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ACID MINE DRAINAGE:

A MATHEMATICAL MODEL

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

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* * * * *

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CHAPTER I

INTRODUCTION

The natural formation of acid as a by-product of mining operations has been observed throughout the world. This acid has been formed by the reaction of oxygen and water with sulfur-bearing minerals, such as pyrite (FeS_2).

The formation of sulfuric acid from pyrite has become a major problem in the coal mining areas of the eastern United States, particularly Ohio, West Virginia, and Pennsylvania. The formation of an acid discharge, popularly known as "acid mine drainage," or simply AMD, is responsible for the ruining of many streams and lakes as recreation areas, for numerous fish kills, and for general wasting of natural resources and beauty. The acidity also causes corrosion of bridge piers, locks, boat hulls, and pumps. (30)

The acid mine drainage problem has been attacked from many angles--ranging from treatment of acid water and sealing of abandoned mines to laboratory scale research. Research on AMD has included studies in the areas of chemical kinetics, microbiology, mineralogy, geology, hydrology, and treatment methods. Thus far most work has been confined to specific areas with little interaction among disciplines. To co-ordinate this diverse information, researchers at Ohio State University have undertaken a systematic analysis of acid mine drainage. The object of the analysis is to develop a mathematical model of acid mine drainage systems.

A useful mathematical model must quantitatively relate the physical and chemical parameters of a pyritic system to the rate of pollution discharge across the boundaries of the system. Such a model would accurately predict the long-term effects of mining operations, abatement procedures, and other conditions imposed on the system.

Of equal importance is the ability to predict surges and peak flows of acid. In many pyritic systems, "normal" runoff can be absorbed without effect on receiving streams. It is the heavy slugs of discharge that periodically cause extensive damage to receiving waters. Prediction of these would allow design of protective neutralizing systems.

The development of a mathematical model of a system usually follows a step-by-step approach. The first step is the identification of what is known about a system (and by inference, what is not known). This may be done by reviewing the literature and work of previous investigators. The second step is filling in the gaps in existing knowledge. The preferred technique is experimentation. However, if the problem is not amenable to experimental solution, approximations can be generated starting from basic scientific principles. The final step is comparing the model behavior with that of the real system. At this time, variables are free to interact, and the validity of the basic assumptions is proved or disproved. Once the model has been refined and can predict previous data, then it is possible to forecast the effects of perturbations imposed on the system.

Such a step-by-step procedure will be followed in developing a model of a pyritic oxidation system. In this case, the examination of existing knowledge includes reviewing both general acid mine drainage literature, and experimental studies of natural pyrite oxidation systems. The experimental work is reported along with numerical computation techniques used to evaluate undefined quantities.

Next, the actual model and computational methods are developed and proved. This has been done for one specific pyrite oxidation system, a drift mine, but the generalization of this model to other types of systems will be shown. Finally, the model will be used to predict results of possible system perturbations.

CHAPTER II

LITERATURE REVIEW

Historical

The problem of acid production in coal mining regions has been the subject of studies since before 1900. The earliest studies were essentially reports of local acid production and high acid concentrations in streams after heavy storms. The reports frequently traced the acid source back to abandoned coal mines, and more specifically to iron pyrite associated with the coal. In some manner, the pyritic sulfur was reacting and oxidizing to form sulfuric acid and iron sulfate.

Early attempts were made to stop this oxidation by using mine sealing techniques. This was done with some success in the 1920's in West Virginia, but in other states records of methods and results have been lost. Moulton(26) has presented a good review of the early studies in Ohio.

Since 1965, Bituminous Coal Research, Inc. (23) has issued annual bibliographies of acid mine drainage.

The next step beyond reporting of acid production was the start of experimental laboratory work. Some of the earlier investigators include Li and Parr (20), McKay and Halpern (22), Burke and Downs (6), and Nelson, Snow, and Keyes (28).

Li and Parr (20) studied the oxidation of pyrite using both air and oxygen atmospheres containing moisture. They found the rate of oxidation in air to be only one-half of that in oxygen, and that the rate increased with the amount of water vapor in the atmosphere. In tests where the pyrite had been wetted, it appeared that the pyrite was more reactive, and that water might be activating the pyrite in some way.

Nelson, Snow, and Keyes (28) passed water-saturated air through beds of crushed coal. They found oxidation rates increased with increasing temperature, but seemed to decrease over a period of days. They attributed this decrease to a build-up of surface products. In other studies, Nelson et al. added ferric ions to coal-water slurries. Although the oxidation rate increased 20 to 25 per cent, the investigators did not feel this indicated ferric ion was acting as an oxidizer.

McKay and Halpern (22) oxidized pyrite in aqueous solutions in the temperature range 100 to 130 °C. They found the overall oxidation rate was proportional to pyritic surface area and oxygen partial pressure, but independent of solution composition. They concluded that the rate controlling step in pyrite oxidation is a heterogeneous surface process involving a chemically adsorbed oxygen molecule. They also observed that the stoichiometric oxidation reaction was:

$$FeS_2 + 7/2\ O_2 + H_2O = H_2SO_4 + FeSO_4 \qquad (2\text{-}1)$$

Oxidation Mechanism

In more recent research, the emphases has been on solution chemistry and the definition of the precise oxidation mechanism. Birle (4), Kim (16), Jutte (15), and Morth (24) studied the basic kinetics of the oxidation of concentrated pyritic material.

Birle (4) performed a general study of the oxidation of iron pyrite. He measured relative surface areas of different structural forms of pyrite. Sulfur ball material of the type found in coal had much greater surface area per unit weight than did highly crystalline museum grade pyrite (fool's gold). Stiles (41) in parallel work showed that the reactivity of pyritic material is proportional to its surface area.

Kim (16) studied the oxidation kinetics of concentrated pyritic material in liquid and vapor phase reactions. The liquid or vapor referred to the phase being recirculated through a pyrite bed. He found that the oxidation rate depended on oxygen concentration. Vapor phase oxidation rates seemed to increase with temperature, but Kim attributed this increase to the increase in humidity.

Morth (24) also worked with liquid and vapor phase reactions. He found that oxidation rate doubled with 10 °C increase in temperature. He observed that vapor phase oxidation increased with humidity, and that at 100 per cent relative humidity, the vapor phase rate is the same as the liquid phase oxidation rate. Morth suggested that water is both a reactant and a reaction medium.

Jutte(15) studied the influence of oxygen concentration of the oxidation rate. The relative oxygen concentration was controlled by applying nitrogen pressure on a liquid phase oxidation. The oxidation rate decreased with increasing pressure. This result led to the conclusion that there was competition between nitrogen and oxygen for a "reactive site." The concept of a "reactive site" has led research into the area of the actual reaction mechanism in addition to the kinetics or rate of reaction.

Electron Transport

Singer and Stumm (34), Smith, Svanks, and Shumate (39), Smith, Svanks, and Halko (38), Sasmojo (29), and Grove (14) have studied the electron transport mechanisms of iron pyrite oxidation. Singer and Stumm (34) investigated the liquid phase oxygenation of ferrous ions and the hydrolysis of the resulting ferric ion. They found that sulfate ions retarded the rate of ferrous ion oxidation, and that high surface area materials such as alumina catalyzed the oxidation. They concluded that ferric ion could not exist in contact with pyrite, and that the overall rate of pyrite dissolution is independent of the surface structure of the pyrite. Finally, Singer and Stumm concluded that the oxidation rate controlling step is the ferrous iron oxidation.

Smith, Svanks, and Shumate (39) studied the anaerobic (oxygen free) oxidation of pyrite using ferric ion as the oxidant. Working with various ratios of ferric and ferrous ions, Smith et al. concluded that the oxidizing species is a surface adsorbed ferric ion. The rate controlling step is the surface transfer of electrons. It was also suggested that aerobic (oxygen) and ferric ion oxidations follow different reaction paths. In a continuation of the above study, Smith, Svanks, and Halko (38) reported that the aerobic oxidation rate was a function only of the oxygen concentration at the reactive site. However, the ferric ion oxidation rate was dependent on the ferric-ferrous ratio and the total iron concentration in solution.

Sasmojo (29) studied the kinetics of both aerobic and ferric ion oxidation and attempted to determine if there was an interdependence between the two reactions. He compared the aerobic oxidation rate in the presence and absence of ferrous ions in solution and found no difference. Then using identical total iron concentration, ferric-ferrous ratios, and pH, Sasmojo measured the ferric ion oxidation rate. This rate was about one-third of the aerobic oxidation rate. He concluded that the rate of pyrite oxidation by oxygen is not controlled by the oxidation reaction of ferrous to ferric ion in solution. Sasmojo studied ferric ion oxidation at varying ferric-ferrous ratios and total iron concentrations. At constant total iron concentration, the rate increased with ferric-ferrous ratio, and at constant ferric concentration, the rate increased with decreasing ferrous concentration. From this, he concluded not only that ferric ions increased the oxidation rate, but that ferrous ions had an inhibiting effect.

Grove (14) also investigated ferric ion oxidation and the effects of the ferric-ferrous ratio. He found that the real variable was the free ferric-ferrous ratio. He defined free ions as those which were not complexed nor associated with the solution anions in any manner. He developed a set of equations to estimate the effects of anions on the free ferric-ferrous ratio.

Smith and Shumate (27) in a final project report have summarized and put in proper perspective the various pyrite oxidation studies performed at Ohio State University. The time interval covered includes the work of Birle through that of Sasmojo. The report is particularly significant since it is a unified presentation of information from different approaches to the problem of defining the sulfide to sulfate raction mechanism.

Microbiological Oxidation

Microbiology has been another area of laboratory scale investigations. Bacteria, such as Ferrobacillus ferrooxidans, enhance the rate of pyrite oxidation. Lorenz and Tarpley (21) and Konecik (17) reported ten to fifty fold increases when these bacteria were added to pyritic systems. Bailey (2) found that bacteria increased the oxidation rate, but only after 70 to 80 per cent of the iron in the reaction medium had been oxidized to the ferric state.

Dugan and Lundgren (12) investigated the metabolism of *Ferrobacillus ferrooxidans*. The organisms were found to use the oxidation of ferrous to ferric ions as their energy source. Hence, the bacterial enhancement of oxidation rate arises from the increase in ferric ions during *F. ferrooxidans* metabolism.

Lau, Shumate, and Smith (19) studied the role of bacteria in the kinetics of pyrite oxidation. They studied the growth of *Ferrobacillus* species in a medium where pyrite was the only source of reduced iron. The bacteria multiplied and increased the rate of pyrite oxidation by maintaining a high (in excess of six) ferric-ferrous ratio in the solution around the pyrite. Lau et al. noted the influence of the water-pyrite ratio on the rate of oxidation. For low ratios, the oxidation rate was limited by the number of bacteria in the water while at high ratios there were excess bacteria and the pyrite surface area influenced the reaction rate. They suggested that bacterial catalysis is much more likely at the surface of a pyritic system such as a refuse pile than in an underground mine environment. This is attributed to the fact that oxygen is the ultimate electron acceptor and must be readily available for bacterial activity to occur.

Geological Studies

Since acid mine drainage causes stream deterioration not in a laboratory, but in the real world, studies in the earth sciences, geology, hydrology, and mineralogy, are as important as laboratory investigations. In such studies, pyrite is not isolated but is distributed in a binder such as coal or shale.

Caruccio and Parizek (8) and Caruccio (7) have conducted extensive investigations of geologic factors in acid mine drainage around Clearfield, Pennsylvania. Two locations were compared, one having acidic strip mine drainage, the other non-acidic drainage. Caruccio and Parizek conducted leaching studies to determine if the acid potential of a coal could be related to its sulfur content. While increased sulfur led to greater acidity, this factor did not explain drainage differences of the observed area.

Caruccio (7) found that finer pyrite grains led to higher acidic activity. He also suggested that shales may generate more acid than coal binders. Coal is relatively "tight" and seals the pyrite from the atmosphere while the relatively permeable shale permits oxidation of the enclosed pyrite. Finally, Caruccio noted that if the ground water in a mining area contains calcium carbonate, alkalinity will develop to counteract acidity. Thus, even if acidic oxidation is occurring, the net effluent will not be acidic.

Vimmerstedt and Struthers (43) studied the weathering of spoils material from Ohio strip mines. They packed the spoils into columns and exposed these to natural weather conditions. The leachate leaving the bottoms of the columns was collected and analyzed for soluble salts, sulfate, and various cations. The investigators found that the amount of leachate and weight of salts followed the annual rainfall pattern. Through regression analysis it was also determined that there was an overall decrease with time in the weight of salts leached. This simply indicated that the pyrite in the samples was being consumed.

Several investigations have checked the effects of coal mining on the hydrology of an entire water shed. Corbett (10) and Agnew and Corbett (1) have studied the hydrology and chemistry of coal mine drainage in Indiana. In particular, they were concerned with flushouts during storms in strip mined areas. Corbett observed that the refuse piles acted as aquifers to store water during storms. The stored water would then be released gradually during dry weather. On the average, about 30 per cent of a given storm was retained in the heavily mined areas as opposed to 15 per cent retention in less mined regions. The peak stream flow during the storm was also considerably less in the stripped area. Corbett did observe that if the refuse piles were already saturated or if there had been heavy compaction during grading of the mined areas, the surface runoff would be enhanced relative to undisturbed land.

Agnew and Corbett (1) emphasized the need for continuous data when studying flushouts and natural systems. Peak flows occurred over a period of hours rather than days. The flushouts increased the concentration of deleterious ions (sulfate, hardness, acidity, and iron) in the receiving streams from 30 to 1000 per cent over normal levels. These concentrations increased at the start of the storm and remained high even after flows had receded. Agnew and Corbett also suggested that some standard method of reporting acidity be determined. In particular, it seemed that both "acidity" and "alkalinity" should be reported rather than just a net acidity. A number of other questions were raised about the analyis of mine waters.

Discussion

The investigations discussed to this point can be considered no more than a sampling of the total acid mine drainage literature. They are typical of the varying points of view which must be considered in any model of pyritic systems. Although methods and interpretation of results may vary, investigators have well defined the kinetics of iron pyrite oxidation.

From the early investigations by Li and Parr (20) to more recent work such as that by Kim (16), Morth (24), Jutte (15), and Morth and Smith (25), the importance of oxygen has been stressed as would be expected in an oxidation reaction. In kinetic terms, the oxidation rate is fractional order with respect to oxygen concentration. Jutte estimated the dependency as three-fourths power. Over the normal range of atmospheric concentrations this can be taken as a linear (or first order) dependence.

The rate of pyrite oxidation has been shown to depend more on the pyrite surface available than on the absolute weight of pyrite present. Stiles (41) came to this conclusion for concentrated, crushed, sieved pyritic material. Caruccio and Parizek (8) observed a similar dependence for pyrite still embedded in coal. Their observation was based on a qualitative estimate of the fineness of pyrite grains rather than on exact measurements.

As the stoichiometric chemical reaction equation (Equation 2-1) showed, water is also a part of the pyrite oxidation reaction system. Kim (16) and Morth (24) investigated the influence of water on the oxidation rate. In liquid phase reactions, water was present in excess and did not enter the oxidation rate equation. It was only in vapor phase reactions where humidity could be varied that water concentration appeared to influence rates. No specific reason for this influence was put forth until investigations of the actual reaction mechanism were undertaken. The mechanism studies led to the conclusion that water was necessary an an oxidation product dissolution medium. The influence of humidity was then related to how much of the pyrite surface contained adsorbed water and was available as a reaction zone. Hence, for the rate limiting step, the basic function of water is to provide a means for the removal of oxidation products.

The determination of the oxidation mechanism involved not only chemists but also geochemists and microbiologists. Here differences in philosophy and technique tended to cause divergent interpretations of similar experimental data. Singer and Stumm (34) in their studies of liquid phase oxygenation of ferrous ions and dissolution of pyrite, concluded that ferric ions could not exist in contact with pyrite. They also stated that the ferric ion was the only actual oxidizing agent even though oxygen might be the ultimate electron acceptor. The first conclusion perhaps is based on a thermodynamic approach where infinite time is allowed for a reaction to .reach equilibrium rather than on a kinetic approach where concentrations are considered as functions of time. There is strong evidence to contradict the conclusion that ferric ions in solution are the only species capable of directly oxidizing pyrite. Morth (24), in studying liquid phase oxidation, placed an Amberlite^{R} IRA-120 ion exchange resin bed in series with the pyrite bed in a recirculating solution. No iron was found in this solution using ortho-phenanthroline spectrophotometric analysis. However, the oxidation rate, as measured by oxygen consumption, was the same as in runs where iron concentrations were at the 1000 parts per million level.

Smith, Svanks, and Halko (38) also refuted Singer and Stumm by showing that there are parallel oxidation mechanisms whereby oxygen and ferric ions simultaneously and independently oxidize pyrite. In addition, Sasmojo (29) showed a direct surface reaction of pyrite with adsorbed oxygen. Finally, as a practical matter, in a real system there is no recirculation of iron-containing water over the pyrite. In experimental work, iron-containing solutions were contacted with pyrite, and the reduced iron then reoxidized to the ferric state after returning to the bulk solution. In nature, the only way that the reduced iron can leave the oxidation site is by gravity flow. If the water flow is away from the oxidation site, it is improbable that the iron ions, when reoxidized, return to the pyritic surface. This is not to deny the possibility that drainage from one mine could come in contact with pyritic material in a lower elevation mine.

Smith and Shumate (27) in discussing the two mechanisms of pyrite oxidation stated that at low ferric-ferrous ratios, oxygen oxidation is dominant. As the ratio increases, the relative importance of ferric ion oxidation increases until at ratios in excess of five, ferric oxidation is dominant. In a natural system, the only way to reach this ratio is through <u>Ferrobacillus</u> species oxidation of ferrous to ferric ions, since at a pH of two or three, the rate of oxygenation of ferrous to ferric ions is too slow to maintain a high ferric concentration in solution. This requirement of bacterial assistance is in accord with Bailey's (2) observation that in a laboratory oxidation system containing <u>Ferrobacillus</u> species, the pyrite oxidation rate increased only after the bacteria had oxidized 70 to 80 per cent of the iron in the reaction medium to the ferric state.

While laboratory investigations were concerned with detailed examination of the oxidation reaction, there have been few detailed studies of what happens once oxidation products have been formed. There is a middle ground such as that taken by Vimmerstedt and Struthers (43) who worked with spoils material. They observed that trickling flow such as that produced by rainfall removes oxidation products. This same observation has been made by nearly everyone who was concerned by acid flushouts after heavy storms. Overall, no great effort has been expended in defining the exact mechanism whereby acid products move from the reaction site to the receiving stream.

Field studies have emphasized that neutralization by naturally-occurring alkalinity is as important as the formation of acid. Caruccio and Parizek (8) and Agnew and Corbett (1) reported that calcium and magnesium carbonates neutralize acidic drainage. The difficulty arises in defining how much acid was originally produced at the source. Should just sulfuric acid be included or should the acidity of metallic sulfates such as ferrous or ferric sulfate also be considered? Sulfuric acid is important because of biological effects, but total acidity determines the cost of treatment. Most analytical techniques determine the total acidity by hot titration to a phenolphthalein end point. Agnew and Corbett (1) also observed that if the acid equivalent of hardness was added to the value of measured acidity in their samples, the sum was quite close to the sulfate level. The implication of this equality is that hardness is indicative of neutralized acidity. The only shortcoming of all these calculations is that none considered the effects of precipitation of iron hydroxy sulfates or other metallic sulfates. The main conclusion that can be drawn is that natural alkalinity of ground water should be considered and that hardness may be taken as a good estimate of the alkalinity which had been available.

Model Oriented Studies

While much has been writen in the area of acid mine drainage, there are a number of studies of particular importance in the development of a mathematical model of a pyritic system.

Smith (36) laid the basis for the development of such a model by discussing the engineering aspects of acid mine drainage. In particular, he showed how basic laboratory rate data and "first principles" of engineering could be used to estimate acid mine drainage discharge rates.

Basic Concepts of Model:

A mathematical model of pyritic systems was first suggested by Shumate, Smith and Brant (33) in 1969. They expressed the belief that a model would greatly reduce the time and expense of studying acid mine drainage. They described pyrite oxidation within the framework of a basic engineering system in the hope of stimulating critical discussion. Shumate et al. summarized five characteristics common to all pyrite systems which must be considered in any model:

1. The oxidation is a heterogeneous reaction involving crystalline pyrite with oxygen in water. The environment at the reaction site determines the reaction kinetics.
2. Oxygen transport is in the gas phase.
3. Pyrite exposed to a vapor phase will oxidize at a rate similar to pyrite in water, provided the relative humidity is near 100 per cent.

4. Removal of oxidation products has no influence on the rate of oxidation.
5. In general, the reaction does not occur on the bulk surface, but on pyrite embedded in a porous structure.

These five criteria are little more than restatements of the research results already discussed. However, they are indicative of the orderly, logical approach which must be used in the development of a mathematical model of a pyritic system. Shumate et al. also suggested methods of relating rates of oxidation, and acid release, to system characteristics. The thrust of the suggestions was to treat a pyritic system as the sum of many micro-systems.

McDaniels Research Complex:

There have been two major investigations of natural systems by workers at Ohio State University. The development of a natural laboratory by Shumate and Smith (31) and the study of a refuse pile by Good (13) have furnished much of the information for development of a mathematical model.

Shumate and Smith have developed the McDaniels Research Complex in Vinton County in southeastern Ohio. The complex, administered by Ohio State University, includes the McDaniels Test Mine and six experimental auger holes. The mine is located in the extensively mined upper reaches of Sandy Run inBrown Township in the Middle Kittanning (No. 6) coal bed. Moulton (24) has described the geology of the area as follows:

> There is a discontinuous shale layer overlying the coal, but a shaly sandstone is present most frequently. The sandstone, though shaly or silty at the base grades upward into a massive, medium grained, well cemented rock. . . . The sandstone over the Middle Kittanning coal bed is about 40 feet thick, and at its top there is a

> thin stained zone which indicates the horizon of the Lower Freeport coal. . . . The general character of the remaining upper part of the geologic section is of sandstone or silt composition, with exception of more or less minor occurrences of shale, limestone, and thin clay and coal beds.

In selecting a mine suitable for field research, investigators examined four mines in the Sandy Run area. The McDaniels Mine was selected because it best met the following four criteria:

1. It was physically separated from all other mines.
2. There was only one opening to be sealed.
3. The strata near the opening were sound so that a tight seal could be constructed.
4. The mine produced a significant quantity of acid mine water.

McDaniels Mine was also relatively small and in a good state of repair.

The test mine is a small drift mine extending 35 to 40 feet into the hillside. The refuse and other material left during mining was removed. A concrete seal was placed on the only entrance to the mine. The seal contains sampling ports and connections for injecting gases for controlling the atmosphere in the mine. The geology and hydrology of the mine was determined. Six observation wells were drilled in the hillside above the mine.

The most important aspect of the test mine work has been the continued periodic measurements of drainage flow rates and chemical analyses for over five years. The data are important both because of their frequency and because they represent a relatively well-defined system. Besides collecting data, Shumate and Smith have attempted to use the mine as one would use a chemical engineering pilot plant to perform experiments.

The main variable available for experimentation was the atmosphere with in the mine. Since the mine is located in a "tight" geologic formation and has only one man-made opening, the initial test was simply to put a seal at the entrance. With a seal, the oxygen concentration in the mine atmosphere dropped to 10 per cent, but no lower. This behavior, which has been observed in a number of other "sealed" mines, has been attributed to "breathing." "Breathing" is the pushing and pulling of air through the fine channels in the overburden by atmospheric pressure variations. To counteract breathing, positive atmospheric control was maintained by injecting gases into the mine to maintain a slight positive pressure relative to the outside atmosphere. The gases that have been injected include oxygen, nitrogen, and air. The oxygen was added to raise the oxygen level. The nitrogen was added to minimize the oxygen level, and air was injected to hold a constant 21 per cent oxygen level.

The expectation of the investigators was that the results of a change in the atmosphere would become apparent in one or two months. This hypothesis was based on the assumption that oxidation was occurring close to water flow channels and that products were washed out soon after formation. It was only after 6 to 8 month delays that anticipated acid load changes occurred. This response lag indicated that oxidation was occurring in areas away from normal flow channels. Product in unleached volumes would only be removed by gravity diffusion as described in Chapter IV. Hence, no changes in acid removal would be noted until the previously accumulated oxidation products had been removed from the system. In light of this conclusion, the most recent experiment, addition of nitrogen to maintain a slight positive pressure of nitrogen at all times, has been in progress since the middle of 1969, over a year ago at this writing. One of the best checks of any model that is developed is that it will show a long lag time similar to the observations at the McDaniels Test Mine. In other experiments, the permeability of the overburden was estimated, and core drill samples were taken from behind the exposed coal faces. These cores showed that pyrite oxidation had occurred as much as fifty feet into the coal away from the bulk atmosphere.

Six experimental auger holes were drilled in the same coal seam as the McDaniels Test Mine, but on the other side of the valley. The flow rate and drainage characteristics from these holes have been monitored since they were drilled in the summer of 1969. The most notable observation has been the change from alkaline to acidic discharges. The change is a sign of increasing acid production rather than a decrease in the natural alkalinity of the ground water. A number of experiments have been proposed and will be studied as soon as "base line" data are collected. A publication describing all of the research at the McDaniels Research Complex is being prepared by Smith and Shumate.(37)

In Situ Oxidation Rates:

Larez (18) determined the oxidation rates of pyrite contained in natural coal and shale. He obtained blocks of coal and shale from the walls of Auger Hole Number 3 at the McDaniels Research Site. The oxygen uptake rate of each of the blocks was measured in a Warburg-type apparatus. The oxygen consumption for shale was about three micrograms per hour per cubic centimeter of solid. For the coal binder, the uptake was only one microgram oxygen per hour per cubic centimeter. In engineering units, these rates are in the range from one-hundredth to one-tenth pound per day per cubic foot solid. This difference in rates was attributed to the higher pyrite content and greater porosity of the shale. Since the blocks used were only about a centimeter in thickness, the observed rates are probably the maximum possible at the operating conditions used. These rates can be used as boundary conditions in developing a model.

Larez exposed the sample blocks to chlorine to kill any bacteria present. This treatment had no influence on the shale block oxygen uptake rate, and slightly decreased the coal rate to 0.7 micrograms per hour per cubic centimeter solid. These results prove nothing concerning the effect of bacteria on acid production and may only indicate the total absence of bacteria.

Refuse Piles:

Good (13) has investigated acidic drainage from the refuse pile of the New Kathleen Mine. This mine, near DuQuoin, Illinois, was operated by the Truax-Traer Coal Company. The pile covers an area of about 40 acres and rises 40 to 65 feet above the surrounding farm land. The pile contains about two million cubic yards of coal refuse. Good described the hydrology and oxidation characteristics of the refuse pile.

Oxidation appeared to occur in a 4 to 10 inch thick outer mantle. The clay was washed out of this layer by rainfall to form a layer of clay just beneath the outer mantle. This clay layer was tightly packed and about an inch in thickness. The layer had low permeability, but there were cracks and crevices where water could enter the main part of the pile. The clay layer did serve as an oxygen and water barrier over most of the pile. The remainder of the pile showed little evidence of oxidation.

The pile had several distinct drainage areas. Instruments were set up to measure the flow rate and water quality from each of these areas. There were also a number of springs around the base whose flow rates were measured. These springs were fed by some sort of internal storage pool in the pile. Test wells in the pile confirmed the existence of such a pool, but did not define its exact nature. This pool was recharged by precipitation and supplied a significant flow rate between storms. Depending on the section of the pile, 40 to 75 per cent of the precipitation was recovered as surface runoff. The runoff was analyzed for sulfate and acidity. Generally, these were at a maximum concentration at the beginning of the storm, and tailed off as the acidic products were removed.

Since the runoff data had some scatter, Good developed a one-tenth acre irrigation sprinkler plot. Precipitation could be simulated by sprinkling uncontaminated water on the plot at any desired rate. Again, the drainage was measured and analyzed. Based on all data, Good estimated that about 30 per cent of the water from a given storm entered the pile and later emerged via springs. The daily acid production was estimated as 200 pounds per acre.

Brown (5) studied the transport of oxygen through layers of soil and material from coal refuse piles. He attempted to model the transport, but he encountered difficulty in estimating the diffusivity of air through the soil. Brown obtained laboratory scale oxidation rates for material from the Truax-Traer pile Good had studied. The small scale rates closely checked those obtained by Good.

The projects discussed in this section have been oriented towards developing information about natural pyrite systems. The results have been in accord with the reaction kinetics developed in laboratory investigations.

Although Smith and Shumate (37) and Good (13) furnished data on acid removal rates, no removal mechanisms were suggested and evaluated. This subject of removal mechanisms and rates is one of the areas where information and theories will be developed as the model is constructed.

CHAPTER III

EXPERIMENTAL PROGRAM

While much experimental information is available on oxidation rates, no work has been done to determine removal rates. To counteract this deficiency, several relatively simple experiments have been performed.

Acid Removal from Isolated Coal Blocks

Blocks of coal were isolated from the main seam in Auger Hole Number 2B at the McDaniels Research Site. One foot square blocks were isolated by cutting channels 6 to 12 inches deep around the blocks, and then filling the channels with polyurethane foam. The foam provides a barrier to oxygen and water vapor. The block is exposed to the atmosphere only on the front face and only to other coal on the rear face. At the time of the foaming, Plexiglas^{R} drainage troughs were placed in the horizontal channels.

Periodically, at 4 to 8 week intervals, the faces of the blocks have been washed. One liter of water was placed in a polyethylene squeeze bottle and the block was sprayed. The wash water was collected and returned to the laboratory for analysis. About 65 to 75 per cent of the water was recovered; the remainder was lost by splashing. The recovered water was assumed to be the average composition, and all calculations have been based on one liter of wash water.

The wash water was analyzed for acidity by hot titration to the phenolphthalein endpoint, and for sulfate by barium sulfate precipitation. The wash water was acidified, and atomic absorption spectrophotometry was used to determine the iron concentration.

The acidity and sulfate are virtually identical since the wash water contained no alkalinity. The acid removal rates for a block are shown in Figure 1 as a function of time. After an initial peak at the beginning of the test in March, 1970, the rate fell off through the summer. In October, the rate began to rise and reached a peak in January, 1971. This seasonal variation corresponds to the variation observed by Smith and Shumate (37) in the drainage from the auger holes at the McDaniels Research Site. This similarity indicates that large scale acid removal rates can be explained by microscale rate variations as in the case of oxidation rate calculations. A detailed explanation of removal mechanisms and rates will be presented in Chapter IV.

Removal Rates in High Humidity Chamber

During the cutting of channels in the above experiment, several large blocks of coal were dislodged. Two blocks, about 1 x 2 x 4 inches in size, were placed in the bottom of a desiccator. Water, instead of drying agent, was placed in the bottom of the desiccator. With the normal good seal of the desiccator, 100 per cent relative humidity was maintained in the chamber. Periodically, the lid was removed to renew the oxygen supply.

