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Development of a Natural Laboratory for the Study of Acid Mine Drainage

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February, 1968

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Submitted to:
Office of Water Resources Research
U. S. Department of the Interior
Research Project Completion Report
Project No. A-001-OHIO

DEVELOPMENT OF A NATURAL LABORATORY FOR THE STUDY OF ACID MINE DRAINAGE

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Water Resources Center
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ABSTRACT

DEVELOPMENT OF A NATURAL LABORATORY FOR THE STUDY OF ACID MINE DRAINAGE

A small drift mine in Vinton County, Ohio, has been characterized and instrumented to permit a detailed study of the influence of oxygen concentration, microgiological factors, and hydrologic features on rate of pyrite oxidation within the system.

This experimental mine will be treated as a pilot-scale reactor to obtain information in a natural environment on the kinetics of the reaction responsible for acid mine drainage.

Six observation wells were dug and core samples taken at selected points surrounding the mine to establish ground water table and the aquifer supplying the mine.

Base rate data of acid run-off as a function of water flow rate and water level in observation wells were collected.

The mine was sealed and maintained under a slight positive pressure of nitrogen. Oxygen concentration dropped to less that 2 % in three months. When "sealed" in a conventional manner, the atmosphere in the mine never dropped below 10 % oxygen after being closed for several years.

Acid run-off decreased approximately 50 % after six months under nitrogen pressure. The response time of the mine to imposed changes and characterization of reaction sites, in terms of physical and chemical environment, as well as location, are now being studied.

Smith, E. E. and Shumate, K. S.
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THE STUDY OF ACID MINE DRAINAGE
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DEVELOPMENT OF A NATURAL LABORATORY FOR THE STUDY OF ACID MINE DRAINAGE

Studies related to the cause and alleviation of acid mine drainage have been either: 1) laboratory-scale investigations in which the reactive material was removed from its natural environment, or 2) demonstration-type studies in which the effect of mine "sealing" and flooding, change in water flow patterns, etc. for specific geologic and hydrologic conditions are observed on full-scale mining operations.

This project was designed to obtain experimental information on an intermediate or pilot-scale facility. The " pilot plant " is a small drift mine known as the McDaniel's Test Mine located in Vinton County, Ohio, This mine has been characterized and instrumented to permit detailed and precise measurements of differences brought about by controlled conditions within the test facility.

Although an actual mine is utilized in this project, it is not a demonstration project. The experimental conditions to be imposed and characteristics of the mine are not, nor are they intended to be, typical of that in conventional operations.

This experimental mine should be viewed as a pilot-scale " reactor " in which the kinetics of the reaction taking place within the system can be analyzed from both a fundamental and engineering point of view. As in a typical pilot plant, the conditions within the reactor can be varied beyond the normal operating range in order to develop fundamental information on reaction kinetics, a situation not possible in demonstration projects.

The facility and experimental program are unique in the study of acid mine drainage. They are a necessary step in developing basic engineering data for the design procedures for abatement of acid mine drainage from abandoned drift mines.

OBJECTIVES

The overall objective of this project is to determine the kinetics and rate-controlling factors of acid mine discharge under natural conditions. The rate-controlling factors in a natural environment can be different from those observed in laboratory studies.

To accomplish this overall goal, specific objectives may be listed:

1. Effect of oxygen concentration on rate of discharge from mine.
2. Influence of microbiological factors on rate of acid discharge from mine.
3. Location of reactive sites in relation to exposed coal face and characterization of conditions predominating at the reactive site (i.e. vapor phase or liquid phase oxidation, and mechanism by which reaction products are removed from reactive sites)

ACCOMPLISHMENTS

Analysis of System:

A " natural " laboratory of this type is necessary in order to relate basic laboratory-scale kinetic studies to the kinetics of acid discharge from actual mining operations.

For example, laboratory investigations have determined vapor phase and liquid phase oxidation rates of pyrite as a function of oxygen concentration. But without some method of determining the nature of the reaction sites in a mine, neither the type of reaction, nor the diffusional resistance (hence concentration) of oxygen involved in acid formation can be predicted. In addition, mechanisms by which oxidation products reach effluent waters cannot be predicted without some knowledge of reaction sites.

In other words, it is impossible to predict the kinetics of acid mine discharge rates without more information on the rate-limiting mechanisms that are important in a natural system. While the natural conditions for studying the chemical reaction may be duplicated in a laboratory, the physical parameters can only be evaluated in a controlled, natural environment as exemplified by the McDaniel's Test Mine.

The role of bacteria in rate of acid discharge cannot be determined until the physical environment and its influence on reaction rate is known. Laboratory data have shown that bacteria can increase pyrite oxidation rate by several orders of magnitude, but if acid discharge is not limited by the oxidation reaction, bacteria would have no effect on rate of acid discharge, even if the pyrite oxidation is a microbiological reaction.

Here again the kinetic information of a natural system cannot be determined from laboratory data since the physical parameters cannot be assessed at the present time.

Characterization of Site:

Prior to May 8, 1965, the mine had been flooded to a depth of approximately three feet above the outlet valve in the mine seal (which was constructed in 1957) . On May 8, the valve was opened and the mine drained. Before draining the mine, samples were taken of the atmosphere in the mine above the impounded water. During the draining operation, samples were taken of the drainage which was concurrently treated with slaked lime to decrease deterioration of water quality in the stream below the mine. On May 18, the manhole cover in the seal was removed, and the interior of the mine was examined. The mine was found to be structurally sound, and plans were made for an accurate planimetric survey of the mine interior. Reference spads were set in the mine roof, and a reference line extended through the seal into the open area in front of the mine. The planimetric survey was finished on June 3, and reference points were placed on the hillside above the mine. The outline of the mine was traced on the hillside, which allowed the selection of sites for five of six observation wells. The location of the sixth well was determined at the time of the drilling of the wells. A planimetric map of the mine and the prepared observation wells is given in Figure 2 in the Appendix.

Having determined the location of the prepared wells, the requisite depths of the wells were estimated, and it was found that the budget would allow the holes to be cored, thereby yielding the maximum possible amount of detailed information on the sub-surface geology of the area surrounding the mine. The drilling was completed during the first week in August.

Boring logs plus soil sample and rock cores indicate that the 24' to 35' of sandstone overlaying the coal seam is the primary aquifer supplying the McDaniel's Mine. The observation wells provide a means of establishing the approximate contour of the ground water table. Only one well (No. 6) shows a significant head of water above the coal. Investigations indicate that water level measurements at well No. 6 provide a satisfactory means of estimating ground water flow into the mine when the outflow cannot be measured directly. Weekly observation of water flow and total acid concentration from the mine have been made (see Figures 5A , B, C) to establish base rate data and give the basis for determining effect of changes imposed on the system.

Samples of the coal plus shale and clay partings at three points in the mine were collected and examined for " forms of sulfur ". Results of analyses are tabulated in the Appendix. By this analysis the degree and depth of fractures from blasting practiced when the mine was active, it appears that interior areas of the coal seam may be exposed several feet from the working face. Water " drips " from the mine ceiling were collected and analyzed to determine the quality of water reaching the mine before it encounters the coal seam.

In addition to planimetric mapping of the mine's interior (Figures 3 and 4), elevation bench marks have been established in the Big Four Hollow in which the mine is located, and out-crop elevations determined down to State Highway 278 (Figure 1). The dip of strata and topography in the general area of the mine has thus been established.

Site Preparation:

During the latter stages of active mining, gob from the operation was piled against the coal faces not being worked instead of being carted from the mine. In order to have a good measure of the coal seam exposed and to gain a better-defined environment within the mine, it was decided to remove this refuse. This turned out to be quite a job. It is estimated that over25 tons of material were removed by hand. Removal of the rear wall of the mine seal wall was necessary. The job was completed early in September, 1965.

Construction of an adit was started and completed as soon after the gob was removed as the contracter was available. The adit replaced the frame structure which originally covered the mine seal. The adit which enclosed the mine seal was constructed of cement block, and has an 8' by 8' room separated from the mine entrance. The room is equipped for use as an analytical laboratory and housing for recording instruments.

A single phase 220 VAC power line was contracted and run back to the mine.

The original seal was constructed of hollow concrete block and painted with "Thoroseal". When preparing the back wall of the seal (which was removed during the gobbing operation) for mounting the sampling line panel, it was discovered that the second and third tier of block were disintegrating-- apparently from the inside out. Evidently, the acid water had leaked into the hollow core of these blocks. Where the core was grounted, no evidence of attack was apparent. Damaged portions of the seal were replaced with solid block, and the entire inside surface coated with a bituminous sealer.

The portion of the seal grouted to the mine entrance was in excellent condition and required little repair.

A new manhole cover and seal was purchased and installed and a stainless steel panel for mounting sampling lines was mounted on the mine seal wall.

The " permeability " of the mine to air was determined by raising the pressure in the mine to approximately 20 cm. of water and observing the rate of pressure decline. From these data it was possible to calculate the amount of gas required to maintain a given pressure differential between mine and atmosphere.

Assuming no net change in atmospheric pressure over a week's period, it was found that 600 cu.ft. of air per week would be lost if a differential pressure of 1.0 mm. of water were maintained. This is equivalent to slightly less than 3 "K" cylinders of oxygen or nitrogen, which may be readily transported and installed once a week.

The pressure within the mine is controlled by a water manometer. The contact in the water manometer is one side of the input to a sensitive relay which activates a solenoid valve on the gas supply when the pressure in the mine falls below the desired pressure differential.

A rain gauge and recorder for water level in Bore Hole No. 6 was installed at the site.

Experimental Results:

Since October 6, 1966, the pressure in the mine has been controlled at 1mm. water pressure by nitrogen injection.

In approximately two months, the oxygen concentration decreased to 3 %, and has varied between 1% and 2% since January 1, 1967.

This is the first time a mine has been truly " sealed ". Simply putting a vapor barrier over the main openings cannot prevent interchange of air in and out of the mine since " breathing " caused by variation in atmospheric pressure replenished the supply of oxygen. A vapor seal on this same mine, which was in place for over five years, did not reduce the oxygen below 10%.

No significant changes was noted in acid run-off for the first several months. Since water discharge rate was increasing, it is possible that oxidation products produced months earlier were being flushed from their reaction sites. Then too, there was no basis on which to judge the response time of the mine to impressed changes. Therefore the same nitrogen pressure was maintained to more definitely establish the change in acid run-off with oxygen concentration.

The quantity of nitrogen required to maintain a positive pressure in the mine decreased during the winter months. This was due in part to a less permeable overburden as the moisture content at the surface strata increased. In addition, condensation of water from the moist air in the mine in the manometer leg changed the setting of the manometer so that the actual pressure differential was probably less than 1mm. of water and in fact may have actually gone negative on some occasions.

In view of this, the differential pressure in the mine was raised to 2 or 3 mm. water pressure on May 13, 1967. Within two weeks, a definite decrease in acid concentration of run-off was observed.

Concentration of acid leveled-off about 50% below the base values of the year before.

Interpretation of Results:

In order to interpret results, information developed through other research projects at The Ohio State University should be mentioned.

During the last five years, a study to describe the basic mechanism and kinetics of pyrite oxidation has been underway. Information on the effect of temperature, as well as oxygen, water, and bacterial concentration, on pyrite oxidation rate for both vapor phase and liquid phase systems has been obtained.

Morth and Smith (1) reported the effect of oxygen concentration on oxidation rate in the absence of bacteria and diffusional resistance. The rate data they obtained was correlated by the Hougen and Watson (2) " active site " equations. These data indicate that the chemically rate-controlled oxidation of pyrite is a continuous (approximately proportional) function of oxygen concentration; and the rates are similar in either saturated liquid or saturated vapor oxidation.

