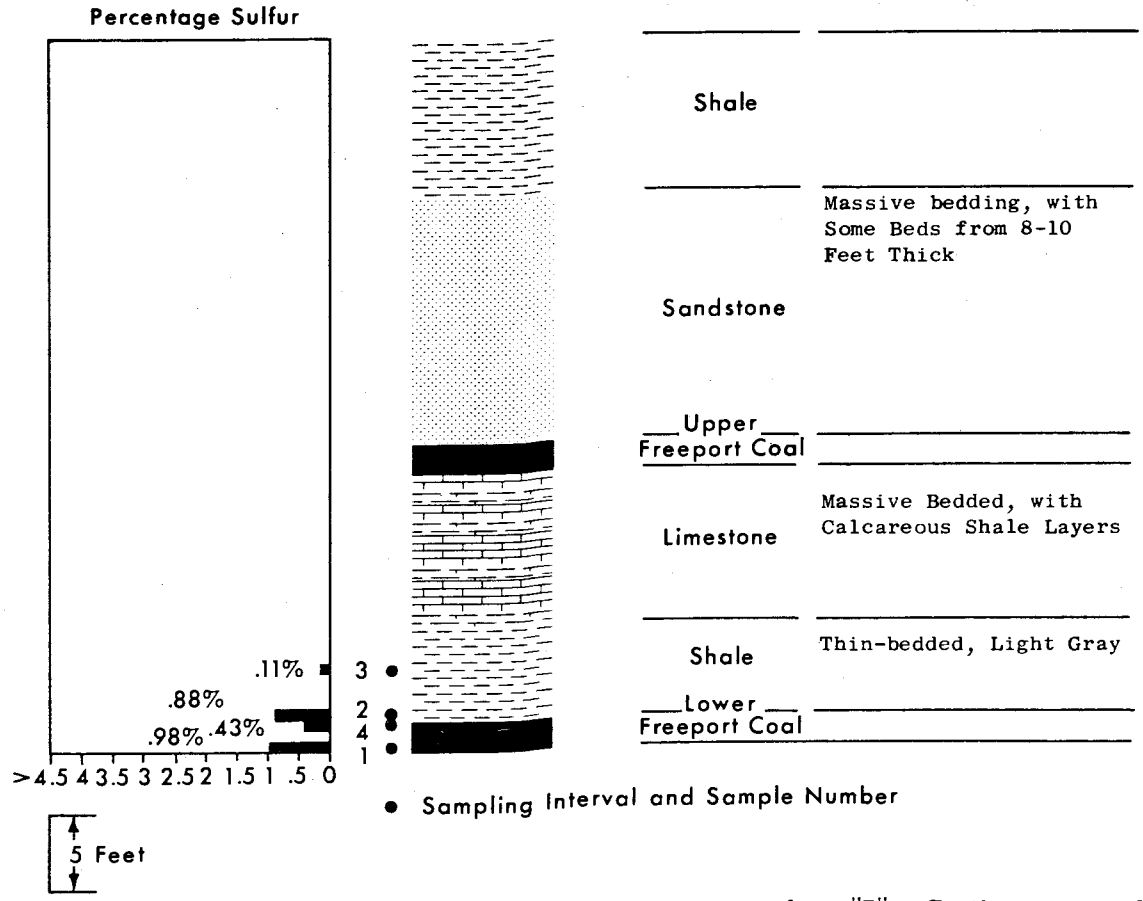
Figure 33



Mine contains two levels, actively mined during the summer of 1966.

STRATIGRAPHIC PROFILE OF MINE RM-3

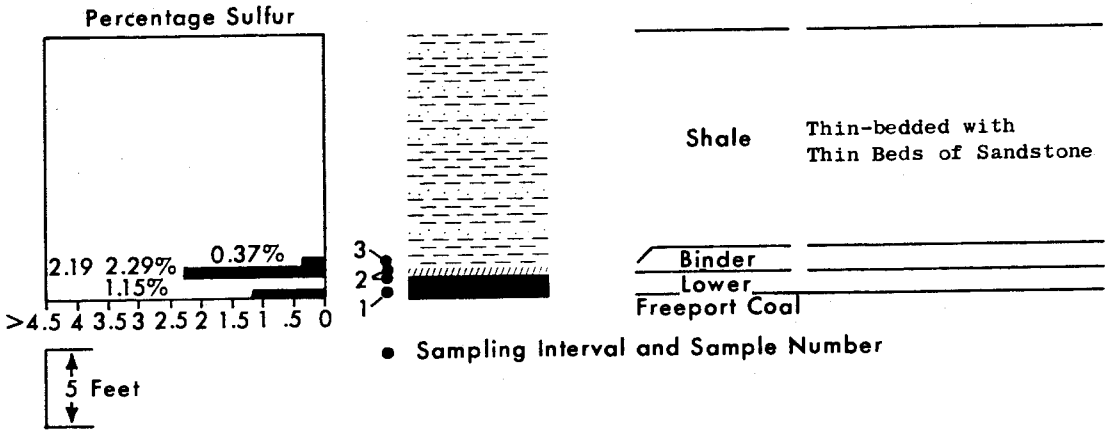
Figure 34



Miner claims the basal coal is the "D" seam and the upper coal as "E". Further states that a limestone underlies the "E" seam. Actively mined during February, 1966.

STRATIGRAPHIC PROFILE OF MINE RM-4

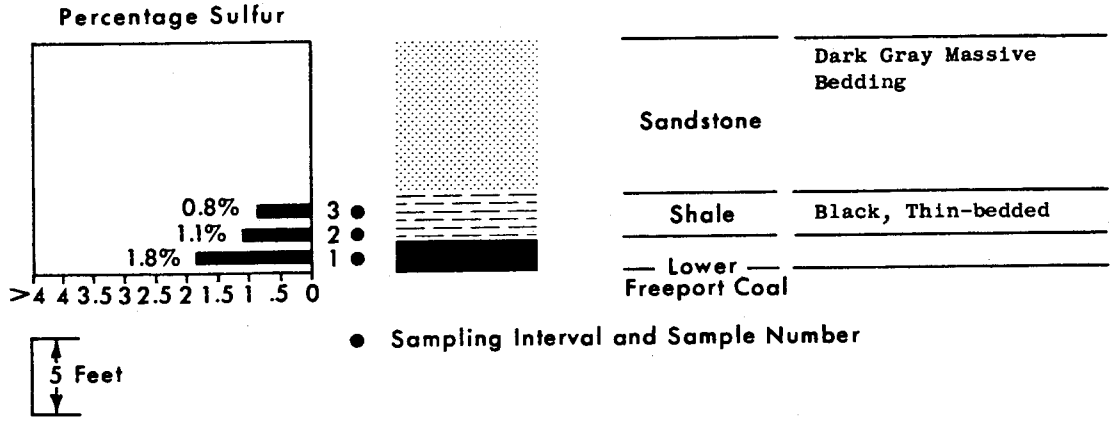
Figure 35



The strip mine, has been partially back filled. A deep mine has penetrated the seam, which has been abandoned and serves as an air shaft for a later deep mine.

STRATIGRAPHIC PROFILE OF MINE RM-5

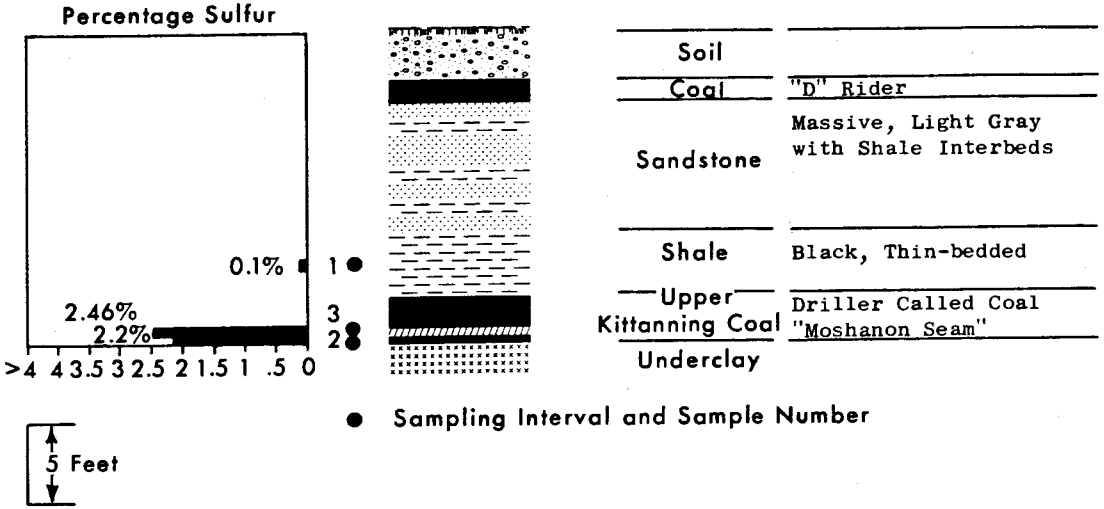
Figure 36



Mine has many open pits and at the time of sampling was being back filled. (December, 1965)