Although the blocks were sitting above the water, they gradually became wet, and occasionally drops of water would fall back into the main body of water. This experiment was continued for several months. At the

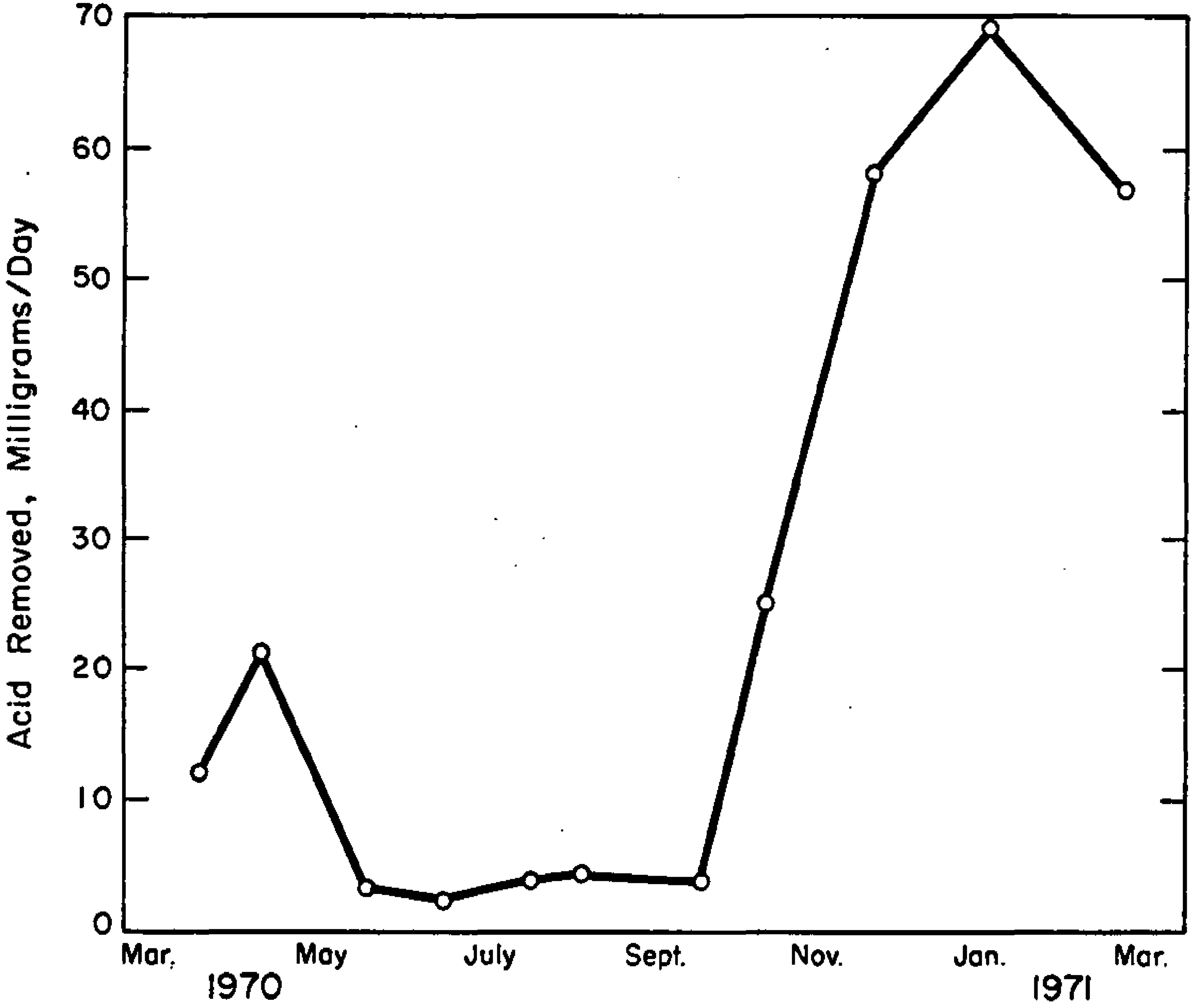


Figure 1 -- Rate of Acid Removal from Isolated Coal Block

conclusion of the run, the bottoms of the blocks were rinsed with distilled water. This water was added to the water in the chamber and analyzed in the normal manner for acidity, sulfate, and ferrous and ferric iron.

During the first test of 196 days length, the acid removal rate for both blocks was 14.4 milligrams per day, the sulfate removal was 2.4 milligrams per day, and the iron rate was 3.3 milligrams per day. The ferric-ferrous ratio was 1.6. When the test was repeated for a 72 day period, the acid removal rate was 5.5 milligrams per day and the sulfate rate was 4.2. The iron rate increased to 13.1 milligrams per day, while the ferric-ferrous ratio was only 0.24. These two sets of data have much scatter, but they do give an order of magnitude estimate of the rate of the gravity diffusion type of removal mechanism which will be presented in Chapter IV.

The weight of the blocks was about 200 grams. When a removal rate per day per gram of coal is calculated, values are in the range of 1 to 10 micrograms per day. It is interesting to observe that Larez' (18) estimates of oxygen uptake by coal and shale samples fell in this same range. This agreement is particularly significant since there has been very little other experimentation with naturally occurring materials regarding oxidation and product removal rates.

Sulfate and Acidity Analyses

In their work with acid mine drainage in Indiana, Agnew and Corbett (1) raised questions about methods of analyzing drainage. In particular, they observed that calcium and magnesium hardness ($CaCO_3$ and $MgCO_3$) should be considered in drainage analyses. Their results showed that the sum of acidity plus hardness, in consistent units, was equal to the sulfate.

To check this observation, samples from McDaniels Mine and the six auger hole mines at the McDaniels Research Site were taken in the usual manner. A small portion of the sample was acidified to prevent precipitation. The usual sulfate and acidity analyses were run on the bulk sample. Atomic absorption spectrophotometry was used to determine calcium and magnesium in the acidified samples. The acidity, sulfate, and calcium and magnesium data are tabulated in Table 1. The concentration of each has been converted to an equivalent calcium carbonate basis as is usually done for the acidity determination. The sum of acidity and hardness are in excellent agreement with the sulfate values in all cases. These results are in accord with the observations of Agnew and Corbett. (1)

Comments

These relatively simple and crude experiments have provided information about the rate of product removal from a small volume of coal. These data, along with all of the oxidation information, will be used in the development of a model of a pyritic system in the following chapters.

The calculations involving water hardness have shown that the alkalinity of the receiving waters must be considered in our model.

TABLE 1

DRAINAGE ANALYSES DATA

Source (Date)	Metal Ions, ppm Ca	Metal Ions, ppm Mg	Equivalent $CaCO_3$, ppm Ca	Equivalent $CaCO_3$, ppm Mg	Acidity, ppm $CaCO_3$	Total $CaCO_3$ Equivalents	Sulfate, ppm
McDaniels Mine (12-15-69)	15	10	36	40	72	146	133
McDaniels Mine (8-6-70)	16	9	38	35	87	160	154
Auger Hole No. 1 (8-12-70)	70	22	168	87	265	520	533
Auger Hole No. 2A (8-12-70)	118	57	290	225	1665	2180	2108
Auger Hole No. 2B (8-12-70)	25	11	60	43	60	163	169
Auger Hole No. 3 (8-12-70)	107	23	126	91	270	497	491
Auger Hole No. 4 (8-12-70)	90	27	216	106	152	474	453
Auger Hole No. 5 (8-6-70)	81	22	194	87	225	506	525
Auger Hole No. 6 (8-6-70)	111	35	266	138	347	751	757

CHAPTER IV

THEORETICAL BASES OF A PYRITIC SYSTEM MODEL

"Iron pyrite reacts in the presence of oxygen and water to form iron sulfate and sulfuric acid. These products are removed and frequently have deleterious effects on the receiving body of water." The preceding phrases are a verbal model of acid mine drainage. A mathematical model of acid mine drainage starts with the verbal model and precisely quantifies and computationally defines each event in the verbal model.

The items to be quantified include how much oxygen reacts with how much pyrite at what rate in the presence of how much water? Additional questions include in what manner and how fast do the acidic products get to the receiving waters ? These factors as well as others suggested by the previously discussed research investigations will be evaluated in the following sections.

There are different kinds of pyritic systems such as drift mines, auger holes, deep mines, and refuse piles. A single model capable of describing all of these systems would be cumbersome and difficult to use. Therefore, a model will be developed to describe one particular system. Suggestions and techniques for generalizing the model to fit other systems will then be offered.

A drift mine was selected for the initial model. This system was chosen because Smith and Shumate (37) have obtained detailed and fundamental information about a drift mine, and McDaniels Test Mine can furnish a check on the validity of the model. In addition, the auger holes at the McDaniels

Research Site will provide an opportunity to test the generality of the initial model.

An acid mine drainage system has two major subsystems: 1) pyrite oxidation, and 2) oxidation product removal. Each of these areas will be discussed separately. The oxidation presentation, based on experimental and theoretical information, is applicable to all pyritic systems. The removal section is based on general knowledge, but has less experimental data to support the presentation than does the oxidation discussion.

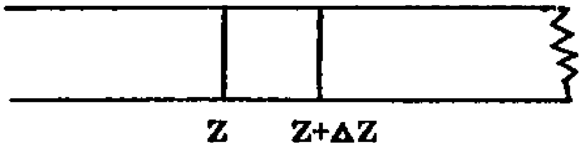
Derivation of Oxygen Concentration Gradient

The reaction mechanism and the kinetics of the oxidation of concentrated pyritic material have been described in the review of previous laboratory work. Certain conclusions will be reiterated to aid in the development of the oxidation model.

One observation was that the oxidation rate was proportional to the oxygen concentration. In the mine environment it is possible to measure a bulk oxygen concentration in the main cavity. However, this concentration is only applicable to oxidation occurring on exposed coal surfaces. Since oxidation products have been observed along cleavage planes within coal away from an exposed face, oxidation obviously occurs well back in the hill. Therefore, some method of estimating oxygen concentration within the pyrite-containing material must be developed. Since no direct analyses are readily available, a mathematical analysis will be used.

The analysis begins by assuming that oxidation occurs along the walls of small channels in the coal or shale. The channel has cross sectional area, A, and extends distance, L, into the binder. Reaction occurs the length of the channel at a rate proportional to the oxygen concentration, C_{Ox}. The rate may also be assumed so slow that no oxygen gradient exists across the area A.

Consider an element in the channel of ΔZ length as shown in the sketch below:



The oxygen entering this volume at Z is $AN_{Ox_Z}\,\Delta\theta$ where N_{Ox} is pound moles per hour per square foot and $\Delta\theta$ is the time increment in hours. The oxygen leaving the volume at $Z + \Delta Z$ is $AN_{Ox_{Z+\Delta Z}}\,\Delta\theta$. The oxygen consumed by reaction is $k_R C_{Ox}\, A\Delta Z\Delta\theta$ where k_R is the reaction rate constant with units of reciprocal hours and C_{Ox} is the oxygen concentration in pound moles per cubic foot of gas. The accumulation of oxygen in the volume is $\Delta C_{Ox} A\,\Delta Z$. These terms can be collected in the form: input minus output equals reaction plus accumulation.

$$AN_{Ox_Z}\Delta\theta \;-\; N_{Ox_{Z+\Delta Z}}\Delta\theta \;=\Delta C_{Ox}A\Delta Z \;+\; k_R C_{Ox} A\Delta Z\Delta\theta$$

If all terms are divided by $A\Delta Z\Delta\theta$, and the limits are taken as the differential elements approach zero, the following equation is obtained:

$$\frac{\partial N_{Ox}}{\partial Z} - k_R\, C_{Ox} = \frac{\partial C_{Ox}}{\partial \theta} \qquad (4\text{-}1)$$

The oxygen concentration term, C_{Ox}, can be replaced by $X_{Ox}C$ where C is the total gas concentration in pound moles per cubic foot and X_{Ox} is the mole fraction of oxygen in the gas. This substitution yields the general equation:

$$\frac{\partial N_{Ox}}{\partial Z} - k_R X_{Ox}\, C = \frac{\partial C_{Ox}}{\partial \theta} \qquad (4\text{-}2)$$

Equation 4-2 is a general relationship which can only be solved by making specific assumptions and substitutions for given situations. For this analysis, it is reasonable to assume that there is no time dependence; an assumption that will be verified in the course of the analysis. A second condition for the solution is that an "effective" diffusivity, D, which is independent of position and concentration, be defined such that

$$N_{Ox} = - CD \frac{\partial X_{Ox}}{\partial Z} \quad . \qquad (4\text{-}3)$$

This condition is based on the fact that coal and shale contain voids and channels which are neither straight nor uniform. Because of the non-uniformity of the diffusion path, the normal distinctions of diffusion area, path length, and counter-diffusion become blurred. Bird, Stewart, and Lightfoot (3) have discussed the concept of effective diffusivity in detail. They presented a similar situation of the first order consumption of a gas inside porous catalyst pellets.

When the two modifications are applied to Equation 4-2 and derivatives taken, the following equation is obtained:

$$CD \frac{d^2 X_{Ox}}{d Z^2} = k_R X_{Ox} C \quad . \qquad (4\text{-}4)$$

This may be rearranged easily to give:

$$\frac{d^2 X_{Ox}}{d Z^2} - \frac{k_R X_{Ox}}{D} = 0 \quad . \qquad (4\text{-}5)$$

The general solution to Equation 4-5 is:

$$X_{Ox} = A \exp\left((k_R / D)^{1/2} Z \right) + B \exp\left(-(k_R / D)^{1/2} Z \right) \qquad (4\text{-}6)$$

The integration constants may be evaluated by used of the two boundary conditions.

B. C. 1: At $Z = L$, $X_{Ox} = 0.0$

B. C. 2: At $Z = 0$, $X_{Ox} = X_{Ox_0}$

From B. C. 1, it is apparent that A is zero. Then, using B. C. 2,

$$X_{Ox_0} = B \exp(-(0)) = B \quad \text{or}$$

$$X_{Ox} = X_{Ox_0} \exp(-(k_R / D)^{1/2} Z) \tag{4-7}$$

In the evaluation of the oxygen gradient, some value must be assigned to the effective diffusivity. Workers in soil mechanics (see Brown (5)) have suggested using $D = 0.6\, D_{AB}$, where D_{AB} is the normal oxygen in air diffusivity.

Another solution to Equation 4-2 may be developed by assuming that the atmospheric pressure varies at the mouth of the channel. If the ambient pressure increases, air containing 21 per cent oxygen will be pushed into the pore. If the outside pressure decreases, part of the air in the confined volume will be pulled out. This is now an unsteady state problem which is more easily handled by numerical than by analytical solution techniques. One simplifying assumption is that the pressure alternately increases and decreases uniformly with time, i.e., a "sawtooth" function. As in the previous analytical development, the effective diffusivity will be used to describe other motion of the oxygen molecules. These assumptions give for the oxygen movement:

$$N_{Ox} = -DC \frac{\partial X_{Ox}}{\partial Z} + X_{Ox}(N_{Ox} + N_N) \tag{4-8}$$

The first term on the right hand side of the equation is the molecular diffusion of oxygen into the channel, and the second term is the bulk flow of oxygen and nitrogen being pushed and pulled by the pressure variations.

At atmospheric pressure the moles (Δn) of an "Ideal" gas entering the channel mouth is equal to $V/RT \Delta P(\theta)$, where V is the channel volume, R is the gas constant, T is the ambient temperature, and $\Delta P(\theta)$ is the change in atmospheric pressure as a function of time. When V is replaced by $A \cdot L$ and the entire equation divided by area to convert to a flux, we obtain:

$$\frac{\Delta n}{A} = (N_{Ox} + N_N) = \frac{AL\ \Delta P(\theta)}{ART}$$

$$= \frac{L\ \Delta P(\theta)}{RT} \quad (4\text{-}9)$$

Finally it may be assumed that effects of gas entering (or leaving) the channel are uniformly reflected over the length of the channel, i.e., each incremental volume gains an additional 1/V moles of gas. This in terms of the flux is:

$$(N_{Ox} + N_N)_Z = \frac{L\ \Delta P(\theta)}{RT}\ (1 - Z/L) \quad (4\text{-}10)$$

$$(N_{Ox} + N_N)_Z = \frac{\Delta P(\theta)}{RT}\ (L - Z) \quad (4\text{-}11)$$

Equation 4-11 may be substituted in to Equation 4-8 and the derivative taken.

$$\frac{\partial N_{Ox}}{\partial Z} = -CD\frac{\partial^2 X_{Ox}}{\partial Z^2} + \frac{\Delta P(\theta)(L-Z)}{RT}\frac{\partial X_{Ox}}{\partial Z} - X_{Ox}\frac{\Delta P(\theta)}{RT} \quad (4\text{-}12)$$

Equation 4-12 is substituted into Equation 4-2 to give the second order unsteady state equation:

$$C\frac{\partial X_{Ox}}{\partial \theta} = CD\frac{\partial^2 X_{Ox}}{\partial Z^2} - \frac{\Delta P(\theta)(L-Z)}{RT}\frac{\partial X_{Ox}}{\partial Z} + X_{Ox}\frac{\Delta P(\theta)}{RT}$$

$$- k_R X_{Ox} C \quad (4\text{-}13)$$

Three boundary conditions are required for the solution of Equation 4-13. Two are the same distance and mole fraction parameters as used in the analytical solution. The third is a time and mole fraction parameter describing the oxygen gradient at zero time.

B. C. 1: At $Z = L$, $\theta = \theta$; $X_{Ox} = 0$

B. C. 2: At $Z = 0$, $\theta = 0$; $X_{Ox} = X_{Ox_0}$

B. C. 3: At $Z = Z$, $\theta = 0$; $X_{Ox} = X_{Ox_0} \exp(-(k_R/D)^{1/2} Z)$

Equation 4-13 is of such complexity that there are no straight forward analytical solutions. However, numerical techniques using a digital computer can be used to generate solutions for different values of the independent variables L and $\Delta P(\theta)$. Implicit finite differences are used to estimate all derivatives, and a solution is obtained by iterative techniques. The setup of the numerical solution and the computer program "GRADIENT" are shown in Appendix A.

The output of the program "GRADIENT" is sets of oxygen gradients for given L and $P(\theta)$ values. An integrating function in the program estimates the daily oxygen consumption in the channel at the stated conditions. Since "GRADIENT" generates much data rapidly, the most important information will be summarized using Figures 2 to 7.

The $\Delta P(\theta)$ function was treated as a sawtooth variable that linearly moves between some maximum and minimum value. The maximum has been fixed at 745 mm Hg pressure and the minimum is established by the ΔP. Figure 2 shows the maximum and minimum oxygen gradients for a daily pressure change of 12 mm Hg and an L of 200 feet. At the minimum pressure, the channel has been partially evacuated, and the oxygen gradient is at its lowest level as the highest oxygen content air has been pulled out. At the maximum, relatively oxygen rich (21 per cent) atmospheric air has been forced into the channel to raise the gradient. For comparison, the gradient from the analytical solution (no breathing) is also shown. The analytical gradient is slightly closer to the minimum than to the maximum. Calculations for more normal, 1 to 3 mm Hg, daily pressure changes give maximum and minimum gradients closer together. At these low pressure variations, the time average of the gradients approaches the analytical gradient.

The channel length L is representative of the volume of gas available for compression and expansion rather than being a perpendicular distance from the channel mouth. Figure 3 shows the influence of L on the amount of oxygen

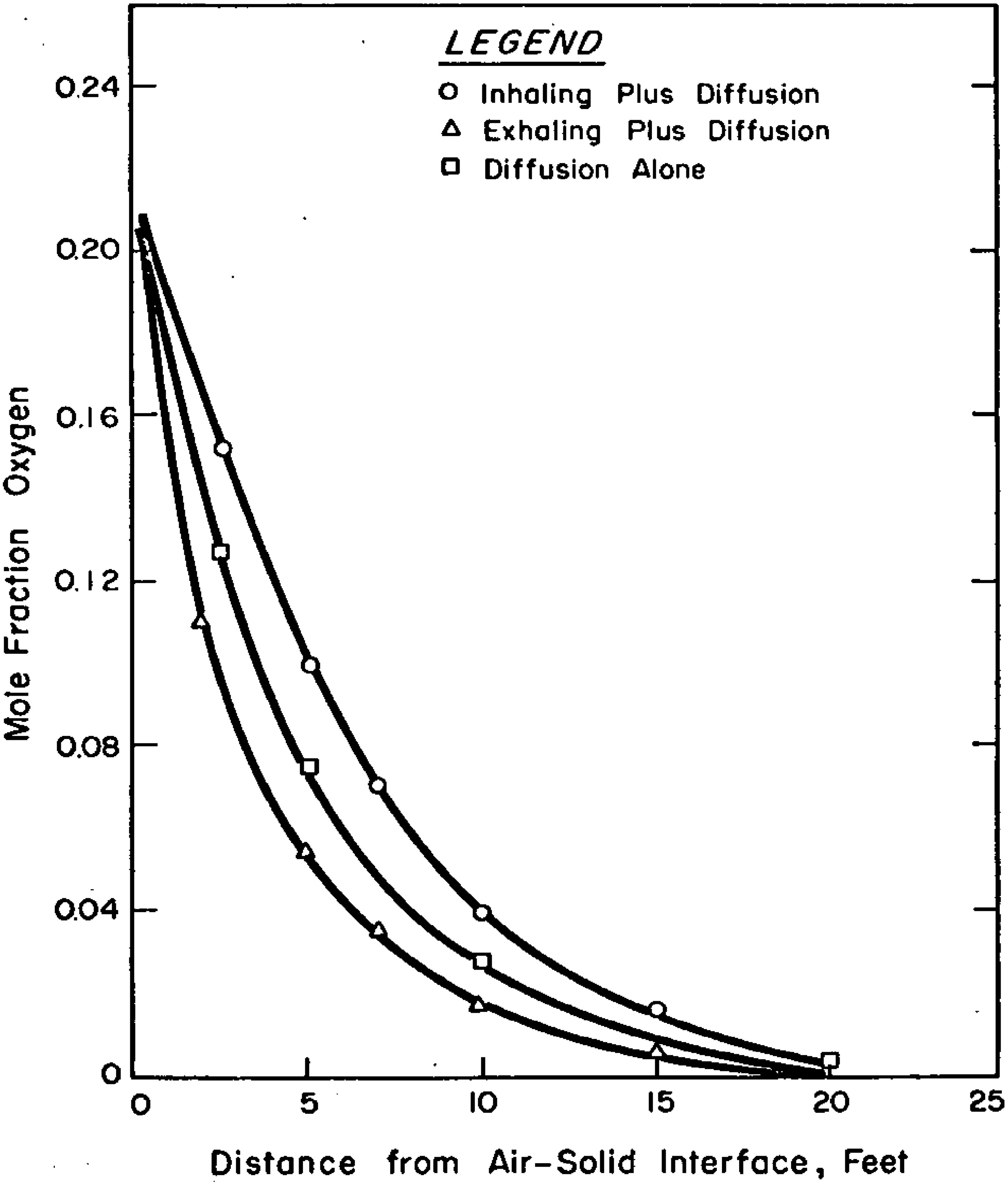


Figure 2 -- Effect of "Breathing" on Oxygen Gradient

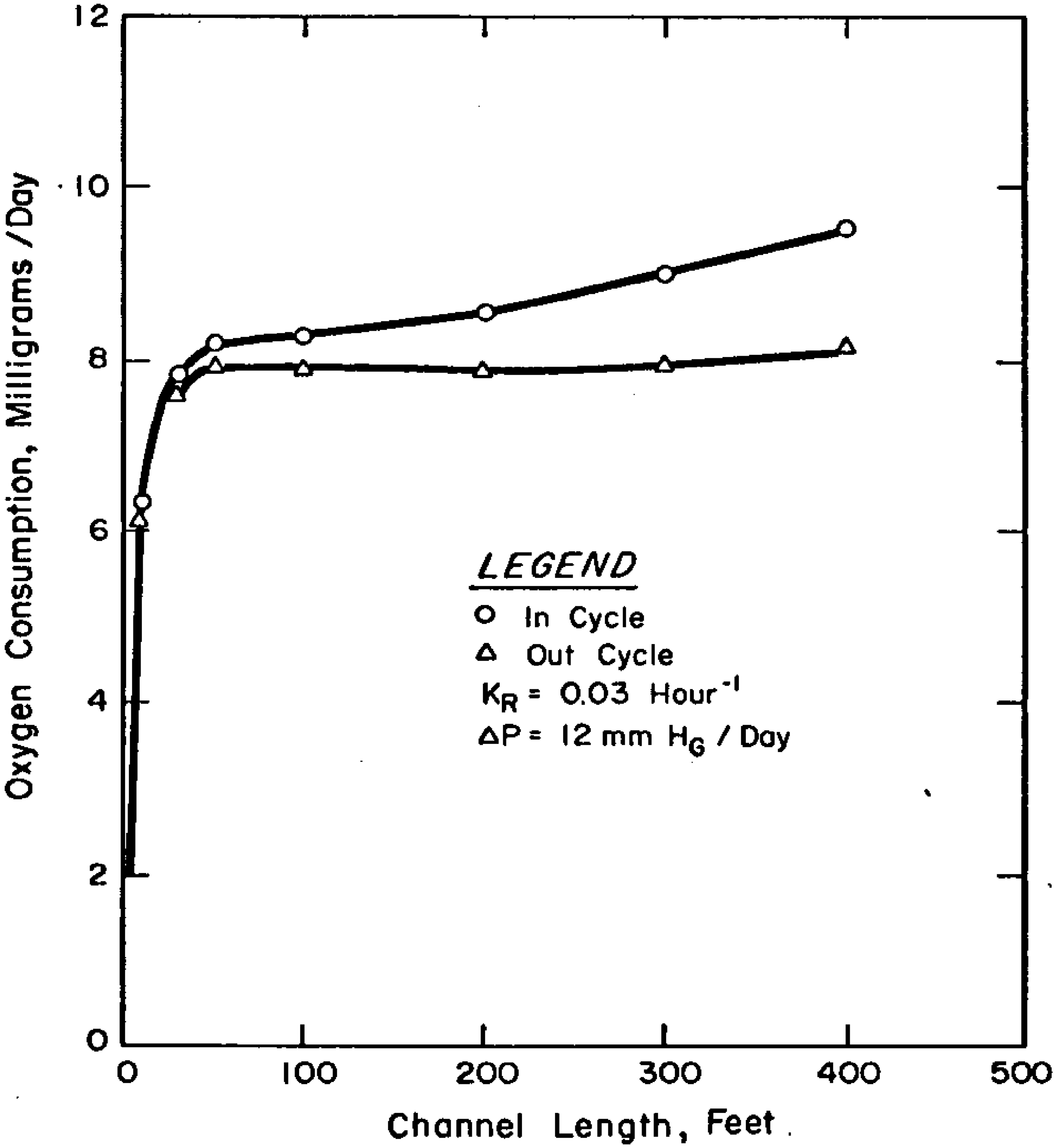


Figure 3 -- Effect of "Breathing" on First Order Oxidation Rate

consumed in the channel. As expected, more oxygen is consumed on the "in" than on the "out" breathing cycles. Longer channels increase the oxidation on the "in" steps, but give less oxidation on the "out" cycles. The net result is a slight increase of oxidation with increasing L.

The evidence presented in Figures 2 and 3 leads to the conclusion that "breathing" has little effect on oxidation in closed end channels. If channels between the atmosphere and a very large void volume, such as a mined out volume, were considered, "breathing" might be of greater importance. This is indicated by the rapidly increasing oxygen consumption at longer pore lengths in Figure 3. In such a case nearly all of the pyrite-containing channel would be swept with a new atmosphere during each pressure change. However, in the current development, it seems reasonable to use the analytical oxygen gradient.

Influence of Reaction Rate Constant

The rate constant k_R also influences the oxygen gradients and amount of oxidation. Generally k_R is defined in terms of the reacting materials. In the case of a heterogeneous reaction a very careful definition is required. The reaction rate equation is written below in the usual symbolic language for a first order reaction:

$$- \frac{d C_{Ox}}{d \theta} = k_R C_{Ox} \qquad (4\text{-}14)$$

The derivative, $\frac{dC_{Ox}}{d\theta}$, is the change in moles per unit volume per unit time. The rate constant, k_R, has the units of reciprocal time, and C_{Ox}, the gas concentration, has the units of moles per unit volume.

Pyrite is embedded in the channel walls in small quantities so the actual concentration must be considered in determining k_R. Since the true pyrite distribution is not known, it is necessary to assume a distribution. For example, in the laboratory, one gram of 60 mesh, concentrated, pyritic material consumed 25 micrograms of oxygen per hour in air at 25 °C. The gram of pyrite can be assumed to be distributed along the walls of some volume, V, of channel, or:

$$\frac{\text{Rate}}{\text{gram pyrite}} \times \frac{\text{gram pyrite}}{\text{Volume}} = k_R \frac{\text{mole oxygen}}{\text{Volume}}$$

$$\frac{25\text{x}10^{-6}}{\text{V}} \frac{\text{gram oxygen}}{\text{hour}} = k_R \times \frac{0.21 \text{ x } 32 \text{ grams oxygen}}{22.4 \text{ liters}}$$

$$k_R = \frac{8.3 \text{ x } 10^{-4} \text{ liter}}{\text{V hour}}$$

If a channel cross sectional area one one square millimeter is considered, it is likely that the reactivity equivalent of one gram of crushed pyrite would be found in a length of 100 meters. This would give a volume of 0.01 cubic meter, or a k_R value of 0.083 per hour. Since this can only be considered an educated guess, Figure 4 has been drawn to show the effect of the rate constant on oxygen gradients. The higher the rate constant, the more rapidly the gradient drops to zero. The influence of rate constant on the amount of oxidation is shown in Figure 5 as a logarithmic plot. This plot has a slope of 0.5 indicating that the rate is proportional to the square root of the rate constant. This is the result for any rate calculation using a concentration term based on Equation 4-7. The preceding observation leads to the conclusion that for a reasonably accurate oxidation model, the rate constant should be known within an order of magnitude.

Effects of Reaction Order

All of the discussion to this point has been based on the premise of first

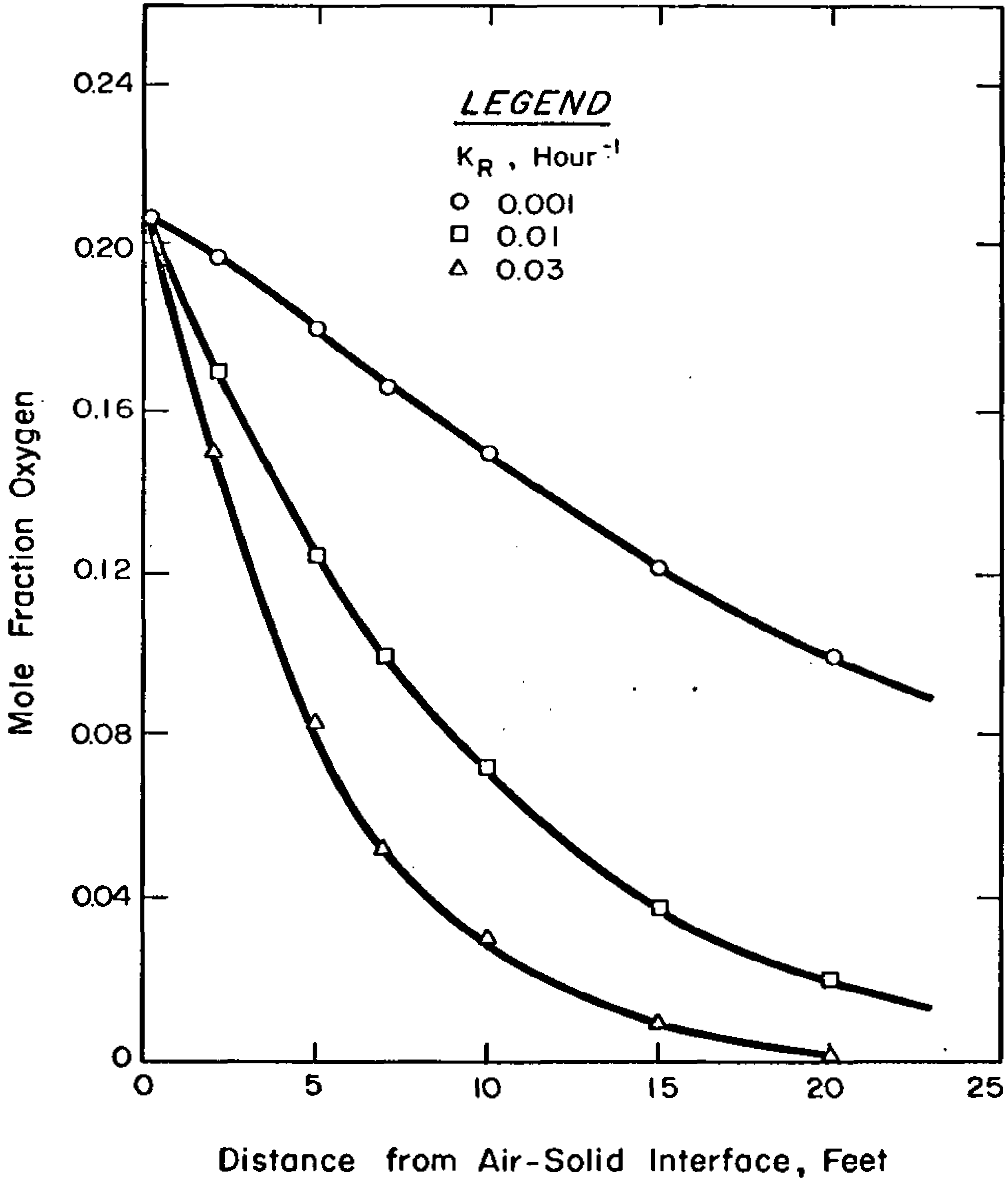


Figure 4 -- Effect of First Order Rate Constant on Oxygen Gradient

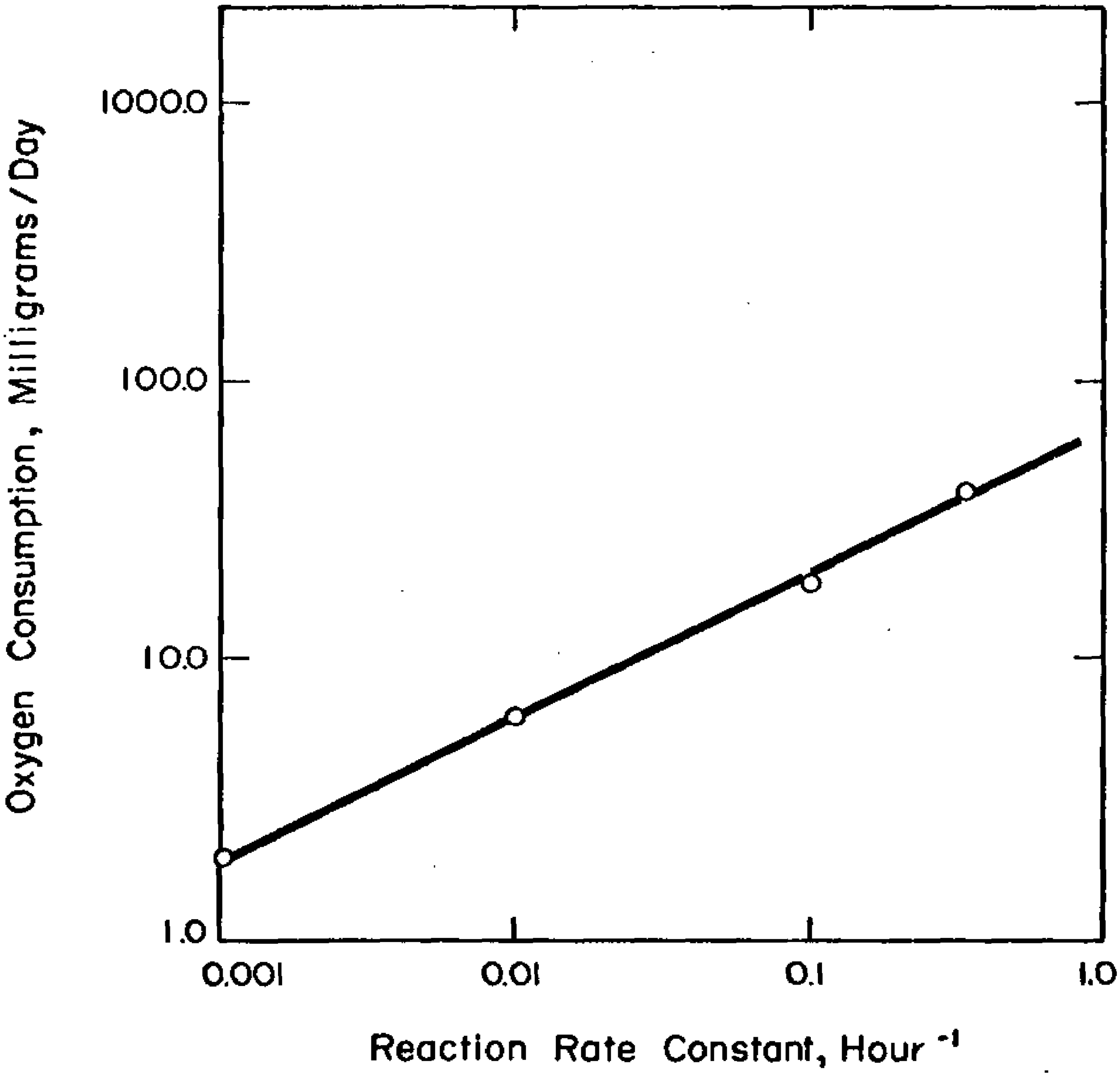


Figure 5 -- Effect of Rate Constant on First Order Oxidation Rate

order, or oxygen concentration dependent, reaction kinetics. However, in microbiological work, particularly that of Lau <u>et al.</u> (19), it has been observed that above a certain minimum concentration of oxygen, the oxidation of pyrite is independent of the oxygen concentration. The oxidation rate appears to be some function of the <u>Ferrobacillus</u> concentration, or zero order with respect to oxygen.