Konecik (3) made a detailed study of the effect of Ferrobacillus ferroxidans on the kinetics of pyrite oxidation. He found that the influence of bacteria is relatively uneffected by oxygen concentration until the dissolved oxygen falls well below one part

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[1] . Morth, A. H. and Smith, E. E., " Kinetics of the Sulfide to Sulfate Reaction, " Paper presented to 151st National ACS Meeting, Pittsburgh, Pennsylvania, March 22-31, 1966.

[2] Hougen, O. A., Watson, K. M., " Chemical Process Principles-Part III, " John Wiley & Sons, Inc., New York (1947)

[3] Konicek, M. G., " The Biological Oxidation of Iron Pyrite, " M.S. Thesis, Ohio State University (1966).

per million. That is, the rate of pyrite oxidation in a system whose rate is controlled by bacterial activity is virtually independent of oxygen concentration above a value of 1. 0 ppm.

Based on these observations, data giving the effect of oxygen concentration on the rate of acid production from the McDaniel's mine can be used to indicate the relative importance of the bacterial or chemical rate in this natural environment. In other words, if the rate of acid run-off from the mine is proportional to oxygen concentration at the reaction sites, the chemical reaction is rate-controlling. If the rate of acid production is independent of oxygen concentration, bacterial reaction is indicated as the rate-controlling reaction.

Note also that the oxygen concentration at the reaction site must be known before the type of reaction can be inferred from acid production data. If diffusional resistances are rate-controlling, both chemical and bacterial reaction rate would be (approximately) proportional to oxygen concentration.

As discussed earlier, (4) it is very likely that diffusional resistances play a big part in determining oxidation rate in an underground mine such as the McDaniel's site. Evidence was given indicating that the majority of reaction sites are located several feet or more from the exposed face of the coal. Therefore both gas phase diffusion as well as oxygen diffusion through a laminar flowing water phase could be rate-controlling. It was also shown that the dissolved oxygen in the water entering the mine is practically zero, and even if it were saturated could only account for a small percentage of the total oxidation that takes place.

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[4] Smith, E. E., " Engineering Aspects of Acid Mine Drainage, " Second Annual Symposium on Water Resources Research, Ohio State University, June 1966.

The data presented in Figures 5B and 5C indicates that the decrease in acid production when the mine was under 1 to 2 % oxygen, was approximately 50% of the rate in a normal atmosphere. This is only one-fourth the decrease expected if one assumes the concentration at the reaction sites is the same as that in the mine.

However, if gas phase diffusional resistance is important in determining rate at reaction sites away from the mine face, the concentration of oxygen at these reaction sites when the air in the mine was atmospheric could be well under 21%. That is, the actual change in concentration of oxygen at the majority of the reaction sites when the oxygen concentration in the mine was changed from 21 to 1% may have been much less than 21 to 1.

The decrease in acid concentration caused by an increase in differential pressure between the mine and atmosphere also indicates a difference in oxygen concentration in the mine and at the reaction sites. When the porous media containing the pyrite was purged by increasing the nitrogen pressure, acid concentration dropped.

Presumably an oxygen concentration gradient exists thru the porous media separating the mine from the atmosphere. If there is little or no vapor flow through the channels, the oxygen concentration would vary from that in the mine to that in the atmosphere.

Until the active reaction sites are better identified and characterized, it is not possible to positively interpret acid production rate as indicated by acid run-off.

Another complicating factor is the obvious delay in removal of oxidation products from the reaction sites. As shown by Figures 5A, B, and C in the Appendix, acid concentration increases with rate of water flow. If products were removed as formed, the quantity of acid would remain relatively constant, i.e. as run-off rate increased, acid concentration would decrease because oxidation rate is probably constant. While this definitely indicates a delay in response, the actual response time cannot be judged from these data.

FUTURE RESEARCH

Research at this facility is being continued with support through the FWPCA. Studies to find response time of the mine, and the identification and characterization of reaction sites are now underway.

The response time is to be determined by imposing a stepwise input of oxygen concentration and following the response of acid concentration.

Core drilling equipment has been ordered to examine the sulfur-bearing strata surrounding the mine to determine 1) extent of weathering as a function of distance from the exposed coal face, and 2) the permeability of the strata at the point where evidence of oxidation is found. Directional permeability, i.e. to the mine and to the atmosphere, will be measured where possible.

Effect of oxygen concentration, as well as chlorine gas purge, will be used to establish effect of microbiological factors or rate of acid production.

APPENDIX

Sulfur Analysis
From
McDaniel's Test Mine

Drill (Face) Samples:

Sample Location No. 1 (Ten feet to left of entrance)

		% of Sulfur *			
Level	**Depth**	**Total**	**Sulfate**	**Pyritic**	**Organic**
Overburden	0-3 "	7.74	0.97	6.43	0.34
Top 1/3	0-3 "	2.02	0.21	1.10	0.71
Top 1/3	3-12"	1.81	0.19	0.91	0.71
Shale parting	0-3 "	4.26	0.86	3.03	0.37
Shale parting	3-12"	10.74	0.93	9.51	0.30
Middle 1/3	0-3 "	1.94	0.20	0.91	0.83
Middle 1/3	3-12"	2.78	0.29	1.61	0.88
Lower 1/3	0-3 "	3.49	0.60	2.37	0.52
Lower 1/3	3-12"	4.05	0.79	2.68	0.59
Sample Location No. 2 (left-center, back wall)					
Top 1/3	0-3 "	2.45	0.28	1.49	0.68
Middle 1/3	0-3 "	2.82	0.28	1.86	0.68
Shale Parting	0-3 "	2.28	0.08	1.87	0.33
Lower 1/3	0-3 "	3.52	0.49	2.36	0.67
Sample Location No. 3 (28 feet from entrance along right wall)					
Top 1/3	0-3 "	4.35	0.51	3.12	0.72
Top 1/3	3-12"	3.26	0.41	2.18	0.67
Middle 1/3	0-3 "	3.16	0.46	2.05	0.65
Lower 1/3	0-3 "	2.55	0.31	1.59	0.65

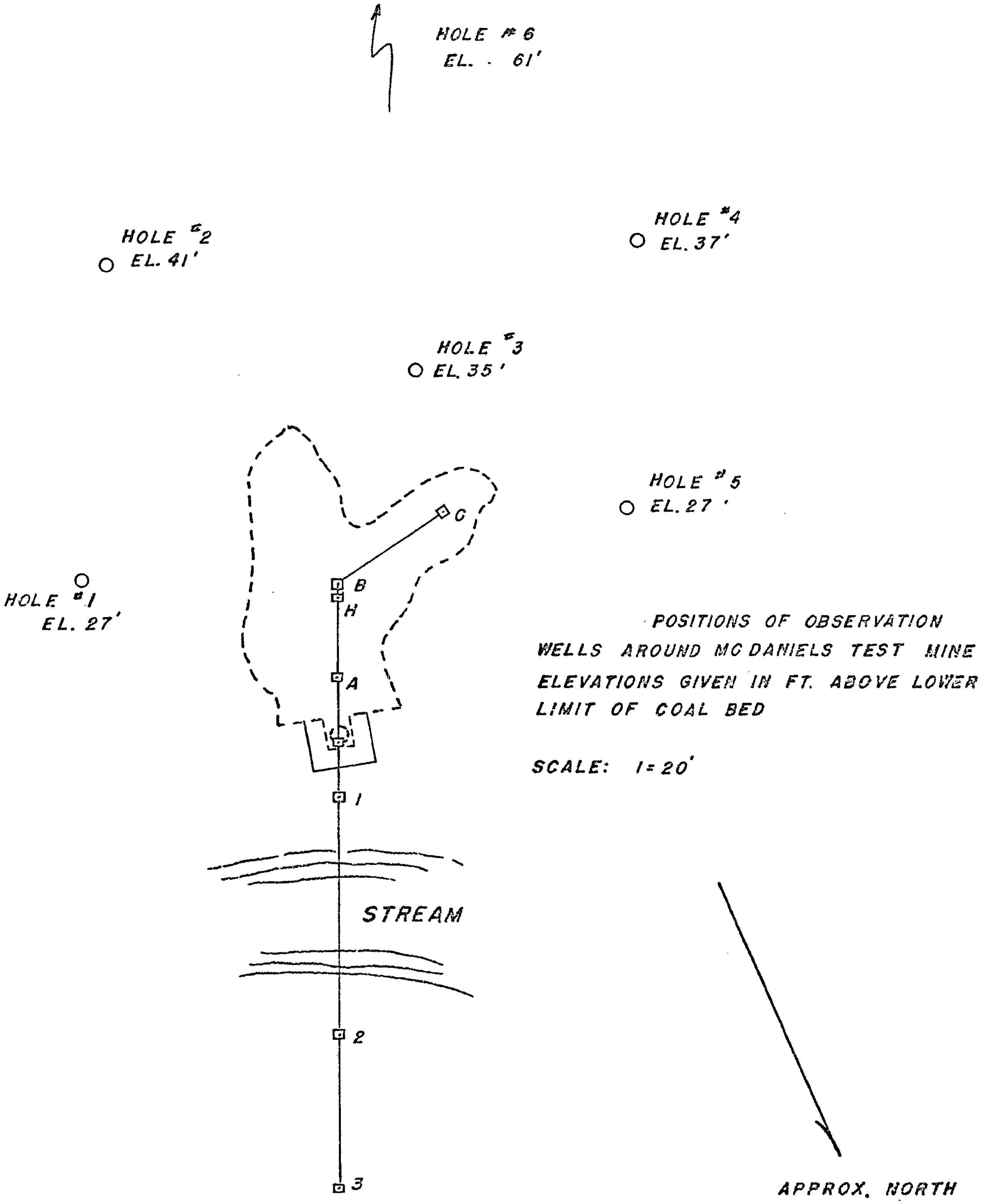
Core Samples

Core No. 1		% of Sulfur			
Description	**Level**	**Total**	**Sulfate**	**Pyritic**	**Organic**
Top-above Shale	26.6'	9.69	0.66	8.58	9.69
Shale parting	26.8'	5.18	1.15	4.03	0.00
Middle coal	27-29.5'	4.20	0.40	3.25	0.55
Bottom coal	29.5-30.2'	3.53	0.49	2.46	0.58

Core No. 2		% of Sulfur			
Description	Level	Total	Sulfate	Pyritic	Organic
Top coal layer	(approx. 6")	5.98	0.90	4.41	0.67
Middle coal		5.10	0.40	4.07	0.63
Shale parting	(6" from bottom)	0.40	0.03	0.12	0.25
Bottom coal	(last 6")	3.07	0.31	2.20	0.56
Core No. 3					
Top 4" coal		8.87	0.64	7.83	0.40
Shale parting	4" from top	11.30	1.14	9.98	0.18
Middle layer	5.05				
Shale parting	(4" thick, 6" from bottom)	3.04			
Bottom coal		4.18			
Core No. 4					
Top 4"		6.63			
Middle coal		4.40			
Shale parting	(6" from bottom)	1.06			
Bottom coal		2.80			
Core No. 5					
Very top		16.96			
Top shale	(24.4-27')	0.72			
Middle coal	(24.4-27')	5.05			
Shale parting	(27.5')	0.61			
Bottom coal	(27.5-28.0')	2.62			
Core No. 6					
Top coal	(first 4")	6.11			
Shale parting	(4" from top)	1.04			
Middle coal		4.81			
Shale parting	(6" from bottom)	0.26			
Bottom coal	(lower 6")	2.98			