STRATIGRAPHIC PROFILE OF MINE RM-6

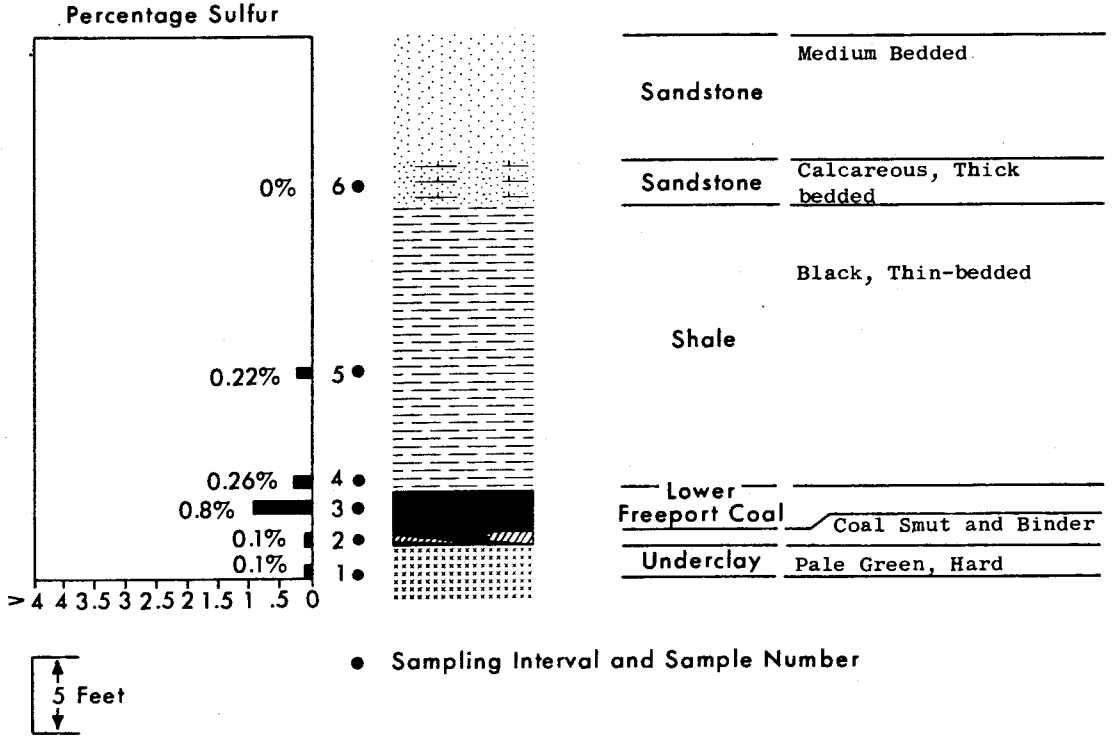
Figure 37



This mine is at the western most end of mine RM-8. Mine RM-8 was not sampled because the mine was being back filled at the time of visit, (summer, 1965,); however,water samples were obtained. The lower coal at RM-9 was being mined with an auger when the rock samples were collected.

STRATIGRAPHIC PROFILE OF MINE RM-9

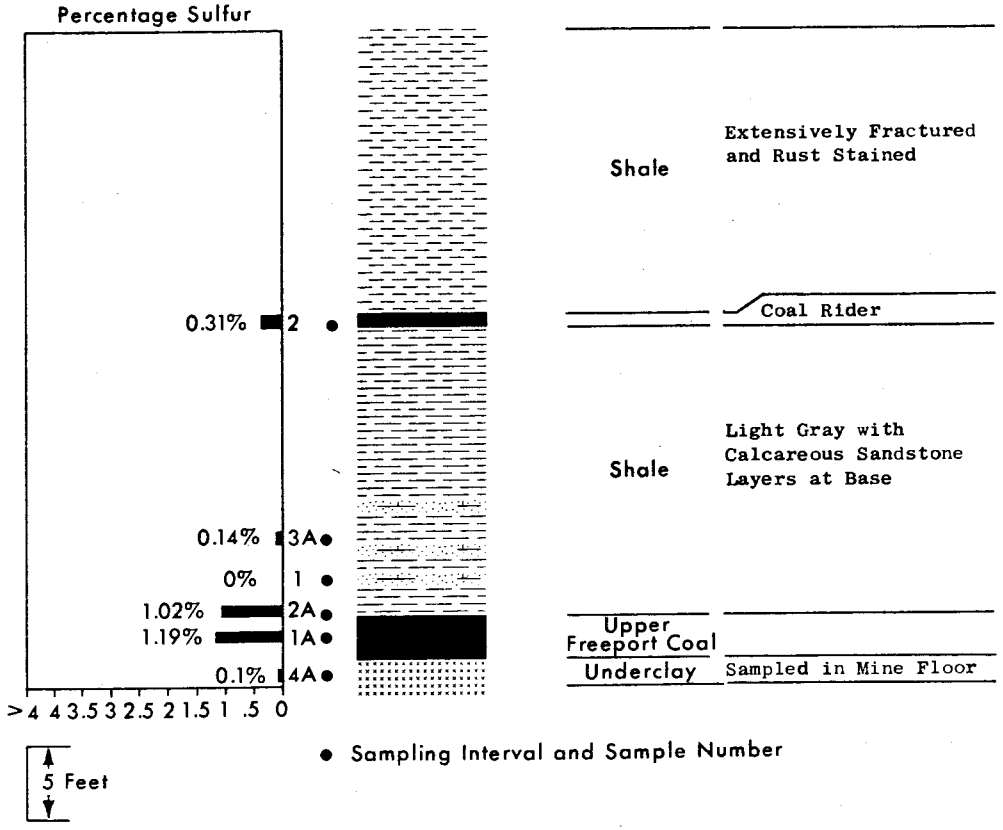
Figure 38



Samples taken from the coal seam at lower level of strip mine which was being auger mined at the time of collection (June, 1966).

STRATIGRAPHIC PROFILE OF MINE RM-15

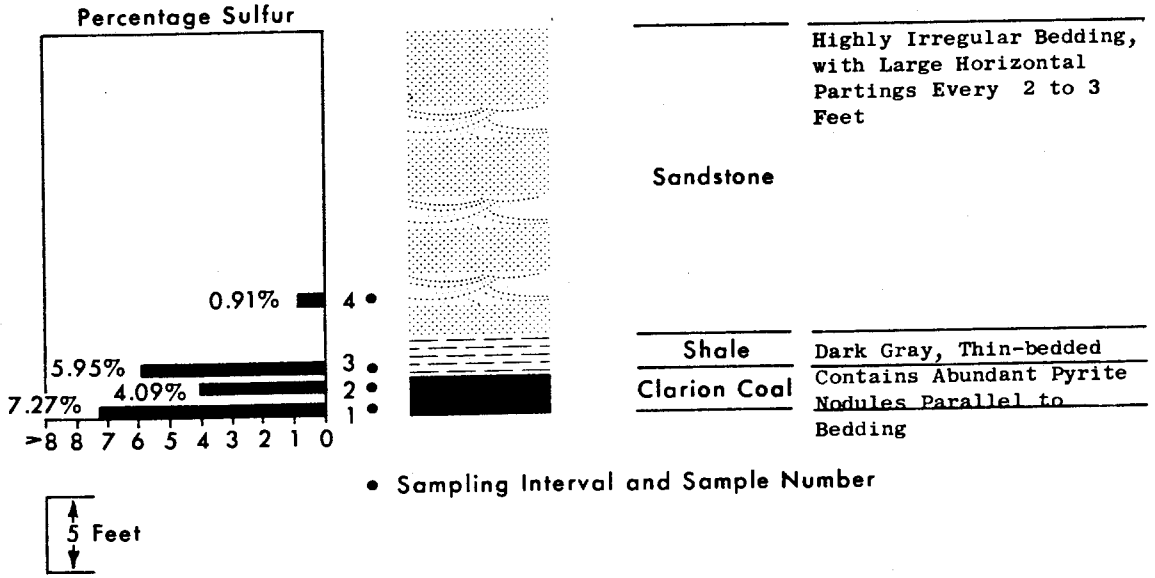
Figure 39



Same location as RM-15, this column represents the upper level of the mine from which the samples were collected. Samples 1A-4A were collected about 75 feet westward from samples 1 and 2.