The "GRADIENT" program was modified to do zero order calculations of oxidation above a minimum oxygen level and first order below that level. Based on Lau <u>et al.</u>'s work, 2 per cent oxygen was used as the cut-off point. The oxidation rate above 2 per cent oxygen was considered to be the same as the rate observed at normal (21 per cent) atmospheric oxygen level.

The results generated using these assumptions lead to the same conclusions as the first order case. Some differences in form do exist. For example, the zero order oxygen concentration gradients shown in Figure 6 are steeper than the first order curves in Figure 4. The most important difference between the two orders is shown in Figure 7 where the amounts of oxidation are plotted against pore length for the different orders. The zero order reaction gives a consistently higher level of oxidation than does the first order. This occurs because the zero order concentration gradient, the driving force for diffusion, is steeper as more oxygen enters the channel to be used in oxidation.

The difference between zero and first order rates is not important in the development of a model for three reasons. As a practical matter, the 30 per cent difference is minor compared to some of the other influences such as rate constants. More importantly, Smith (35) and others have stated that the significant bacterial activity, ferrous to ferric oxidation, occurs in the

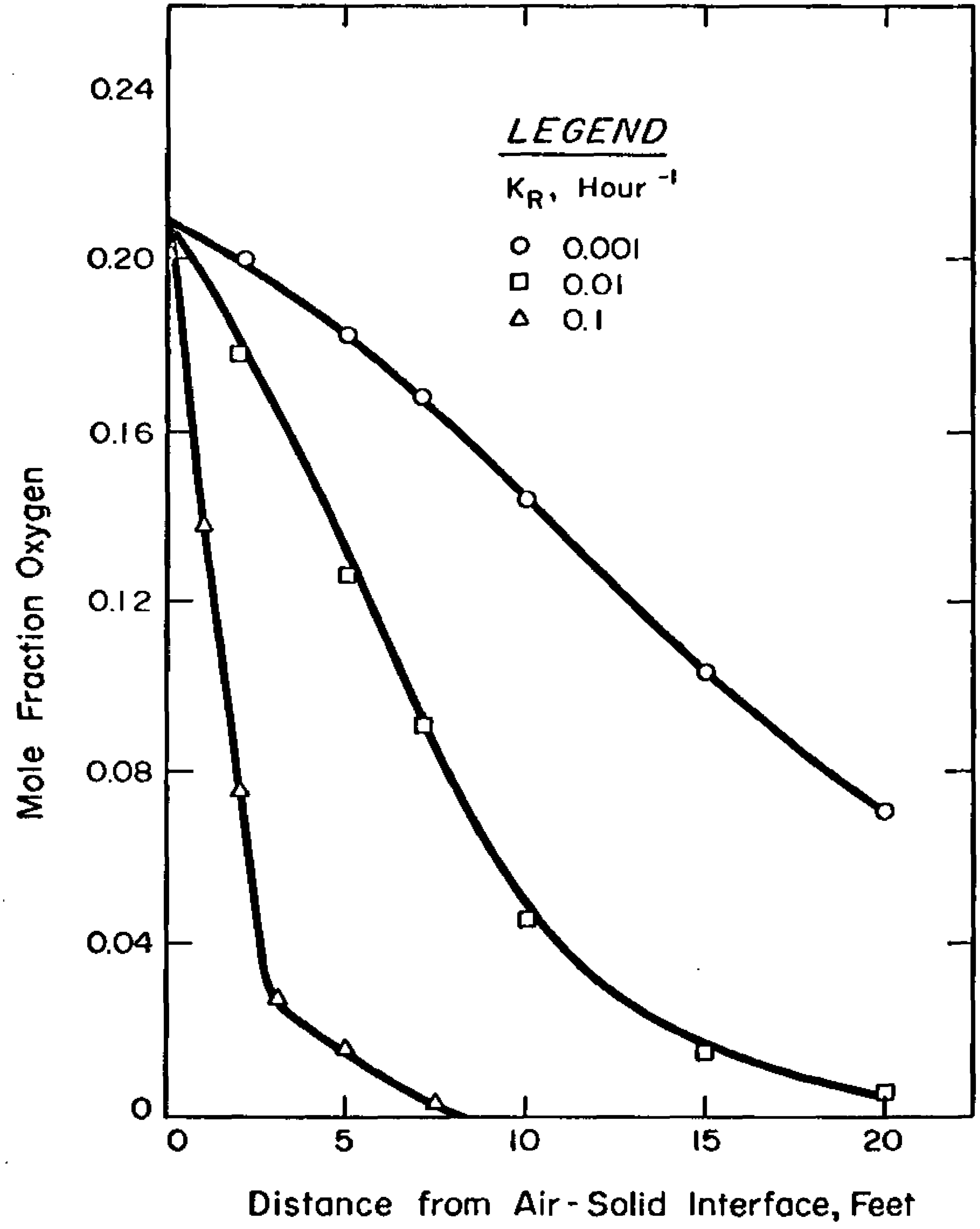


Figure 6 -- Effect of Zero Order Rate Constant on Oxygen Gradient

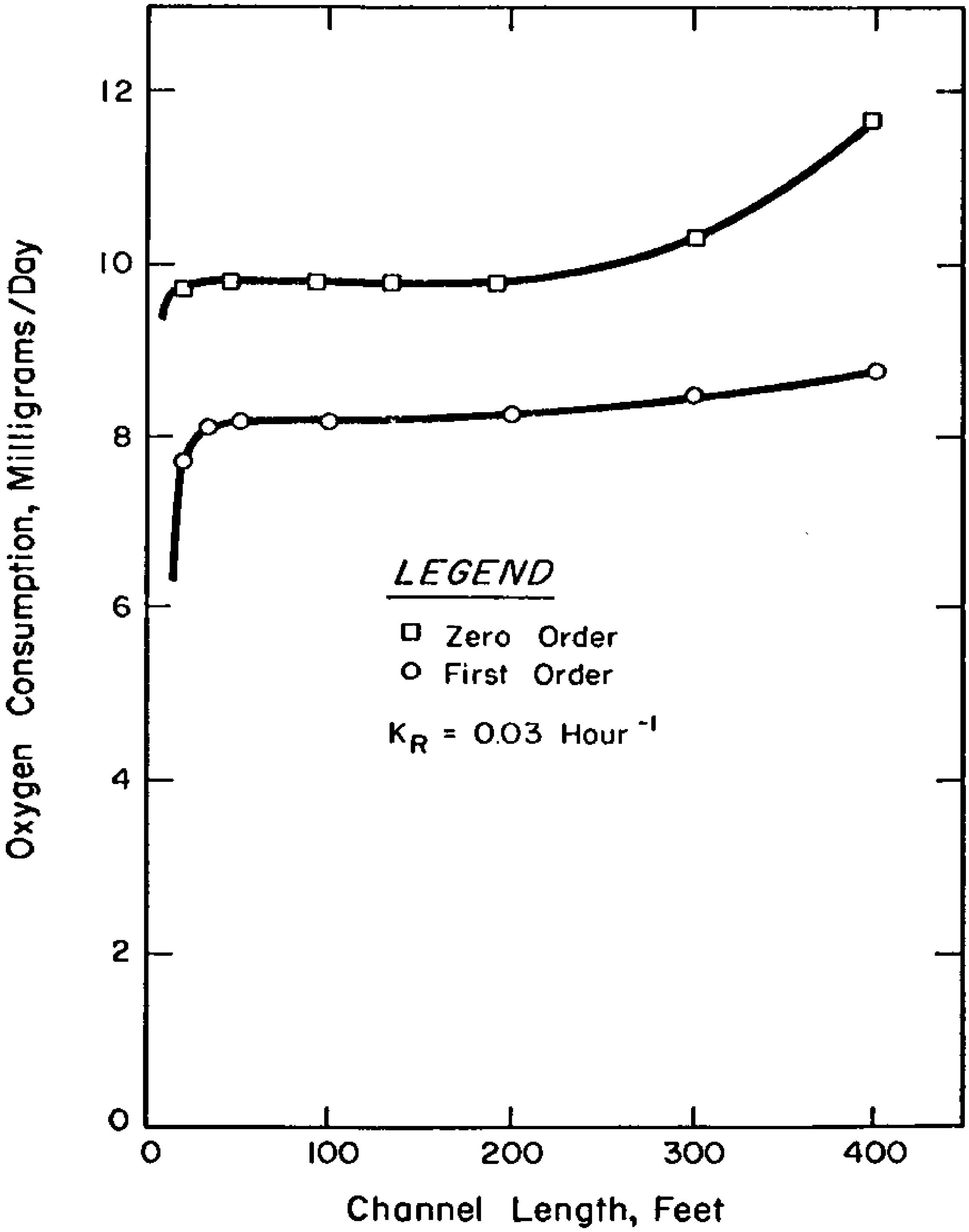


Figure 7 -- Effect of Pore Length on Oxidation Rate

drainage rather than on the surface of the oxidizing pyrite. This means that in a natural system the pyrite is oxidized, the products move to a receiving stream or pool, and then the bacteria oxidize ferrous ions to the ferric state. In the laboratory research, the bacterial enhancement of oxidation rates was observed only in systems where the culture medium was recirculated over the pyritic material. In a natural system recirculation does not occur. Finally, in a natural system, the water-to-pyrite ratio is low at the reaction sites. Under this condition, as explained by Lau et al. (19), there will be relatively few bacteria growing, and therefore, no enhancement of the oxidation rate.

Oxidation Product Removal

Generally speaking, the removal of pyrite oxidation products has been investigated much less than oxidation of pyrite. The basic removal problem is to describe and evaluate the flow rate of oxidation products through various porous media by both water movement and by molecular diffusion in aqueous solution (i.e., without net flow of water).

The rate of removal is primarily a function of the hydrologic characteristics of the system. Conditions describing the extremes of removal rate compared to oxidation rate can be imagined as varying from oxidation sites in close proximity to flowing ground water to sites far removed from the water table which are never inundated or flushed by flowing water. All other factors being equal, oxidation rates at these sites would be the same, but the rate of acid transport to the effluent stream would be quite different. To estimate the rate of transport, we must first describe possible transport mechanisms.

Removal Mechanisms:

On the basis of laboratory observations and physical considerations, it is possible to visualize three parallel transport mechanisms. The first is simply a direct washing. As ground water percolates through flow channels in the coal seam, products from the walls of the pores are dissolved. These products may have formed at times when the channel was not filled with water or the products may have diffused from adjacent channels that are not normally used for water flow. As flow increases, more channels are utilized, and more product is removed.

The second removal mechanism is the flushing of products from an inundated volume. The inundation occurs as the water table rises during the spring thaws or during heavy rains and covers a previously non-saturated volume. The oxidation products gradually dissolve and are carried to the receiving stream. This mechanism is partially responsible for the high acid loads observed during the spring.

The final removal mechanism arises from the fact that the oxidation products form a highly localized concentrated acid and salt solution. This solution is hygroscopic and will absorb moisture from the air. Since the relative humidity in a mine atmosphere is usually 100 per cent, ample water is available for absorption. In addition, when warm air from outside enters a mine and is cooled, moisture may be removed by condensation. Eventually, sufficient moisture is collected at the oxidized surface, and droplets of acidic solution form. As the drops become heavier, they begin to flow by gravity and eventually reach the receiving streams. This mechanism has been observed in laboratory studies where water saturated air was recirculated over a bed of pyritic material. After about one week, acidic brown liquid began to drip from the pyrite bed. The removal by condensation, or gravity diffusion in the nomenclature of this model, is assumed to occur uniformly throughout a pyritic system, but only the drops leaving the bottom of the system are included in the net removal of acid.

While experimental data and theoretical calculations could be used to closely estimate oxidation rates in a pyritic system, less data are available for estimating the rate of removal by each of the described removal mechanisms. However, using "common sense" and the engineering approach of Smith (36), removal rates can be estimated in terms of what is physically reasonable.

Gravity diffusion both adds and removes products from a volume of coal or shale. The rate of removal by this method can be estimated in two ways. The laboratory experiment with small coal block in a 100 per cent relative humidity chamber gave a removal rate, R_{Rem}, of about 100 milligrams acidity per day per square foot of coal drainage surface. If the rate of gravity diffusion is considered proportional to the quantity of oxidation products stored in a volume, the above removal rate is a maximum estimate since it represents a volume at the air-solid interface where the oxygen concentration and oxidation rate are at a maximum. If the rate of removal by gravity diffusion is assumed proportional to the concentration of stored products, the total removal rate from a one foot wide row of volumes perpendicular to the interface may be estimated by integrating the exponential oxidation gradient of Equation 4-7:

$$\text{Total removed} = R_{Rem} \int_0^L \exp\left(-\left(k_R / D\right)^{1/2}\right) dZ$$

Inserting the value of k_R equal to 0.8 per day for coal, a diffusivity of 10.0 square feet per day, and the R_{Rem} value of 100 milligrams acidity per day and noting that at great values of L there are no oxidation products to be removed, then:

$$\text{Total removed} = (100/(0.8/10)^{1/2})\ \exp(-(0.8/10)^{1/2})$$

$$= 343 \text{ milligrams acid per day per foot of interface.}$$

For the estimated wall length of 100 feet at McDaniels Mine this gives 34 grams per day or about 2 pounds per month.

The second method of estimating gravity diffusion is to examine acid output data from McDaniels Mine for periods such as late summer and early autumn when the ground is relatively dry and ground water flows are low. Under these conditions, leaching and inundation removal of oxidation products are minimal, and gravity diffusion is the dominant removal method. Over the 1966 to 1970 period, acid loads in this dry season have been in the range of two to four pounds per month at McDaniels Mine. Since this ranges agrees with the rate estimated in the laboratory study, a relationship must be included in the model to give this rate of removal by gravity diffusion.

The removal of products by percolation or by flushing both require that there be a description of underground water flow patterns. Hydrologic equations have been developed to describe flow patterns in watersheds covering hundreds of square miles. Even in these large areas, the non-isotropic nature of the earth forces generalizations in the flow descriptions. When the relatively small, at most two or three acres, drainage area of McDaniels Mine is considered, flow can best be described as "through cracks and crevices." (32) It has been suggested that the best mathematical description of this behavior can be obtained by assuming a model and determining how well the model correlates previous precipitation and flow data.

Underground Water Balance

The basis that will be used for a model of ground water flow is a material balance: In - Out = Accumulation. This balance can be expanded and rearranged to describe the rate of water flow through a mine. To aid the visualization of the water material balance, McDaniels Test Mine will be used as the basis for calculations.

The input term in the water balance is a function of the amount and rate of precipitation and of the characteristics of the receiving ground. The output term depends on drainage flows, evaporation, and transpiration. The accumulation term approaches zero over a period of years, but has a finite value over shorter periods of time. The accumulation may be considered as the time for passage of water from the surface after precipitation through the ground to sub-surface flow paths. The accumulation also represents a driving force or "head" for underground flows.

The input of water can be estimated successfully using currently available hydrologic models (11, 44). The amount and duration of precipitation can be measured. The rate and total uptake of water by the soil, infiltration capacity, can be determined. The infiltration capacity, f_p, decreases exponentially from a maximum initial rate, f_{Max}, to a constant rate. For the McDaniels area an f_{Max} of 0.5 inch per hour has been estimated during the normal growing season(32). When the ground is wet, the infiltration capacity drops to lower values as the soil flow channels become saturated, and clay particles begin to swell and constrict pores (44). Since the infiltration is laminar flow, the rate is also viscosity dependent. Viscosity of water in turn is temperature dependent. The dependence is of the form

$$\text{Viscosity} = A \exp (B / \text{Temperature})$$

where A and B are constants for the liquid in question. Hence, there will be a seasonal variation of infiltration capacity arising from temperature variations in addition to the cyclic variations caused by plant growth demands for water. When the ground is frozen, the infiltration capacity approaches zero.

The output of water is harder to describe since only the dependent variable, drainage from McDaniels Mine, can be directly measured. The evapotranspiration losses, evaporation plus water vapor given off during plant growth, can not easily be measured. However, techniques have been developed for estimating evapotranspiration. Thornthwaite and Mather (42) compiled and analyzed all of the existing evapotranspiration data from the United States. On the basis of this compilation, they developed a method to predict potential evapotranspiration (PE). Their correlation requires data on the average monthly temperature, latitude, soil type, and vegetative cover for the region in question.

The temperature data are used to estimate the solar energy received by the ground, and the latitude determines the daily time available for plant growth. From this data a potential (maximum) evapotranspiration is calculated. From the type of vegetation and soil, a provisional water holding capacity (PWHC) is obtained. The PWHC represents the ability of the root structure to hold or bind water in the soil. The soil and vegetation of the Vinton County, Ohio, area are probably best described by Thornthwaite and Mather's category of sandy loam and open forest. For this combination, a PWHC of 10 inches of water is suggested.

The PE calculation techniques are fairly simple. The estimated evapotranspiration is subtracted from the water content of the soil. The actual water content must be known at some time, or else the water content can be assumed equal to the PWHC during the wettest part of the year. As the PE is subtracted from the root water storage, the storage level falls below the PWHC. When the surface dries, there is less water available for evaporation and the PE is reduced also. During a prolonged dry period, the root storage asymptotically approaches zero. When precipitation occurs, the root storage is recharged up to the PWHC. In the system being analyzed, excess infiltrated water is then considered to be available for drainage flows. The logic of this assumption can be verified by digging into the soil after a summer shower. While the surface is moist, the soil at a depth of a foot is dry and powdery.

Precipitation occurring during cold weather is a special problem. When the ground freezes, the water contained in the freezing ground is held and prevented from reaching the area of underground flows. The rain or snow falling on frozen ground either remains as frozen water or runs off into surface streams. The frozen water may infiltrate the soil when the ground thaws during warmer weather, but a large fraction may run off as surface water if there is a rapid thaw or a relatively large amount of frozen water.

Potential evapotranspiration and mean monthly rainfall for the McDaniels area are compared in Figure 8. In the hot summer months there is a deficiency of precipitation compared to the PE. In the cooler months there is excess precipitation and the underground flow reservoirs can be recharged. The calculation of the PE curve is shown in Appendix B. Data have been abstracted from Thornthwaite and Mather's presentation so that the PE can be repeatedly calculated for the McDaniels Test Site. The subroutine "PEVAP" has been written to determine a PE for each month of the year. "PEVAP" is described in Chapter V in the section on programming.

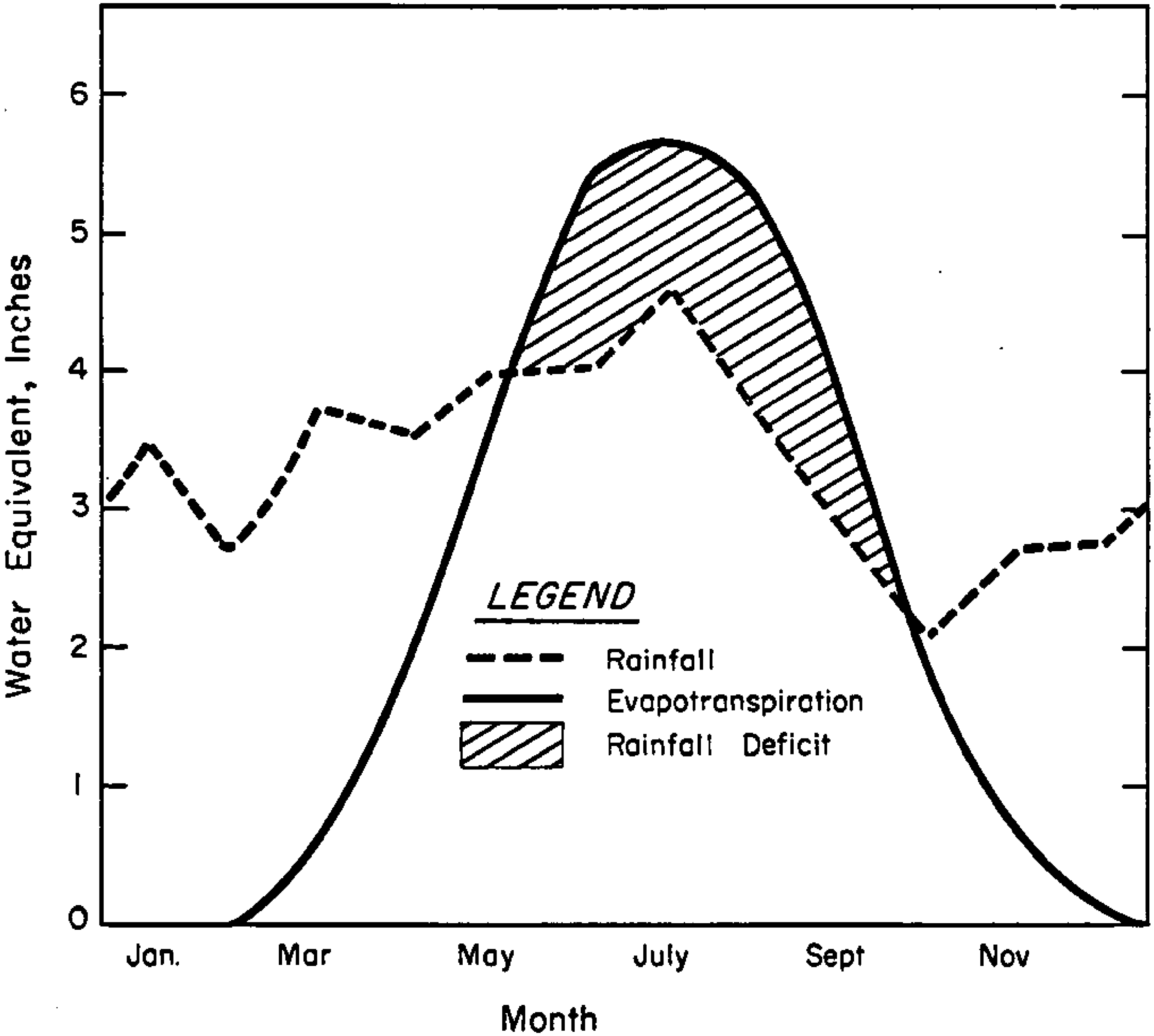


Figure 8-- Comparison of Rainfall and Potential Evapotranspiration

The accumulation term in the water balance represents the water contained in the geologic structure. Materials such as shale and sandstone are not solid, but porous, and can hold water in these pores. There are also cracks and crevices which can hold water. As was mentioned previously, the water moving down from the surface or being held as frozen water or snow can also be considered part of the accumulation in the mass balance.

Estimation of Drainage Flows:

Since the main concern of this analysis is the estimation of drainage flow from the McDaniels Mine, the material balance can be rearranged to give:

Output = Input - Accumulation .

Breaking down the output term further gives:

Drainage = Input - Accumulation - Evapotranspiration

The information required to use the above equality for predicting groundwater flows may be summarized as follows:

Input = f(Precipitation, Infiltration capacity, Temperature)

Accumulation = f(Temperature, Geologic Features)

Evapotranspiration = f (Temperature, Vegetation, Precipitation)

The nature of these relationships has largely been explained so the formulation of a prediction technique can now proceed. The one relationship which was not quantitatively described was the effect of geologic structure on the accumulation. Since no information exists to define this relationship, an empirical correlation must be used. In terms of what is observed, the model must provide for the general storage of water and the delay between precipitation and measurable flow changes. It must also provide for longer term storage of frozen water.

One storage representation is a set of three tanks: A, B, and C. Tank A receives precipitation when the ambient temperature is above freezing. Tank B represents surface storage of snow and ice when the ground is frozen. Tank C is the general storage volume from which water is continually released as drainage flow. A fraction of the contents of Tank A are transferred to Tank C each day. This partial transfer builds in a delay representing the time it takes for precipitation to move through the ground. The contents of Tank B are gradually transferred to Tank C as the ground thaws. With even a simple three tank model, arbitrary constants must be evaluated. Since there are limited physical bases for evaluating the constants, they may be assigned values which best simulate existing data.

The computer subroutine "REMOVE" has been developed from the information presented in the discussion of the water balance. The subprogram, which is described in Chapter V, uses basic meteorological data and the storage model to generate daily flow estimates. The daily flow estimates are then used to determine product removal rates by leaching and inundation. These calculations will be discussed when the total drift mine model is described in the following chapter.

CHAPTER V

DEVELOPMENT OF DRIFT MINE MODEL

Several approaches are possible in developing a model of a pyritic system. The major source of variations arises in the choice of the bases to be used. The choice of a co-ordinate system depends on factors such as computational facility, spatial visualization, and physical reality. The easiest choice is to list all possible variables with a tabulation of data and feed the mass of numbers to a computerized multiple regression analysis. This statistical approach offers computational facility, but sometimes at the sacrifice of physical reality. Since the goal of this research is to maintain physical meaning so that different sites can be compared, a statistical approach must be ruled out.

For the sake of generality and physical significance, the best approach is to work with Cartesian co-ordinates. The physical orientation of the system can be easily described in these co-ordinates. Physical and chemical variables such as water flow, oxygen gradients, and the water table are also easily defined in rectangular co-ordinates.

Computational neatness can be assured by the careful definition of the variables. For example, a technique to calculate the oxygen gradient in terms of the distance from the air-solid interface has already been explained in Chapter IV.

Description of Micro-System

Let us begin development of the computational model by examining a sketch of a pyrite containing coal seam as shown in Figure 9. Generally, the coal seam is divided into a number of layers of coal and shale. The water table may intercept the coal seam. The coal seam extends a relatively great distance from the air-solid interface.

One of the layers is shown in expanded form in Figure 10. The stratum is of such size that oxidation and removal conditions can vary widely over the stratum. Therefore, the stratum is subdivided into several layers, and these layers are then divided into blocks. The basic assumption of the whole model must now be stated: An average set of conditions exists over each volume and can be used in any calculations for that block. The system behavior is then the linear sum of the behavior of all these small reaction volumes.

The block marked "A" in Figure 10 is further expanded in Figure 11. A material balance has been developed about the block to relate the oxidation product formation and removal rates. Oxidation is the chemical reaction of oxygen and pyrite. Gravity diffusion is the very slow downward movement of highly concentrated product solutions. Leaching is the removal of products by ground water trickling through the oxidized volume. Flooding is the removal of products when a volume is inundated. All of these terms have been described in Chapter IV so now they need only be slightly expanded or altered to give a single expression to describe the events in volume "A."