* Moisture-Free Sulfur

Figure 1
Outcrop map showing measured elevations at bottom of coal, and elevations from mine maps
Scale: 1" = 500'



POSITIONS OF OBSERVATION WELLS AROUND MC DANIELS TEST MINE ELEVATIONS GIVEN IN FT. ABOVE LOWER LIMIT OF COAL BED

SCALE: 1=20'

PLANIMETRIC MAP OF MC DANIELS MINE AND OBSERVATION WELLS

FIGURE 2

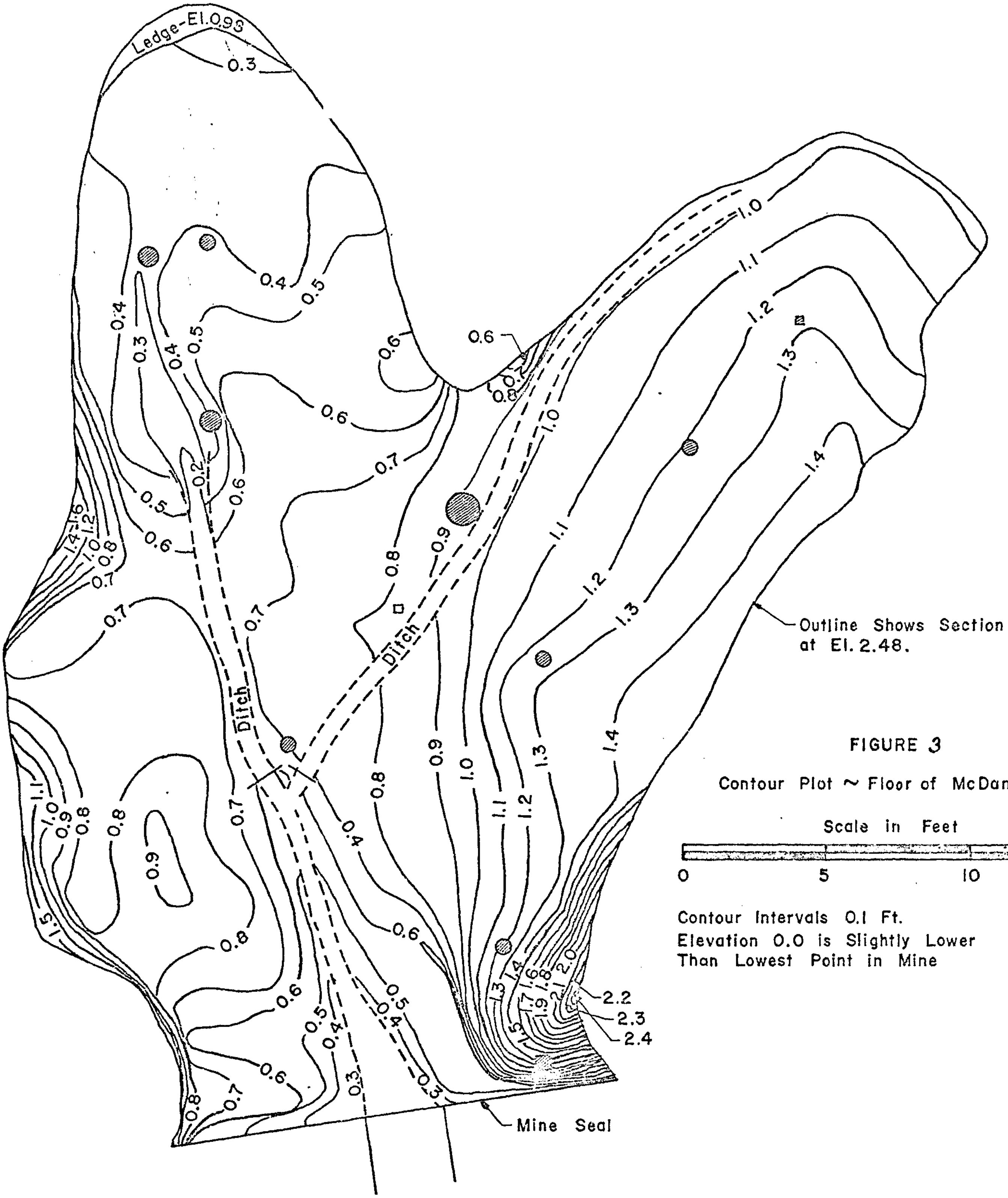
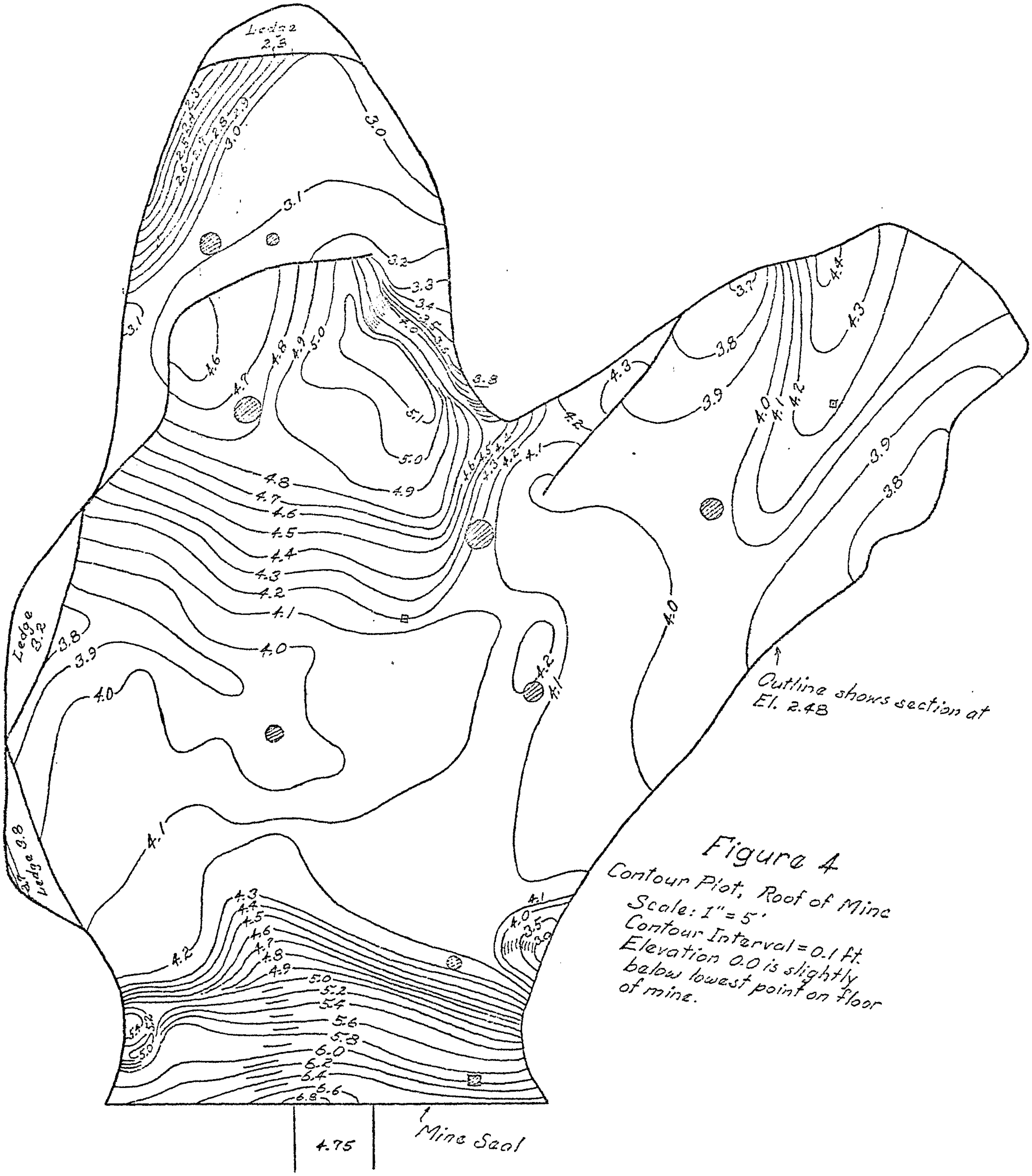


FIGURE 3

Contour Plot ~ Floor of McDaniels Mine

Scale in Feet

Contour Intervals 0.1 Ft.
Elevation 0.0 is Slightly Lower
Than Lowest Point in Mine



Outline shows section at El. 2.48

Mine Seal

Figure 4

Contour Plot, Roof of Mine

Scale: 1" = 5'

Contour Interval = 0.1 ft.

Elevation 0.0 is slightly below lowest point on floor of mine.