STRATIGRAPHIC PROFILE OF MINE RM-16

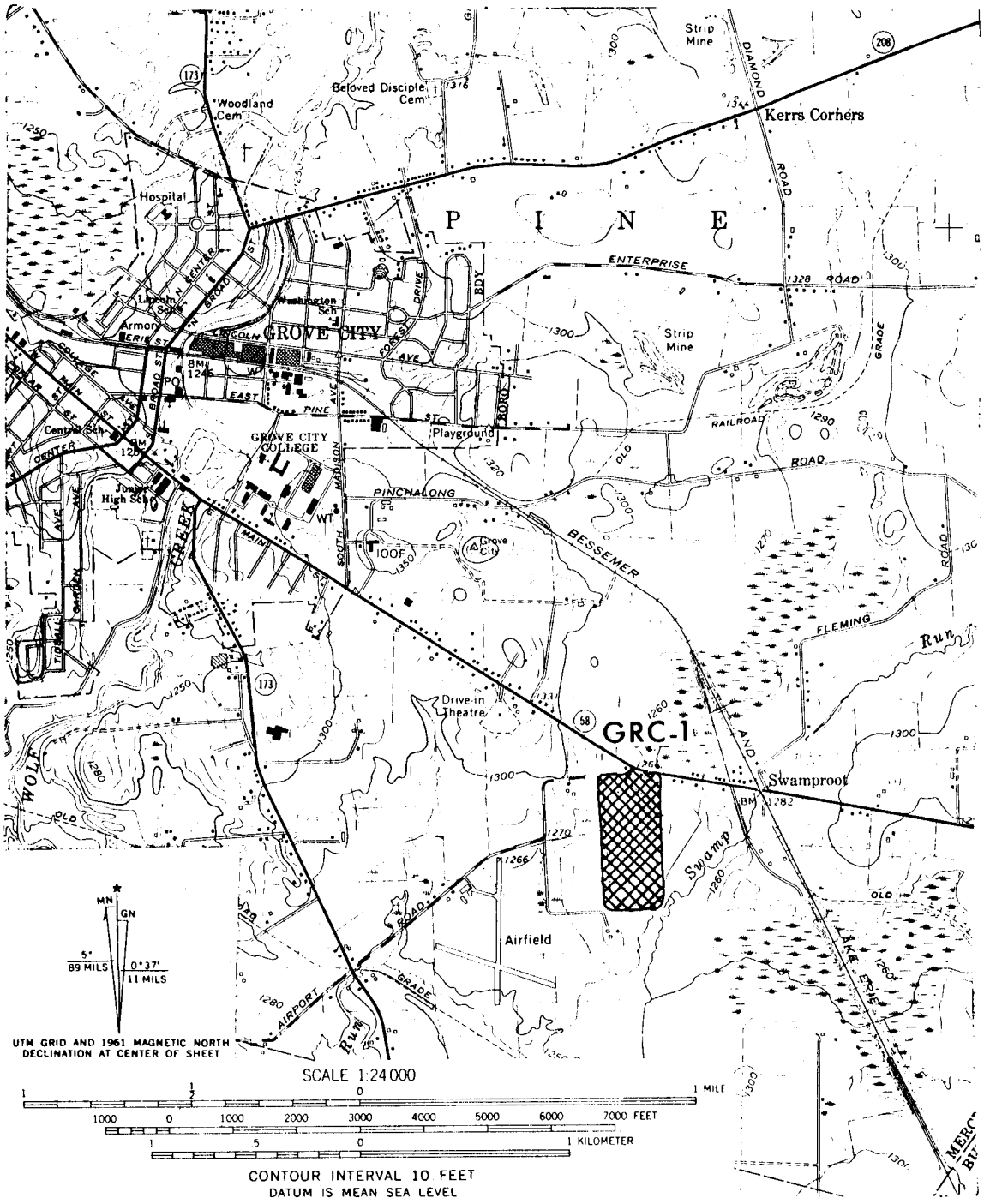
Figure 40



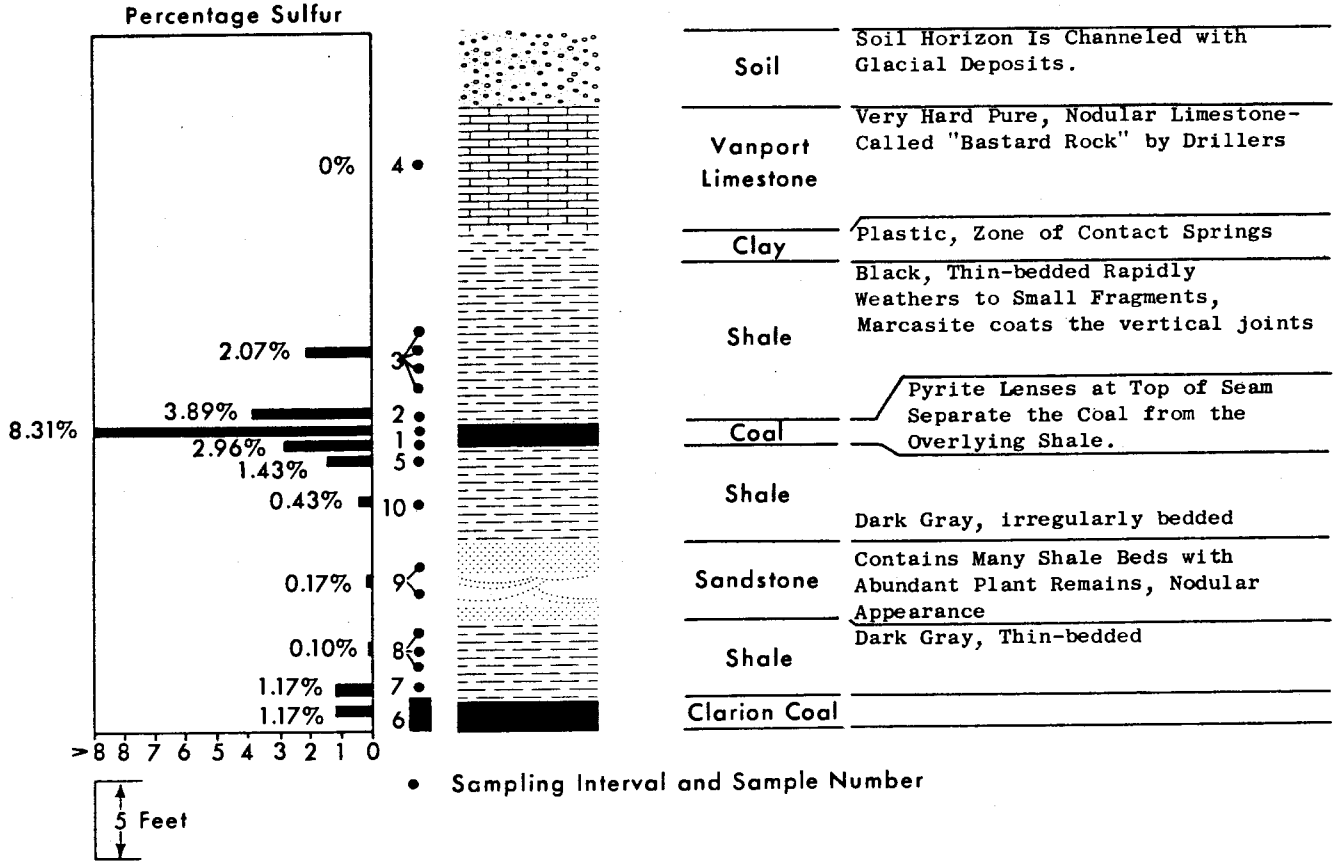
Strip mine located 7 1/4 miles east of Grove City, Pennsylvania on Route 208.