Oxidation rate is a function of the oxygen concentration, the pyrite surface available for oxidation, and the reaction rate constant. The oxygen concentration gradient can be calculated using Equation 4-7. The pyrite available

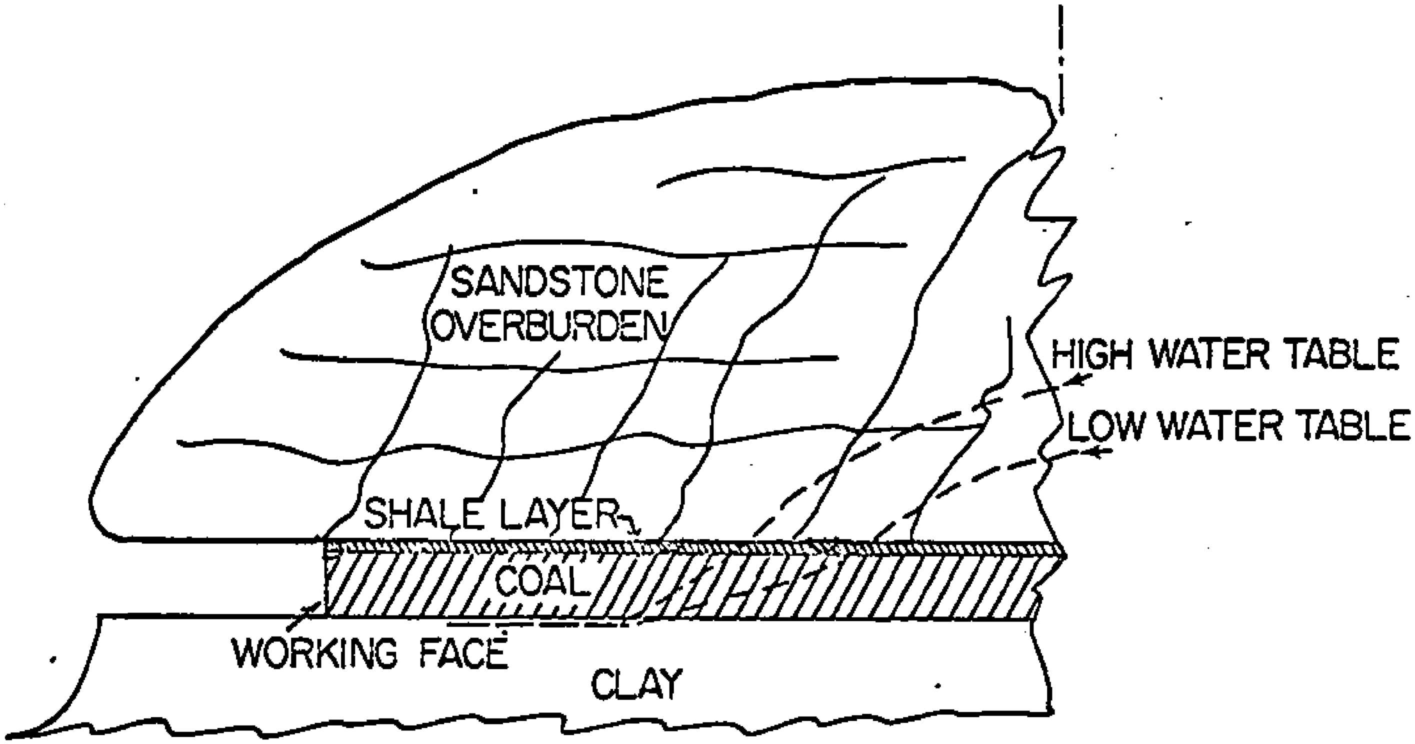


Figure 9 -- Sketch of Underground Pyritc System from Smith and Shumate (37)

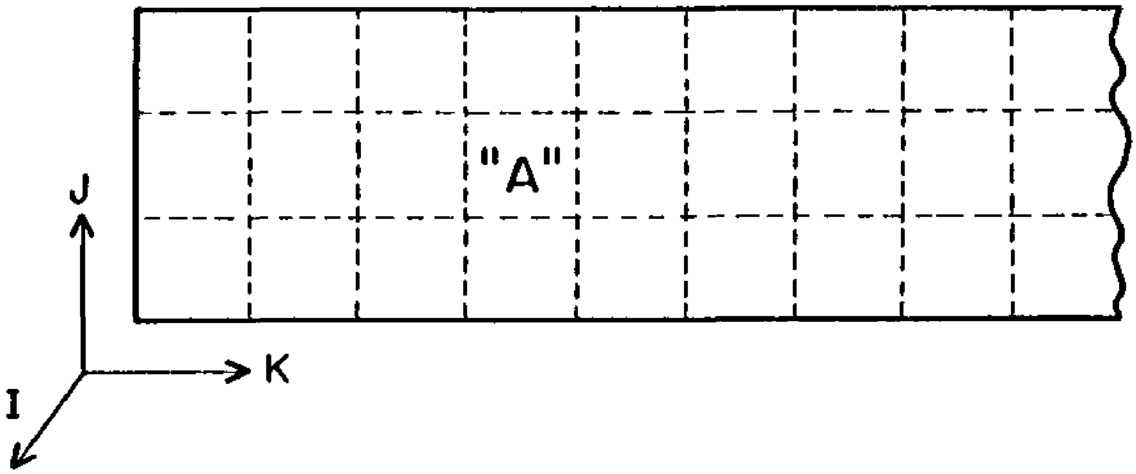


Figure 10 -- Stratum in Seam Divided into Micro-Volumes

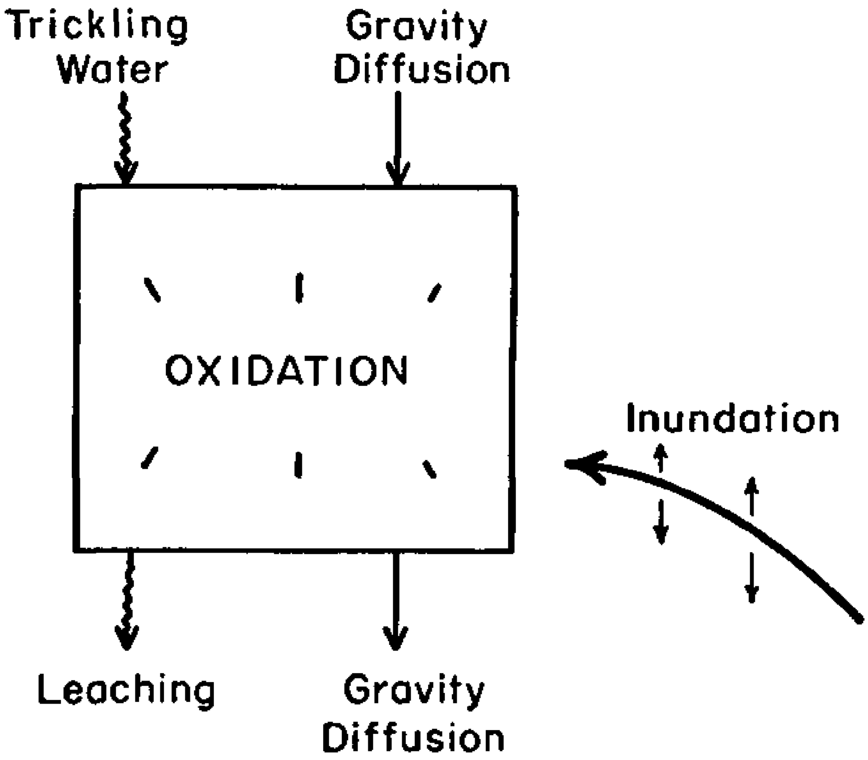


Figure 11 -- Storage Volume Material Balance

and the reaction rate constant can be estimated from data such as that described by Larez. (18)

Previously, a rate constant was calculated by assuming that the reactivity of a gram of pulverized pyrite was distributed along the walls of some void volume. Larez (18), however, reported rates based on a volume of binder material rather than on the basis of pyrite weight or surface area. In this case, the void fraction, ϵ , of the binder must be used in calculating the rate constant. For shale, ϵ is in the range 0.2 to 0.3. (35) For coal, the only data on porosity is that of the micro-structure measured by nitrogen adsorption and other such techniques. Therefore, if has been necessary to make a rough estimate of ϵ for coal. Dr. K. S. Shumate of the Civil Engineering Department of The Ohio State University has suggested that ϵ probably has a relatively low value for coal--in the range 0.005 to 0.02. (32) For computational purposes a value of 0.005 void fraction will be used for coal.

Larez' oxygen uptake rates and the void fraction may be used to estimate a rate constant for the naturally occurring pyrite. We may write the general first order rate equation as:

$$\text{Rate (moles/hour/volume gas)} = k_R\text{(/hour)} \quad C_{Ox}\ \text{(moles oxygen/volume gas)}$$

The experimental rate, Rate_{Exp}, was reported as oxygen uptake per total volume per hour. Since the gas volume equals the void fraction times the total volume:

$$\text{Rate}_{Exp} / \epsilon = k_R\ C_{Ox} \quad .$$

This may be rearranged to give:

$$k_R = \text{Rate}_{Exp} / (\ \epsilon\ C_{Ox}\ )$$

If an oxygen level of 21 per cent is assumed in the bulk air phase, and Larez' oxygen uptake rates of 3 micrograms oxygen per hour per cubic centimeter solid for shale and 1 microgram per hour per cubic centimeter for coal are used, k_R has a value of 0.067 per day for shale and 0.80 per day for coal. The higher value for coal arises because the rate constant is inversely proportional to the void fraction.

In the following pages, a number of variables will be introduced. The model terminology is summarized in Table 2. The basic notation used in the computation model is "J" for the layer number counting upwards from the bottom layer, and "K" for the block number counting in a horizontal direction from the air-solid interface. In addition, the program provides "I" notation for increments along the interface for situations where conditions may vary horizontally along the exposed face.

The quantity of oxidation, which increases the amount of products stored in volume "A" (STORE(I, J, K) in our notation) can be expressed as follows:

$$\mathrm{OXIDN}(I, J, K) = k_R(J)\, C_{Ox}(I, J, K)\, \mathrm{DVOL}(I, J, K) \qquad (5\text{-}1)$$

OXIDN(I, J, K) is the oxygen consumed per day in a block of volume DVOL (I, J, K). $C_{Ox}(I, J, K)$ is the oxygen concentration in the void volume, and $k_R(J)$ is the rate constant for layer J.

A gravity diffusion function which includes a dependence on the quantity of stored products and which assumes no horizontal motion of products is:

$$\mathrm{GRAVOT}(I, J, K) = \mathrm{DIFFG}(J)\, \mathrm{STORE}(I, J, K) \qquad (5\text{-}2)$$

$$\mathrm{GRAVIN}(I, J, K) = \mathrm{DIFFG}(J+1)\, \mathrm{STORE}(I, J+1, K) \qquad (5\text{-}3)$$

GRAVIN and GRAVOT are the gravity diffusion in and out of a volume. STORE(I, J, K) is the pounds of oxidation products, reported as oxygen consumed, stored in the volume, and "J+1" refers to the volume above.

TABLE 2

COMPUTER PROGRAMMING NOMENCLATURE

Main Program Arrays

STORE	Product storage volumes
RATEK	Reaction rate constants of strata
REACT	Oxygen consumption rate of pyrite containing binders
THICK	Thickness of strata
ROCK)	
TYPE)	Literal description of strata
DIFFG	Gravity diffusion rate constant for a layer
WASH	Equilibrium product storage in layer
WATER	Water table
VAP	Monthly value of potential evapotranspiration

Main Program Integer Variables

IN	Input unit number
IO	Printed output unit number
IP	Punched output unit number
IY	Year number storage
NLAYER	Number of layers in coal seam model
NDEPTH	Number of depth increments in model
NFEET	Number of air-solid interface increments
NPUNCH	Punched output control
IYEAR	Year
IDAY	Date

Main Program Real Variables

DTHETA	Time increment length, days
DI	Length of air-solid interface increments, feet
DK	Length of depth increments, feet
TOP	Datum plane for top of coal seam
SLOPE	Slope of coal seam relative to datum plane
ALKALI	Ground water alkalinity, parts per million
AMONTH	Month
OXX	Mole fraction oxygen
FRAC	Fraction of stored products removed daily during flooding
FLOOD	Acid removed during inundation, pounds
DIF	Base gravity diffusion constant
GRAVIN	Gravity diffusion into a volume, pounds
GRAVOT	Gravity diffusion out of a volume, pounds
DSLV	Fraction of products removed each day by leaching
AOUT	Daily acid removal by leaching, pounds
OXIDN	Oxidation in a volume, pounds
-SUM	Variable representing cumulative total
FJ	The ratio of stored products to equilibrium storage level
CON-	Calculational constant

TABLE 2
(continued)

Subroutine Integer Variables

KEEP	Length of month
LAST	Date of previous data input
LTHETA	Days since preceding data input

Subroutine Real Variables

REMOVE	Name of flow calculation subroutine
DAYS	Name of interval determining subroutine
EVAP	Name of evapotranspiration calculation subroutine
TANKA	Storage of water from warm weather precipitation
TANKB	Longer term storage of frozen precipitation
TANKC	Main storage volume
TA	Rate of water transfer from TANKA to TANKC
TB	Rate of water transfer from TANKB to TANKC
RAIN	Precipitation, inches
RTIME	Duration of rainfall, hours
RCAP	Infiltration capacity of soil
TMEAN	Average daily temperature, degrees Fahrenheit
RNET	Net rainfall entering underground storage
PWHC	Provisional water holding capacity of root structure, inches
PWATER	Current water storage in root structure, inches
DEFICT	Deficiency in root water storage
TCAP	Sum of RCAP and DEFICT
EFF	Effect of root storage deficiency on potential evapotranspiration
PEVAP	Potential evapotranspiration, inches of water
AIN	Five day average of water entering underground storage
WSHED	"Watershed" area of mine
FLOW	Drainage flow from mine, gallons per day

DIFFG(J) is the fraction of products stored in layer J which moves by gravity diffusion each day. For different strata, DIFFG(J) is calculated as a constant fraction, DIF, of the oxidation rate constant. This dependence is based on the assumption that gravity diffusion depends on how fast oxidation products form, and inversely depends on the void volume available for product storage. Both of these factors are included in the rate constant. The magnitude of DIF, 0.001, is chosen to give a net monthly removal rate of about two pounds of acid as described in Chapter IV. Calculated values of DIFFG(J) are in the range 0.0005 to 0.001.

Removal by leaching and flooding are both functions of underground water flows. The leaching occurs as water trickles through channels in the oxidized volume. The trickling water picks up oxidation products and enters the receiving stream. The products which are removed may have been formed either along the flow channel walls or have diffused from adjacent "dry" channels. The basic assumption of the leaching model is that most of the water observed as drainage has not contacted the reactive pyrite volume, but merely dilutes the acid. The reasoning is that if the reactive area was continually washed by large volumes of water, the fine channels in the binder would be filled with water. The water then would block the transport of oxygen to the pyrite, and oxidation would virtually cease.

The quantity of products leached depends both on the amount of products present and on the number of flow channels being utilized for flow. The utilization of flow channels is largely controlled by how much liquid is moving. Therefore, AOUT, the quantity of material leached from a volume may be expressed as a function of the storage contents and the rate of water trickling vertically from the surface:

$$AOUT(I,J,K) = STORE(I,J,K) \cdot FJ \cdot DSLV \qquad (5\text{-}4)$$

DSLV is the fraction of stored products removed each day by water trickling downward through the binder and pyrite. The value of DSLV has been obtained by correlating the calculated water infiltration rates with observed variations in acid load at the McDaniels Mine. The best match of observed and predicted acid load was obtained for:

$$DSLV = 0.002\ ARN \qquad (5\text{-}5)$$

where ARN is the water infiltration rate averaged over a five day period. This averaging represents the gradual movement of water down from the surface after precipitation. The time response to rainfall becomes more rapid as the soil becomes saturated with water. The value of DSLV is usually calculated in the range 0.0005 to 0.0015. The term FJ is the ratio of the quantity of stored products to the equilibrium product storage level. The equilibrium storage is the amount of products that would be maintained in an open system where oxidation and removal rates were equal. The equilibrium conditions were estimated by allowing the simulation program to run under conditions of 21 per cent oxygen atmosphere for a three year period. The quantities of product stored at the end of this period were used as the equilibrium storage.

The quantity of products removed by inundation depends on the movement of the water table. The motion of the water table can be related to the underground storage tank model. The variation in the level in Tank C can be used to represent the fluctuations of the water table above a datum level. In the real system, the fluctuations of the water level of Test Well Number 6 in the hillside above McDaniels Mine are indicative of water table changes. It has been suggested that the water table is parabolic in form, rising at an increasing slope from the exposed coal face towards Well 6. (35) Obviously, the total water table can not have this initial concave form since by logical extension of the table there would be a water spout at the end of the table at some point higher on the hill. Beyond Well 6, the water table probably has a more hydrologically reasonable shape such as convex parabolic which becomes essentially horizontal. The true shape of the water table is not critical for this model, but some form must be selected for computational purposes.

Under the assumption that the calculated levels in Tank C directly correspond to the observed levels in Test Well Number 6, an equation can be developed to describe the shape of the water table. The basic equation for a parabola, $y = mx^2 + b$, requires evaluation of two constants, m and b. These may be evaluated by examining data from Well 6.

When y, defined as the height of water in Well 6 relative to the bottom of the coal seam, is 21 feet, water runs out over the top of the coal seam 120 (x) feet away. Since the seam is about 3 feet thick,

$$21 = m\,(120)^2 + 3$$

or upon rearrangement,

$$m = 18 / (120)^2 = 1 / 800 \ .$$

The real point of interest is x, the point where the water table intersects the coal seam, so the parabolic equation must be put in the form

$$x^2 = 800\,y$$

or $$x = (800\,y)^{1/2} \ .$$

Finally this may be converted to a dependence on Tank C. In the four year period simulated by the flow prediction subprogram "REMOVE," the storage term, TANKC, varied in the range 0.9 to 2.5 (inches of stored water).

During the same time interval, the water level in Test Well 6 varied between 15 and 22 feet above the coal seam. If it is assumed that the relationship between the level in Test Well 6 and TANKC is linear, an expression such as

$$y = 15 + 5 (\mathrm{TANKC} - 0.9)$$

can be used to define the relation. This gives

$$x = 28.28 (15\ \mathrm{TANKC} - 13.5)^{1/2} \qquad (5\text{-}6)$$

as the final form to be used in the computational model. The shape of the water table is rather uncertain after it intersects the coal. A linear slope through the seam will be assumed although the actual table depends on where cracks and cleats occur in the seam.

While a storage volume is inundated, the oxidation products gradually dissolve and flow away. The amount of products removed per day is

$$\mathrm{FLOOD(I,J,K)} = \mathrm{FRAC} \cdot \mathrm{STORE(I,J,K)} \ . \qquad (5\text{-}7)$$

FRAC is the fraction of products stored in a volume which are dissolved each day that the volume is inundated. A value of 0.002 per day has been found most appropriate for FRAC. This is a higher value than that of DIFFG (0.0005 to 0.001 range) and that of DSLV (0.0005 to 0.0015 range) since inundation supersedes and includes gravity diffusion and leaching. An upper limit on the rate of removal during inundation arises because of product solubility limitations, and because of the fact that products must still diffuse out of capillary size channels in the inundated volume.

At this point, it is appropriate to discuss in more detail how "suitable" values were obtained for the constants DIF, DSLV, and FRAC. The basis for the evaluation of the constants was the annual acid loads measured at McDaniels Test Mine.

While the three removal mechanisms, leaching, gravity diffusion, and inundation, have been considered as parallel and independent, the total removal must fit the constraints of the observed data. Hence, if one rate is increased, the other two removal rates must be reduced.

In light of the preceding discussion, the general technique for evaluating DIF, DSLV, and FRAC was to pick a value for each and determine how well the annual predictions of acid loads matched the annual loads observed at McDaniels Mine. The key for the initial estimate of the constants was the experimental knowledge that gravity diffusion removed two to four pounds of acid per month combined with an estimate of the total product storage obtained by allowing the program to run for a simulated period of three or four years. The total initial storage was about 150 pounds of acid, and assuming 30 pounds of removal by gravity diffusion per year, a gravity diffusion removal rate of 0.1 pound per day. As an order of magnitude estimate, this gave 0.1/150, or about 0.0007 per day for DIF. To get what was essentially a "trial and error" approach started, initial guesses of FRAC and DSLV were set equal to DIF. These values were the right magnitude, but gave low predictions.

The values of the three constants were raised to bring the annual predictions of acid load in line with observed values. Once the annual loads were in line, the "fine tuning" or matching of short term acid loads was undertaken. The inundation removal term was the most sensitive of the three rates during the first three months of the year. It is, in process control terminology, a derivative function which responds rapidly to changes in the water table. Hence, the inundation constant FRAC could be used to match early year increases in acid load. The leaching constant DSLV is most important in times of high flow so it could be varied to produce the best acid load predictions in April, May, and June.

As each constant was varied, the other two also had to be adjusted. During the general trial and error evaluation, it was observed that any constant could be varied by 30 or 40 per cent of its value without great damage to the annual prediction capability of the model. However such variations in FRAC or DSLV could shift short term prediction peaks by as much as 3 or 4 weeks.

Once all the events probable in a given volume have been defined, the appropriate terms are summed to give the new storage contents in the volume. Under normal circumstances, no flooding, the new product storage in a volume is the sum of the rates in Equations 5-1, 5-2, 5-3, and 5-4 plus the previous storage:

$$\begin{aligned} \mathrm{STORE}(I, J, K) = \mathrm{STORE}(I, J, K) + \mathrm{OXIDN}(I, J, K) + \mathrm{GRAVIN}(I, J+1, K) \\ - \mathrm{GRAVOT}(I, J, K) - \mathrm{AOUT}(I, J, K) \qquad (5\text{-}8) \end{aligned}$$

During inundation, the water forms an oxygen diffusion barrier so that oxidation virtually ceases, and

$$\mathrm{STORE}(I, J, K) = \mathrm{STORE}(I, J, K) - \mathrm{FLOOD}(I, J, K) \qquad (5\text{-}9)$$

The total acid removed from the system is the sum of all AOUT(I, J, K), and FLOOD(I, J, K) where appropriate, terms plus the GRAVOT terms from storage volumes immediately above the water table. The calculation of acid load as the sum of all acid removal rates assumes that oxidation products leave the mine as soon as they enter the ground water. The summation of all these removal terms plus the calculation of new storage quantities are performed by a digital computer. The computer program which does these calculations iteratively to simulate the passage of time will be described in the following section.

Computer Programming of Model

The programming of this or any other model is the restatement of regular mathematical equations in the particular form required by a digital computer. This language of the computer has already been introduced with the I, J, K notation of the first section of this chapter. The computational model of the drift mine will be described in terms of one main program and three subroutines. The main program maintains generality with regard to most pyritic systems, but the subroutines include special provisions for a specific mine site. A flow chart for the main program is shown in Figure 12, and flow charts for the subroutines are shown in Figures 13, 14, and 15.

The main program has two principle sections. The first section handles bookkeeping such as defining variables, establishing computational arrays, and setting initial values. The arrays are the subscripted variables which represent incremental changes in distances or conditions in different locations. The initial conditions to be established include a base datum plane, a minimum water level datum, dimensions of the coal and shale strata, alkalinity of ground water, the "water shed" area drained by the mine, experimental or estimated oxidation rates, and conversion factors. The most critical set of initial values is the estimate of oxidation products stored in the system from previous oxidation. That is to say, we are breaking into a steady state system, and the steady state point is non-zero in value.

To obtain initial storage values, the computer program was allowed to run for a simulated period of three years of oxidation and removal. The oxidation rates were based on 21 per cent oxygen level in the mined-out volume since prior to the start of the observation period, McDaniels Mine had been

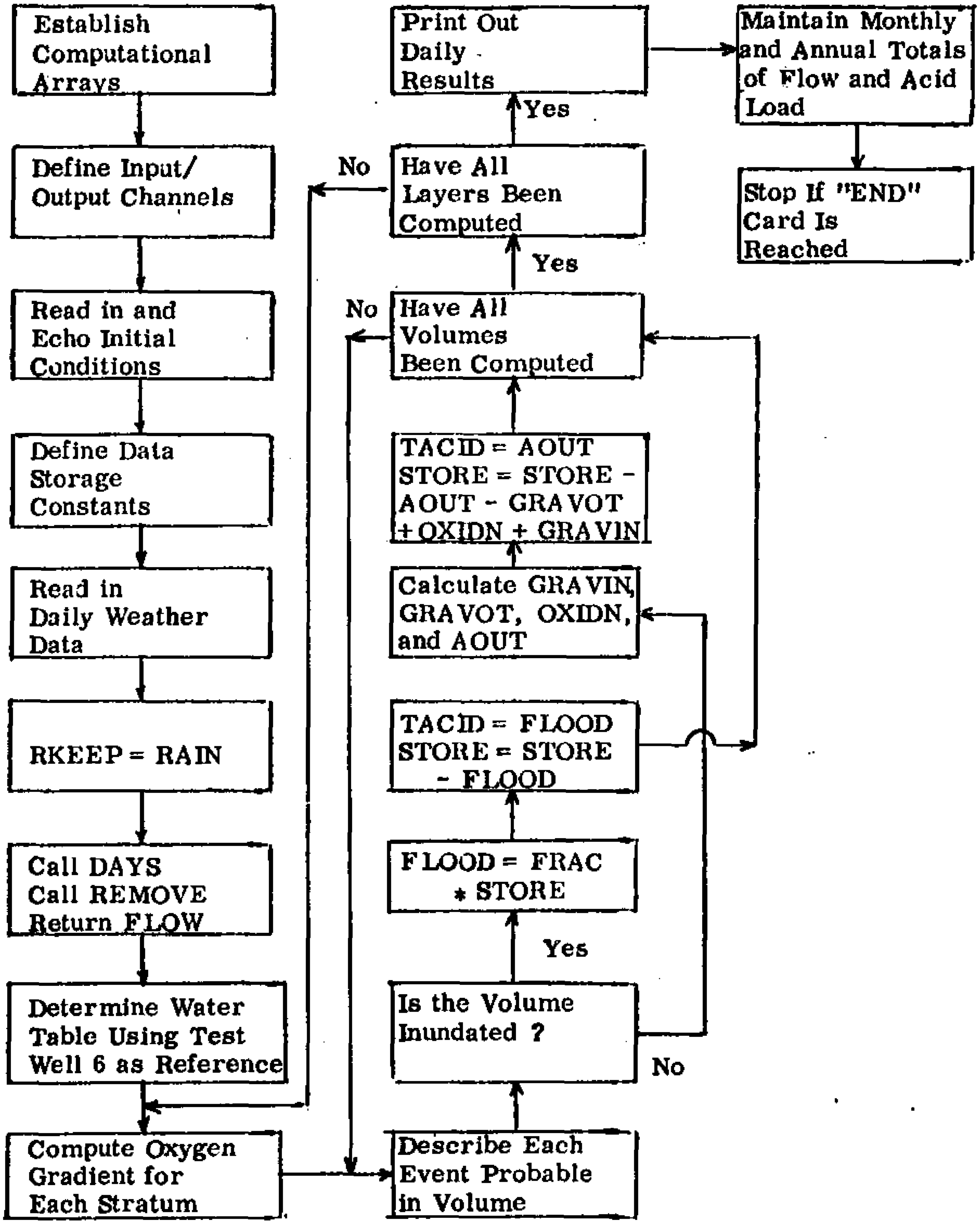


Figure 12 -- Main Program Flow Chart

open to the atmosphere. The final storage values, STORE(I, J, K) were then punched out on standard computer cards in a format suitable for reading-in as data. Once the initial conditions have been established, the simulated daily mine behavior can be calculated.

The second section of the program, which does the day to day simulation, will be described in terms of a typical run. The first step in the simulation is the reading of meteorological data. The date, the inches of precipitation, hours of duration of precipitation, mean daily temperature and oxygen concentration at the air-solid interface are the input data. The program is written in such a manner that only positive information such as precipitation or changes in the temperature or oxygen level need be read in. The input data are examined to determine if any conditions have changed, and the amount of precipitation is recorded.

The subroutine "DAYS" is called to determine the number of days, LTHETA, since the previous data input. The program is run on the condition that precipitation only occurs on the LTHETA day--whether this is one day or one month from the previous precipitation. The program performs the following set of calculations for each day. The computer variables introduced in this section are summarized in Table 2.

1. The subroutine "REMOVE" is called. This routine, described in more detail on page 78, calculates the ground water flow and the quantity of water in underground storage. The factor DSLV, the fraction of stored products removed each day by leaching, is also returned by "REMOVE."
2. The position of the water table in relation to the coal seam is determined. A water level, YZERO, equivalent to the water level in Test

Well 6 is calculated from the value of TANKC using the technique shown on page 66. YZERO is used as one end of a parabolic water table which intersects the coal seam at point XMIN. From XMIN, the water table is taken as a 20 per cent downward slope through the coal seam. The position of the water table in relation to the seam is recorded as WATER(K). The "K" increments are counted horizontally from the air-solid interface.

Steps 1 and 2 have furnished numerical information for calculating product removal rates. The next steps are performed iteratively over the computer array of oxidation storage volumes, STORE(I, J, K), for all volumes above the water table. For inundated volumes, the program skips to Step 7.

3. The oxygen mole fraction, XNN, in the void volume is determined using the oxygen gradient equation. (Equation 4-7) The total volume of the block, DVOL, is calculated. The oxidation, as pounds of oxygen consumed per day, is determined.
4. The quantity of products removed by leaching, AOUT, is calculated using Equation 5-4.
5. The gravity diffusion in, GRAVIN, and out, GRAVOT, are computed using Equations 5-2 and 5-3.
6. The terms calculated in Steps 3, 4, and 5 are summed to obtain the change in product storage. The program then skips to Step 8.
7. The quantity of products removed from an inundated volume is obtained from Equation 5-7. Since there is no oxidation in inundated volumes, the new storage quantity is calculated simply by subtracting the quantity removed from the product storage value.
8. The quantity of acid removed from each storage volume is added to

the running total, TACID, of acid removed. In addition, sub-totals of the amount of acid removed by each mechanism are also kept.

After the calculations have been performed for all of the volumes of the STORE(I, J, K) array, the results are prepared for output.

9. The acid load, TACID, is converted from an oxygen consumption to a "total acid" basis by multiplying by 200/112. This is the stoichiometric ratio of 2 H_2SO_4 to 7/2 O_2 when acidity is expressed as the calcium carbonate ($CaCO_3$) equivalent.
10. The acid load is then corrected for the influence of alkalinity in the entering ground water. A value of 20 parts per million alkalinity has been used for the McDaniels Mine.
11. The daily acid load is added to the cumulative monthly, YSUMA, and annual, YSUM, acid load totals. Similarly, monthly totals of removal by gravity diffusion, GSUM, inundation, FSUM, and leaching, ASUM, are also accumulated.
12. The daily flow, acid load, and precipitation are printed. At the end of each month, a summary including flow, total acid load, inches of water entering underground storage, and the acid removal by each mechanism is printed.
13. Similarly, annual or quarterly summaries may be printed. The sample program in Appendix C shows monthly and annual summaries.

Once the calculations have been performed for one day, the program repeats Steps 1 through 12 LTHETA times. On the LTHETA day, the call of the "REMOVE" subroutine includes the amount of precipitation. "REMOVE" performs all calculations involving rainfall and ground water flows.

Several subroutines have been written to assist the main program. The subprograms were written for either of two reasons. First, some routines are of general use so it is convenient to be able to move them from one main program to another. Second, each subroutine is compiled independently. This feature can greatly simplify "debugging" and identification of errors in the program. Errors can be corrected immediately rather than propagating and giving false error messages in unrelated portions of the program.

The subroutine "DAYS" determines the number of days between two consecutive data inputs. The name of the month and the date are read into the routine which compares the name of the month with the name of the month from the preceding input. If the names of the months are the same, the routine obtains the difference of the two dates and returns this as the elapsed time, LTHETA. If the months are different, the routine determines the number of days in the preceding month from an internal data table. The old date is subtracted from the month length. The difference is added to the new date to give LTHETA. The "DAYS" subroutine simplifies data input since only positive information or changes in conditions need be read because the time between changes can be computed. "DAYS" is a general purpose routine that can be transferred from program to program.

The subroutine "EVAP" determines the potential evapotranspiration at the McDaniels Test Mine. Monthly evapotranspiration rates have been calculated according to the Thornthwaite and Mather (42) technique. These values are read into the main program as data and transferred to the subroutine through a Common statement. The call to the subroutine includes the name of the month. "EVAP" finds the evapotranspiration rate corresponding to the month from an internal data table, and returns this value to the calling program. This routine can be used for other sites if the appropriate

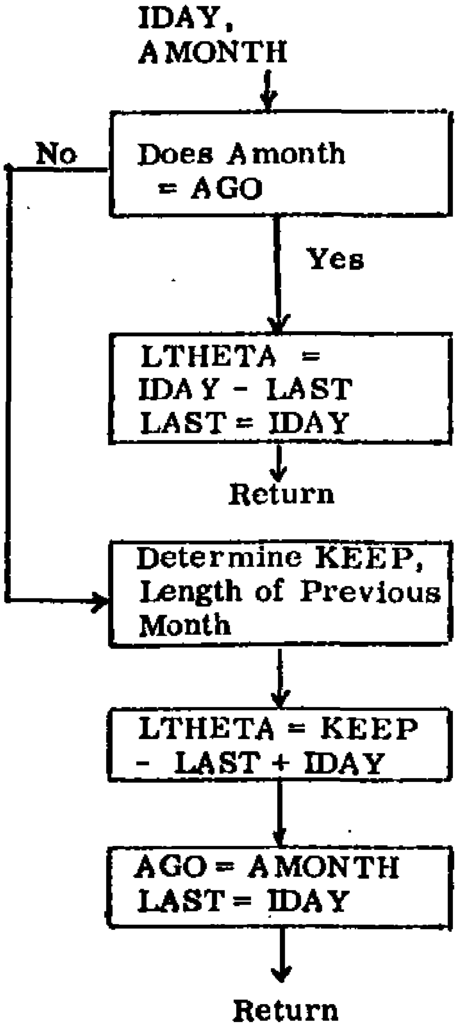


Figure 13 -- Flow Chart of Subroutine DAYS

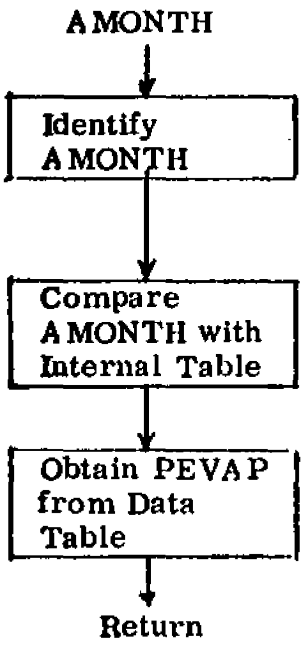


Figure 14 -- Flow Chart of Subroutine EVAP

evapotranspiration rates are calculated or measured and supplied to the program.