Figure 5A

Water Flow Rate and Total Acidity vs. Time

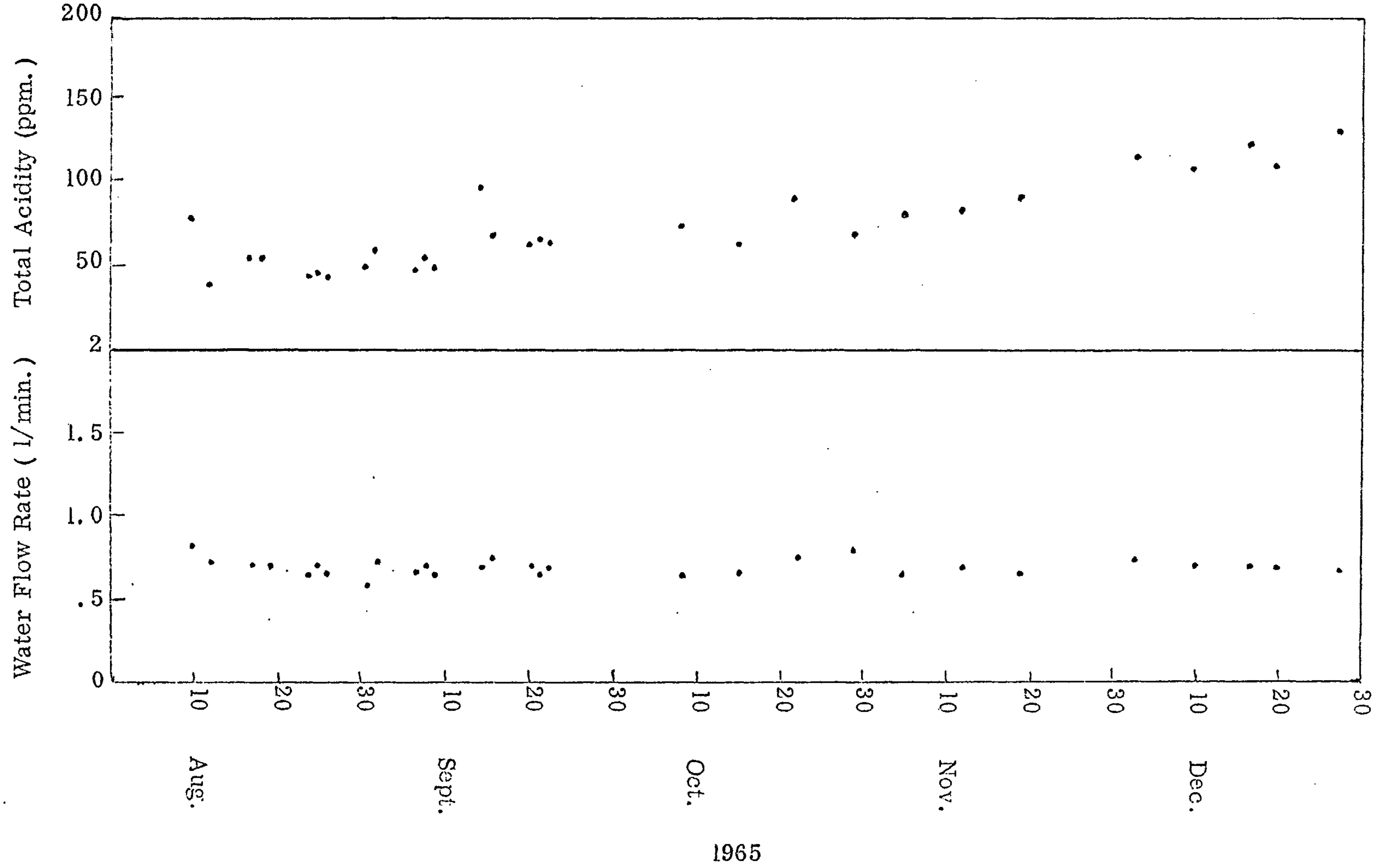


Figure 5B

Water Flow Rate and Total Acidity vs. Time

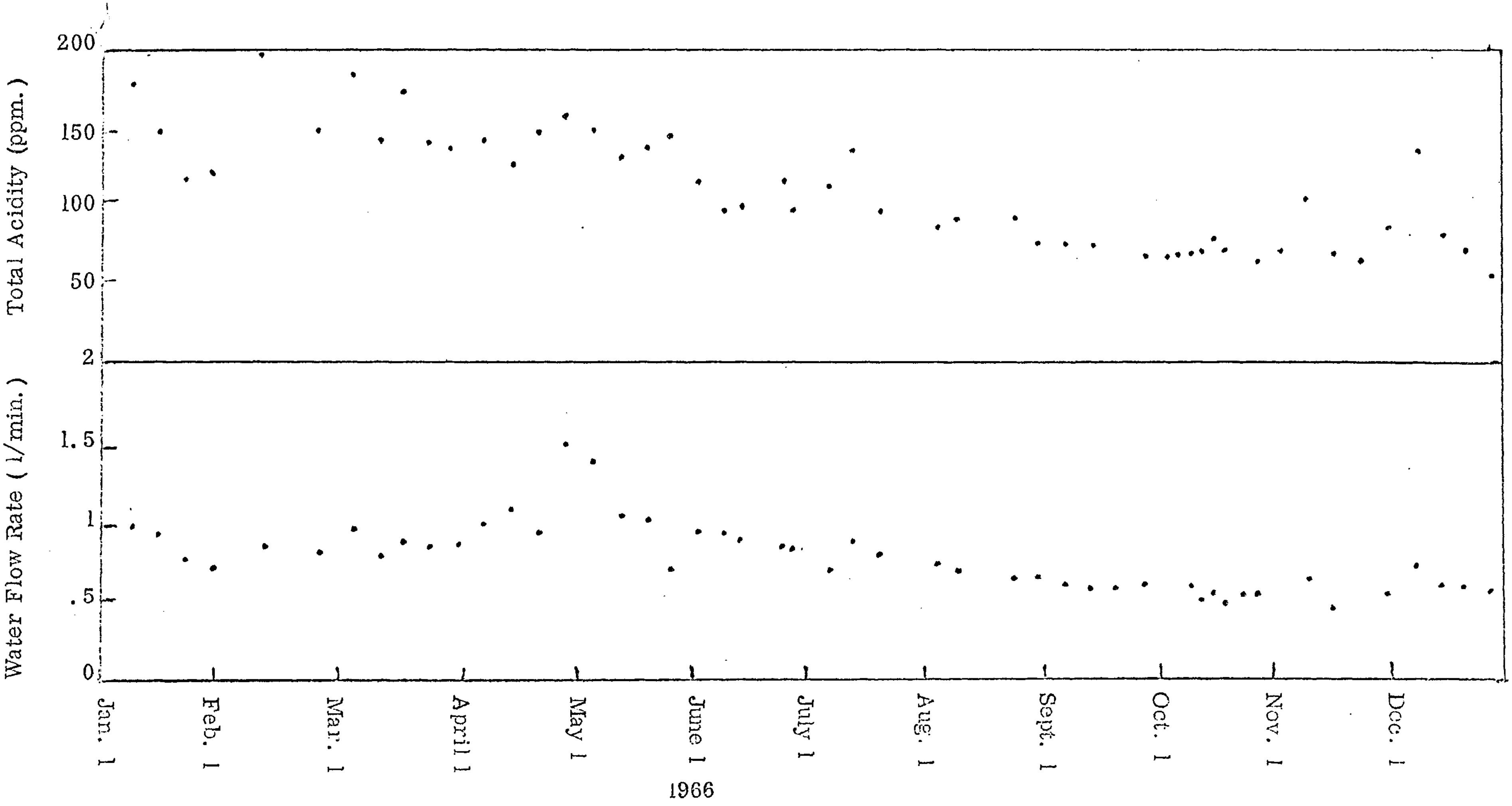


Figure 5C

Water Flow Rate and Total Acidity vs. Time

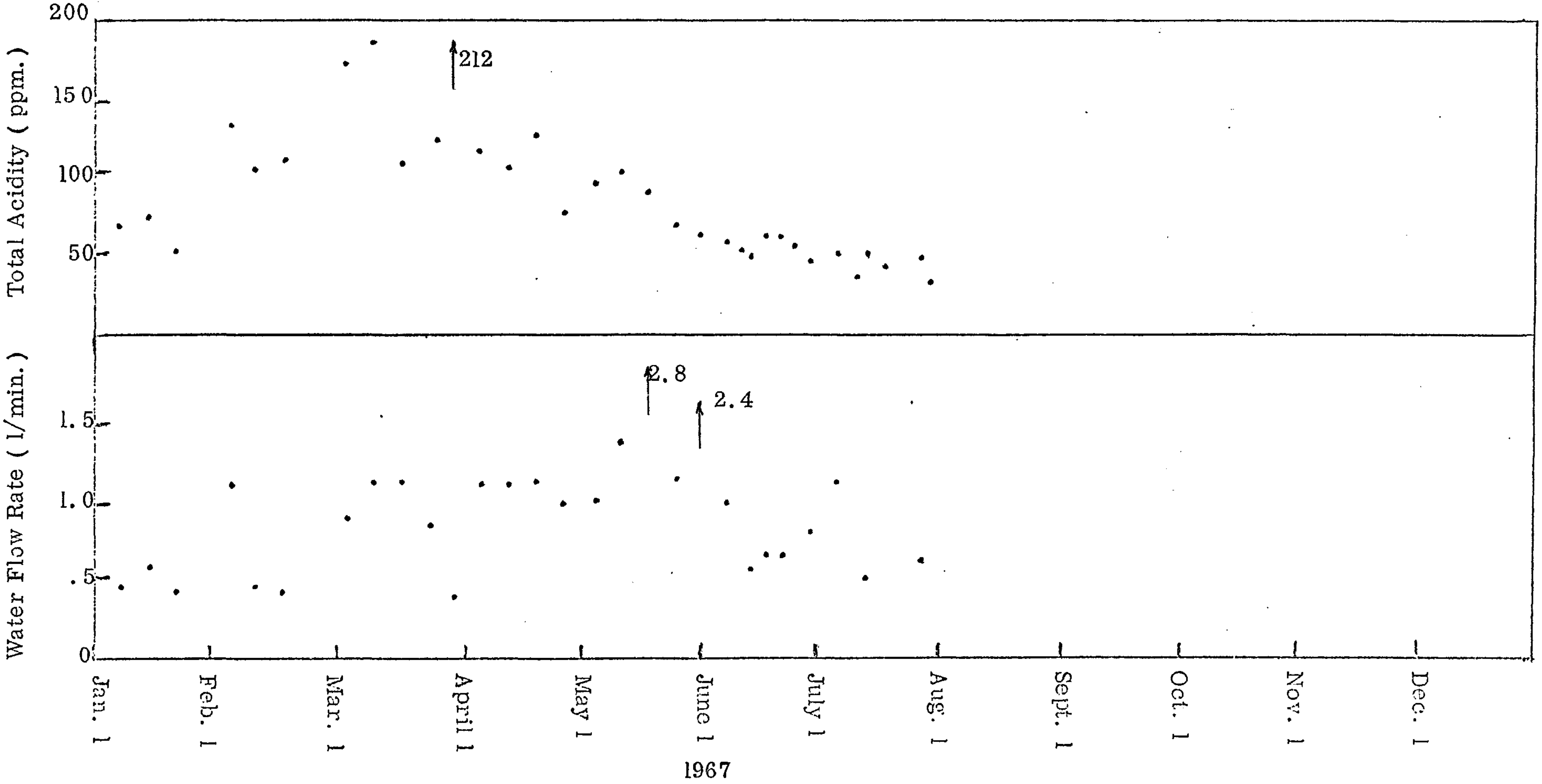
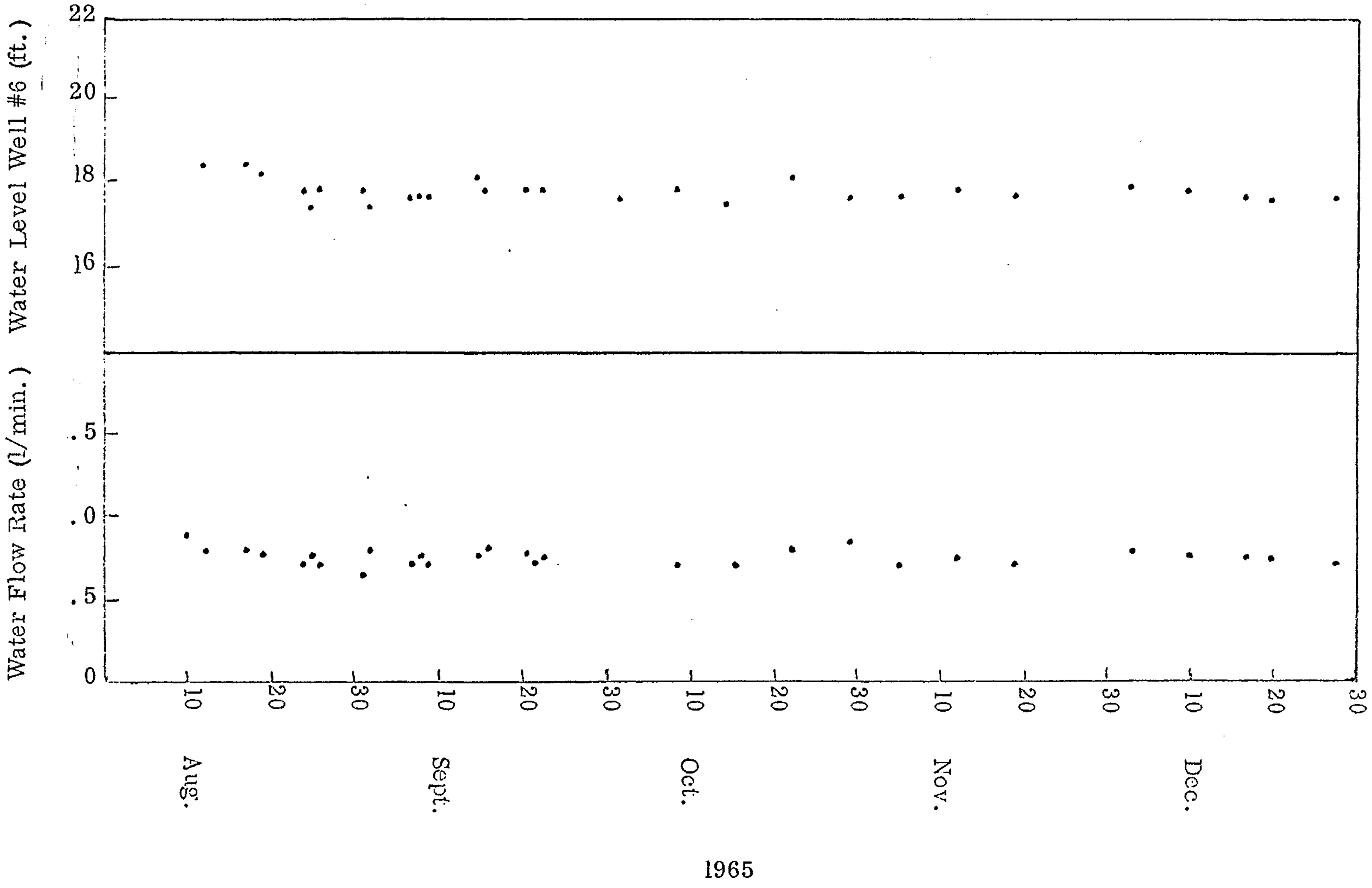
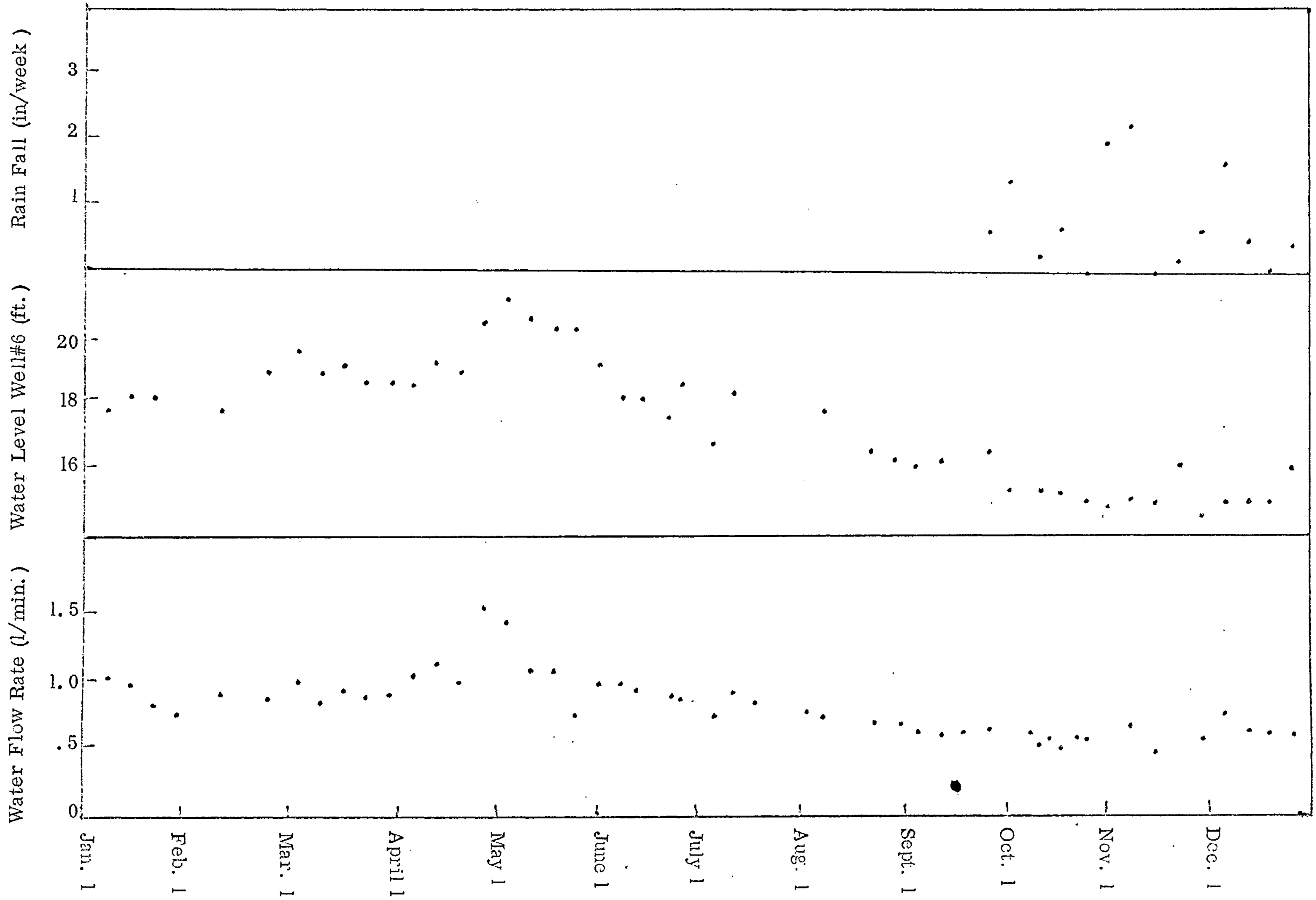