STRATIGRAPHIC PROFILE OF MINE BR-1

Figure 41



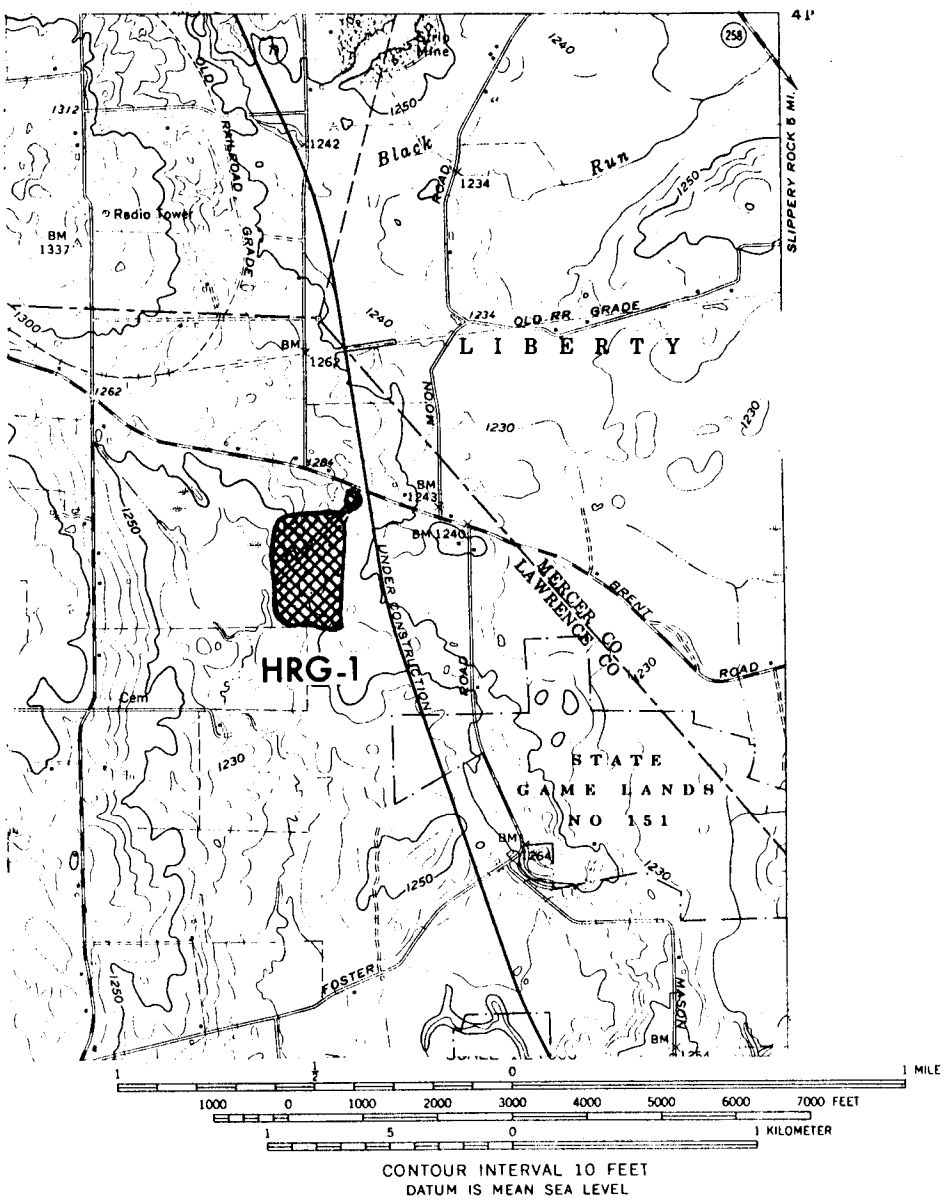
PORTION OF GROVE CITY QUADRANGLE (7½')
SHOWING THE LOCATION OF MINE GRC-1
Figure 42



Located one mile Southeast of Grove City, Pennsylvania on Route 58. Miner reported that a 6" drill hole drilled 69 feet below the mine floor (Clarion Coal) encountered artesian conditions in a sandstone aquifer. Mine is composed of two levels. Actively mined during the fall of 1966.