The major subroutine is "REMOVE." "REMOVE" has been written to calculate drainage flow rates. The program also determines the fraction of stored products to be removed each day by leaching.

On the first call of "REMOVE" initial conditions are established. The short term storage volumes, TANKA and TANKB, are assumed to be zero. The long term water storage, TANKC, may be assigned a zero value or a positive value. An initial value can be estimated by allowing the program to run for a simulated period of 3 to 5 years, as in the estimation of initial product storage. On each succeeding call of the routine, the following set of operations is performed.

1. The daily potential evapotranspiration is determined. The monthly maximum evapotranspiration is obtained by calling "EVAP." The value is then converted to a daily value by dividing by the length of the month. The daily value is then reduced depending on the moisture in the ground. The drier the ground, the less the water near the surface to evaporate or to be used for plant growth.

If there has not been any precipitation on the day being simulated, the program by-passes the following two steps and goes directly to the calculation of ground water flows in Step 4.

2. Infiltration capacity, RCAP, of the ground is calculated. The total capacity of the soil, TCAP, is taken as the sum of RCAP and DEFICT, the deficiency in root water storage. DEFICT is the difference between the provisional water holding capacity, PWHC, and the actual root water storage level, PWATER.

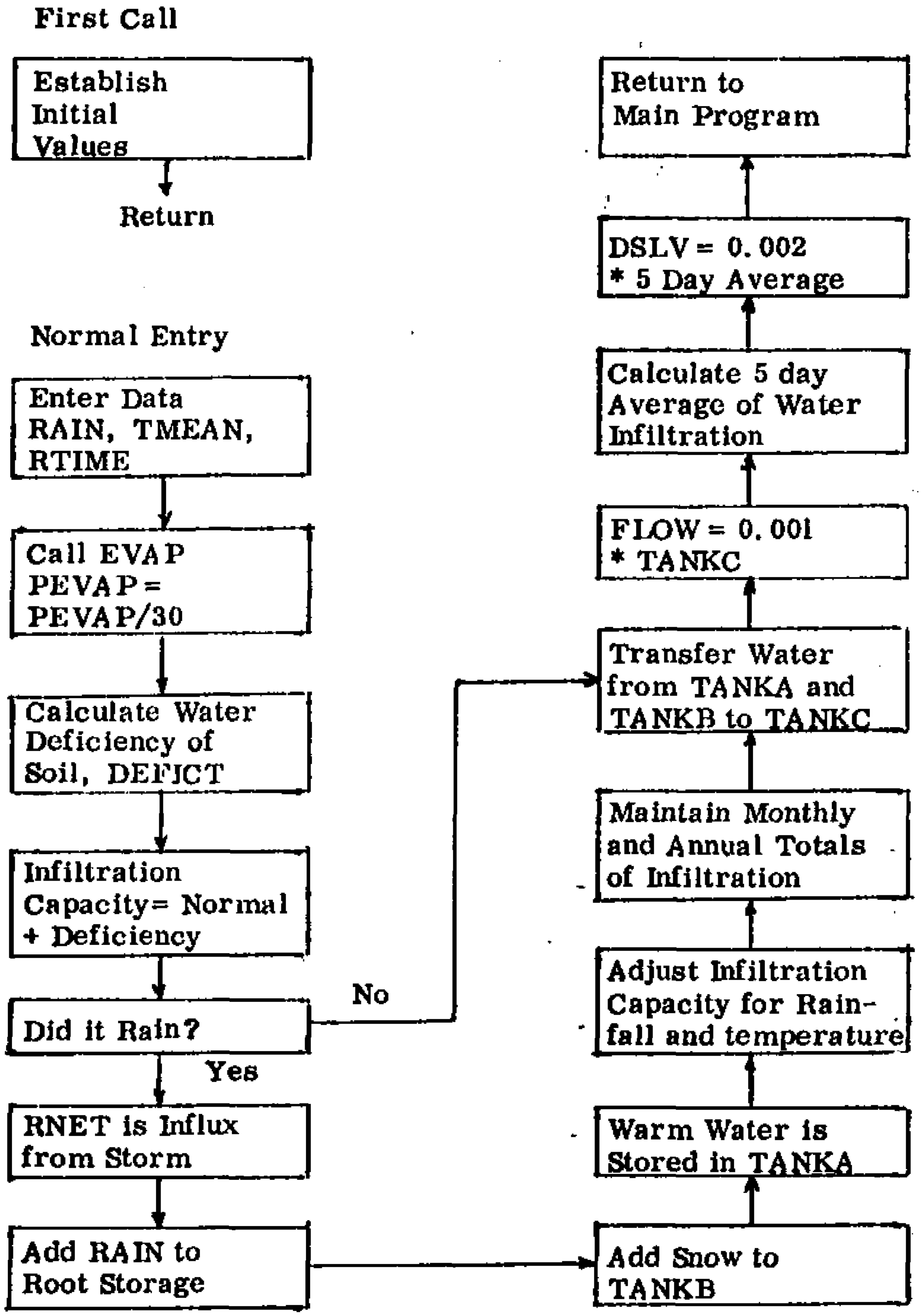


Figure 15 -- Flow Chart of Subroutine Remove

3. The actual rainfall, RAIN, is compared with TCAP, and the lower of the two values isused as the quantity of water, RNET, penetrating the surface of the soil. Excess water is assumed to be lost as surface runoff. Up to 90 per cent, if required, of RNET is used to recharge the water storage, PWATER of the root structure. Excess water, ADD, is added to TANKA, the first storage or delay volume. If the ground is frozen, the excess water is assigned to longer term storage in TANKB.

4. From 20 to 40 per cent of the contents of TANKA is transferred daily to the main underground storage volume, TANKC. The fraction which is transferred is proportional to the value of TANKC. This dependence simulates the more rapid water flow when the ground is wetter.

5. Water held in TANKB is transferred to TANKC only after the temperature rises sufficiently to melt the snow. For areas such as southeastern Ohio, where snows usually melt in a reasonably short time rather than accumulating to great depths, Wisler and Brater (44) have suggested that the rate of melting can be related to the degree days above freezing. They suggest using an estimate of a tenth of an inch of water equivalent for each degree day above freezing . This water is then treated the same as ordinary rain with regard to infiltration rate and capacity.

6. The drainage flow, FLOW, is calculated as a function of TANKC and the drainage area, WSHED, of the mine. The function that gives the best correlation with existing data is a linear dependence. The goodness of fit of real and simulated flow data will be shown in

Figures 16 and 17. In addition to the flow out through McDaniels Test Mine, water flows out through other openings in the overburden. This extra flow is also proportional to underground storage, TANKC. During wet seasons, this additional flow may exceed the flow through the mine. The value of TANKC is decreased in accord with total quantity of calculated flow.

7. DSLV, the fraction of stored products removed daily by leaching, is computed. As shown by Equation 5-5, DSLV is a function of the rate of water addition to ground water storage.
8. Control is returned to the main program.

Although "REMOVE" is based on general hydrologic principles, the constants used in the program can only be evaluated in terms of a real system. Factors obtained by examining real data from McDaniels Test Mine include the "water shed" area of the mine, the response time of drainage flow to precipitation, the water storage capacity of the geologic structure, and a snow melt criterion.

The "water shed" area was estimated by back calculating from the observed yearly totals of drainage flow and precipitation. Water losses such as evapotranspiration were then subtracted from the precipitation to give a "net" rainfall. The net rainfall and observed drainage were then used to calculate the "water shed" of the mine. In the McDaniels case, this area was 27,000 square feet, or about two-thirds of an acre. In terms of a visual observation of the site, this is a reasonable estimate. Since the drainage area of the mine is so small, it was virtually impossible to make exact calculations of water storage or time response. Therefore, the technique of examining real data was used.

With slight modifications "REMOVE" could be used to estimate drainage flow rates from the auger holes at the McDaniels Research Site. The main change will be that each auger hole will have a different size drainage area. It will also be necessary to consider that the holes are tubular and extend a relatively great distance into the hillside in comparison to the wedge shape of McDaniels Mine. The cold weather criterion must also be examined since auger hole flows increase in cold weather rather than maintaining a relatively constant low flow rate as does the test mine. The likely explanation for the increased flow is that the surface of the outcrop in which the holes are drilled freezes, and all water must use the holes as exits.

To apply "REMOVE" to other systems the following information must be available:

1. Infiltration capacity of soil
2. System response time to precipitation
3. Water shed area of mine
4. Water storage capacity of geologic structure
5. Cold weather water behavior criterion

Of these five items, only the water shed estimate is an absolute requirement for other sites. For the other four factors, the McDaniels data are adequate first approximations.

CHAPTER VI

VERIFICATION OF MODEL

The validity of the pyritic systems model which has been developed can be evaluated by using the model to simulate mine drainage behavior for a period during which there are natural data. Such a comparison has been made by simulation of the period from 1967 through 1970 for McDaniels Test Mine.

The computer program was run using the physical description of the mine and meteorological data as inputs. The experimental varations of oxygen in the mine atmosphere were also included in the data. The output from the program was the daily drainage, in gallons, and the acid load, in pounds. In addition, monthly and annual totals of drainage and acid load were printed.

The day by day predictions of the model have been graphically compared with the natural observations. The drainage flow rates are shown in Figures 16 and 17, and the acid loads are compared in Figures 18 and 19. Insufficient short term acid load data are available for 1967 so monthly average values are used for the actual data. A hydrologic year beginning with the October dry season (in Ohio) has been used as the time basis. This choice simplifies visualization of the cyclic nature of acid mine drainage rates.

The data in Figures 16 to 19 show the capability of the model to predict the sharp peaks of drainage and acid load in the spring of each year. Likewise, the figures show the steady decline of flow rates through the summer and fall. The success of the model in predicting short term variations has fulfilled a major objective of this investigation. Such a short term response

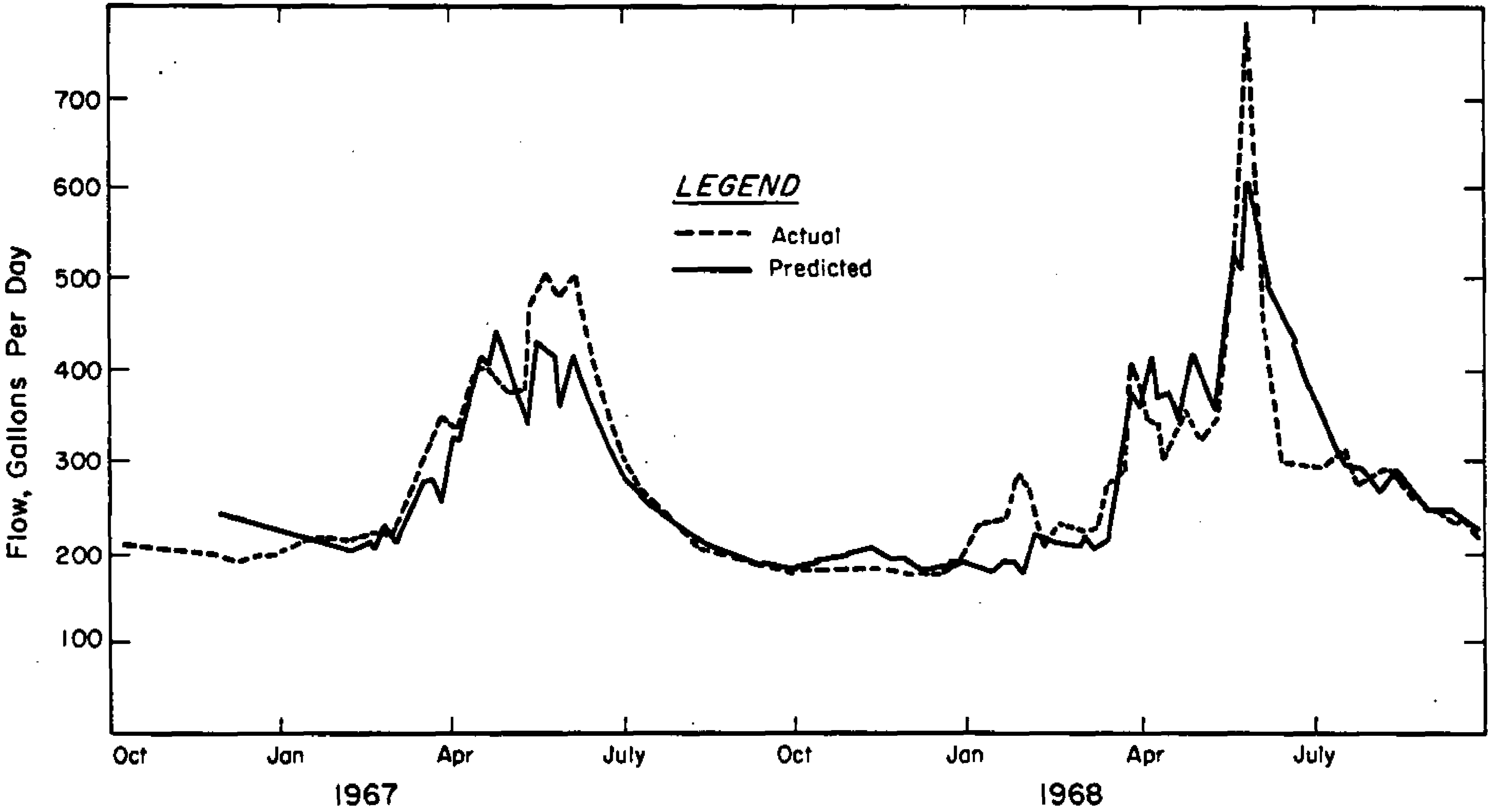


Figure 16 -- Drainage Flows for 1967 and 1968 Hydrologic Years

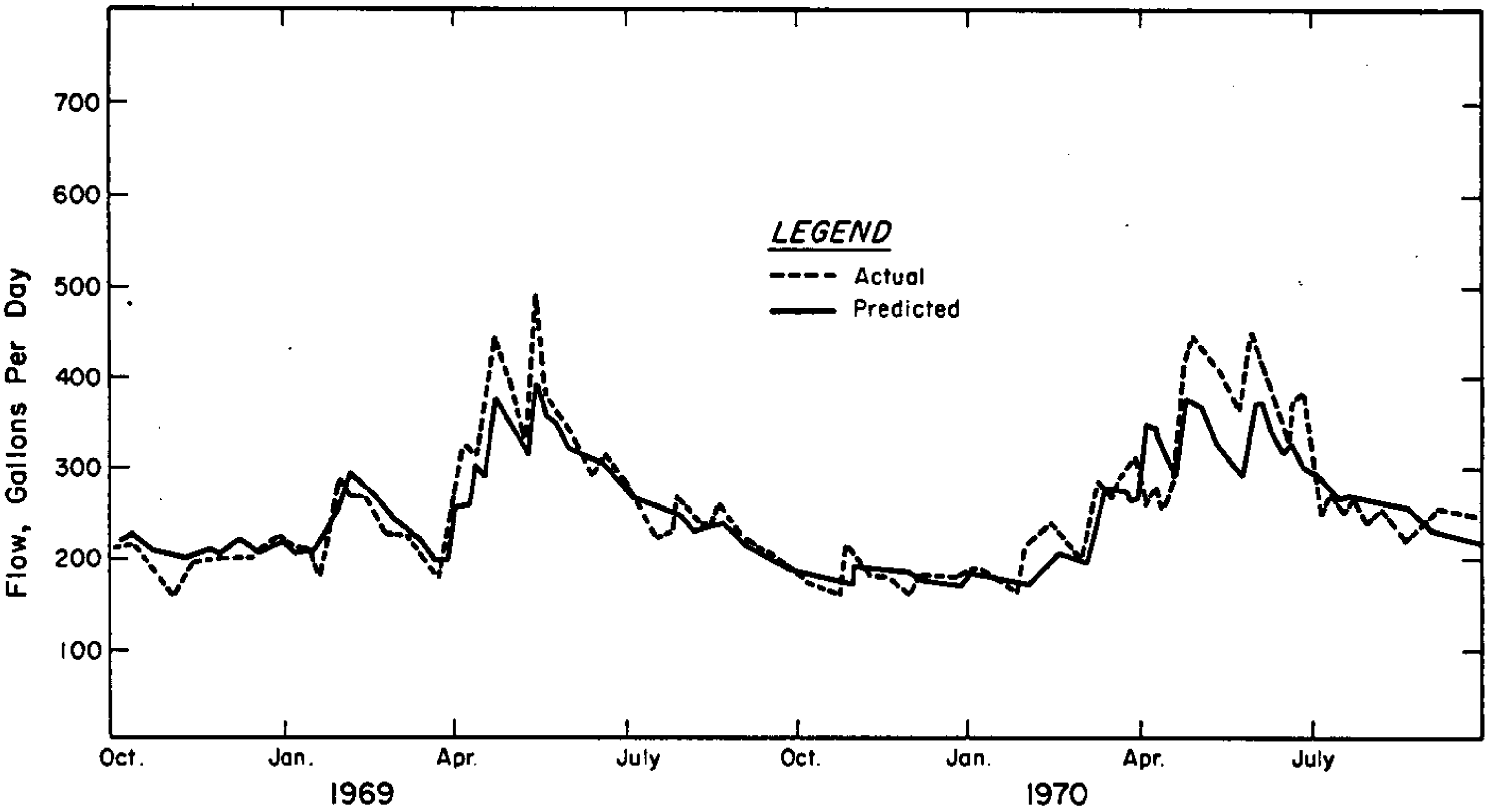


Figure 17 -- Drainage Flows for 1969 and 1970 Hydrologic Years

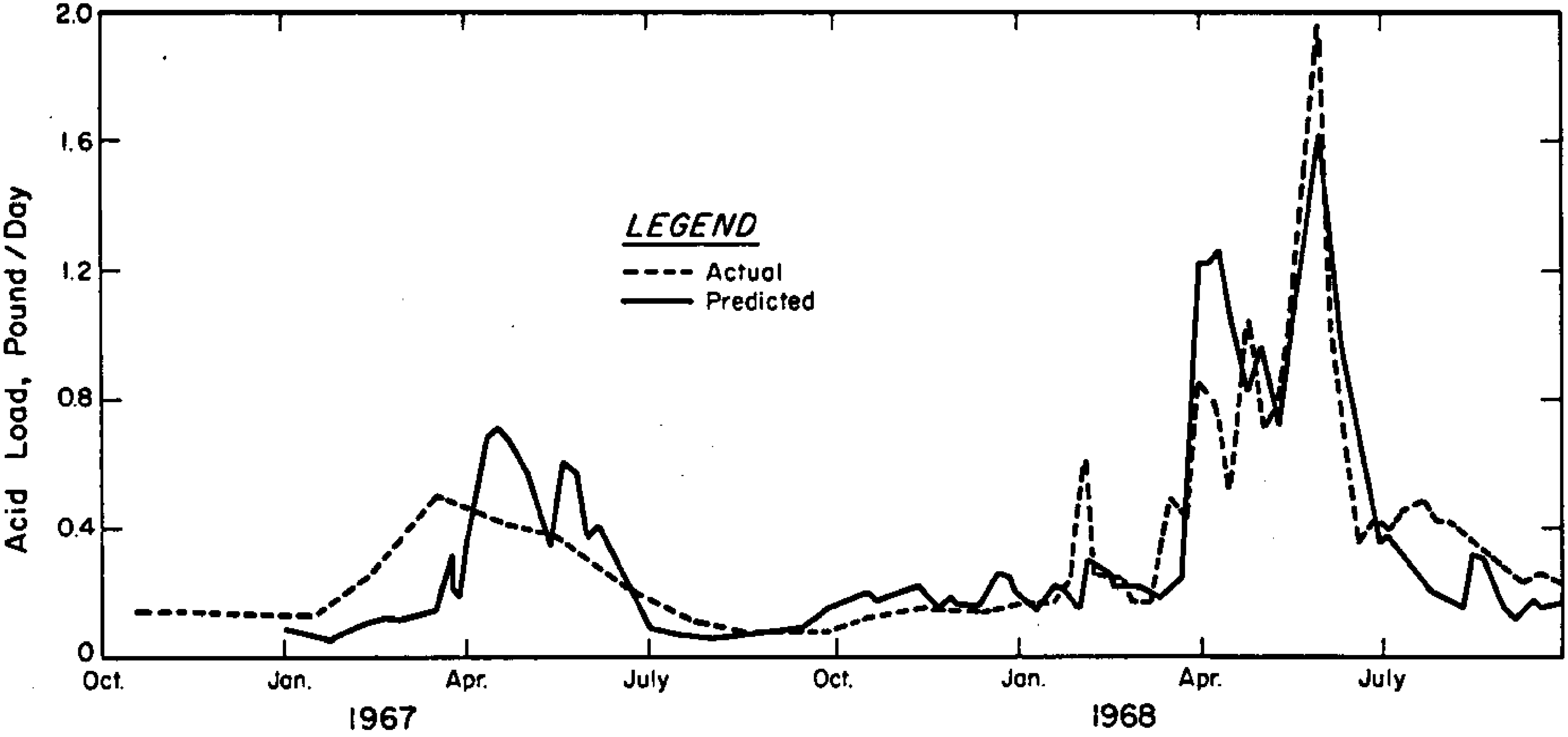


Figure 18 -- Acid Loads for 1967 and 1968 Hydrologic Years

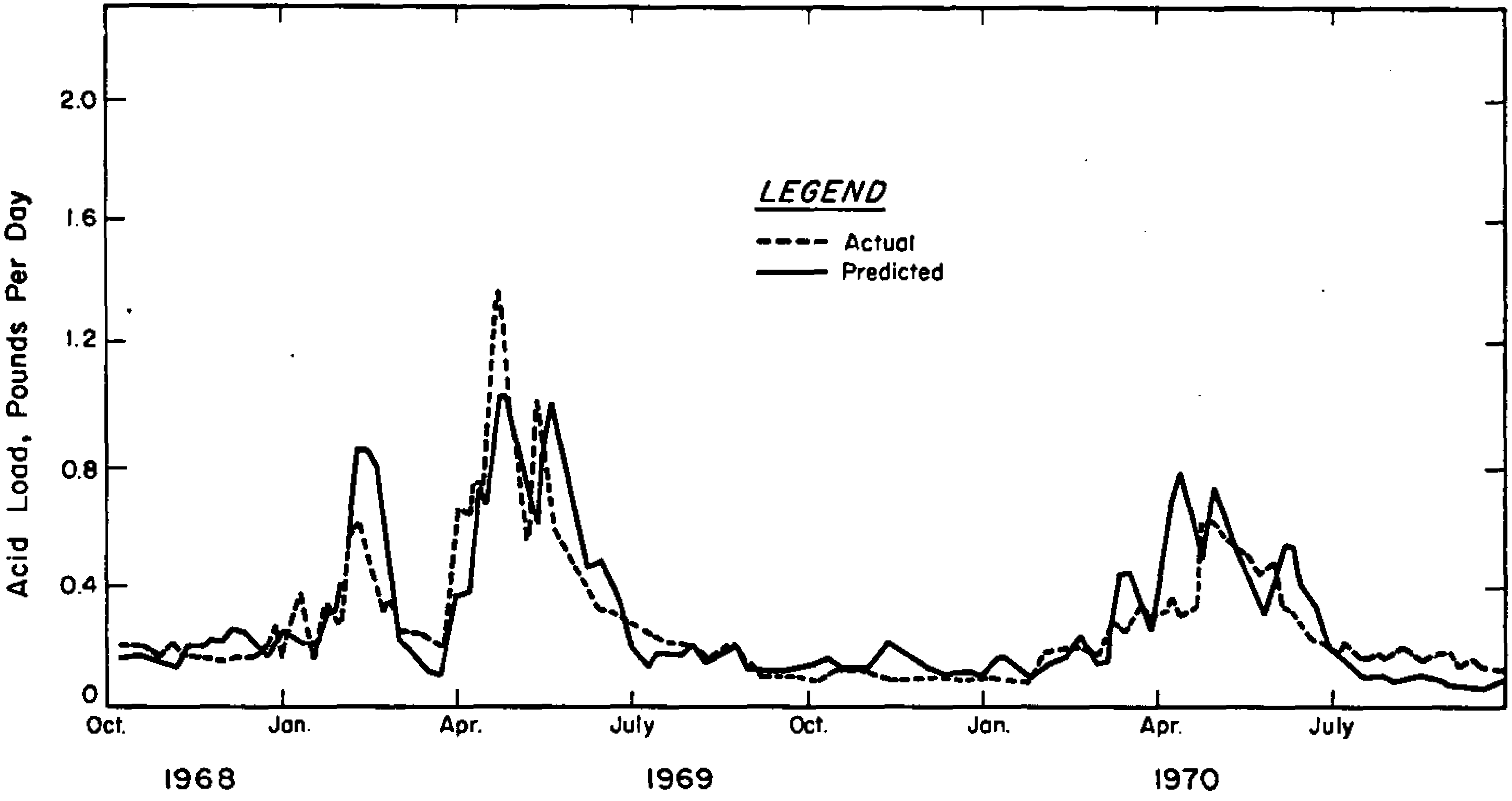


Figure 19 -- Acid Loads for 1969 and 1970 Hydrologic Years

is necessary if the model is to be used to predict peak loads for use in the design of treatment facilities. Similarly, the operation of existing treatment plants may require knowledge of when peak acid loads will occur.

While the agreement of predicted and observed short term data is desirable, the validity of the model in the general case may depend more on the long range predictions. Table 3 summarizes the monthly and annual (on a calendar year basis) drainage flows and acid loads. In this table it can be seen that monthly predictions are generally within 20 per cent of the measured rates, and that annual values agree within 5 per cent. The goodness of fit of long term data is important since there were large year to year variations in acid load because of the variation of oxygen levels in the mine atmosphere.

The practical significance of the agreement of long range predictions and observations is that for unmanned treatment facilities in isolated areas, the model could be used to estimate the quantity of treatment chemicals which must be available. The model can also estimate how often the chemicals must be replenished.

A word of warning should be issued before the model is strongly praised or condemned for the level of agreement with the natural data. The natural measurements are based on flow samples collected for 10 or 15 second intervals once or twice each week. Obviously, the reliability or the comparison would be improved if sampling frequency were increased.

When the acid removal was discussed in Chapter IV, the description of three different removal mechanisms was emphasized. The importance of each of these mechanisms in the actual simulation is shown in Table 4. The annual acid loads are compared with the quantity of acid removed by each

TABLE 3

MONTH BY MONTH COMPARISON OF PREDICTED AND OBSERVED DATA

Date	Drainage Flows, gallons Measured	Drainage Flows, gallons Predicted	Acid Loads, pounds Measured	Acid Loads, pounds Predicted
1968				
January	7560	5712	5.7	5.5
February	6090	5853	9.5	7.0
March	7510	7852	12.6	13.7
April	10350	11513	23.0	31.7
May	16300	14504	39.5	34.6
June	8610	13798	16.8	23.1
July	8700	9794	12.4	8.1
August	8500	8471	11.4	6.9
September	7000	7063	7.2	4.8
October	6360	6605	5.5	5.0
November	5670	6076	4.8	5.6
December	6550	6588	5.4	6.8
Total	99000	104000	154	153
1969				
January	6780	6749	7.9	7.6
February	7200	7891	12.7	17.0
March	6920	7012	9.7	5.0
April	11250	9604	25.4	23.1
May	12000	10631	20.7	22.9
June	9030	8960	10.2	11.2
July	8100	7820	6.7	4.9
August	7240	7300	5.0	5.9
September	5730	6092	3.2	3.9
October	5680	5671	3.4	4.0
November	5520	5775	2.8	5.1
December	5400	5472	2.5	3.5
Total	89000	88960	112.	114.
1970				
January	5850	5631	3.1	4.4
February	6100	5485	5.2	5.0
March	9000	8092	8.5	9.8
April	9870	9792	12.5	18.8
May	11780	9812	14.9	13.7
June	9600	9673	7.7	11.4
July	8740	8471	5.1	3.7
August	7690	7823	5.0	3.1
September	7290	6751	3.7	2.2
October	6940	7080	3.1	2.9
November	8100	7043	4.1	2.5
December	9300	8144	5.2	5.4
Total	99000	93776	78.	83.

method. (The annual totals in Table 4 are less than the sums of the three separate rates since only the total includes the influence of alkalinity in the ground water. For the case of 20 parts per million alkalinity in the water, the acid reduction is about 17 pounds per year for 100,000 gallons of flow.)

TABLE 4

COMPARISON OF ACID REMOVAL RATES

Year	Acid Removal Mechanism Gravity Diffusion (pounds/year)	Inundation (pounds/year)	Leaching (pounds/year)	Observed Total (pounds/year)
1967	31.8	19.6	38.6	74.
1968	48.7	40.6	80.9	153.
1969	45.2	32.2	51.8	114.
1970	30.1	19.2	49.8	78.

Leaching removal is the most important mechanism, contributing about 50 per cent of the acid load. Inundation removal is responsible for 20 per cent of the acid, and the remainder is removed by gravity diffusion. As would be expected from the description of the mechanisms, gravity diffusion fluctuated less from year to year than did the leaching and inundation removal rates. The diffusion is independent of the quantity and frequency of precipitation which serves as the driving force for the other mechanisms. The relative uniformity, or lack thereof, may be seen in more detail by examining the sample output for 1970 shown in Appendix C. For all months, gravity diffusion is always two or three pounds while leaching and inundation removal have sharp peaks in the spring. The rest of the year inundation removal virtually ceases, and leaching removal is at about the same level as gravity diffusion with occasional peaks corresponding to rainy periods. Simulation data for other years also show this pattern. There are even greater peaks in the inundation and leaching rates for the very high acid load year, 1968.

CHAPTER VII

UTILIZATION OF MODEL

Although a model capable of describing past events at a drift mine has been developed, the actual objective of this investigation, namely to make predictions, must still be accomplished. The use of the model of a drift mine for prognosticating falls into two areas:

1 Prediction of what will happen under different conditions at McDaniels Test Mine.

2. Showing how the model may be generalized for use with other pyritic systems.

Predictions

The best test of any model is how well it can foretell what will happen when perturbations are imposed on the system in question. For a drift mine, the perturbation of most interest is the exclusion of oxygen from the atmosphere. At this writing, in early 1971, McDaniels Test Mine has been under a positive pressure of nitrogen for over a year. The oxygen level in the mined-out volume has been reduced to less than one per cent, and the acid loads from the mine have started to decrease. The question to be answered, or predicted, is how long flow from the mine will remain acidic. The answer is "probably a very long time" if one considers that oxygen dissolved in water will continue to enter the mine. Practically speaking, there is very little oxidation occurring, so the real prediction is how rapidly stored products will be removed.

The product removal rate in the model has been related to the infiltration of water from the surface of the ground. The rate of infiltration in turn is dependent on the level of precipitation. Therefore, a number of predictions are possible depending on the estimate of precipitation. The best source of precipitation data is meteorological records from previous years. During the 1965 to 1970 period, the rainfall in southeastern Ohio ranged from 30 to 45 inches per year. In 1968 there were 45 inches of rain including nearly 13 inches in May. In 1967 and 1969, precipitation totaled only 30 inches. Since the annual average rainfall is about 38 inches in the region, the 30 and 45 inch years probably represent extremes. Therefore, duplicates of 1968 and 1969 will be used as sample data for wet and dry years. The prime reason for using existing rainfall data for generating predictions is to insure that the natural pattern of storms and dry spells is included. Another reason for using the existing data is that the program requires temperature data, and these are already available in the data decks for preceding years.

Two sets of predictions have been undertaken. The more important one is determining what will happen if the low oxygen level is maintained in McDaniels Mine. The second set investigates the effect of imposing changes on the system at different points in the hydrological year. The initial product storage and hydrologic conditions for the predictions were established by allowing the program to run through the normal 1967 to 1970 simulation.

The prediction of what will happen if the current low oxygen level is maintained will be useful in evaluating the nitrogen addition experiment of Smith and Shumate. (37) On the basis of an observed decrease in acid load of 30 per cent during the past year, acid loads should be reaching a very low level within two years. To check this hypothesis, the simulation of two years at McDaniels Mine has been run for cases of above and below average rainfall. These cases bracket the expected precipitation and removal rates and give the range of times that will be required to achieve a desired minimum acid load level.