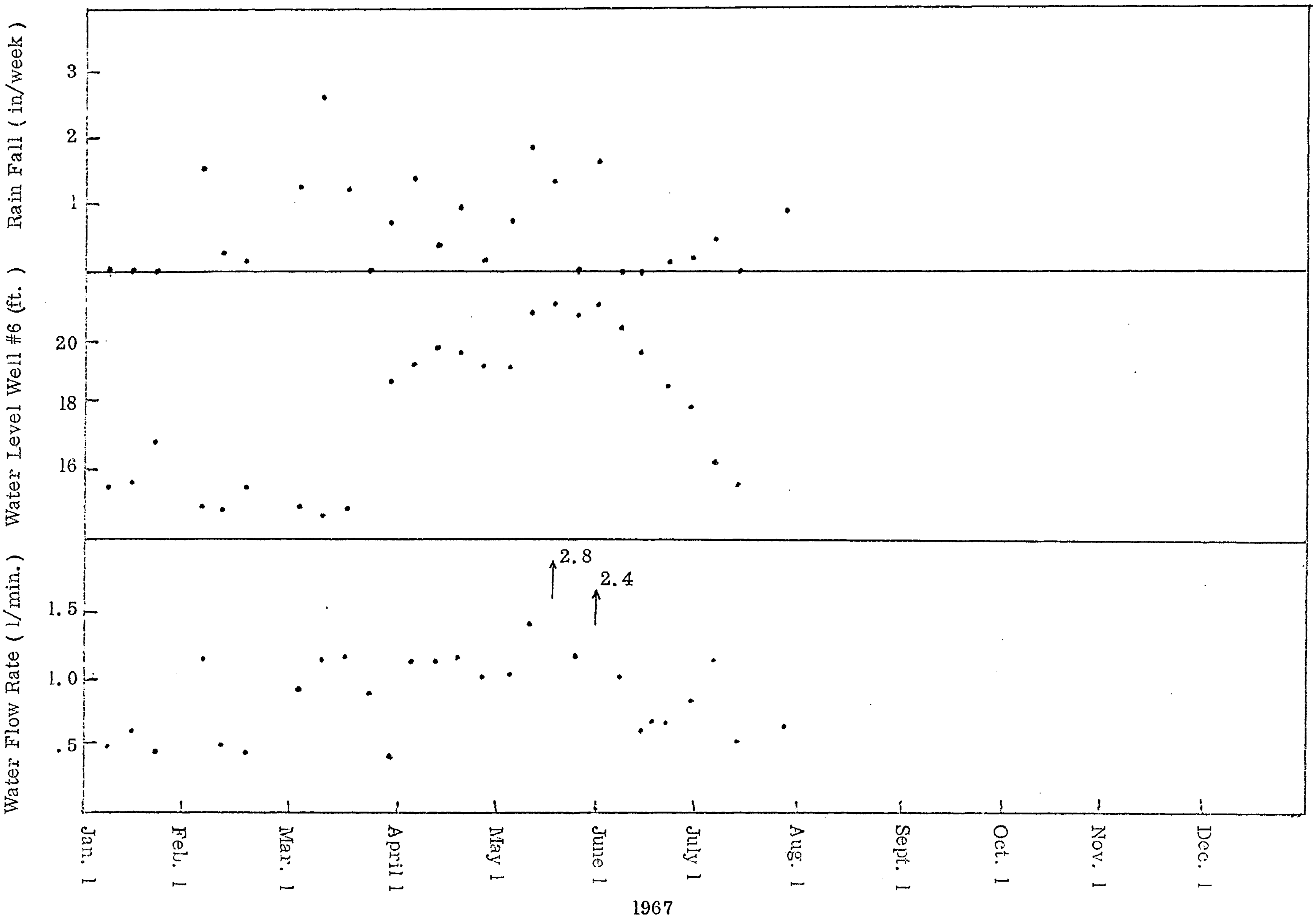
Figure 6 A

Water Flow Rate and Water Level vs. Time





Water Flow Rate, Water Level, and Rain Fall vs. Time
Figure 6B



Water Flow Rate, Water Level, and Rain Fall vs. Time

Figure 6C

The Attached Paper
will be presented at a

Second Symposium on
COAL MINE DRAINAGE RESEARCH
Mellon Institute
Pittsburgh, Pennsylvania
May 14-15, 1968

DEVELOPMENT OF A NATURAL LABORATORY FOR THE STUDY OF ACID MINE DRAINAGE PRODUCTION

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The phenomenon of acid mine drainage has been the subject of intensive study, both in the laboratory and in the field, for the greater part of this century. These studies have been either 1) laboratory scale investigations in which the reactive material was removed from its natural environment, or 2) demonstration type studies in which the effect of proposed abatement measures, such as various types of mine seals, have been observed on full-scale mining operations. Although a wealth of information has been obtained from these studies, many difficulties have been encountered in applying the results toward the controlled alleviation of the acid mine drainage problem at the source, particularly in the case of underground mines.

For example, laboratory investigations have determined vapor and liquid phase oxidation rates of pyrite as a function of oxygen and water concentration, and the catalytic effect of certain autotrophic bacteria found naturally in mine drainage has been widely noted in the laboratory. These results cannot, however, be applied directly to the mine situation because the nature and location of the reaction sites are not known, and therefore, the specific conditions at the reaction site cannot be predicted. For example, oxygen concentrations at the reactive sites are dependent on the nature of the oxygen transport mechanism and of the transport medium. Further, it is entirely possible that bacteria may be generally active in the sequence of mass transport and chemical reactions associated with pyrite oxidation, but that the transport of oxygen to the bacteria might be the rate controlling step in the overall reaction chain. In addition to questions regarding transport of reactants and conditions at the reactive sites, the mechanisms by which oxidation products reach the mine drainage effluent cannot be predicted without knowledge of the nature and location of these sites.

With respect to demonstration type studies, the observed effects of trial abatement procedures represent the overall effect of potentially pertinent but poorly defined physical, chemical, and biological variables, which would be expected to vary widely from one situation to another. Therefore, while an effect on acid production rate may be observed, it is neither possible to identify the specific rate-limiting step in the reaction chain responsible for the change, nor in the absence of this information, to generalize widely on the applicability of a given abatement procedure.

In short, the development of engineering procedures for the abatement of acid mine drainage at the source depends on the identification of the rate controlling mechanisms pertinent to the reaction as it occurs in the mine environment. Once these mechanisms are identified, it will be possible to extrapolate laboratory research findings to the field environment with greater confidence, and hopefully to predict and interpret more satisfactorily the kinetics of acid mine discharge rates under conditions of impressed environmental changes, as in demonstration projects.