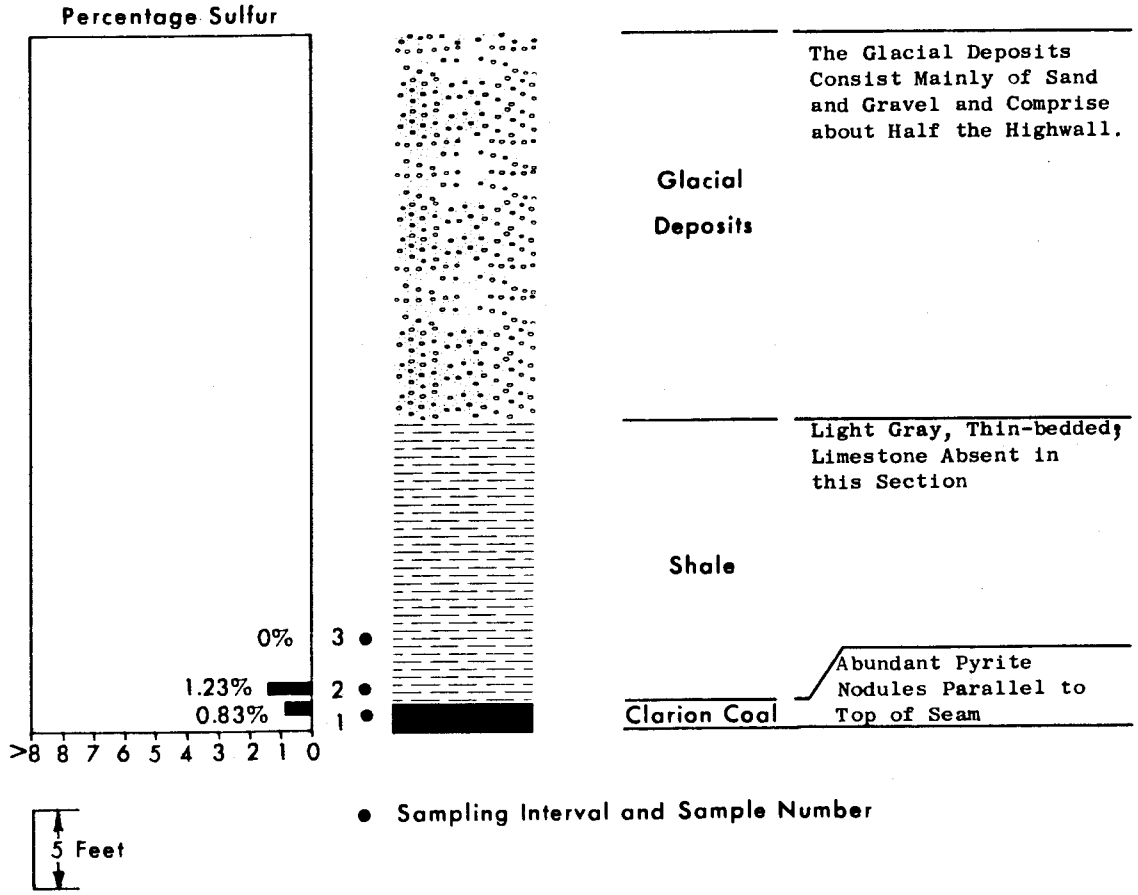
STRATIGRAPHIC PROFILE OF MINE GRC-1

Figure 43



PORTION OF HARLANSBURG QUADRANGLE (7½')
SHOWING THE LOCATION OF MINE HRG-1

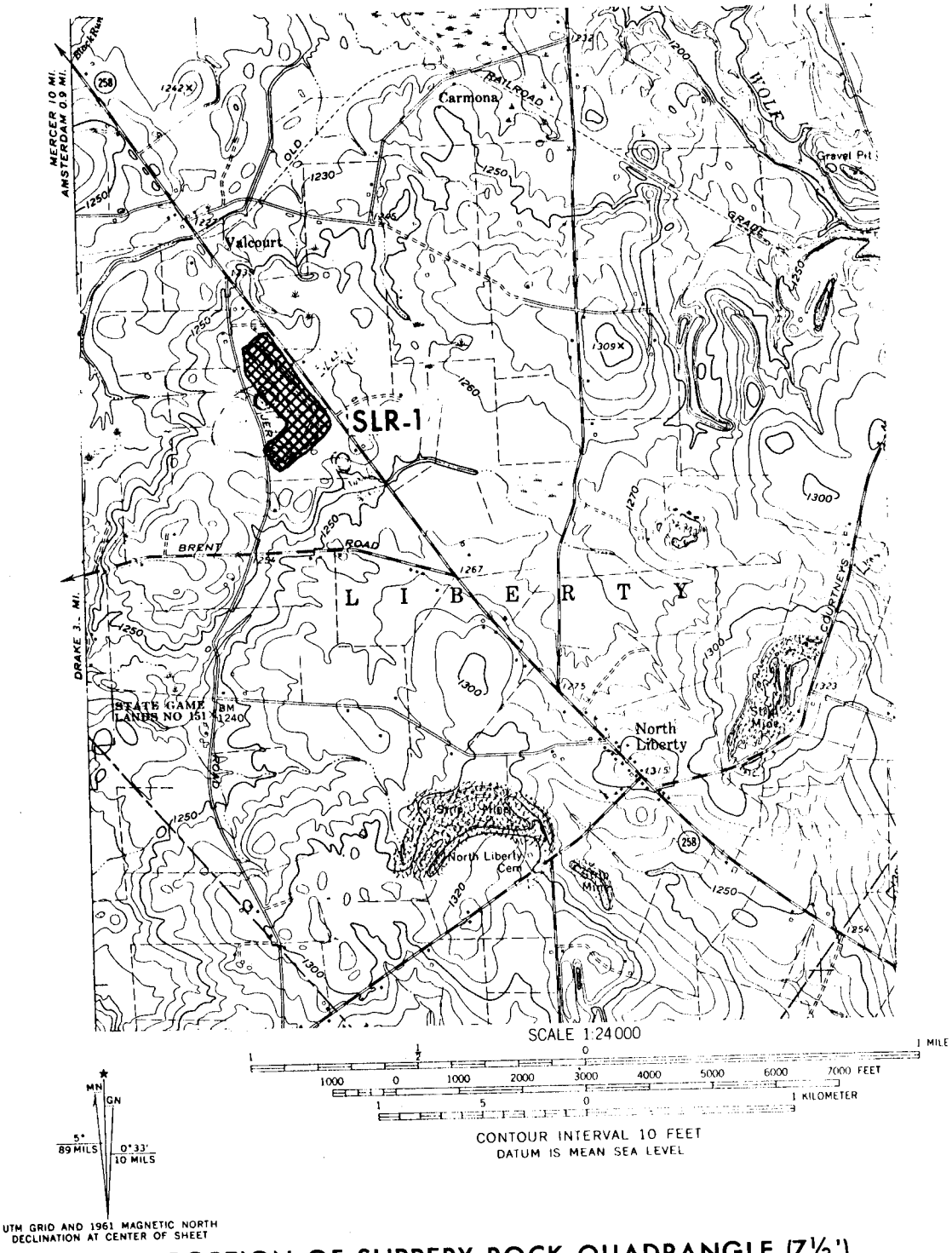
Figure 44



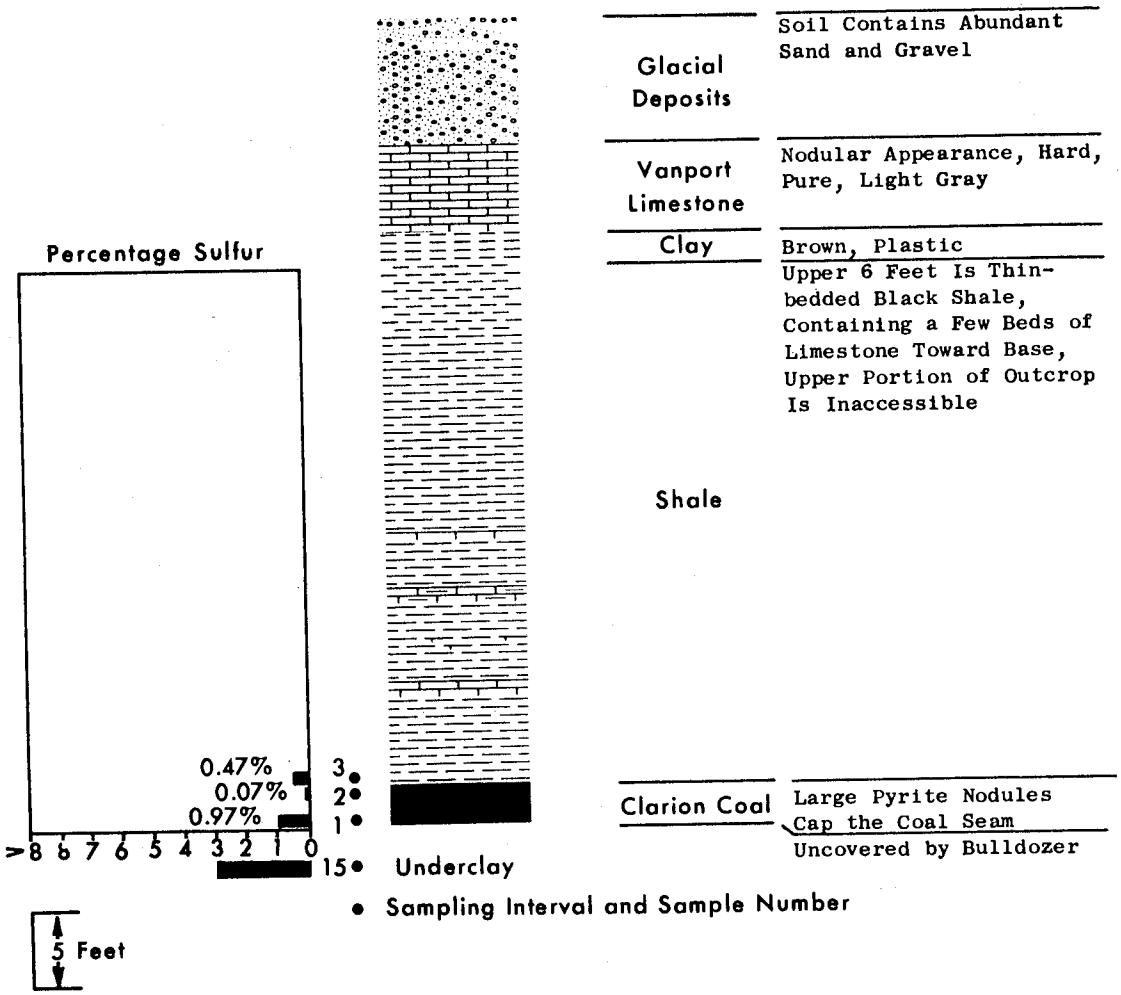
Strip mine located 6 miles northeast of Harlansburg, Pennsylvania.
Actively mined during the fall of 1966.

STRATIGRAPHIC PROFILE OF MINE HRG-1

Figure 45



PORTION OF SLIPPERY ROCK QUADRANGLE (7½')
SHOWING THE LOCATION OF MINE SLR-1
Figure 46



Strip mine located 4 miles northeast of Slippery Rock, Pennsylvania on Route 258. Actively mined during the fall of 1966.