The results for the two cases are remarkably similar. About 35 pounds of acid removal is predicted for 1971 and about 20 pounds for 1972 in each case. Since the results are identical, only the predictions for the high rainfall case are shown in Figure 20. The expectation of a substantially higher rate for the wet year was based on the high acid loads in 1968 which included a period when oxygen was being injected into McDaniels Mine.

The breaks in the curve in Figure 20 indicate periods when the program predicts alkaline drainage from McDaniels Mine. The actual fulfillment of this prediction depends on the validity of the estimate that ground water entering the mine contains 20 parts per million alkalinity. Also to be verified at some point in the future is the tacit assumption that no acid is diffusing into or otherwise entering the drainage from outside the stated boundaries of the system. Whether or not the observed drainage ever becomes alkaline at McDaniels Mine, the acid load should be down to 20 or 25 pounds per year by 1972. On a concentration basis, this is about 20 parts per million acidity in the drainage.

In the second simulation experiment the effects of the timing of changes in the concentration of oxygen in the mine atmosphere were studied. The situation that has been studied assumes that the oxygen level at the McDaniels

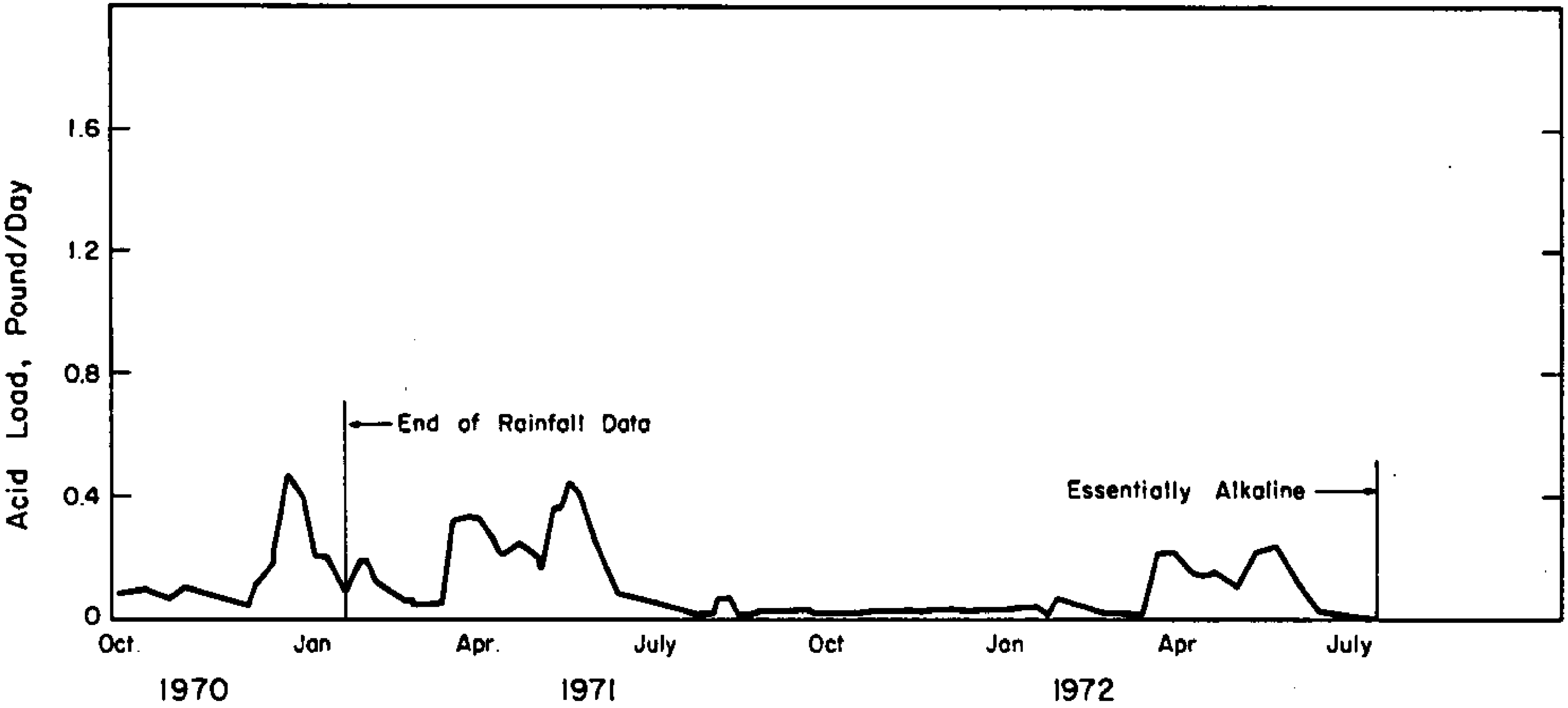


Figure 20 -- Acid Load Predictions for 1971 and 1972 Using 1968 Rainfall Data

Mine was returned to 21 per cent as in normal air. Two cases have been examined:

1. The oxygen level was raised on January 1, 1971. In this case the change immediately precedes the wettest part of the year.
2. The oxygen level was raised on July 1, 1971. In this case the change follows the rainy season.

For this experiment, the average rainfall year, 1970, was used as the data source.

The results of this experiment are shown in Figure 21. For Case 1, where the oxygen level was changed in January, there is a rapid system response in terms of increased acid load. The curve plotted for Case 2 during the first half of 1971 represents the acid load if the nitrogen addition had been continued during that period. For Case 2, the response to increased oxygen levels appears more slowly. However, if the Case 2 curve in Figure 21 is compared with the continued addition curve in Figure 20, it is apparent that there are slight increases in acid load even when the reintroduction of oxygen into the mine was done during the dry season. Significant increases in acid load for Case 2 do not appear until the wet spell in late December.

In the second year of the simulation, differences in acid load for the two cases become smaller. However, the fact that differences in acid load still exist a year after oxygen was restored to the mine atmosphere can be taken as evidence of the slowness of the time response of the system. This delay in change of drainage composition is in accord with the observations of Smith and Shumate (37) in the natural laboratory study. They had estimated lag times for McDaniels Mine in the range from six months to one year.

The simulation experiments that have been run are examples of tests

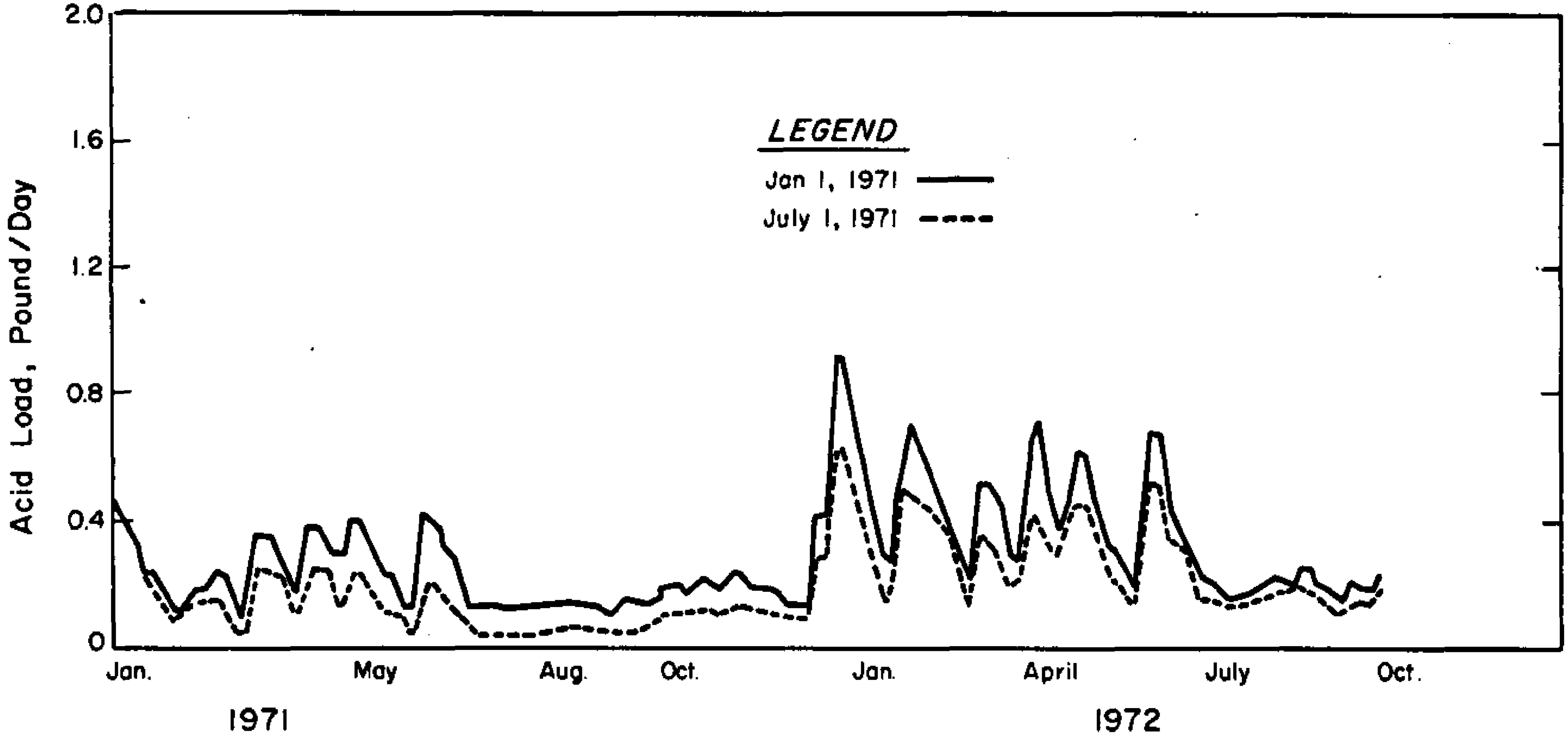


Figure 21 -- Effect of Timing of Increase of Oxygen Level on Acid Load Predictions for 1971 and 1972

that can be performed with our model. Other investigations could include the use of zero order oxidation rate (oxygen concentration independent) or evaluating the effects of "leakages" of oxygen into the mine through the overburden. The most important use of the model still to be described is the application to other pyritic systems. This topic will be discussed in the following section.

Generalization of Model

A model has been developed which well describes the flow of acidic mine drainage from a specific drift mine. This model includes physical, chemical, hydrological, and meteorological features of the mine environs. To convert this specific model to a general model of pyritic systems, two levels of generality must be considered. The first level is that of geometric similarity to other drift mines. At this level, our model is virtually a general model. The second level of generality is chemical similarity to any other system containing oxidizable pyrite--such as refuse piles or auger holes. At this level, the spatial configuration is different and limits the use of coordinate based features of the drift mine model, to say nothing of possible mechanistic differences.

Geometric Similarity:

The utilization of the model in cases of geometric similarity can be considered in terms of the underlying assumptions and input data requirements for the two parts of the model--oxidation and product removal. The oxidation model requires physical and chemical information about the mine. Physical data include the length of the exposed coal face, the number and thickness of coal and shale layers in the seam, and the porosity of the pyrite-containing strata. Chemical data include pyrite reactivity and oxygen concentration in the mined-out volume. If the required information is not available, certain approximations can be made. For example, in a mine containing only open rooms, the perimeter of the mine cavity can be used to estimate the length of exposed coal face. If the mine contains pillars or passageways, the surfaces of these must be considered as part of the exposed area. The perimeter of a pillar could be used as a measure of the exposed length, but it must be remembered that the volume to surface ratio is lower for a pillar than for a wall. Hence, there will be less oxidation products formed per unit area of pillar than for the same area of regular wall. Using the length of exposed coal face is based on the assumption of a uniform atmosphere in the mined-out volume. The computer program has been written to handle varying conditions along the exposed surface (this is the "I" direction), but the time required for computer calculations increases linearly with each increment of change in conditions along the surface.

In the absence of porosity and reactivity data, oxidation rate data of the type that Larez (18) reported may be used. In fact, the computer program for this model has been written under the assumption that such data will be used.

Actual data are required to describe the number and thickness of coal and shale layers in the seam. Finally, there must be an estimate of the bulk oxygen concentration in the mine. Starting with the bulk oxygen level and reactivity data, the oxygen gradients within the strata can be calculated using Equation 4-7.

The rate of removal is determined as the sum of the rates of removal by three mechanisms. The usefulness of this part of the model in the general case must be evaluated in terms of the suitability of each mechanism.

The dependence of the gravity diffusion rate on the concentration of stored products is fundamental to the definition of diffusion. The value, DIFFG(J), used for the fraction of products moved daily by gravity diffusion, was chosen on the basis of experimental observation and by correlation of acid loads under low water flow conditions at McDaniels Mine. The fact that two independent evaluation techniques yielding similar values of the gravity diffusion coefficient indicate that the value could have general applicability.

The leaching removal mechanism has been related to the trickling of water downward from the surface after precipitation. The validity of this mechanism in the general case largely depends on the strata overlaying the coal seam. If there is an impervious layer which blocks the percolation, no water is available for leaching. Where there is a highly fractured sandstone overburden, as at McDaniels Mine, percolation is rapid, and leaching is an important removal mechanism. Since there are very few totally impermeable formations, leaching removal will occur in most mines. The overburden will influence the time delay between precipitation and observed changes in the leaching rate. The constants in the model derived from McDaniels data represent a time delay of two to four days depending on the wetness of the soil. For overburden less permeable than fractured sandstone, the time delay will be greater and the observed response will be flatter; that is, there will be no sharp increases in acid load after a storm.

Products can only be removed by inundation if the coal seam lies in the range of movement of the water table. Evaluation of this removal mechanism for different sites requires specific information about the location of the pyritic material relative to the water table. In our test case, water table fluctuations have been described by using a correlation based on measured water levels in a test well and the program water storage variable, TANKC. This is a specific correlation for a particular mine. An important reason for using this correlation has been to simplify the evaluation of other parts of the model. As has been explained in Chapter VI, inundation removal is at a maximum early in the year and at a very low level the remainder of the year. On an annual basis, inundation removal accounts for about 20 per cent of the total acid removal. If precise estimates of inundation removal are required at other sites, test wells or other hydrological techniques must be used to determine the location and fluctuations of the water table relative to the coal seam. (32) If exact removal values are not needed, or water table data are not available, qualitative estimates of the elevation of the coal seam relative to springs or surface flow may be used to determine the importance of inundation removal.

In general, the removal rates are dependent on underground water movement. The calculation of water flow variations in our model is based on fundamental information such as infiltration capacity, potential evapotranspiration, and meteorological data. A number of techniques have been described for determining infiltration capacity. (11) Thornthwaite and Mather (42) have presented a method to estimate potential evapotranspiration if the latitude and vegetative cover are known for the site in question. Monthly summaries of weather data are published by the Environmental Data Service. (9) From the fundamental information, the day to day flow variations can be predicted. In the model, the magnitude of peak flows, relative to "base" flows, has been controlled by the assumption that as underground water storage increased, more drainage outlets became available through the overburden. These paths could be through cracks, crevices, and porous strata. This assumption required that an empirical constant be evaluated from correlations of existing McDaniels flow data. Application of the flow rate prediction model to other mines requires at least a qualitative evaluation of this assumption of alternate flow paths during the "wet" season.

Precipitation falling as snow is treated as being delayed until temperatures above freezing occur. The rate at which the snow melts is proportional to the number of degrees above freezing. (44) The melted snow is treated as an equivalent amount of rainfall as far as flow rate calculations are concerned. This way of computing snow melt is based on the assumption that in the McDaniels Mine area, southeastern Ohio, snow melts throughout the winter rather than accumulating to great depth, and then melting in the spring. Depending on the type of winter, other techniques have been described for calculating snow melt runoff rates. However, the actual estimate of water flow is usually obtained by correlation of data for each site. (44)

Finally to use our model, the investigator must obtain an estimate of the "water shed" area of the mine being studied. This value controls the magnitude of flow predictions, but has no influence on the rate of product removal or formation. The area does influence the concentration of acidity in the drainage. The concentration of acid is an important biological consideration. Since McDaniels Mine is a relatively small hole--six hundred square feet--in a relatively large hill, there is no practical way to directly estimate the area which drains through the mine. (32) Therefore, the drainage area was determined by an indirect calculation. Drainage and rainfall rates were known, and evapotranspiration could be estimated. (42) A material balance of water was developed. From this a "water shed" area of 27,000 square feet, or about two-thirds or an acre, was determined.

The use of back calculation to estimate the drainage area implies that some flow data must be available for other sites before our model can be used. However, the alternative, direct calculations using hydrological theory, requires data that may be even less available. Such data include information of the sub-surface structure and the water table. There are special cases, such as a large mine draining an entire hill, where direct observation could be used to estimate the water shed area. In short, our investigation, being conducted from a chemical engineering point of view, does not possess the competence to develop new hydrological concepts. It is our hope that those trained in the complex and diverse field of hydrology will be available to guide the application of the model at different sites.

<u>Summary of Data Requirements:</u>

The basic information required to use our oxidation and removal model for another drift mine includes the following items:

1. Prevailing oxygen concentration in mined out volume
2. Number and thickness of coal and shale layers in seam
3. Rate constants and porosity of each layer
4. Area of air-solid interface
5. Meteorological data
6. "Water shed" area of mine
7. Position of mine relative to water table

These data can be plugged into the model and calculations made using the constants developed from McDaniels Mine data. It is not unreasonable to expect the model to estimate annual acid loads to within plus-minus fifty per cent of the true value. The monthly predictions would only be an order of magnitude estimate.

Non-Drift Mine Systems

A situation where there is geometric similarity with a drift mine is auger hole mines such as those at the McDaniels Test Site. The model should describe these holes very well since they are in the same coal seam and a geologically similar situation. Since precipitation data will not vary from those used in the McDaniels simulation, the model can be used directly if the length of exposed seam and drainage area data are estimated. Checking the model with these auger holes is a logical extension of this study. Here there is an opportunity to start with zero product accumulation and determine if the observed increase in acidity with time can be predicted.

In the situation where geometric similarity to a drift mine is absent, usefulness of our model is limited. For example, in refuse piles the pyritic material is more highly concentrated than in a mine, and oxidation products form above the level of normal ground water flows. It can be seen at once that the removal portion of the model will not be directly applicable. It will be easier to describe a new model with different computational methods than to modify the drift mine program to fit a refuse pile. The similarities that do exist between drift mine and refuse pile systems will be emphasized in the presentation of suggestions for a model of a refuse pile.

Refuse Pile:

The following discussion of a refuse pile draws extensively on the work of Good (13) at the New Kathleen pile of Truax-Traer. The oxidation in the refuse pile occurs in a zone about 10 inches thick at the surface of the pile instead of extending as much as fifty feet into the binder as in a coal seam. (35) A clay mantle which blocks oxygen transport is the stated reason for the limited reaction zone. However, the concentration of pyrite is so great in the refuse that it is entirely possible that the oxygen gradient goes to zero in this short distance. If data on the bulk porosity of the refuse and the pyritic content were known, the oxygen gradient could be calculated using the exponential expression, $X_{Co} = X_{Co_0} \exp (- (k_R / D)^{1/2} Z)$, developed for coal and shale binders. However, Good has presented rate information on the basis of pounds of acid formed per day per acre of refuse pile area. On a smaller scale, Brown (5) took samples from the New Kathleen pile and obtained laboratory scale oxidation rates. Since the laboratory conditions are well defined, Brown's data can be used to estimate a rate constant for the exponential gradient calculation. Brown's laboratory rates check Good's field data quite well.

While there is a similarity in the area of oxidation between refuse piles and drift mines, major differences arise in the removal mechanisms. In drift mines, underground water flows are responsible for continuous removal of oxidation products. In refuse piles, oxidation occurs, for the most part, above the level of ground water flows. A fourth removal mechanism, physically impossible underground, becomes dominant. This is the direct washing by precipitation on the refuse pile. This is analogous to the underground leaching by trickling water. The rain water washing mechanism is efficient since the water, uncontaminated by acid, contacts a region of high product concentration, and the resultant acidic solution quickly flows away by gravity. The key point brought out by Good (13) and Corbett (10) is that not all of this acidic solution immediately runs off into receiving streams.

Instead, a fraction of from 15 to 30 per cent of the drainage flows into the pile and is temporarily stored. This stored water is gradually released as flow or springs at the base of the pile.

The drainage flow behavior of a refuse pile can be modeled by starting with a material balance as was done for the drift mine. Similar factors must be considered, including rate and frequency of precipitation, infiltration capacity, temperature, and evaporation. Transpiration will not be very important since the acidic conditions at the surface of a refuse pile are not conducive to plant growth. A storage tank model could be used to describe the head or driving force available for flow from the pile. If a storage tank model were used, the tanks could only be assigned limited volumes. In other words, like a sponge, the pile can only hold so much water. Any additional water runs off immediately. This immediate acid runoff is of major importance since it is the sudden shock of acidity which causes much damage to the receiving stream.

The storage tank concept has physical validity since Good, using test well measurements, observed distinct water storage volumes in the New Kathleen refuse pile. The number and capacity of storage tanks in a model could be determined empirically for a specific pile. This information might be generalized for refuse piles on the basis of a storage volume per unit area of refuse pile. To summarize, Good (13) and Brown (5) have presented sufficient information for the development of a model of drainage flow and acid load from a refuse pile. Such a model could give a very good estimate of the quick runoff and acid release during or immediately after a storm. The daily flows from internal storage could be estimated to within a factor of two or three.

Strip Mine System:

Another type of pyrite system geometrically dissimilar to a drift mine is a strip mine. Development of a strip mine model requires an extensive background in hydrology. In this type of mining, the cuts taken and the spoil banks left behind distort natural water flow patterns. The oxidation or acid load can still be estimated by the techniques described in Chapter IV.

Sternberg and Agnew (40) have undertaken the development of a model of drainage in a surface mined area. They obtained solutions for changes in ground water elevation and ground water flow that would occur in response to a uniform rate of deep percolation over the spoil bank. The solution for ground water flow can be used to predict maximum and minimum flows from the spoil bank to the last cut.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

A mathematical model has been developed which can be used to describe the drainage flow rates and acid loads from a drift mine. The McDaniels Test Mine was used to develop this model. The model's predictions of acid load and drainage flows match existing data within twenty per cent on a monthly basis and within five per cent on an annual basis. The model has been used to generate predictions of acid loads from McDaniels Mine for future years under varying levels of precipitation and different concentrations of oxygen in the mine atmosphere.

The development of a mathematical model of an acid mine drainage system has led to the following conclusions:

1. Basic scientific principles and laboratory data can be used to develop a quantitative model of a natural pyrite oxidation system.
2. While no two pyritic systems are identical, all can be described beginning with fundamental rate equations.
3. Since real, non-uniform systems are being modeled, basic principles must be augmented with empirical assumptions and correlations.
4. Because acid load and drainage flow rates can vary rapidly with environmental changes, the frequency of system monitoring is as important as the length of the time interval being monitored.
5. For $25 worth of computer time, five years of mine drainage

behavior can be simulated. This offers an inexpensive method of estimating the effect of changes, such as varying oxygen level, on the acidity of drainage from a drift mine. This technique can also be used to screen experiments and identify the most promising abatement procedures.

CHAPTER IX

FUTURE WORK

1. The predictions for McDaniels Mine should be checked by continued monitoring of the system.
2. The monitoring of the flows and acid loads from McDaniels Mine should be on a continuous rather than on a weekly basis. This will better define the short term response of the system to perturbations such as precipitation.
3. The model should be tested using the auger holes at the McDaniels Research Site. The model should also be tested using data from other drift mines.
4. Since Good (13) has furnished a basic analysis of a refuse pile, this information should be converted to a mathematical model.

APPENDIXES

APPENDIX A

GRADIENT COMPUTER PROGRAM

During the investigation of the influence of "breathing" on pyrite oxidation, a complicated differential equation was derived. This second order, variable coefficient, unsteady state equation is shown here again:

$$C \frac{\partial X_{Ox}}{\partial \theta} = CD_{AB} \frac{\partial^2 X_{Ox}}{\partial Z^2} + \frac{\Delta P(\theta)\,(L-Z)}{RT} \frac{\partial X_{Ox}}{\partial Z} - X_{Ox} \frac{\Delta P(\theta)}{RT}$$

Since there are no straight forward analytical solutions to this equation, it has been solved using finite difference approximations and digital computation. Crank-Nicolson implicit finite differences have been used to estimate all derivatives. Using the notation "I" for steps in the Z (distance) domain, and "J" for steps in the θ (time) domain, the following approximations are obtained:

$$\frac{\partial X}{\partial Z} = \frac{1}{\Delta Z} \left[X(I+1,\ J+1) - X(I,\ J+1) \right]$$

$$\frac{\partial^2 X}{\partial Z^2} = \frac{0.5}{(\Delta Z)^2} \Big[X(I+1,\ J+1) - 2X(I,\ J+1) + X(I-1,\ J+1) + X(I+1,\ J) - 2X(I, J) + X(I-1, J) \Big]$$

The next step is the collection of coefficients of each time and distance term. The collection of constants for the equation is shown in Table 5. The six sets of coefficients are general and are equally valid for a point X(M, N). To evaluate an X(I, J), this means that the five surrounding X values must be known. However, this evaluation can not be done directly since the J+1 terms are in the next time step. Therefore, it is necessary to solve for all the J+1 terms first, and then back substitute. This may be easily done since the matrix in Table 5 is tridiagonal having non-zero elements only on the main diagonal and on the diagonals immediately above and below the main diagonal. The solution of this matrix is obtained using the "TRIDAG" subroutine of the Ohio State University Chemical Engineering package. To use "TRIDAG," boundary conditions must be known, and a standard setup followed. Since the solution to the matrix is implicit, the (I, J+1) terms are defined as the main diagonal.

The setup of "TRIDAG" for our system is as follows:

Boundary Conditions

1. For $J = 1$, $X(I) = X_0 \exp(-(k_R / D)^{1/2} I \Delta Z)$.
   This is a restatement of the analytical oxygen gradient, a good initial approximation.
2. For $J = 1, 2, \ldots N$, $X(1) = X_0$. The first concentration increment is the bulk concentration for all time steps.
3. For $I = N$, where N is much greater than 1, $X(N) = X(N+1)$. In other words, at a great distance from the air-solid interface, the oxygen concentration gradient is zero.

Column Vectors

1. A(N) = coefficients in lower diagonal (I-1, J+1).
2. R(N) = coefficients in main diagonal (I, J+1).
3. C(N) = coefficients in upper diagonal (I+1, J+1).
4. D(N) = coefficients of known values such as X(0, J), X(N, 1), X(1, J), and so forth.

TABLE 5

FINITE DIFFERENCE COEFFICIENT MATRIX

Terms	X(I-1, --)	X(I, --)	X(I+1, --)
X(--, J)	$\frac{0.5\,CD_{AB}}{(\Delta Z)^2}$	$-\frac{CD_{AB}}{(\Delta Z)^2} + \frac{C}{\Delta\theta}$	$\frac{0.5\,CD_{AB}}{(\Delta Z)^2}$
X(--, J+1)	$\frac{0.5\,CD_{AB}}{(\Delta Z)^2}$ $+\frac{\Delta P\,(L-Z)}{RT}$	$-\frac{CD_{AB}}{(\Delta Z)^2} + \frac{C}{\Delta\theta}$ $-k_R C + \frac{\Delta P}{RT}$	$\frac{0.5\,CD_{AB}}{(\Delta Z)^2}$ $-\frac{\Delta P(L-Z)}{RT}$

The "GRADIENT" program functions by calculating the vectors A, R, C, and D. Once these vectors are evaluated, the subroutine "TRIDAG" is called. "TRIDAG" solves the matrix described by A, R, C, and D and returns the solution vector X(N), the oxygen mole fraction gradient. The program prints the values of X(N) and then repeats the calculations for as many time steps as are desired.

The program includes provision for varying the channel length, L, and for using different size time and distance increments. A printout of the program and samples of the output are shown on the pages immediately following in this appendix.