The work presented in this paper represents the results, to date, of a study designed to determine the kinetics and rate controlling factors of acid mine discharge under natural conditions, using a pilot scale facility intermediate between laboratory studies and demonstration-scale projects. The "pilot plant" is a small drift mine known as the McDaniel's Test Mine, located in Vinton County, Ohio. The mine has been characterized, sealed and instrumented to permit the control of flooding depth and vapor phase composition within the mine, and to facilitate the measurement of changes brought about by the controlled variation of conditions. The experimental conditions to be imposed and the characteristics of the mine are not, nor are they intended to be, typical of those in conventional operations. Rather, this mine should be viewed as a pilot-scale "reactor" in which the kinetics of the reaction taking place within the system can be analyzed from both a fundamental and engineering point of view. As in a typical pilot plant, the conditions within the reactor can be varied beyond the normal operation range in order to develop fundamental information on reaction kinetics, a situation not possible in demonstration projects.

DESCRIPTION OF THE McDANIEL'S TEST MINE

The McDaniel's Mine lies in the Middle Kittanning (No. 6) coal, and was mined by hand, without the use of conventional power tools. A contour map of the floor of the mine is shown in Figure 1. As this map indicates, the two rooms extend only 35 to 40 feet into the hillside, and are irregular in shape. The coal in the seam at this locality is typical of the extensively mined Middle Kittanning coal in the Vinton County area. The seam varies in thickness up to about 40 inches and the roof shale between the coal and the sandstone overburden is discontinuous in places. The thickness of the sandstone overlying the mine itself varies from 24 feet at the seal to 35 feet at the back of the mine. The coal seam is underlain by impervious fire clay, and is several feet above the maximum elevation attained by surface drainage in the immediate area. It has been established that the only entry of water into the mine is through the sandstone overburden. The mine is driven straight into the side of a high ridge, and it is the elevation of the ground water table in the sandstone overburden, above and behind the mine, which controls the flow of ground water into the area around the mine. In this mine there is no possibility of cross flow from other underground mines.

The concrete block seal was put in place in 1957, and was equipped with a drainage valve arrangement which allowed the level of flooding in the mine to be held at any desired point. Soon after completion of the seal, the drainage valve was closed, and the water level allowed to rise until it found exit points other than through the seal. The water level attained was coincident with the top of the coal seam, indicating that water loss when the mine is in a flooded state is predominantly through the materials overlying the coal. Due to the contours of the mine roof, there exists a sizable gas volume above the water even when the mine is flooded to the maximum attainable level. This would promote "breathing" through the sandstone overburden, due to fluctuations in atmospheric pressure.

The mine was maintained in a fully flooded state until May, 1965, when it was drained prior to initation of the work presented below. Although water and gas samples were taken from the mine at intervals during the 1957-1965 period, few conclusions as to the effectiveness of the sealing and flooding can be drawn, due to inadequacy of baseline records prior to sealing. It is pertinent to note, however, that during the flooded period, the oxygen concentrations in the gas space above the water stabilized at approximately 10 per cent. It is felt that this concentration was maintained through the breathing action of the mine. The dissolved oxygen concentration in the water trapped in the mine dropped to zero, and did not deviate from this value.

Following the draining of the mine, the seal and mine interior were closely examined. The mine itself was found to be structurally sound, and the seal, which had begun to show signs of deterioration, was repaired with relative ease. During the later stages of active mining, however, gob from the operation had been piled against the coal faces not being worked instead of being carted from the mine. In order to have a good measure of the coal seam exposed and to gain a better defined environment, this refuse was removed. An accurate survey was made of the mine, and samples of the coal and associated strata were taken from three locations at and behind the coal face and examined for forms of sulfur. These analyses, together with visual examination of the coal face, indicate that interior areas of the coal seam may be exposed several feet from the face. Concomittant with preparatory work within the mine, six wells were cored through the sandstone and coal and into the underclay at selected positions around the mine These wells had the dual purpose of providing cores for analysis and determination of the dip of the coal strata, as well as to serve as observation wells for the delineation of the ground water table. Following coring, the wells were sealed back to several inches above the top of the coal to serve the latter purpose. The five wells closest to the mine show little or no head of water above the coal, indicating that ground water movement in the immediate vicinity of the mine is predominantly through joints in the sandstone and in the coal seam itself. Analysis of the cores indicated that this situation should be expected. On the other hand, the sixth well (observation well No. 6), located at a point behind the mine where the sandstone overburden has a thickness of 60 feet, demonstrates a phreatic surface varying from 15 to 21 feet above the coal throughout the annual hydrologic cycle.

OBJECTIVES AND EXPERIMENTAL PROCEDURES

Specific objectives associated with this work are to determine:

1. The effect of oxygen concentration on the rate of acid discharge from the mine.
2. The influence of microbiological factors on the rate of acid discharge from the mine.
3. The location of reactive sites in relation to the exposed coal face, and the characterization of conditions predominating at the reactive site (*i.e.*, vapor

phase or liquid phase oxidation, and the mechanism by which reaction products are removed from the reactive sites).

During the period from August 10, 1965 to October 6, 1966, the mine was left open to the atmosphere, and baseline data were collected on mine drainage acidity (hot titration to phenolphthalein endpoint) and flow rate. Concurrently water level records for well no. 6 were maintained. Similar data have been collected to the present time, with the effort being made to take samples, flow rate, and water level readings at least once per week.

On October 6, 1966, the mine was sealed, flushed with nitrogen, and maintained under a positive nitrogen pressure of one millimeter of water, relative to the prevailing atmospheric pressure. Approximately three 'K' cylinders of nitrogen per week (approximately 600 ft^3) were required to maintain this pressure. Mine atmosphere oxygen concentrations for this period are given in Table I.

On August 1, 1967, the nitrogen pressure was discontinued, and the mine was flushed with oxygen. From August 1, 1967 to November 18, 1967, an oxygen-rich atmosphere (greater than 21 per cent) was maintained by the periodic valving of oxygen into the sealed mine. Although a constant positive pressure of oxygen was not maintained, pressures well in excess of one millimeter of water were reached during the periodic additions of oxygen (one full 'K' cyclinder, released over a period of several hours). Mine atmosphere oxygen concentrations for this period are given in Table II.

From November 18, 1967, to the present, the mine has been held at 21 per cent oxygen by the continuous addition of air, with the maintenance of a positive pressure of approximately one inch of water, relative to atmospheric pressure. At no time since May, 1965 has water been allowed to accumulate within the mine to a significant level.

RESULTS AND DISCUSSION

It was originally intended to accumulate concurrent ground water table elevation and mine drainage flow rate data, in the hope that a correlation could be established between the two. Water table level data could then be used to estimate ground water influx rates during future stages of this work when the mine seal drain will be closed and the mine flooded. However, it was found that subsequent to the sealing of the mine on October 6, 1966, iron precipitates occasionally fouled the water trap employed to maintain free water drainage through the seal. This resulted in erratic flow measurements, particularly during periods of high flow. A correlation has therefore been made at this time between flow rate and water table level, as it is felt that the water table level is a more valid indicater of ground water influx rates than grab samples of mine drainage flow rates. The available flow rate versus water level data for the period August, 1965 through December, 1967 are presented in Figure 2. The correlation curve shown was fit by eye, with no attempt being made to fit a specific mathematical form to the data. Referring to Figure 2, it is significant that there is no indication of a linear relationship between water table level and flow rate, but rather that the drainage rate shows an increasing rate of increase as the water table level rises. This has been interpreted as an increasing effective permeability in the ground water flow system, due to the intersection of the ground water table with an increasing number of joints and fractures in the sandstone and coal as the water table rises. Thus, it is suggested that during periods of higher ground water table levels, water flows through regions in the immediate vicinity of the mine which are not flushed by ground water during periods of lower flow.

Effluent acidity and flow rate data for the entire seventeen month experimental period are presented in Figure 3. In this figure, the open data points indicate direct flow measurements, while the solid line connecting solid points represents adjusted flows, derived from observed water levels in well no. 6 by using the correlation curve shown in Figure 2. During the periods for which water level measurements are available, it is felt that these adjusted flows give the best indication of ground water influx rates to the mine.

A conceptual model of the physical environment of the reactive sites is suggested by these data. For purposes of presentation here, the model will first be described, followed by a discussion of the data.

The model is formulated as follows:

1. The reactive sites of pyrite oxidation may be, and in this mine, probably are some distance back of the working face. Oxygen is transferred to the site predominately by either molecular diffusion through the gas phase, or by convective transport, induced by the breathing of the mine with fluctuations in atmospheric pressure. It is significant to note that oxygen concentrations in the mine itself thus give no direct indication of concentrations at the reactive site.

2. The reactive sites are not, in general, submerged in flowing ground water, but are largely exposed to the gas phase, with a relative humidity of approximately 100 per cent. Most of the pyrite oxidation occurs, then, under 'vapor phase' conditions.

3. The products of oxidation are carried to regions of flowing ground water and thence into the mine drainage by a relatively slow process. This process might be the seepage of condensate from the site to the flowing ground water. Thus, if reaction rates are altered at the site, there will be a lag time before the acidity of the mine drainage reflects this change.

4. During periods of low ground water flow, pyrite in certain regions may actively undergo oxidation, but the oxidation products may be stored in the immediate vicinity until they are carried away during periods of higher ground water flow rate. It is indicated that as ground water flow increases, the water finds additional routes of flow, and thus leaches larger and larger regions of active pyrite oxidation. This postulate implies that mine drainage acidity is a direct reflection of pyrite oxidation rate only during periods of constant or decreasing ground water flow. During periods of flow surges

or increasing flow, mine drainage acidity will reflect both oxidation rate and the rate of leaching of stored oxidation products.

Using the above conceptual model as a basis, interpretations of the mine drainage acidity and flow rate data can be made. Figure 4 shows the total discharge rate of acid from the mine, expressed in pounds of acidity per month (as $CaCO_3$) versus time. These values were calculated from average monthly acidities and average monthly adjusted flow rates, shown in Table III. The per cent of oxygen in the mine atmosphere is also shown in Figure 4, as well as an unscaled plot of relative mine drainage flow rates. The open data points indicate months when ground water flow rates were constant or decreasing, and thus are indications of pyrite oxidation rates. It must be recognized that the lag time between the formation of oxidation products and the transport of the products to flowing ground water must be taken into account in analyzing these data. Thus, an acid production rate shown for a given month is an indication of the pyrite oxidation rate at some previous time.

The solid data points indicate acid production rates for months in which increasing flows were noted, and therefore reflect both pyrite oxidation rate and oxidation product storage. Restricting our analysis to the open data points, it is seen that there was an increase in acid production rate during the months of August through December, 1965, a period during which the drainage rate was essentially constant. The mine had been flooded until May, 1965, and it is felt that this increase in acid production rate was an indication of a new pyrite oxidation rate equilibrium being attained after the mine was drained. The remaining open data points, however, should reflect pyrite oxidation rates under the conditions impressed by the mine atmosphere oxygen concentrations indicated in Figure 4. The data for these months are plotted in Figure 5 as monthly averages of mine drainage acidity versus flow rate. It is pertinent that the data tend to lie in two separate regions on the plot. Straight lines have been drawn through both sets of data, although a linear function is not necessarily the best fit. Looking first at the upper set of data, shown by solid points, it is seen that these points represent the period from June, 1966 through January, 1967, and October through December, 1967. The lower set of data, shown by open points, represent the period June through September, 1967. It is the opinion of the authors that the separation of these two sets of data indicate the effect of the lowered oxygen concentration during the period October 6, 1966 to August 1, 1967.