STRATIGRAPHIC PROFILE OF MINE SLR-1

Figure 47

APPENDIX C

Hydrologic and Aqueous Geochemical Data

Table 14 - List of Private Wells Inventoried in the Clearfield Study Area

Sample Number	Owner	Type of Well	Elev. Above Sea Level(ft)	Total Depth of Well(ft)	Diam. of Well (in)	Length of Casing if present(ft)	Aquifer	Static Water Level Date	Static Water Level Depth(ft)	Sample Collected and Analyzed
CH-1	Robert Cline	Dug	1250	6	24	-	Recent All.	6/65	2	No
CH-2	H. Siebenrock	Drilled	1500	215	6	-	Up. Kit-M. Kit.	-	-	No
CH-3	Dayton Shifter	Drilled	1470	185	8	-	Mid. Kit.	1956	85	No
CH-4A	Elva Godin	Drilled	1460	102	6	-	Mid. Kit.	1960	94	Yes
CH-4B	Elva Godin	Dug	1467B. M.	35	24	-	Mid. Kit.	9/65	25	No
CH-5A	Joseph Wilson	Dug	1480	12	28	-	Mid. Kit.	10/65	8	No
								6/66	6	Yes
CH-5B	Joseph Wilson	Drilled	1480	65	6	-	Mid. Kit.	-	-	No
CH-6	Doryce Shifter	Drilled	1480	150	6	20	Mid. Kit.	1965	30	Yes
CH-7	D. Cochran	Drilled	1480	Well Buried		-	-	-	-	-
CH-8	Roy Ogden	Dug	1450	16	48	-	Mid. Kit.	9/65	13	No
CH-9A	J. Carl Ogden	Drilled	1480	78	6	25	Mid. Kit.	1966	10	Yes
CH-9B	J. Carl Ogden	Dug	1495	-	24	-	Up. Kit.	1966	1	Yes
CH-10A	Clyde Ardary	Drilled	1440	Well Idle		-	Lo. Kit.	-	-	No
CH-10B	Clyde Ardary	Drilled	1440	60	6	-	Lo. Kit.	-	-	No
CH-10C	Clyde Ardary	Drilled	1440	145	6	24	Cl. -Lo. Kit.	11/65	85	No
CH-11	-	Dug	1340	-	24	3	Mercer	9/65	1/2	No
CH-12	Albert Ogden	Dug	1710	16	36	16	Lo. Kit.	6/66	10	Yes
CH-13	Charles Green	Spring	1670	-	-	-	Clarion	-	-	Yes
CH-14	Arthur L. Ogden	Dug	1660	-	30	-	Clarion	6/66	1	Yes
CH-15	W. Sommerville	Drilled	1640	99	6	-	Cl. -Lo. Kit.	6/66	37	Yes
CH-16	Club Resort	Dug	1480	-	28	-	Mercer	6/66	1	Yes
CH-17	Amon Pifer	Dug	1490	6	32	-	Clarion	6/66	4	Yes
CH-18	Luther Ogden	Dug	1490	-	36	-	Clarion	6/66	1	Yes
CH-20	Morris Hile	Dug	1542	16	24	9	Mid. Kit.	6/66	3	Yes
CH-21	Ethel Hile	Drilled	1530	52	6	-	Mid. Kit.	-	-	Yes
CH-22	John Hile	Dug	1530	4.7	41	-	Mid. Kit.	6/66	1-1/2	Yes
CH-23	P. N. Morrison	Drilled	1570	158	6	to rock	U. Kit.	12/64	120	Yes
CH-24	D. Gearhart	Drilled	1520	50	6	20	U. -Mid. Kit.	-	-	Yes

Table 15 - Analyses of Water Samples

Ground Waters

Sample Number	Method of Collection	Date	Temp. °C	pH	Eh (mv) +	Specific Resistance (ohms)	Alkalinity (mg/l as HCO_3-)	Acidity (mg/l as H+)	Sulfate (mg/l as SO_4=)	Calcium (mg/l as Ca^{++})
CH-4A	KS	6/12/66	-	6.70	-	5,800	84	0	0	10
CH-5A	Bailer	6/12/66	10	5.30	285	17,000	4	0	14	2
CH-6	KS	6/12/66	15	6.75	110D	4,500	100	0	17	5
CH-9A	KS	6/12/66	-	6.95	80D	3,400	170	0	0	2
CH-9B	Bailer	6/12/66	10	5.20	285	3,400	4	0	85	12
CH-10C	Bailer	11/01/65	-	5.20	-	-	-	-	-	-
CH-11	Bailer	9/09/65	-	4.5	-	-	-	-	-	-
CH-12	Bailer	6/06/66	11	5.30	-	25,000	5	0	0	0
CH-13	Bot. Im.	6/06/66	10	4.85		6,200	4	0.08	61	Tr
CH-14	Bot. Im.	6/06/66	10.5	5.44	-	24,000	6	0	0	0
CH-15	KS	6/06/66	18	5.60	-	5,600	12	0	27	0
CH-16	Bot. Im.	6/06/66	9	4.85	-	28,000	6	0	0	0
CH-17	Bailer	6/06/66	10	5.60	-	27,000	5	0	0	0
CH-18	Bot. Im.	6/06/66	9	4.80	-	4,300	3	0.08	72	0
CH-20	Bailer	6/12/66	14	6.20	225	8,000	21	0	23	6
CH-21	KS	6/12/66	14	6.50	165D	6,000	38	0	23	11
CH-22	Bot. Im.	6/12/66	11	5.48	260	6,700	8	0	33	7
CH-23	KS	6/12/66	13	7.00	150D	5,200	50	0	33	11
CH-24	KS	6/12/66	14	6.50	150D	2,000	32	0	53	38
RM-7	Bot. Im.	4/15/67	13.5	8.30	-	2,800	75	0	0	50

KS - Sample taken from Kitchen Spigot
Bot. Im. - Sample taken by immersing bottle in water
"D" following the Eh readings indicates the needle was drifting while measurements were being made

Table 16 - Analyses of Water Samples

Mine Drainage and Pools

Sample Number	Source Sampled	Date	Temp. °C	pH	Eh (+mv.)	Specific Resistance (ohms)	Alkalinity (mg/l as HCO_3^-)	Acidity (mg/l as H^+)	Sulfate (mg/l as $SO_4^=$)	Calcium (mg/l as Ca^{++})
CM-6	Pool at highwall	11/17/65	-	3.1	-	-	-	-	-	-
		8/04/66	22	3.8	175D	1800	0	0.45	330	46
CM-6	Pool #1 outlet	8/05/66	17	3.50	250	1100	0	1.3	680	71
CM-6	Pool #3	8/04/66	19	3.50	235	1100	0	1.4	665	76
CM-6	Pool #4	8/04/66	16	3.55	205	1050	0	1.43	650	80
CM-6	Pool A	8/04/66	17	3.5	240	1100	0	1.4	650	74
		4/15/67	-	3.65	-	1100	0	1.30	600	above 50
CM-6	Pool A outflow	8/04/66	16	3.5	275	1100	0	1.35	680	64
CM-6	Pool B	8/04/66	16.5	3.5	225	1040	0	2.1	720	76
		4/15/67	-	3.60	-	1200	0	1.35	650	70
CM-6	Pool C	8/04/66	21	3.5	275	540	0	2.4	1270	170
CM-6	Pool C outlet	8/04/66	15	3.65	380	580	0	2.7	1270	153
For specific locations of pools sampled in Mine CM-6 refer to Plan View Map of CM-6 (Figure 20).										
CM-8	Pool	9/22/65		3.2	-	500	0	-	-	-
CM-10	Pool	8/15/67	15.5	4.1	-	8400	0	0.15	40	5
RM-1	Shaft drainage	12/02/65	-	8.2	-	-	-	-	-	-
		4/15/67	-	7.9	-	4500	71	0	0	33
RM-5A	Shaft drainage	12/11/65	5	6.75	-	9000				
RM-5B	Ground water bleed at seam	4/15/67	8.5	6.55	-	8600	9	0	0	14

Table 16 (continued)

Number	Source	Date	Temp.	pH	Eh	Resistance	Alkalinity	Acidity	Sulfate	Calcium
RM-5C	Air Shaft drainage	4/15/67	8	7.25	-	7000	25	0	28	19
RM-5D	Stream above mine	4/15/67	10	7.0	-	11000	27	0	less 10	12
RM-6	Pool (mine filled)	12/10/66	3	5.85	-	8000	-	-	-	-
RM-7	Shaft (stripped)	9/18/66	11.5	7.5	85	1950	123	0	0	66
RM-7	Drainage of shaft and strip mine	4/15/67	9.5	7.2	-	1900	102	0	less 20	81
	Ground water	4/15/67	13.5	8.3	-	2800	75	0	0	50
RM-8	Pool in mine	9/16/65	-	6.5	-	9400	-	-	-	-
	Highwall bleed	9/16/65	-	6.6	-	9000	-	-	-	-
	Water near refuse	9/16/65	-	2.4	-	800	-	-	-	-
RM-17	Pool (new mine)	4/15/67	-	7.80	-	4700	36	0	0	30
CLM-1	Pool	9/30/66	13	2.35	-	-	0	8.7	4000	350
GRM-1	Highwall bleed	10/06/66	10.5	7.65	210D	-	112	0	125	50
GRM-2	Pool near Rt. 58	10/06/66	11	7.1	105	-	130	0	125	94
GRM-3	Pool at mine end	10/06/66	-	7.45	-	-	170	0	100	68
HRM-1	Pool	10/06/66	10	7.8	225	-	220	0	55	100
HRM-2	Pool	10/06/66	10.5	7.1	225	-	240	0	60	81
KM-1	SE Highwall bleed	9/19/66	12	3.15	-	480	0	4.05	2860	108
KM-2	Pool SE Highwall	9/19/66	16.5	2.9	450	800	0	2.75	1000	93
KM-3	Bleed of West Wall	9/19/66	13	4.15	385	300	0	7.1	4800	360
KM-4	Bleed of East Wall	9/19/66	17	3.95	420	360	0	8.65	5660	198
KM-5	Stream from mine	9/19/66	-	2.80	-	325	0	8.5	5000	265
SLM-1	Pool #1 by coal	10/06/66	12	7.05	240	-	224	0	140	98
SLM-2	Pool #2 by Highwall	10/06/66	11	6.45	50	-	152	0	740	117
SLM-3	Pool #3 in Talus	10/06/66	10.8	6.35	85	-	382	0	150	290
SLM-4	Pool #4 in Talus	10/06/66	10.8	6.6	115	-	388	0	140	300

"D" following the Eh reading indicates the needle was drifting while the measurement was being made.