MAIN

```
C  THIS PROGRAM ESTIMATES OXYGEN MOLE FRACTION
C     IN A LONG CHANNEL.  CRANK NICOLSON FINITE
C     DIFFERENCE APPROXIMATIONS ARE USED FOR THE
C     DERIVATIVES.  THE RESULTING SERIES OF EQUATIONS
C     ARE SOLVED USING THE 'TRIDAG' SUBROUTINE
C
C  THE EQUATION BEING SOLVED IS
C     C*DX/DT = C*DAB* (D2X/DZ2) - K*X*C + X*DELP/(RT)
C     - DELP/(RT) * (L-Z) * (DX/DZ)
C
      DIMENSION A(1000), R(1000), C(1000), D(1000),
     1 X(1000), XSTORE(100,4), TSUM(100)
C
C  IN IS INPUT UNIT NUMBER
C     THIS IS UNIT NUMBER 5 AT OHIO STATE UNIVERSITY
      IN = 5
C  IO IS OUTPUT UNIT NUMBER
C     THIS IS UNIT NUMBER 6 AT OHIO STATE UNIVERSITY
      IO = 6
      IO = 6
C
C  READ INITIAL CONDITIONS AND OTHER DATA
C  L IS LENGTH OF CHANNEL
C  N IS NUMBER OF INCREMENTS PER FOOT
C  NORDER IS ORDER OF REACTION
C  M AND MIN CONTROL ITERATIONS AND PRINTED OUTPUT
C
      READ(IN,1001)  L, N, M, MIN , NORDER
      NSTORE = NORDER
C
C  DTHETA IS TIME INCREMENT IN HOURS
C  P IS AMBIENT PRESSURE, MM. HG.
C  T IS AMBIENT TEMPERATURE, DEGREES FAHRENHEIT
C  RATEK IS REACTION RATE CONSTANT
C  DAB IS OXYGEN IN AIR DIFFUSIVITY
      READ(IN,1000) DTHETA, P, T, RATEK, DAB
      NL = N*L
C  GAS CONSTANT MM.HG.FT**3 / GM.MOLE DEGREE RANKINE
      E = 760. * 359. / (454. * 492.)
C
      WRITE(IO,2002) DTHETA,E,P,T,RATEK,NORDER,L
      WRITE (IO, 2005)
      ZN = N
C  CALCULATE DELTA Z
      DZ = 1.0 / ZN
C  SAWTOO CAUSES DELTA P TO CHANGE SIGN DAILY
      SAWTOO  = -1.
      NHOURS = 48
      NHRS = NHOURS
      COUNT = 16.0
```

```
C   ASSUME A DAILY DELTA P OF BIGDP MM. HG.
          VOL = 8.33
          BIGDP = 12.
          DELTAP = BIGDP / NHOURS
          NHOURS = NHOURS + 1
C
C   ESTABLISH INITIAL EXPONENTIAL GRADIENT
C
          X( 1) =  .21
          ROOT = SQRT ( RATEK / CAB )
          NN = NL + 2
          DO 110  I = 2, NN
          K = I
          Z = DZ * ( I - 1 )
          X( I ) = .21 * (EXP (-ROOT * Z ) )
          IF (X( I) .LT. 1.E-40) GO TO 111
  110     CONTINUE
          GO TO 113
  111     DO 112 I = K, NN
  112     X( I ) = 0.0
  113     CONTINUE
   48     CONTINUE
C
C   START A SERIES OF CYCLES
C
          DO 30  MM = 1, M
          SUM = 0.0
          DELTAP  =  DELTAP *  SAWTOO
          TIME = 0.0
C   START A 24 HOUR CYCLE
          DO 47  NTIME  = 1, NHOURS
          P = P + DELTAP
          RHO = 1.34 *(P/ 760.) * (492.0 / 515.0)
          CTOTAL = P/ (E*T)
C   CALCULATE SECOND ORDER CONSTANT
          CON1 = 0.5*CTOTAL*DAB  / (DZ**2)
C   CALCULATE TRANSPORT CONSTANT
          CON2 = DELTAP /(E*T)
C   CALCULATE TIME CONSTANT
          CON3  = CTOTAL / DTHETA
C
C   CALCULATE CONSTANT FOR INFLUENCE OF REACTION ORDER
          CON4 = .21* RATEK * CTOTAL*( 1 - NORDER )
C   CALCULATE TRIDAG COEFFICIENTS
C   A, B, AND C ARE COEFFICIENTS OF UNKNOWN TERMS
C   D IS SOLUTION TERM.
          DO 1  I = 1, NL
          C(I)  =  CON1  - CON2*(NL - I)
```

```
      A(I)  =  CCN1  + CON2*(NL - I   )
      IF ( X(I) .LT. 0.02 ) NCRDER  = 1
    1 R(I)  = -2*CON1  +  CON2 - CON3 - RATEK *
     1 CTOTAL * NCRDER
      NORDER = NSTORE
C   INTEGRATE QUANTITY OF OXYGEN CONSUMED IN CHANNEL
      IF (NORDER .EQ. 1 ) GO TC 301
      DO 300  I = 1, NL
      IF ( X(I) .LT. 0.02 ) NORDER  = 1
      SUM = SUM + 0.21*RATEK*DTHETA * (1-NORDER) *
     1 RHO * DZ
      SUM = SUM + DZ/ 6.0 * (X(I+2) + 4.0 * X(I+1)
     1 + X(I)) * RATEK * DTHETA * NCRDER
  300 CONTINUE
  301 CONTINUE
      NCRDER = NSTCRE
      IF ( NORCER .EQ. 0 ) GO TO 302
      DO  99  I = 1, NL, 2
      SUM = SUM + DZ/ 3.0 * (X(I+2)+4.*X(I+1) +
     1 X(I)) * RATEK * DTHETA * RHO * NORDER
   99 CONTINUE
  302 CONTINUE
      J =NL- 1
      D(1)  =-CON1* ( X( 1) - 2*X( 2)  + X( 3)) - CON3
     1 *X(2) -(CON1 +CON2 * (NL-1)) * X(1) + CON4
      DO 4  I =2,J
      IF ( X(I) .LT. 0.02 ) CCN4 = 0.0
      D(I)  = -CON1*(X(I) - 2.*X( I + 1) + X(I +
     1 2)) - CON3 * X(I+1) + CCN4
      NK  =  I + 1
      IF(ABS( D(I)) .GT.  1.E-20)  GO TO 4
      DO 5  LL = I, NL
    5 D(LL) = 0.0
      GO TO 8
    4 CONTINUE
    8 CONTINUE
      D(NL) =  -CCN1 *(X(NL -1) - 2.* X(NL))  -
     1 CON3 * X(NL) + CON4
C   ESCAPE FROM DO LCOP AT END OF 24 HOUR CYCLE
      IF( NTIME .EQ. NHOURS ) GO TC 30
C   PRINT INITIAL AND FINAL SETS OF CONCENTRATION DATA
      IF( MM .EQ. 1 ) GO TO 21
      IF ( MM .LT.  MIN) GC TC 20
   21 CONTINUE
      IF(NTIME - 1 ) 9, 9, 15
C   WRITE OUT EVERY 8TH TIME INCREMENT
   15 FLAG = ( NTIME - 1 ) / COUNT
      NFLAG = FLAG
      FLAG = FLAG - NFLAG
      IF ( ABS (FLAG) .GT.  0.01 )  GO TO 20
    9 WRITE (IC,2000) MM , TIME, P
```

```
C  WRITE OUT FIRST 20 CONCENTRATION INCREMENTS
      DO 10  I = 1, 20
      DIST = DZ *(I - 1 )
      WRITE(IO,2001) DIST,X(I),A(I),R(I),C(I),D(I)
  10  CONTINUE
C  WRITE OUT EVERY FCURTH DISTANCE INCREMENT
      DO 11  I = 21, NK, 4
      DIST = DZ *(I - 1 )
C  PRINT ONLY NCN ZERC RESULTS
      IF( X(I) .LE. 0.0001)  GO TO 20
  11  WRITE(IO,2001) DIST,X(I),A(I),R(I),C(I),D(I)
  20  CONTINUE
C  STORE CAILY CATA FOR LATER PRINTOUT
      IF( NTIME .NE. NHRS ) GO TC 80
      XSTORE (MM, 1) = X(2)
      XSTORE (MM, 2) = X(15)
      XSTORE (MM, 3) = X(35)
      XSTORE (MM, 4) = X(100)
  80  CONTINUE
      CALL TRIDAG( A, R, C, D, X, NK)
C  TRIDAG IS AN OHIO STATE SUBROUTINE FOR SOLVING
C     TRIDIAGONAL MATRICES SUCH AS THOSE ARISING FROM
C     IMPLICIT SOLUTIONS OF MASS TRANSPORT EQUATIONS
      DO 150  I = 1, NN
      IF( X(I) .LT. 0.0 ) X(I) = 0.0
 150  CONTINUE
      TIME = TIME + DTHETA
      TSUM(MM) = SUM * 120.  / 112. * VOL
  47  CONTINUE
  30  CONTINUE
      WRITE(6, 2003)
      DO 31  MM = 1, M
  31  WRITE (IO,2004) MM, XSTORE(MM, 1), XSTORE(MM,
     1 2), XSTORE(MM,3), XSTORE(MM,4), TSUM(MM)
      STOP
1000  FORMAT( 5F10.6)
1001  FORMAT( 5I5)
2000  FORMAT(////  '  THIS IS DAY ',I5, '  AFTER  ',
     2 F8.3, '  HOURS', // 12X, ' THE PRESSURE IS  ',
     2 F7.3, '  MMHG.' , ///15X, 'DEPTH', 10X,
     3 'O2 FRACTION', 8X, 'A(I)',15X,'R(I)', 13X,
     4 'C(I)',  15X,  'D(I)')
2001  FORMAT(1H0,10X, F10.3, 10X, F 10.6, 4E17.8)
2002  FORMAT(1H1, 'DT  =',F4.2, '  HR.' // ' GAS ',
     1 'CONSTANT  =', F6.4,// ' INITIAL PRESSURE  =',
     2 F6.1, '  MM.HG.', // ' TEMPERATURE  =',F6.0,
     3 '  DEGREES R.',// ' RATE CONSTANT =', F10.8,//
     4 ' ORDER CF REACTION IS ', I2,//' LENGTH  IS',
     5 I3, '  FEET' )
```

```
 2003    FORMAT ( 1H1, '  X(I) VALUES ARE TABULATED ',
       1 'BELOW FCR THE LAST',// ' DAILY TIME INCREM',
       2 'ENT  AT THE 2ND, 13TH, 35TH, AND 100TH ',
       3 'DISTANCE  INCREMENTS', // ' A FORM OF STEADY',
       4 ' STATE IS REACHED WHEN VALUES FOR ALTERNATE',
       5 ' DAYS ARE THE SAME', //' THIS IS USUALLY ',
       6'OCCURS AFTER 20 TO 30 DAYS ',// ' THE FINAL ',
       7 'COLUMN IS THE PYRITE OXIDIZED IN MGMS/DAY',
       7 ///15X, 'DAY',6X,'O2 FRACTION',6CX,'OXIDATION')
 2004    FORMAT  (16X, I3, 5( 8X, F9.6))
 2005    FORMAT ( 1H1)
         END
```

```
        X(I) VALUES ARE TABULATED BELOW FOR THE LAST DAILY
   TIME INCREMENT AT THE 2ND AND 15TH DISTANCE INCREMENTS.
   A FORM OF STEADY STATE IS REACHED WHEN VALUES FOR
   ALTERNATE DAYS ARE THE SAME.  THIS USUALLY OCCURS AFTER
   15 TO 20 DAYS.  THE FINAL COLUMN IS THE PYRTIE OXIDATION
   IN MILLIGRAMS  OXYGEN CONSUMED PER DAY

                             TABLE 6

        DAY          OXYGEN MOLE FRACTION              OXIDATION

          1       0.113937         0.002585           9.899684
          2       0.185306         0.007099          12.941030
          3       0.113768         0.001857           9.487527
          4       0.185298         0.007087          12.830996
          5       0.113781         0.001784           9.475357
          6       0.185298         0.007075          12.825077
          7       0.113779         0.001774           9.472585
          8       0.185298         0.007072          12.823798
          9       0.113779         0.001772           9.471957
         10       0.185298         0.007071          12.823528
         11       0.113779         0.001771           9.471822
         12       0.185298         0.007071          12.823472
         13       0.113779         0.001771           9.471774
         14       0.185298         0.007071          12.823464
         15       0.113779         0.001771           9.471774
         16       0.185298         0.007071          12.823457
         17       0.113779         0.001771           9.471774
         18       0.185298         0.007071          12.823457
         19       0.113779         0.001771           9.471774
         20       0.185298         0.007071          12.823457


                DT  =  0.50 HOUR
                GAS CONSTANT  = 1.2215
                INITIAL PRESSURE  = 745.0 MM HG
                TEMPERATURE = 515. DEGREES RANKINE
                RATE CONSTANT = 0.0300
                ORDER OF REACTION IS 0
                LENGTH IS 400 FEET
```

```
THIS IS DAY      1  AFTER      8.000   HOURS

          THE PRESSURE IS  740.750  MMHG.

               DEPTH             C2 FRACTION

                0.0                0.210000

                1.000              0.131294

                2.000              0.082267

                3.000              0.050897

                4.000              0.030540

                5.000              0.017995

                6.000              0.012162

                7.000              0.012830

                8.000              0.012316

                9.000              0.011611

               10.000              0.010808

               11.000              0.009877

               12.000              0.008842

               13.000              0.007755

               14.000              0.006675

               15.000              0.005651

               16.000              0.004721

               17.000              0.003904

               18.000              0.003205

               19.000              0.002620

               20.000              0.002135
```

APPENDIX B

ESTIMATION OF POTENTIAL EVAPOTRANSPIRATION

The use of the Thornthwaite and Mather (42) method for estimation of potential evapotranspiration (PE) requires monthly average temperatures and the latitude for the site. Information on the type of soil and vegetative cover in the region are also required. The PE technique was developed by an analysis of data from all over the United States. The correlations which were developed have been published in the form of a manual of tables.

The best way to use the PE tables is to construct a table of data as they are read. The data shown in Table 7 below are listed in six columns.

TABLE 7

ESTIMATION OF POTENTIAL EVAPOTRANSPIRATION

Month	T_{mean}, Degrees F	Calculation Constants* A	B	C	Inches Potential Evapotranspiration
January	33.5	0.06	0.0	25.4	0.0
February	34.7	0.16	0.0	25.1	0.0
March	42.1	1.19	0.02	30.9	0.62
April	53.3	3.68	0.06	33.3	2.00
May	62.8	6.44	0.10	37.0	3.70
June	71.4	9.34	0.14	37.3	5.22
July	74.7	10.56	0.15	37.9	5.69
August	73.3	10.04	0.15	35.5	5.34
September	66.9	7.78	0.12	31.2	3.74
October	55.6	4.30	0.07	28.8	2.02
November	43.3	1.41	0.03	25.2	0.75
December	34.2	0.11	0.0	24.8	0.0

*Calculation constants are explained in text on page 125 .

The first two columns in Table 7 contain the name of the month and the monthly average temperature in degrees Fahrenheit. The second, third, and fourth columns contain calculational constants. The significance of these columns, labelled A, B, and C in Table 7, is as follows:

Column A -- Intensity of incident sunlight. This is a function of the temperature and is read from Table 1 in Section I of the PE manual. In physical terms, this variable is an estimate of the energy available to evaporate water.

Column B -- Daily unadjusted PE. This term is read from Table 3 in Section II on the manual. It is a function of the sunlight intensity, type of soil, and vegetation.

Column C -- Correction factor to convert daily unadjusted PE to monthly values. This factor is based on the latitude and represents the number of twelve hour days of sunlight per month. The correction is based on the fact that plant growth, and transpiration, requires sunlight. This term is obtained from Table 6 in Section III.

The sixth column is the adjusted PE in units of inches of water per month. This value is obtained by multiplying Columns B and C together. The values in the sixth column are those which are used in any further calculations. These are the values which have been read into the "PEVAP" subroutine as data.

Thornthwaite and Mather have also presented tables for scaling down the potential evapotranspiration for cases where the soil is less than saturated as is the assumption in the initial calculation. These scaling factors have been written into the "PEVAP" subroutine.

APPENDIX D

DRIFT MINE PROGRAMMING
and
SAMPLE OUTPUT FOR 1970

MAIN

```
C
C  THIS IS THE MAIN PROGRAM FOR THE CALCULATION OF
C    ACID MINE DRAINAGE IN A DRIFT MINE.  CERTAIN
C    CONSTANTS USED IN THIS PROGRAM HAVE BEEN
C    OBTAINED BY CORRELATION OF DATA FROM MCDANIELS
C    TEST MINE.  THE MINE IS ADMINISTERED BY THE
C    OHIO STATE UNIVERSITY.
C
C  ESTABLISH ARRAYS
      DIMENSION STORE( 5, 15, 30), ALT(15), WATER(30),
     1 THICK( 15), REACT( 15), RATEK(15),  ROCK(15),
     2 TYPE(15),PYCON(15), DIFFG(15), WASH( 15)
      REAL  BLANK, END, YEAR, JAN, FEB, MAR, APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CA/ BLANK,END,YEAR,JAN,FEB,MAR,APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CB/ AMONTH, AG,RAIN, RTIME, TMEAN,AGO,
     1 TANKC, RSUM, RSUMA, FLAG, AFLAG, WSHED, PWHC,
     2 PWATER, LAST, KEEP, LTHETA, IDAY
      COMMON /CC/ VAP(12)
C
C  DEFINITION OF COMPUTATIONAL ARRAYS
C  WATER    IS WATER TABLE LEVEL ARRAY
C  REACT IS THE OXIDATION OF THE STRATUM EXPRESSED AS
C  MICROGRAMS OF OXYGEN CONSUMED / CC SOLID / HOUR
C  RATEK IS THE REACTION RATE CONSTANT OF THE STRATA
C  THICK IS THE THICKNESS OF THE  STRATA
C  ROCK TYPE IS A VERBAL DESCRIPTION OF THE STRATA
C  PYCON IS THE VOID  FRACTION OF THE STRATUM
C  STORE  IS OXIDATION PRODUCT STORAGE ARRAY
C  ALT IS ELEVATION OF STRATUM RELATIVE TO DATUM PLANE
C
C
C  IN IS INPUT CHANNEL
C    AT OHIO STATE THIS IS UNIT 5
      IN = 5
C  IO IS PRINTED OUTPUT CHANNEL
C    AT OHIO STATE THIS IS UNIT 6
      IO = 6
C  IP IS PUNCHED OUTPUT CHANNEL
C    AT OHIO STATE THIS IS UNIT 7
      IP =   7
C
      IY = 0
      AGO = BLANK
      AG = BLANK
C  READ NUMBER OF STRATA, DEPTH,AND LENGTH INCREMENTS
      READ(IN,5300) NLAYER, NDEPTH, NFEET, NPUNCH
```

```
C  READ SIZE OF DEPTH AND LENGTH INCREMENTS
      READ(IN,5302) DI, DK
C  ALKALI IS PPM ALKALINITY IN GROUND WATER
C  TOP IS TOP OF COAL SEAM
      READ(IN, 5302) ALKALI, TOP, SLOPE
C  WSHED IS 'WATER SHED' AREA OF MINE
C  PWHC IS PROVISIONAL WATER HOLDING CAPACITY
C  IT HAS THE ESTIMATED VALUE OF 10 INCHES
      READ(IN, 5302) WSHED, PWHC, PWATER
C  READ IN MONTHLY POTENTIAL EVAPOTRANSPIRATION VALUES
      READ(IN, 5310) (VAP(I), I=1,12)
C
C  READ INPUT DATA OF STRATA
      NL = NLAYER + 1
      DIFFG( NL) = 0.0
C  FRAC IS FRACTION OF STORED PRODUCTS REMOVED BY
C     INUNDATION EACH DAY
      FRAC = 0.02
      DIF = 0.02
      SOX = 0.0
      KEEP = 30
      LTHETA = 1
      KAT = 0
      WMIN = 10.
      H = SQRT( 800. )
      ALT(NLAYER + 1) = TOP
      DO 1200  J = 1, NLAYER
      READ(IN,5301)  ROCK(J), TYPE(J), ALT(J),
     1 REACT(J), PYCON(J)
1200  CONTINUE
C  INITIALIZE STORAGE
      DO 1201 I = 1, NFEET
      DO 1201 K = 1, NDEPTH
1201  STORE( I, NL, K) = 0.0
C
C  ECHO INPUT DATA AND INITIAL CONDITIONS
      WRITE(IO, 6200)NLAYER, NDEPTH,DK, NFEET,DI,
     1 WSHED, ALKALI
C
      WRITE(IO, 6300)
C  CALCULATE RATE CONSTANT
C  CORRECT TO MINE TEMPERATURE FROM EXPERIMENTAL
C     LABORATORY TEMPERATURE
      TEMP = 0.15
C  FTGMOL IS FT**3 VOLUME OCCUPIED BY GM MOLE GAS
      FTGMOL = 359. / 454.
      CCPRFT = (2.54 ** 3 ) * 1728.
      CONA = CCPRFT* FTGMOL /(0.21 *32. ) * TEMP
      DO 1202 J =1, NLAYER
      REACT(J) = REACT(J) *1.E-6 * 24.
      RATEK(J) = REACT(J) * CONA / PYCON(J)
      DIFFG(J) = DIF * RATEK(J)
      THICK(J) = ALT(J+1) - ALT(J)
```

```
C  ECHO INPUT DATA
1202    WRITE(IO,6301) J, ROCK(J), TYPE(J), ALT(J),
      1 RATEK(J), PYCON(J)
        DIFFG(3) = DIFFG(10)
C  AT THIS POINT, THE SYSTEM HAS BEEN PHYSICALLY
C     AND CHEMICALLY DESCRIBED
C
C  BEGIN CALCULATION OF OXIDATION
        P = 454.
C  DIFF IS GAS DIFFUSIVITY IN FT**2 PER DAY
        DIFF = 0.692 * 24. * 0.6
C  CORRECT GAS CONCENTRATION TO MINE CONDITIONS
        GASC = 32. / 359. * 492./ 515.
        DO 1205  J = 1, NLAYER
1205    READ(IN,7000) (STORE(I,J,K), K=1, NDEPTH)
        DO 1500 I = 1, NFEET
        DO 1498 J = 1, NLAYER
        DO 1496 K = 1, NDEPTH
        STORE(I,J,K) = STORE(I,J,K) * CI
1496    SOX = SOX + STORE(I,J,K)
        WRITE(IO,6305) (STORE(I,J,K) , K=1, NDEPTH)
        WASH(J) = STORE(I,J,1)
1498    CONTINUE
1500    CONTINUE
1600    CONTINUE
        WRITE(IO, 6302) SOX
C
C  BEGIN DAILY CALCULATIONS OF OXIDATION AND OUTPUT
C
C  DEFINE OPERATIONAL CONSTANTS
        WRITE(IO, 6349)
        TSUM = 0.0
1605    CONTINUE
        WSUM = 0.0
        YSUM = 0.0
        FSUM = 0.0
        RSUM = 0.0
        YSUMA = 0.0
        FSUMA = 0.0
        RSUMA = 0.0
        GSUM = 0.0
        FLSUM = 0.0
        DO 2500  L = 1,1000
C
C  READ DAILY WEATHER DATA
        READ(IN,5401)AMONTH, IDAY, RAIN, RTIME,
      1 TMEAN, OXY, IYEAR
        IF( OXY .GT. 0.0 ) OXX = OXY
C  ESCAPE FROM PROGRAM AT END OF DATA
        IF(AMONTH - END) 2250, 2200, 2250
2250    CONTINUE
        IF(AMONTH - YEAR ) 2255, 3050, 2255
2255    CONTINUE
```

```
      CALL DAYS
      RKEEP = RAIN
      RAIN = 0.0
      DO 3005 M = 1, LTHETA
      IF( M .EQ. LTHETA ) RAIN = RKEEP
      IF( KAT .NE. 0) GO TO 2305
C  REMOVE IS A SUBROUTINE TO  ESTIMATE FLOW DATA
      CALL  REMOV  (DSLV, FLOW, M)
      GO TO 3005
2305  CALL  REMOVE (DSLV, FLOW, M)
2306  CONTINUE
C  DETERMINE POSITION OF WATER TABLE
C  YZERO IS EQUIVALENT TO BORE HOLE # 6
C  XMIN IS MOST FORWARD REACH OF WATER LEVEL ABOVE COAL
C  WATER(KA) IS POSITION OF TABLE THROUGH COAL SEAM
      YZERO = WMIN + 5. * TANKC
      XMIN = H * SQRT ( YZERO - 3.0 )
      XMIN = XMIN + 5.0
      XMIN = 120. - XMIN
      IF( XMIN .LT. 1.0 ) XMIN = 1.01
      DO 2310 KA = 1, NDEPTH
      DF = KA * DK
      KB = KA
      IF(DF .GT. XMIN ) GO TO 2308
2310  WATER (KA) = ALT(1)
      GO TO 2316
2308  DO 2315 KA = KB, NDEPTH
      WATER( KA) = WATER(KA - 1) + 0.2 * DK
      IF(WATER(KA) .GT. TOP) WATER(KA) = TOP
2315  CONTINUE
C
2316  CONTINUE
C  TACID IS RUNNING TOTAL OF ACID OUTPUT
      TACID  = 0.0
      DO 2000 I =1, NFEET
      DO 1995 J =1, NLAYER
      DVOL = THICK(J) * DI * DK
C  COMPARE ACID STORAGE WITH EQUILIBRIUM ACID STORAGE
      FJ = STORE(I,J,1) / WASH(J)
      IF(FJ .GT. 1.1 ) FJ = 1.1
C  CALCULATE OXYGEN GRADIENT IN EACH LAYER
      DO 1990 K = 1, NDEPTH
      TNN = K
      DNK =  ( TNN - 0.5 )*DK
      XNN = OXX* EXP(-SQRT(RATEK(J)/ DIFF) *DNK)
C
C  THE FOLLOWING CALCULATIONS DESCRIBE EACH EVENT
C    PROBABLE IN THE BLOCKS
C  GRAVOT IS GRAVITY DIFFUSION OUT OF BLOCK
C  GRAVIN IS GRAVITY DIFFUSION INTO BLOCK
C  FLOOD IS QUANTITY OF PRODUCTS REMOVED WHEN A
C    BLOCK IS INUNDATED
C  AOUT IS AMOUNT OF PRODUCTS REMOVED BY LEACHING
C  STORE(I,J,K) IS PRODUCT STORAGE ARRAY
```

```
C
C
C  DETERMINE POSITION OF BLOCK RELATIVE TO WATER
C     TABLE AND OBTAIN SUM OF APPROPRIATE TERMS
C
1647    CONTINUE
        HITE = ALT(J) + SLOPE *CK * K
        IF(HITE - WATER(K)  ) 1648, 1655, 1655
1648    CONTINUE
        ALEFT = STORE(I,J,K) *(1.-FRAC)**DTHETA
        FLOOD= STORE(I,J,K) -ALEFT
        AOUT = FLOOD
        STORE(I,J,K) = STORE(I,J,K) - FLOOD
C  MAINTAIN RUNNING TOTAL OF INUNDATION REMOVAL
        FLSUM = FLSUM + FLOOD* 196. / 112.
        IF(FLSUM .LT. 1. E-10 ) FLSUM = 0.0
1653    GO TO 1989
1655    OXIDN = RATEK(J) * GASC * XNN * DVOL*
      1 PYCON(J) * DTHETA
        GRAVOT = DIFFG(J) * STORE(I,J,K) *DTHETA*FJ
        GRAVIN = DIFFG(J+1) * STORE(I,J+1,K) *
      1 DTHETA * FJ
1660    AOUT = STORE(I,J,K) * DSLV* FJ
        STORE(I,J,K)=STORE(I,J,K) + OXIDN+ GRAVIN -
      1 GRAVOT - AOUT
        WSUM = WSUM +AOUT * 196./ 112.
        UP = HITE - WATER(K)
        IF(UP .GT. 0.2 .AND.J .GT.1) GO TO 1989
        AOUT = AOUT + GRAVOT
        IF(STORE(I,J,K) .LT.1.E-10)STORE(I,J,K)=0.0
C  KEEP RUNNING TOTAL OF GRAVITY DIFFUSION REMOVAL
        GSUM = GSUM + GRAVOT* 196./112.
1989    CONTINUE
        TACID = TACID + AOUT
1990    CONTINUE
1995    CONTINUE
2000    CONTINUE
        ALK = FLOW * ALKALI * 8.33E-6
C  CONVERT ACID LOAD FROM AN OXYGEN CONSUMPTION
C  BASIS TO  EQUIVALENT ALKALINITY BASIS
        TACID = TACID * 196. / 112. - ALK
        TSUM = TSUM + TACID
        TACID = TSUM / 5.
        TSUM = TSUM - TACID
2002    CONTINUE
        FSUM = FSUM + FLOW
        FSUMA = FSUMA + FLOW
        YSUM = YSUM + TACID
        YSUMA = YSUMA + TACID
        IDAY = LAST + M
C
```

```
C  PRINT OUT SUMMARY OF DAILY RESULTS
C
           IF( AG - AGO ) 2020, 2010, 2020
   2010    WRITE(IO,6350)AGO, IDAY, FLOW, TACID, RAIN
           GO TO 3000
   2020    IF(IDAY .GT. KEEP ) GO TO 2030
   2025    WRITE(IO,6350) AG, IDAY, FLOW, TACID, RAIN
           GO TO 3000
   2030    IDAY = IDAY - KEEP
           WRITE(IO,6350)AGO, IDAY, FLOW, TACID, RAIN
   3000    CONTINUE
           IF( IDAY .NE. KEEP ) GO TO 3005
           WRITE(IO, 6241) FSUMA , YSUMA, RSUMA
           WRITE(IO, 6245) FLSUM, GSUM, WSUM
           WRITE(IO, 6349)
           WSUM = 0.0
           GSUM = 0.0
           FLSUM = 0.0
           RSUMA = 0.0
           YSUMA = 0.0
           FSUMA = 0.0
   3005    CONTINUE
           LAST = IDAY
           KAT = 1
   2500    CONTINUE
   3050    CONTINUE
           IY = IYEAR
           WRITE(IO, 6370) IYEAR , FSUM, YSUM, RSUM
           DO 2201 I = 1, NFEET
           DO 2201 J = 1, NLAYER
   2201    WRITE(IO,6305) (STORE(I,J,K), K=1,NDEPTH)
           GO TO 1605
   2200    WRITE(IO,6360 )
           IF (NPUNCH .EQ. 0) STOP
           DO2217 I = 1, NFEET
           DO2217 J = 1, NLAYER
           WRITE(IP, 7000)(STORE(I,J,K), K=1,NDEPTH)
   2217    CONTINUE
           STOP
   5300    FORMAT(4I5)
   5301    FORMAT ( 2A4, 2X, F5.0, 2F10.5 )
   5302    FORMAT(8 F10.5)
   5310    FORMAT (12F5.2)
   5401    FORMAT( 1X, A4, 1X, I2, 2X, 4F10.5, I4)
   6200    FORMAT( 1H1, 10X, 'THE INITIAL CONDITIONS '
         1 ,'AND VARIABLES USED IN THIS MODEL ',///
         2 10X, 'THE NUMBER OF LAYERS IS ', I3,/10X,
         3 'THE NUMBER OF DEPTH INCREMENTS IS', I3,/ 15X,
         4 'EACH INCREMENT =', F5.2, ' FEET',/ 10X,'THE',
         5 ' NUMBER OF PERIMETER INCREMENTS IS', I3,/15X,
         6 'EACH INCREMENT =', F7.2, ' FEET',/ 10X,
         7 'THE WATER SHED IS ',F10.0, ' SQUARE FEET',/
         8 10X,'THE PPM CACO3 ALKALINITY IS ', F6.2, //)
```

```
6241   FORMAT(//  , 5X,'GALLCNS CF FLCW DURING MONTH'
      1,' IS', F10.0,/ 5X, 'POLNDS OF ACID DLRING '
      2,'MONTH IS', F6.1,/  5X,'INCHES OF RAIN ',
      3 'ENTERING STORAGE IS', F6.2 // )
6245   FORMAT(5X,'ACID REMOVED BY INUNDATION',F8.3,/
      1 5X,'ACID REMCVED BY GRAVITY DIFFUSION',F8.3,/
      2 5X,'ACID REMOVED BY LEACHING', F8.3,///)
6300   FORMAT(1H1, ' THE FOLLOWING IS A DESCRIPTION',
      1 ' OF THE MINE',/' BEING MCDELEC.  THE LAYERS' ,
      2 ' ARE COUNTED FROM THE BOTTOM.  ', //
      4 ' LAYER MATERIAL ELEVATION  K(RATE)', 3X,
      5 'VOID ', / 2CX, 'FEET' )
6301   FORMAT(2X,I2, 3X, 2A4, 3X, F5.1, 4X, F8.6,
      1 2X, F7.3 )
6302   FORMAT(// F1C.4 ///)
6305   FORMAT ( 10 (3X, F8.4))
6349   FORMAT(1H1, ///5X, 'CATE', 6X,
      2 'FLOW,GPD',2X, 'ACID,LBS',4X, 'RAIN, IN.',///)
6350   FORMAT(3X, A4, I5, 3X, F6.0, 4 ( 3X, F10.5 ))
6351   FORMAT(3X, A4, I5, 3X, F6.0, 4 ( 3X, F10.5 )////)
6360   FORMAT (1H1, '  TERMINATION CARD REACHED ' )
6370   FORMAT(//// 5X,'SUMMARY OF CATA FOR ', I4,//
      1 5X,'GALLONS OF FLOW DLRING YEAR IS', F10.0,//
      2 5X,'POUNCS OF ACID DURING YEAR IS',F10.0,//
      3 5X,'INCHES OF RAIN ENTERING STCRAGE IS' ,
      4 F6.2, ////)
7000   FORMAT (8F10.8 )
7001   FORMAT(F10.8)
       END



       BLCCK DATA
       REAL  BLANK, END, YEAR, JAN, FEB, MAR, APR,
      2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
       COMMON/CA/ BLANK,END,YEAR,JAN,FEB,MAR,APR,
      2 MAY, JUNE, JULY, AUG, SEPT, CCT, NCV, DEC
       DATA BLANK, END, YEAR, JAN, FEB, MAR, APR,
      1 MAY, JUNE, JULY, AUG, SEPT, CCT,NCV, CEC/
      2 '    ', 'END ', 'YEAR', 'JAN ', 'FEB ','MAR ',
      3 'APR ', 'MAY ', 'JUNE', 'JULY', 'AUG ','SEPT',
      4 'OCT ', 'NOV ', 'DEC '/
       END
```

DAYS

```
      SUBROUTINE DAYS
      REAL  BLANK, END, YEAR, JAN, FEB, MAR, APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CA/ BLANK,END,YEAR,JAN,FEB,MAR,APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CB/ AMONTH, AG,RAIN, RTIME, TMEAN,AGO,
     1 TANKC, RSUM, RSUMA, FLAG, AFLAG, WSHED, PWHC,
     2 PWATER, LAST, KEEP, LTHETA, IDAY
      IF( AGO .EQ. BLANK ) GO TO 2240
C  CHECK TO SEE IF MONTH HAS CHANGED
2210  IF( AGO   - FEB) 2215, 2214, 2215
2214  KEEP = 28
      GO TO 2230
2215  IF(AGO .EQ. SEPT .OR. AGO .EQ. NOV .OR. AGO
     1 .EQ. APR .OR. AGO .EQ. JUNE) GO TO 2218
      KEEP = 31
      GO TO 2230
2218  KEEP = 30
2230  CONTINUE
      IF( AMONTH - AGO ) 2205, 2201, 2205
2201  LTHETA = IDAY - LAST
      GO TO 2235
2205  LTHETA =  KEEP - LAST + IDAY
2235  CONTINUE
2240  CONTINUE
      AG = AGO
      AGO = AMONTH
      FLAG = 0.0
      AFLAG = 0.0
      IF(AGO .EQ. OCT  ) AFLAG = 1.
      IF(AGO .EQ. NOV  ) AFLAG = 1.
      IF(AGO .EQ. DEC  ) AFLAG = 1.
      IF(AGO .EQ. JAN  ) AFLAG = 1.
      IF(AGO .EQ. FEB  ) AFLAG = 1.
      IF(AGO .EQ. MAR  ) AFLAG = 3.
      IF(AGO .EQ. APR  ) AFLAG = 2.
      RETURN
      END
```