Referring to Figure 4, it is significant to note that even though the lowering of the oxygen concentration began in October , 1966, the effect was still not being detected in January, 1967. This lag is believed to be due to the lag in transport of oxidation products to the flowing ground water, and to the slow rate of decrease of oxygen concentration in the mine.

Referring again to Figure 4, it is seen that although the oxygen concentration was increased in August, 1967, the effect was not significantly noted until October, 1967. Again, this is felt to be a function of the lag time of oxidation product transport.

With regard to the positive slope of the curves shown in Figure 5, it appears that the pyrite oxidation areas leached at the higher flows have greater activities than those leached at the lower ground water flow rates. This is in no way in opposition to the conceptual model presented.

CONCLUSIONS

The work presented in this paper represents the preliminary development of techniques for the utilization of the McDaniel's Test Mine 'pilot-scale' facility, and certainly, no sweeping conclusions can be drawn at this time. We have, on the other hand, gained pertinent information.

First, it is evident that 'base-line' data must be carefully gathered over, at the least, one complete hydrologic cycle, and that 'apparent' oxidation or acid discharge rates may well be a function of the hydrologic characteristics of a region. They may therefore, vary significantly with time, with no real change in rates at the reactive sites. This should be carefully considered when evaluating mine sealing results.

Secondly, it is felt that the conceptual model of the physical system, while incomplete, is essentially valid. The transport of oxygen to reactive sites by breathing of the mine, which will occur if the overburden is permeable and there is a significant gas phase volume in the mine, is an especially critical factor in the evaluation of proposed abatement procedures. The data and model presented here, while not conclusive, indicate that oxygen transport to the reactive sites is indeed the rate controlling step in pyrite oxidation.

Third, there is a significant lag time between changes in environmental conditions associated with oxygen concentrations at the reactive site, and reflection of this change in the mine drainage characteristics. This, together with hydrologic considerations, puts severe limitations on the amount of data which can be generated from a test facility of this type. Nevertheless, it is felt that data of this type are a necessary prerequisite to the understanding and solution of the mine drainage problem.

Fourth, it has been shown that a decrease in oxygen concentration, in the mine itself, to less than two per cent decreases acid production by only 40 to 50 per cent. It should be emphasized, however, that this concentration is not necessarily that at the reaction site.

ACKNOWLEDGEMENTS

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Table I

Mine Atmosphere O_2 Concentrations, Per Cent
October 6, 1966 through July 29, 1967

Date	% O_2	Date	% O_2	Date	% O_2
10/6/66	16.4	12/17	2.7	4/29	2.3
10/8	15.7	1/7/67	2.1	5/7	1.9
10/12	15.0	1/21	4.0	5/13	2.8
10/15	13.5	2/5	2.9	5/20	1.9
10/18	13.0	2/11	3.3	5/27	5.0
10/21	14.8	2/18	4.9	6/10	2.8
10/26	11.7	3/4	4.8	6/20	0.7
10/29	9.2	3/11	5.1	6/24	2.0
11/5	7.0	3/18	7.0	6/27	2.4
11/12	5.7	3/25	6.4	7/8	2.1
11/19	5.0	4/1	6.5	7/15	1.7
11/26	4.2	4/8	5.9	7/29	0.9
12/10	2.8	4/15	2.9		

Table II

Mine Atmosphere O_2 Concentrations,
Per Cent, August 1, 1967 through
November 18, 1967

Date	% O_2	Date	% O_2
8/1/67	24.2	9/23	30.7
8/5	30.3	10/1	26.4
8/10	36.5	10/7	29.0
8/12	38.7	10/11	40.6
8/19	30.7	10/14	42.6
8/23	41.7	10/19	36.6
8/26	43.0	10/21	27.6
8/30	37.0	10/28	25.4
9/9	32.2	11/4	26.9
9/16	30.5	11/18	22.1

Table III

Average Monthly Mine Drainage Acidity,
mg/l as $CaCO_3$, and Average Monthly Mine
Drainage Flow Rate, Gallons per day

Month	Acidity	Flow Rate
6/66	112	324
7/66	121	297
8/66	97	275
9/66	79	231
10/66	77	207
11/66	85	198
12/66	78	196
1/67	72	211
6/67	64	395
7/67	53	268
8/67	39	198
9/67	48	190
10/67	72	185
11/67	92	185
12/67	90	185

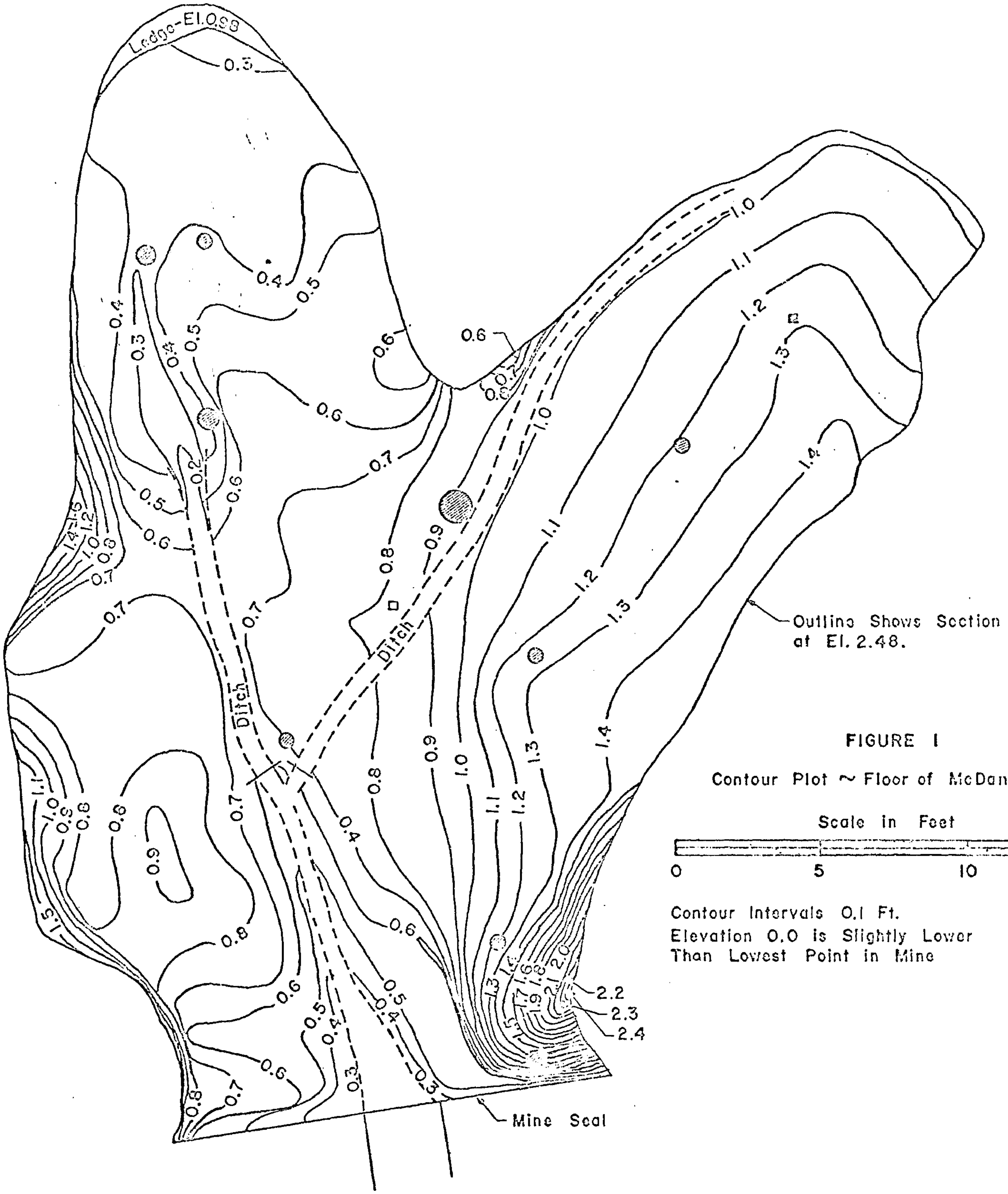

FIGURE I

Contour Plot ~ Floor of McDaniels Mine

Scale in Feet

Contour Intervals 0.1 Ft.
Elevation 0.0 is Slightly Lower Than Lowest Point in Mine