Table 17 - Analyses of Water Samples

Streams

Sample Number	Source*	Date	Temp. °C	pH	Specific Resistance (ohms)	Alkalinity (mg/l as HCO_3^-)*	Acidity (mg/l as H^+)*	Sulfate (mg/l as $SO_4^=$)	Calcium (mg/l as Ca^{++})
						*with PHS as source these are expressed as $CaCO_3$ equiv.			
CT-1	Sample	8/17/65	-	6.0	-	-	-	-	-
CT-2	Sample	8/22/65	-	4.2	-	-	-	-	-
CT-3	PHS*	2/13/52	-	4.55	-	4	20	100	
	Sample	8/17/65	-	4.5	-	-	-	-	-
	Sample	9/22/65	-	3.3		-	-	-	-
CT-4	Sample	9/22/65	-	6.05	-	-	-	-	-
CT-5	Sample	9/22/65	-	3.95		-	-	-	-
CT-9	Sample	8/17/65	-	6.00	-	-	-	-	-
	Sample	6/06/66	13	5.10	20,000	2	0.01	Tr	Tr
CT-11	PHS	9/21/48		3.2	-	-60	190	-	-
CT-12	PHS	9/21/48	-	5.94	-	12	26	-	-
CT-13	PHS	9/21/48	-	5.01	-	16	26	-	-
CT-14	PHS	9/07/48	-	4.2	-	10	18	-	-
	PHS	9/21/48	-	4.3	-	8	24	-	-
	PHS	1/06/49	-	4.95	-	8	14	-	-
	PHS	2/24/49	-	7.95	-	20	4	-	-
	PHS	3/02/49	-	4.78	-	12	16	-	-
	PHS	5/12/49	-	4.82	-	12	20	-	-
CT-15	PHS	1/06/49	-	4.9	-	8	10	-	-
	PHS	2/24/49	-	7.65	-	12	4	-	-
	PHS	3/02/49	-	5.0	-	8	10	-	-
CT-16	PHS	5/12/49	-	4.2	-	4	40	-	-
CT-17	PHS	5/12/49	-	4.8	-	8	22	-	-
CT-18	PHS	12/19/50	-	3.9	-	-2	160	-	-

* See Page 213

Table 17 (continued)

Number	Source*	Date	Temp.	pH	Resistance	Alkalinity	Acidity	Sulfate	Calcium
CT-19	PHS	12/19/50	-	3.9	-	-16	216	-	-
CT-20	PHS	12/19/50	-	3.48	-	-16	64	-	-
CT-21	PHS	4/17/51	-	6.1	-	8	2	-	-
CT-22	PHS	8/02/55	-	3.52	-	-24	176	640	-
CT-23	PHS	11/30/55	-	4.7	-	6	8	85	-
CT-24	Sample	6/06/66	18	3.5	760	0	2.7	1120	Tr
CT-25	Sample	6/12/66	18	4.35	3,600	0	0.25	97	13
RT-1	Sample	12/02/65	-	6.62	-	-	-	-	-
RT-2	Sample	11/17/65	-	5.80	-	-	-	-	-
	Sample	12/02/65	-	6.80	-	-	-	-	-
RT-3	Sample	11/65	-	2.70	-	-	-	-	-
RT-4	Sample	9/65	-	6.0	-	-	-	-	-
RT-5	PHS	3/02/49	-	4.95	-	10	14	-	-
	PHS	5/23/55	-	4.30	-	4	30	210	-
RT-6	PHS	7/27/51	-	7.12	-	72	-6	-	-
	PHS	9/03/54	-	7.50	-	68	-14	65	-
	PHS	8/18/55	-	6.98	-	74	-10	72	-
RT-7	PHS	7/27/51	-	7.3	-	72	-16	-	-
	PHS	10/20/53	-	7.3	-	82	-18	100	-
	PHS	8/18/55	-	7.2	-	78	-16	110	-
RT-8	PHS	7/09/53	-	6.31	-	30	-4	12	-
RT-9	PHS	7/09/53	-	6.6	-	28	-2	64	-

* See Page 213

Table 17 (continued)

Number	Source	Date	Temp.	pH	Resistance	Alkalinity	Acidity	Sulfate	Calcium
RT-10	PHS	10/13/53	-	3.3	-	-30	140	690	-
	PHS	7/07/55	-	4.31	-	8	16	385	-
RT-11	PHS	11/20/53	-	7.13	-	60	-10	180	-
	PHS	7/12/54	-	7.02	-	72	-12	78	-
	PHS	9/03/54	-	7.4	-	94	-8	260	-
RT-12	PHS	9/03/54	-	3.45	-	-12	88	750	-
RT-13	PHS	9/03/54	-	7.15	-	80	-16	95	-
RT-14	PHS	9/03/54	-	7.3	-	66	-6	160	-
RT-15	PHS	6/30/55	-	6.48	-	46	-8	185	-
RT-16	Sample	11/66	-	4.15	1060	0	0.6	500	126

*PHS for source indicates the data were obtained from the files of the Mine Drainage Section of the Public Health Service in Harrisburg, Pennsylvania. Acidity is the volumetric titration with a standard solution of known normality of Sodium Hydroxide in a hot solution to the end point with phenolphthalein indicator. Alkalinity is the volumetric titration in a cold solution with a standard solution of known normality of sulfuric acid to an end point of pH value of 4 with bromphenol blue indicator. Negative acidity values are alkalinities; negative alkalinity values are acidities. Both are expressed as mg/l as $CaCO_3$. To convert Acidity as $CaCO_3$ to H^+ divide by 100. To convert Alkalinity as $CaCO_3$ to HCO_3^- multiply by 0.61.

*Sample as the source indicates the data were obtained from measurements made in this study using the chemical analyses described in the text.

CLEARFIELD, PA.

CLEARFIELD QUADRANGLE
PENNSYLVANIA—CLEARFIELD CO.
7.5 MINUTE SERIES (TOPOGRAPHIC)

SCALE 1:24000
1 0 1 MILE
1000 0 1000 2000 3000 4000 5000 6000 7000 FEET
1 .5 0 1 KILOMETER
CONTOUR INTERVAL 20 FEET
DATUM IS MEAN SEA LEVEL

7° MAGNETIC NORTH TRUE NORTH
APPROXIMATE MEAN DECLINATION, 1959

EXPLANATION

	Symbol	Name	Thickness	Description
	Qa	RECENT ALLUVIUM	Variable	Unconsolidated Stream Sand and Gravel
	Pc	CONEMAUGH GROUP	Lower 225 Feet Only	Cyclic Repetitions of Soft Clay, Freshwater Limestone, Coal, Shale and Sandstone. Base Is the Top of the Upper Freeport Coal.
ALLEGHENY GROUP	Pf	FREEPORT FORMATION	Usually 25 to 70 Feet	Includes Upward, the Lower Freeport Clay and Associated Fresh-water Limestone, the Lower Freeport Coal, Non-marine Shale, Sandstone, the Upper Freeport Clay and Associated Fresh-water Limestone and the Upper Freeport Coal.
	Puk	UPPER KITTANNING FORMATION	Usually 30 to 80 Feet	Includes Upward, the Upper Kittanning Clay and Associated Fresh-water Limestone (Johnstown Limestone), the Upper Kittanning Coal, Siltstone and Sandstone.
	Pmk	MIDDLE KITTANNING FORMATION	Usually 30 to 80 Feet	Includes Upward, the Middle Kittanning Clay, the Middle Kittanning Coal, Semi-marine Shale or Claystone, the Middle Kittanning Rider Coal, and Sandstone.
	Plk	LOWER KITTANNING FORMATION	Usually 40 to 80 Feet	Includes Upward, the Lower Kittanning Clay, the Lower Kittanning Coal, a Semi-marine Shale, the Lower Kittanning Rider Coal and Sandstone
	Pcn	CLARION FORMATION	Usually 50 to 110 Feet	Includes Upward, the Clarion Clay, the Clarion Coals
POTTSVILLE GROUP	Pm	MERCER FORMATION	Usually 30 to 80 Feet	High-alumina Flint Clays, Lower Mercer Coal, Shales, Siltstones and Sandstones, and Upper Mercer Coal
	Pre-m	PRE-MERCER		Undivided Connoquenessing - Pocono Formations

Formational contacts are taken at the base of the underclay, except the Freeport Formation whose top is the top of the uppermost coal.

Base Map from U.S. Geological Survey Clearfield 7½' Quadrangle
Geology from "Geologic Map of the Clearfield Quadrangle," (In Press),
Author - Albert Glover
Publisher and Source - Pennsylvania Geological Survey

GEOLOGIC MAP OF THE CLEARFIELD AREA

PLATE I



GLEN RICHEY, PA.

1 0 1 MILE

1000 0 1000 2000 3000 4000 5000 6000 7000 FEET

1 .5 0 1 KILOMETER

7° TRUE NORTH MAGNETIC NORTH

APPROXIMATE MEAN DECLINATION, 1944

Contour interval 20 feet
Datum is mean sea level

SCALE 1:24000

PENNSYLVANIA
(CLEARFIELD COUNTY)

GLEN RICHEY QUADRANGLE

7½-MINUTE SERIES

EXPLANATION

	Symbol	Name	Thickness	Description
	Qa	RECENT ALLUVIUM	Variable	Unconsolidated Stream Sand and Gravel
	Pc	CONEMAUGH GROUP	Lower 225 Feet Only	Cyclic Repetitions of Soft Clay, Freshwater Limestone, Coal, Shale and Sandstone. Base Is the Top of the Upper Freeport Coal.
ALLEGHENY GROUP	Pf	FREEPORT FORMATION	Usually 25 to 70 Feet	Includes Upward, the Lower Freeport Clay and Associated Fresh-water Limestone, the Lower Freeport Coal, Non-marine Shale, Sandstone, the Upper Freeport Clay and Associated Fresh-water Limestone and the Upper Freeport Coal.
	Puk	UPPER KITTANNING FORMATION	Usually 30 to 80 Feet	Includes Upward, the Upper Kittanning Clay and Associated Fresh-water Limestone (Johnstown Limestone), the Upper Kittanning Coal, Siltstone and Sandstone.
	Pmk	MIDDLE KITTANNING FORMATION	Usually 30 to 80 Feet	Includes Upward, the Middle Kittanning Clay, the Middle Kittanning Coal, Semi-marine Shale or Claystone, the Middle Kittanning Rider Coal, and Sandstone.
	Plk	LOWER KITTANNING FORMATION	Usually 40 to 80 Feet	Includes Upward, the Lower Kittanning Clay, the Lower Kittanning Coal, a Semi-marine Shale, the Lower Kittanning Rider Coal and Sandstone
	Pcn	CLARION FORMATION	Usually 50 to 110 Feet	Includes Upward, the Clarion Clay, the Clarion Coals
POTTSVILLE GROUP	Pm	MERCER FORMATION	Usually 30 to 80 Feet	High-alumina Flint Clays, Lower Mercer Coal, Shales, Siltstones and Sandstones, and Upper Mercer Coal
	Pre-m	PRE-MERCER		Undivided Connoquenessing - Pocono Formations

Formational contacts are taken at the base of the underclay, except the Freeport Formation whose top is the top of the uppermost coal.

Base Map from U.S. Geological Survey Glen Richey 7½' Quadrangle

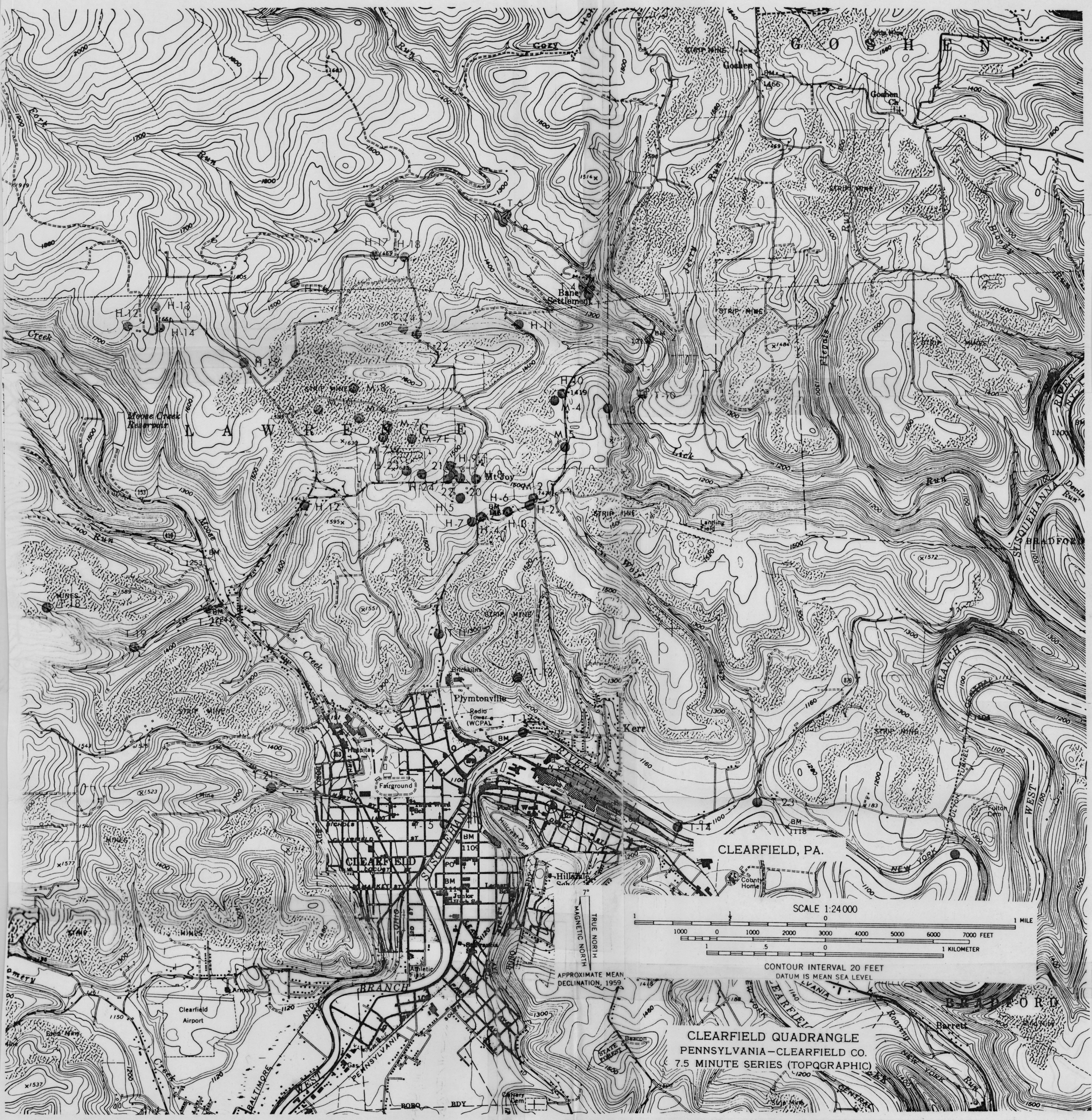
Geology from "Geologic Map of the Northern Half of the Houtzdale Quadrangle"

Author - William E. Edmunds

Publisher and Source - Pennsylvania Geological Survey

GEOLOGIC MAP OF THE GLEN RICHEY AREA

PLATE II



LEGEND

T = Water Sample Collected from a Stream

H = Water Sample Collected from Domestic Supply

M = Water and/or Rock Samples Collected from a Mine

WATER AND ROCK SAMPLING LOCATION MAP OF THE CLEARFIELD AREA

Plate III



LEGEND

T = Water Sample Collected from a Stream

M = Water and/or Rock Samples Collected from a Mine

WATER AND ROCK SAMPLING LOCATION MAP OF THE GLEN RICHEY AREA INCLUDING THE KREBS MINE

Plate IV