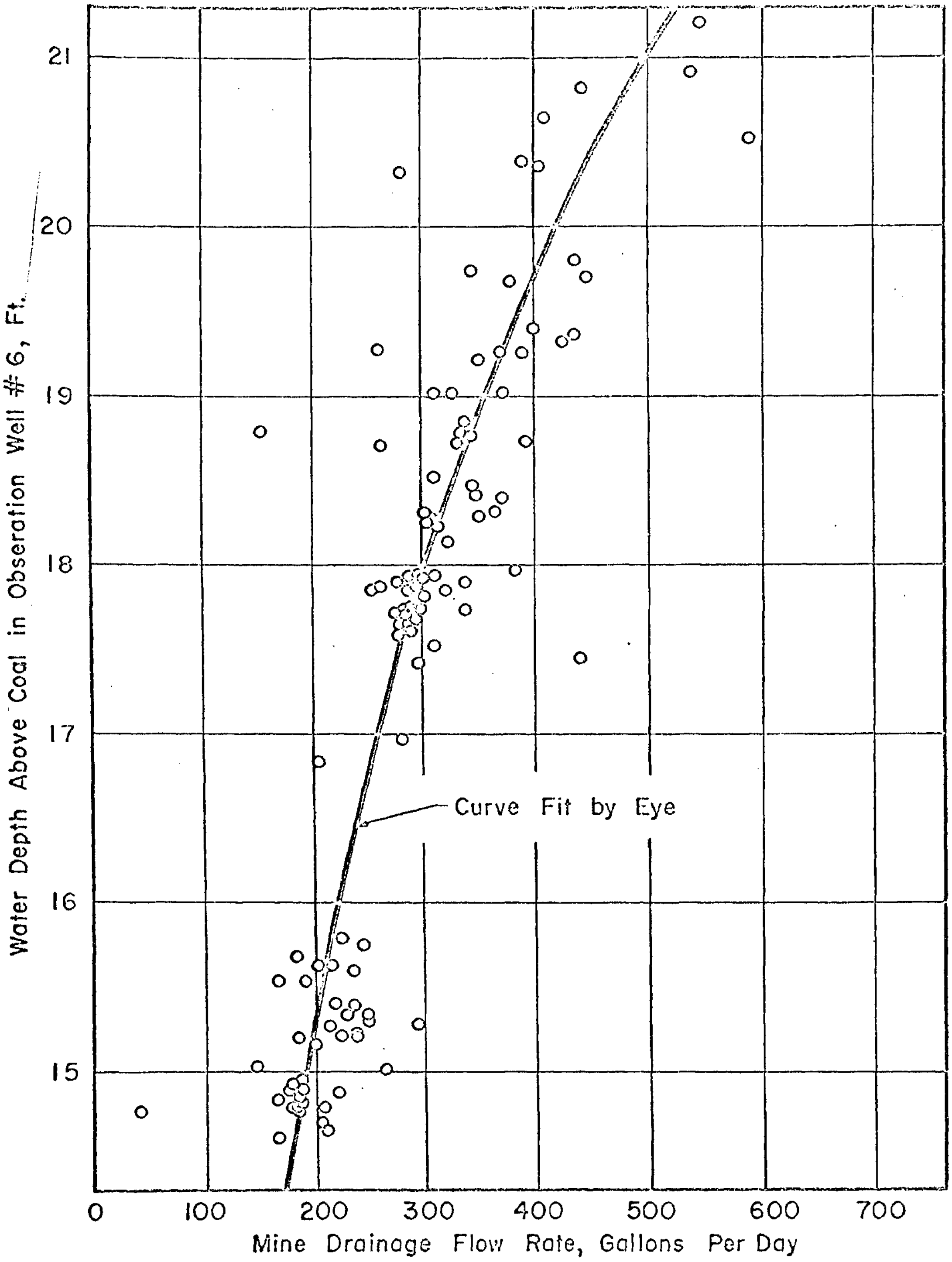

Figure 2

Depth of Water in Well # 6
vs
Mine Drainage Flow Rate

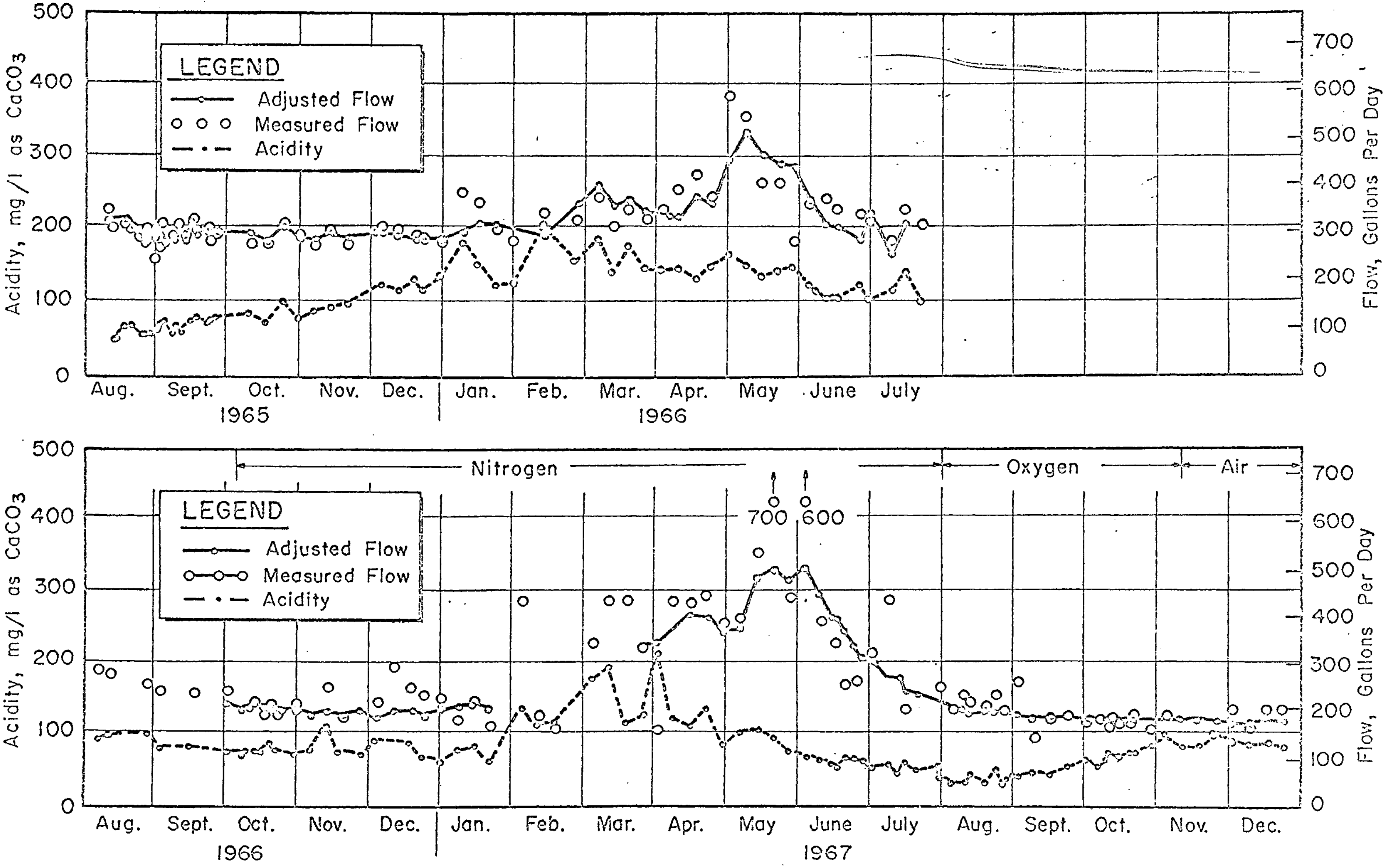

Figure 3

Mine Drainage Acidity and Flow Rate Versus Time

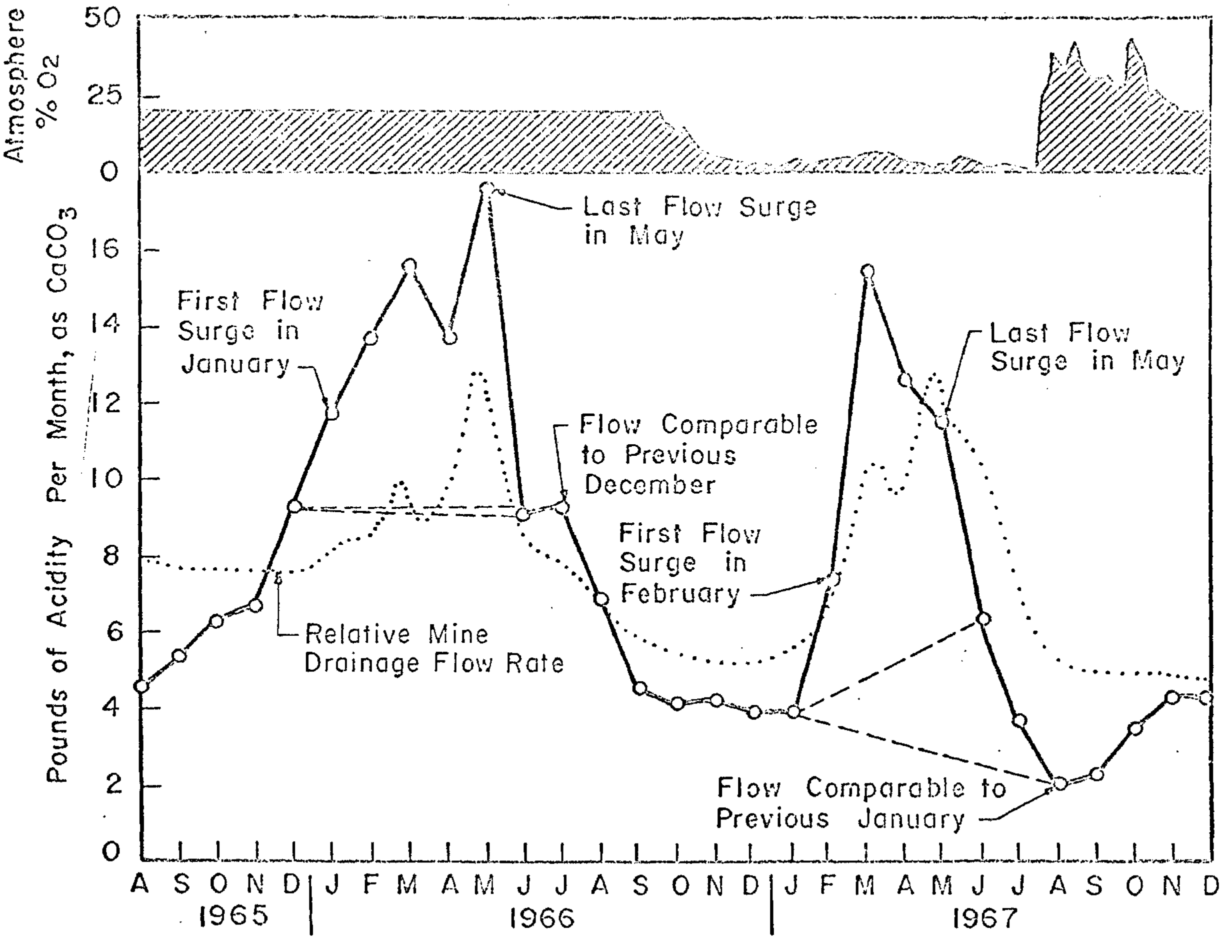

Figure 4

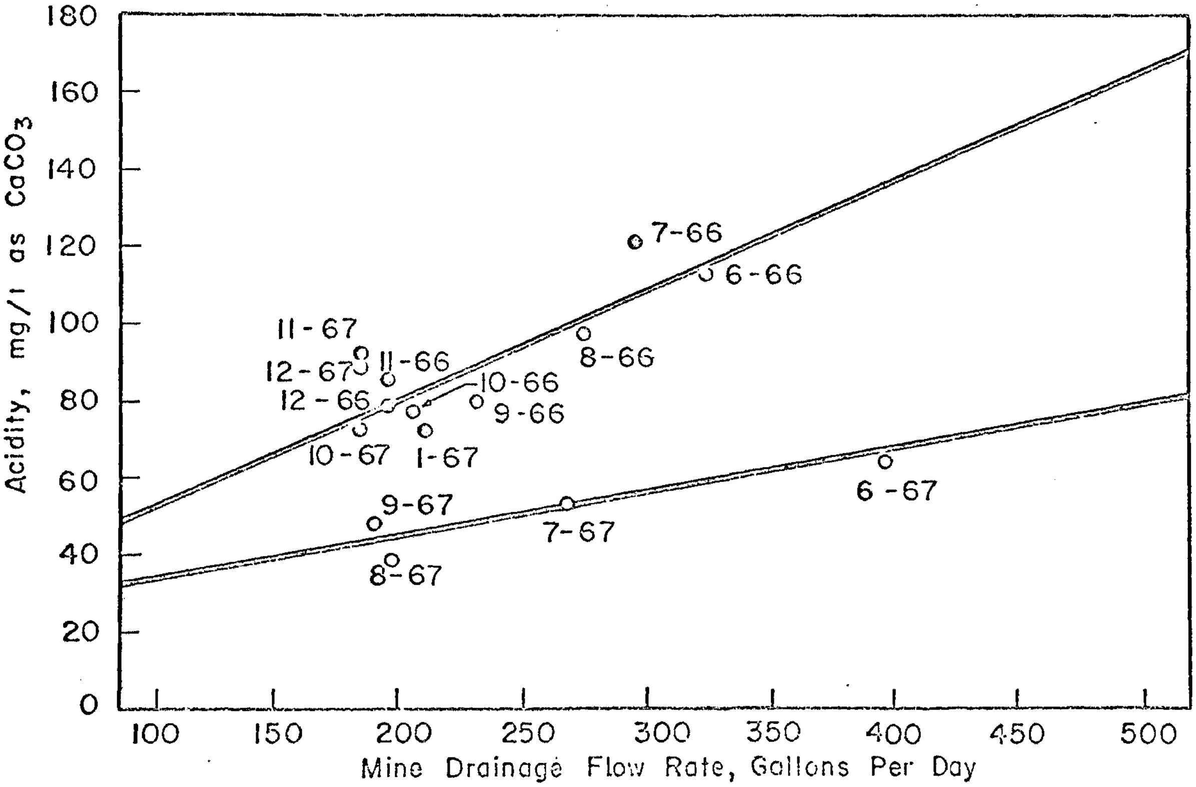

Figure 5