EVAP

```
      SUBROUTINE EVAP (PEVAP)
C   SUBROUTINE ESTIMATES POTENTIAL EVAPOTRANSPIRATION
C   USING THORNTHWAITE METHOD
      REAL  BLANK, END, YEAR, JAN, FEB, MAR, APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CA/ BLANK,END,YEAR,JAN,FEB,MAR,APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CB/ AMONTH, AG,RAIN, PTIME, TMEAN,AGC,
     1 TANKC, RSUM, RSUMA, FLAG, AFLAG, WSHED, PWHC,
     2 PWATER, LAST, KEEP, LTHETA, IDAY
      COMMON /CC/ VAP(12)
      IF( AMONTH - JAN ) 2, 1, 2
    1 PEVAP = VAP( 1)
      RETURN
    2 IF( AMONTH - FEB ) 4, 3, 4
    3 PEVAP = VAP( 2)
      RETURN
    4 IF( AMONTH - MAR ) 6, 5, 6
    5 PEVAP = VAP( 3)
      RETURN
    6 IF( AMONTH - APR ) 8, 7, 8
    7 PEVAP = VAP( 4)
      RETURN
    8 IF( AMONTH - MAY ) 10, 9, 10
    9 PEVAP = VAP( 5)
      RETURN
   10 IF( AMONTH - JUNE) 12, 11, 12
   11 PEVAP = VAP( 6)
      RETURN
   12 IF( AMONTH - JULY) 14, 13, 14
   13 PEVAP = VAP( 7)
      RETURN
   14 IF( AMONTH - AUG ) 16, 15, 16
   15 PEVAP = VAP( 8)
      RETURN
   16 IF( AMONTH - SEPT) 18, 17, 18
   17 PEVAP = VAP( 9)
      RETURN
   18 IF( AMONTH - OCT ) 20, 19, 20
   19 PEVAP = VAP(10)
      RETURN
   20 IF( AMONTH - NOV ) 22, 21, 22
   21 PEVAP = VAP(11)
      RETURN
   22 PEVAP = VAP(12)
      RETURN
      END
```

```
      SUBROUTINE REMOV (DSLV, FLOW, M )
C
C  REMOVE IS A SUBROUTINE TO  CALCULATE FLOW RATES
C    AND FRACTION OF POODUCTS REMOVED BY LEACHING
C
      REAL  BLANK, END, YEAR, JAN, FEB, MAR, APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CA/ BLANK,END,YEAR,JAN,FEB,MAR,APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CB/ AMONTH, AG,RAIN, RTIME, TMEAN,AGO,
     1 TANKC, RSUM, RSUMA, FLAG, AFLAG, WSHED, PWHC,
     2 PWATER, LAST, KEEP, LTHETA, IDAY
      EXTERNAL EVAP
C
C  DEFINE FLOW RATE VARIABLES AND ESTABLISH INITIAL VALUES
C  INITIAL CONDITIONS ARE ONLY ESTIMATES TO SPEED UP
C   CALCULATIONS AND REMOVE OLD VALUES FROM
C   COMPUTER STORAGE
C
C  FLOW IS GALLONS PER DAY FLOW FROM SYSTEM
C  TANKA IS WARM WEATHER WATER DELAY STORAGE
      TANKA = 0.0
C  TANKB IS FREEZING WEATHER WATER STORAGE
      TANKB = 0.0
C  TANKC IS SOURCE OF GROUND WATER FLOW
      TANKC = 0.5
C  TAA IS FACTOR TO REPRESENT FASTER TRANSFER OF WATER
C   WHEN GROUND IS WETTER
C  TA IS DAILY TRANSFER FROM TANKA TO TANKC
      TA = 0.0
C  TB IS DAILY SNOWMELT TRANSFER TO TANKC
      TB = 0.0
C  CAP IS MAXIMUM HOURLY INFILTRATION RATE
      CAP = 0.5
C  TCAP IS DAILY MAXIMUM INFILTRATION CAPACITY
C    EXCLUSIVE OF ROOT STORAGE REQUIREMNTS
      TCAP = 0.7
C  RCAP IS TOTAL DAILY INFILTRATION CAPACITY
C  PNET IS AMOUNT OF WATER AVAILABLE FOR INFILTRATION
C  DELAY IS ESTIMATE OF RAINFALL OF PRECEDING DAYS
      DELAY = 0.5
C  RSUM IS MONTHLY TOTAL OF WATER INFILTRATION
C  RSUMA IS ANNUAL SUM OF WATER INFILTRATION
C  DEFICT IS DEFICIENCY OF WATER IN ROOT STORAGE
C  EFF IS FRACTIONAL REDUCTION IN EVAPORATION BECAUSE
C    OF DEFICIENCY IN ROOT STORAGE
C  CON5 IS A CALCULATIONAL CONSTANT
      CON5 = WSHED * 7.5 / 12.0
C  A IS A CALCULATIONAL CONSTANT
      A = 4203. / 528.
```

```
C  DEFINE ADDITIONAL REMOVAL VARIABLES
C
C  DSLV IS FRACTION OF STORED PRODUCTS REMOVED BY
C   LEACHING EACH DAY
C  RIN IS INFILTRATION DELAY AND SMOOTHING FUNCTION
       RIN = 0.0
C  AIN IS FIVE DAY AVERAGE OF WATER INFILTRATION
       AIN = 0.0
       ADD = 0.7
       RETURN
       ENTRY REMOVE (DSLV, FLOW, M)
C  CALCULATE DAILY POTENTIAL EVAPOTRANPIRATION
C  EVAP IS SUBROUTINE TO CALULATE POTENTIAL EVAPORATION
C     IT RETURNS A MONTHLY AVERAGE POTENTIAL VALUE
       CALL EVAP (PEVAP )
C  SUBTRACT EVAPORATION FROM ROOT STROAGE
       DEFICT = PWHC - PWATER
C  POTENTIAL EVAPOTRANSIRATION DEPENDS ON MOISTURE
C  CONTENT OF GROUND
C
       EFF = 1. /EXP( 0.9*DEFICT/PWHC)
3060   CONTINUE
       PEVAP = PEVAP * EFF
       PEVAP = PEVAP/ 30.
       PWATER = PWATER - PEVAP
       RCAP = TCAP + DEFICT / 2.0
C  IF THERE IS NO RAINFALL, BYPASS INFILTRATION STEP
       IF(RAIN .EQ. 0.0) GO TO 3115
C  INFILTRATION RATE DECAYS EXPONENTIALLY
C  INTEGRATE TO GET INFLUX FROM STORM
       IF(RTIME .GT. 2.0 ) GO TO 3100
C  CALCULATE RNET
       RNET = CAP * (1.0 - EXP(-RTIME) )
       GO TO 3101
3100   RNET = CAP *(1.0 + EXP(-2.)* (RTIME - 3.0) )
3101   IF( RNET .GT. RCAP ) RNET = RCAP
       IF( RNET .GT. RAIN ) RNET = RAIN
       DEFICT = DEFICT / 2.0
       IF (RNET - DEFICT) 3110, 3120, 3120
C  NO MATTER HOW DRY GROUND IS, SOME WATER ENTERS SOIL
3110   PWATER = PWATER + 0.875 * RNET
       ADD = RNET / 8.
       GO TO 3130
3115   ADD = 0.0
       GO TO 3130
C  AUGMENT ROOT STORAGE WITH NEW RAINFALL
3120   PWATER = PWATER + DEFICT
       ADD = RNET - DEFICT
       IF (TMEAN .GE. 33.) GO TO 3130
3128   CONTINUE
C  ADD FREEZING WATER TO TANKB
       TANKB = TANKB + ADD
       RNET = 0.0
3130   CONTINUE
```

```
C  DETERMINE EFFECT OF TEMPERATURE ON INFILTRATION
      FV = EXP(A- 4203. /(TMEAN+460.) )
      TCAP = 0.7 * FV
C  REDUCE INFILTRATION CAPACITY DURING WINTER MONTHS
      IF(TMEAN .LE. 40. ) TCAP = 0.1
C  REDUCE INFILTRATION CAPACITY BY PRECEDING INFILTRATION
      TCAP = TCAP - DELAY
      IF (TCAP .LT. 0.0 )TCAP = 0.0
C  CALCULATE INFLUENCE OF RECENT PRECIPITATION OR MELTING
      DELAY = DELAY + ADD + TB
      DELAY = 0.7 * DELAY
C  INCLUDE RAINFALL IN INFILTRATION TOTALS
      RSUM = RSUM +ADD
      RSUMA = RSUMA + ADD
C
C  CALCULATE OUTFLOW
C  INCLUDE RECENT RAINFALL AND THAW CONDITIONS
C
C  CALCULATE TA
      TAA = 0.2 + 0.2 * TANKC
      TA = TAA * TANKA
      TB = 0.0
      IF( TANKB .EQ. 0.0) GO TO 3160
      TANKB = 0.98 * TANKB
C  CALCULATE TB
      IF(TMEAN .LT. 32.) GO TO 3160
      TB = 0.1 * (TMEAN - 32.)
      IF(TB .GT. TANKB) TB = TANKB
      TANKB = TANKB - TB
      IF(TANKB .LT. 1. E-10) TANKB = 0.0
      RCAP = TCAP - ADD
      IF( TB .GT. RCAP) TB = RCAP
C  INCLUDE SNOWMELT IN INFILTRATION TOTALS
      RSUM = RSUM + TB
      RSUMA = RSUMA + TB
3160  CONTINUE
C  TC IS TOTAL WATER TRANSFER TO TANKC
      TC = TA + TB
      TANKC = TANKC + TC
      FLOW = 0.01 * TANKC
      TANKC = TANKC * ( 1.0 - 0.0075  * TANKC)
      TANKA = TANKA - TA + ADD
      FLOW = FLOW * CONS
C  CALCULATE DSLV
      DSLV = 0.01 * AIN
```

```
C   DETERMINE NEW VALUE OF WATER INFILTRATION FUNCTION
          IF(AFLAG .EQ. 1.0) ADD = 0.75 * ADD
          IF(AFLAG .EQ. 2. ) ADD = 0.75 * ADD
          IF(AFLAG .EQ. 3. ) ADD = 0.50 * ADD
          RIN = RIN + ADD + TE / 2.
          ADD = RIN / 5.0
          RIN = RIN - ADD
          AIN = 0.75 * AIN
          AIN = AIN + ADD
C   RETURN TO MAIN PROGRAM
          RETURN
          END
```

```
   DATE        FLOW,GPD   ACID,LBS     RAIN, IN.

 JAN     1      187.       0.14014       0.0
 JAN     2      191.       0.15675       0.0
 JAN     3      193.       0.17073       0.0
 JAN     4      193.       0.18082       0.0
 JAN     5      193.       0.18680       0.0
 JAN     6      192.       0.18898       0.03000
 JAN     7      191.       0.19822       0.09000
 JAN     8      190.       0.19580       0.0
 JAN     9      189.       0.18180       0.0
 JAN    10      188.       0.17648       0.0
 JAN    11      187.       0.17006       0.13000
 JAN    12      187.       0.16414       0.0
 JAN    13      186.       0.15831       0.0
 JAN    14      185.       0.15243       0.0
 JAN    15      183.       0.14650       0.0
 JAN    16      182.       0.14057       0.0
 JAN    17      181.       0.13475       0.0
 JAN    18      179.       0.12913       0.03000
 JAN    19      178.       0.12400       0.0
 JAN    20      177.       0.11931       0.0
 JAN    21      176.       0.11500       0.0
 JAN    22      174.       0.11104       0.0
 JAN    23      173.       0.10743       0.15000
 JAN    24      173.       0.10542       0.0
 JAN    25      172.       0.10418       0.10000
 JAN    26      172.       0.10407       0.05000
 JAN    27      172.       0.10471       0.02000
 JAN    28      172.       0.10556       0.0
 JAN    29      171.       0.10617       0.73000
 JAN    30      171.       0.10735       0.0
 JAN    31      171.       0.10841       0.0


   GALLONS OF FLOW DURING MONTH IS      5631.
   POUNDS OF ACID DURING MONTH IS    4.4
   INCHES OF RAIN ENTERING STORAGE IS  0.09


   ACID REMOVED BY INUNDATION    0.004
   ACID REMOVED BY GRAVITY DIFFUSION    3.335
   ACID REMOVED BY LEACHING    1.909
```

```
   DATE          FLOW,GPD   ACID,LBS      RAIN, IN.

 FEB     1       170.        0.10899        0.0
 FEB     2       169.        0.10903        0.60000
 FEB     3       174.        0.11469        0.10000
 FEB     4       177.        0.12287        0.0
 FEB     5       179.        0.13089        0.07000
 FEB     6       180.        0.13792        0.0
 FEB     7       180.        0.14306        0.02000
 FEB     8       179.        0.14620        0.27000
 FEB     9       183.        0.15244        0.54000
 FEB    10       191.        0.16432        0.04000
 FEB    11       196.        0.17791        0.0
 FEB    12       198.        0.18947        0.0
 FEB    13       199.        0.19757        0.02000
 FEB    14       199.        0.20237        0.04000
 FEB    15       208.        0.20649        0.28000
 FEB    16       213.        0.21438        0.0
 FEB    17       215.        0.22364        0.0
 FEB    18       215.        0.22995        0.0
 FEB    19       214.        0.23265        0.0
 FEB    20       212.        0.23003        0.0
 FEB    21       211.        0.22478        0.0
 FEB    22       209.        0.21745        0.0
 FEB    23       207.        0.20865        0.0
 FEB    24       205.        0.19892        0.0
 FEB    25       203.        0.18907        0.0
 FEB    26       202.        0.17731        0.0
 FEB    27       200.        0.16690        0.0
 FEB    28       198.        0.15704        0.0

    GALLONS OF FLOW DURING MONTH IS       5485.
    POUNDS OF ACID DURING MONTH IS   5.0
    INCHES OF RAIN ENTERING STORAGE IS  0.44

    ACID REMOVED BY INUNDATION    0.084
    ACID REMOVED BY GRAVITY DIFFUSION   3.065
    ACID REMOVED BY LEACHING   2.931
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```
      DATE          FLOW,GPD   ACID,LBS     RAIN, IN.


   MAR       1        196.         0.14785        0.0
   MAR       2        195.         0.13909        0.11000
   MAR       3        200.         0.13566        0.0
   MAR       4        202.         0.13444        0.61000
   MAR       5        233.         0.16025        0.17000
   MAR       6        261.         0.21687        0.0
   MAR       7        276.         0.27908        0.0
   MAR       8        281.         0.34362        0.0
   MAR       9        282.         0.39245        0.0
   MAR      10        281.         0.42699        0.0
   MAR      11        278.         0.44924        0.0
   MAR      12        275.         0.44757        0.54000
   MAR      13        276.         0.44263        0.09000
   MAR      14        278.         0.44995        0.0
   MAR      15        277.         0.43834        0.0
   MAR      16        275.         0.42529        0.0
   MAR      17        272.         0.41105        0.0
   MAR      18        270.         0.39595        0.25000
   MAR      19        274.         0.38369        0.0
   MAR      20        274.         0.37254        0.0
   MAR      21        272.         0.36162        0.0
   MAR      22        270.         0.35055        0.0
   MAR      23        267.         0.32995        0.06000
   MAR      24        264.         0.31153        0.0
   MAR      25        262.         0.29485        0.11000
   MAR      26        261.         0.28065        0.0
   MAR      27        259.         0.26810        0.0
   MAR      28        257.         0.25005        0.75000
   MAR      29        261.         0.24419        0.31000
   MAR      30        269.         0.25273        0.0
   MAR      31        271.         0.26070        0.0


      GALLONS OF FLOW DURING MONTH IS        8072.
      POUNDS OF ACID DURING MONTH IS     9.8
      INCHES OF RAIN ENTERING STORAGE IS   1.02


      ACID REMOVED BY INUNDATION     4.292
      ACID REMOVED BY GRAVITY DIFFUSION     3.585
      ACID REMOVED BY LEACHING    3.678
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```
     DATE          FLOW,GPD   ACID,LBS      RAIN, IN.


   APR      1        271.        0.26673        0.15000
   APR      2        277.        0.27587        1.76000
   APR      3        318.        0.40289        0.0
   APR      4        336.        0.51431        0.0
   APR      5        341.        0.60547        0.0
   APR      6        340.        0.67552        0.16000
   APR      7        339.        0.72678        0.05000
   APR      8        336.        0.76133        0.0
   APR      9        332.        0.78143        0.0
   APR     10        327.        0.78963        0.0
   APR     11        322.        0.78839        0.0
   APR     12        318.        0.77999        0.0
   APR     13        313.        0.76636        0.14000
   APR     14        311.        0.74999        0.06000
   APR     15        308.        0.73200        0.0
   APR     16        304.        0.68321        0.0
   APR     17        300.        0.64017        0.0
   APR     18        297.        0.58158        0.0
   APR     19        293.        0.53165        0.30000
   APR     20        292.        0.49091        0.54000
   APR     21        312.        0.51937        0.0
   APR     22        319.        0.54601        0.0
   APR     23        320.        0.56753        0.37000
   APR     24        330.        0.58869        0.54000
   APR     25        365.        0.62209        0.0
   APR     26        377.        0.65529        0.0
   APR     27        378.        0.69184        0.0
   APR     28        374.        0.69909        0.25000
   APR     29        373.        0.70864        0.0
   APR     30        369.        0.71004        0.0


     GALLONS OF FLOW DURING MONTH IS      9792.
     POUNDS OF ACID DURING MONTH IS   18.8
     INCHES OF RAIN ENTERING STORAGE IS  1.39


     ACID REMOVED BY INUNDATION  12.719
     ACID REMOVED BY GRAVITY DIFFUSION    3.478
     ACID REMOVED BY LEACHING    6.072
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```
     DATE          FLOW,GPD   ACID,LBS     RAIN, IN.

    MAY     1       364.        0.70397      0.0
    MAY     2       358.        0.69166      0.16000
    MAY     3       354.        0.67578      0.0
    MAY     4       350.        0.65691      0.0
    MAY     5       345.        0.63579      0.0
    MAY     6       339.        0.61323      0.0
    MAY     7       334.        0.58995      0.0
    MAY     8       329.        0.56658      0.0
    MAY     9       325.        0.54361      0.0
    MAY    10       320.        0.52142      0.0
    MAY    11       315.        0.50026      0.0
    MAY    12       311.        0.48030      0.30000
    MAY    13       310.        0.46396      0.37000
    MAY    14       312.        0.45263      0.05000
    MAY    15       311.        0.44398      0.0
    MAY    16       308.        0.43618      0.48000
    MAY    17       310.        0.43200      0.0
    MAY    18       308.        0.42864      0.04000
    MAY    19       306.        0.40252      0.0
    MAY    20       302.        0.38012      0.0
    MAY    21       299.        0.36018      0.0
    MAY    22       295.        0.32914      0.0
    MAY    23       291.        0.30226      0.0
    MAY    24       287.        0.27877      0.65000
    MAY    25       291.        0.26329      0.0
    MAY    26       291.        0.25207      0.03000
    MAY    27       289.        0.24313      0.0
    MAY    28       286.        0.22677      0.0
    MAY    29       283.        0.21236      1.48000
    MAY    30       333.        0.27978      0.0
    MAY    31       355.        0.35095      0.0

     GALLONS OF FLOW DURING MONTH IS      9812.
     POUNDS OF ACID DURING MONTH IS  13.7
     INCHES OF RAIN ENTERING STORAGE IS  0.85

     ACID REMOVED BY INUNDATION    7.317
     ACID REMOVED BY GRAVITY DIFFUSION    3.006
     ACID REMOVED BY LEACHING    3.591
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     DATE          FLOW,GPD   ACID,LBS      RAIN, IN.


   JUNE     1      362.        0.41436        0.0
   JUNE     2      361.        0.45466        0.12000
   JUNE     3      358.        0.50123        0.45000
   JUNE     4      360.        0.52744        0.10000
   JUNE     5      358.        0.54330        0.0
   JUNE     6      354.        0.54915        0.0
   JUNE     7      349.        0.54624        0.0
   JUNE     8      344.        0.53624        0.0
   JUNE     9      338.        0.52089        0.0
   JUNE    10      333.        0.50180        0.0
   JUNE    11      328.        0.49034        0.0
   JUNE    12      324.        0.45766        0.0
   JUNE    13      319.        0.43465        0.25000
   JUNE    14      317.        0.41379        0.15000
   JUNE    15      316.        0.39546        0.80000
   JUNE    16      323.        0.38436        0.0
   JUNE    17      323.        0.37623        0.0
   JUNE    18      320.        0.36871        0.0
   JUNE    19      316.        0.36064        0.0
   JUNE    20      312.        0.35155        0.0
   JUNE    21      308.        0.34144        0.0
   JUNE    22      304.        0.31192        0.0
   JUNE    23      300.        0.28587        0.0
   JUNE    24      296.        0.25341        0.0
   JUNE    25      292.        0.22557        0.0
   JUNE    26      288.        0.20165        0.27000
   JUNE    27      288.        0.18304        0.78000
   JUNE    28      294.        0.17365        0.0
   JUNE    29      295.        0.16872        0.0
   JUNE    30      293.        0.16544        0.0


    GALLONS OF FLOW DURING MONTH IS      9673.
    POUNDS OF ACID DURING MONTH IS    11.4
    INCHES OF RAIN ENTERING STORAGE IS   0.36


    ACID REMOVED BY INUNDATION     4.559
    ACID REMOVED BY GRAVITY DIFFUSION    2.720
    ACID REMOVED BY LEACHING    5.028
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    DATE         FLOW,GPD    ACID,LBS      RAIN, IN.


  JULY     1       291.        0.16228        0.0
  JULY     2       287.        0.15854        0.23000
  JULY     3       286.        0.15034        0.12000
  JULY     4       285.        0.14392        0.75000
  JULY     5       291.        0.14848        0.0
  JULY     6       292.        0.15361        0.0
  JULY     7       290.        0.15744        0.0
  JULY     8       287.        0.15379        0.0
  JULY     9       284.        0.14905        0.0
  JULY    10       280.        0.14320        0.0
  JULY    11       277.        0.13408        0.06000
  JULY    12       274.        0.12522        0.0
  JULY    13       271.        0.11655        0.0
  JULY    14       268.        0.10683        0.0
  JULY    15       265.        0.09767        0.30000
  JULY    16       265.        0.09123        0.64000
  JULY    17       270.        0.09205        0.0
  JULY    18       271.        0.09481        0.0
  JULY    19       270.        0.09747        0.0
  JULY    20       268.        0.09775        0.31000
  JULY    21       269.        0.10038        0.0
  JULY    22       267.        0.10096        0.0
  JULY    23       265.        0.10049        0.0
  JULY    24       262.        0.09876        0.32000
  JULY    25       263.        0.09812        0.0
  JULY    26       262.        0.09732        0.0
  JULY    27       259.        0.09578        0.50000
  JULY    28       262.        0.09685        0.0
  JULY    29       262.        0.09830        0.10000
  JULY    30       261.        0.09969        0.50000
  JULY    31       265.        0.10362        0.0


     GALLONS OF FLOW DURING MONTH IS      8471.
     POUNDS OF ACID DURING MONTH IS    3.7
     INCHES OF RAIN ENTERING STORAGE IS  0.47


     ACID REMOVED BY INUNDATION   0.623
     ACID REMOVED BY GRAVITY DIFFUSION    1.590
     ACID REMOVED BY LEACHING   2.614
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```
       DATE        FLOW,GPD   ACID,LBS      RAIN, IN.


       AUG     1      265.        0.10748        0.0
       AUG     2      264.        0.10598        0.0
       AUG     3      261.        0.11065        0.21000
       AUG     4      261.        0.11093        0.0
       AUG     5      259.        0.11011        0.0
       AUG     6      257.        0.10723        0.0
       AUG     7      254.        0.10329        0.0
       AUG     8      251.        0.09848        0.0
       AUG     9      249.        0.09269        1.70000
       AUG    10      253.        0.09185        1.00000
       AUG    11      262.        0.09825        0.0
       AUG    12      264.        0.10611        0.0
       AUG    13      264.        0.11290        0.0
       AUG    14      262.        0.11746        0.0
       AUG    15      260.        0.11946        0.0
       AUG    16      257.        0.11816        0.0
       AUG    17      254.        0.11502        0.0
       AUG    18      252.        0.11039        0.03000
       AUG    19      249.        0.10457        0.0
       AUG    20      247.        0.09825        0.0
       AUG    21      244.        0.09163        0.12000
       AUG    22      243.        0.08589        0.88000
       AUG    23      248.        0.08532        0.0
       AUG    24      249.        0.08668        0.0
       AUG    25      249.        0.08815        0.0
       AUG    26      247.        0.09883        0.0
       AUG    27      245.        0.08838        0.0
       AUG    28      242.        0.08677        0.0
       AUG    29      240.        0.08393        0.0
       AUG    30      237.        0.08036        0.0
       AUG    31      235.        0.07628        0.0


         GALLONS OF FLOW DURING MONTH IS        7823.
         POUNDS OF ACID DURING MONTH IS     3.1
         INCHES OF RAIN ENTERING STORAGE IS  0.31


         ACID REMOVED BY INUNDATION     0.128
         ACID REMOVED BY GRAVITY DIFFUSION     1.707
         ACID REMOVED BY LEACHING    2.443
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        DATE         FLOW,GPD   ACID,LBS     RAIN, IN.


        SEPT     1       232.        0.07192        0.0
        SEPT     2       230.        0.06733        0.0
        SEPT     3       228.        0.06283        0.05000
        SEPT     4       226.        0.05884        0.50000
        SEPT     5       229.        0.05960        0.05000
        SEPT     6       230.        0.06018        0.0
        SEPT     7       229.        0.06209        0.0
        SEPT     8       228.        0.06354        0.0
        SEPT     9       226.        0.06420        0.70000
        SEPT    10       231.        0.06869        0.0
        SEPT    11       232.        0.07419        0.0
        SEPT    12       232.        0.07892        0.0
        SEPT    13       231.        0.08202        0.0
        SEPT    14       229.        0.08348        0.06000
        SEPT    15       227.        0.08377        0.0
        SEPT    16       226.        0.08289        0.0
        SEPT    17       224.        0.08096        0.0
        SEPT    18       221.        0.07814        0.19000
        SEPT    19       221.        0.07600        0.10000
        SEPT    20       221.        0.07461        0.17000
        SEPT    21       222.        0.07439        0.0
        SEPT    22       221.        0.07426        0.0
        SEPT    23       220.        0.07372        0.0
        SEPT    24       218.        0.07256        0.0
        SEPT    25       216.        0.07078        0.0
        SEPT    26       214.        0.06849        0.0
        SEPT    27       212.        0.06576        1.29000
        SEPT    28       222.        0.07144        0.0
        SEPT    29       227.        0.07992        0.0
        SEPT    30       228.        0.08820        0.0


          GALLONS OF FLOW DURING MONTH IS      6751.
          POUNDS OF ACID DURING MONTH IS    2.2
          INCHES OF RAIN ENTERING STORAGE IS  0.39


          ACID REMOVED BY INUNDATION    0.015
          ACID REMOVED BY GRAVITY DIFFUSION    1.750
          ACID REMOVED BY LEACHING    1.579
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        DATE          FLOW,GPD   ACID,LBS      RAIN, IN.


        OCT      1        228.          0.09474         0.0
        OCT      2        227.          0.09898         0.0
        OCT      3        225.          0.10086         0.30000
        OCT      4        226.          0.10209         0.0
        OCT      5        226.          0.10208         0.0
        OCT      6        224.          0.10074         0.0
        OCT      7        223.          0.09816         0.0
        OCT      8        221.          0.09449         0.0
        OCT      9        219.          0.09012         0.0
        OCT     10        217.          0.08531         0.55000
        OCT     11        220.          0.08290         0.45000
        OCT     12        225.          0.08365         0.0
        OCT     13        227.          0.08519         0.0
        OCT     14        227.          0.08634         0.81000
        OCT     15        233.          0.09070         0.10000
        OCT     16        237.          0.09575         0.0
        OCT     17        238.          0.09983         0.0
        OCT     18        237.          0.10222         0.0
        OCT     19        235.          0.10275         0.0
        OCT     20        233.          0.10157         0.0
        OCT     21        231.          0.09865         0.42000
        OCT     22        233.          0.09699         0.13000
        OCT     23        234.          0.09587         0.0
        OCT     24        233.          0.09445         0.0
        OCT     25        232.          0.09239         0.0
        OCT     26        230.          0.08930         0.0
        OCT     27        228.          0.08565         0.0
        OCT     28        226.          0.08158         0.0
        OCT     29        224.          0.07725         0.60000
        OCT     30        227.          0.07561         0.73000
        OCT     31        235.          0.07873         0.0


          GALLONS OF FLOW DURING MONTH IS       7080.
          POUNDS OF ACID DURING MONTH IS    2.9
          INCHES OF RAIN ENTERING STORAGE IS  0.51


          ACID REMOVED BY INUNDATION    0.023
          ACID REMOVED BY GRAVITY DIFFUSION    1.882
          ACID REMOVED BY LEACHING    2.100
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DATE          FLOW,GPD   ACID,LBS     RAIN, IN.


     NOV      1      239.        0.08303        0.0
     NOV      2      239.        0.08684        0.60000
     NOV      3      244.        0.09292        0.10000
     NOV      4      247.        0.09871        0.06000
     NOV      5      247.        0.10324        0.0
     NOV      6      246.        0.10589        0.0
     NOV      7      244.        0.10655        0.0
     NOV      8      242.        0.10539        0.0
     NOV      9      240.      . 0.10196        0.0
     NOV     10      237.        0.09757        0.09000
     NOV     11      236.        0.09295        0.04000
     NOV     12      234.        0.08830        0.0
     NOV     13      232.        0.08358        0.04000
     NOV     14      230.        0.07870        0.48000
     NOV     15      233.        0.07652        0.32000
     NOV     16      237.        0.07667        0.0
     NOV     17      237.        0.07744        0.0
     NOV     18      236.        0.07791        0.0
     NOV     19      235.        0.07768        0.0
     NOV     20      233.        0.07662        0.25000
     NOV     21      233.        0.07595        0.13000
     NOV     22      233.        0.07565        0.0
     NOV     23      232.        0.07508        0.03000
     NOV     24      231.        0.07377        0.0
     NOV     25      229.        0.07199        0.0
     NOV     26      227.        0.06975        0.04000
     NOV     27      225.        0.06731        0.0
     NOV     28      223.        0.06466        0.0
     NOV     29      221.        0.06178        0.0
     NOV     30      219.        0.05883        0.10000


GALLONS OF FLOW DURING MONTH IS       7043.
POUNDS OF ACID DURING MONTH IS    2.5
INCHES OF RAIN ENTERING STORAGE IS  0.28


ACID REMOVED BY INUNDATION   0.044
ACID REMOVED BY GRAVITY DIFFUSION    1.858
ACID REMOVED BY LEACHING    1.674
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        DATE         FLOW,GPD   ACID,LBS      RAIN, IN.


     DEC      1      218.        0.05634       0.0
     DEC      2      217.        0.05409       0.0
     DEC      3      215.        0.05197       0.10000
     DEC      4      214.        0.05038       0.20000
     DEC      5      214.        0.04992       0.0
     DEC      6      214.        0.04985       0.0
     DEC      7      212.        0.04973       0.0
     DEC      8      211.        0.04941       0.0
     DEC      9      209.        0.04883       0.0
     DEC     10      207.        0.04799       0.0
     DEC     11      205.        0.04695       0.0
     DEC     12      204.        0.04576       1.00000
     DEC     13      238.        0.06292       0.0
     DEC     14      258.        0.08900       0.0
     DEC     15      267.        0.11698       0.0
     DEC     16      270.        0.14452       0.26000
     DEC     17      270.        0.16498       0.24000
     DEC     18      268.        0.17862       0.0
     DEC     19      266.        0.18174       0.0
     DEC     20      263.        0.18086       0.04000
     DEC     21      261.        0.17700       0.53000
     DEC     22      276.        0.17759       0.88000
     DEC     23      282.        0.18779       1.04000
     DEC     24      323.        0.26020       0.0
     DEC     25      340.        0.32330       0.0
     DEC     26      345.        0.37418       0.0
     DEC     27      344.        0.41230       0.0
     DEC     28      340.        0.43848       0.0
     DEC     29      336.        0.45423       0.0
     DEC     30      331.        0.46135       0.0
     DEC     31      326.        0.46161       0.0


        GALLONS OF FLOW DURING MONTH IS      8144.
        POUNDS OF ACID DURING MONTH IS    5.4
        INCHES OF RAIN ENTERING STORAGE IS   1.19


        ACID REMOVED BY INUNDATION    2.877
        ACID REMOVED BY GRAVITY DIFFUSION    2.116
        ACID REMOVED BY LEACHING    3.423
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SUMMARY OF DATA FOR 1970

GALLONS OF FLOW DURING YEAR IS     93776.

POUNDS OF ACID DURING YEAR IS        83.

INCHES OF RAIN ENTERING STORAGE IS  7.30
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APPENDIX D

INSTRUCTIONS FOR USE OF MAIN PROGRAM

The use of our program for prediction of flow rates and acid loads at other sites is described in this appendix. The discussion presumes that the reader is familiar with the technical content of the model and needs only "nuts and bolts" information to use the computer program for his system.

The application of this program requires that the user furnish three kinds of information:

1. Specific program statements as described below
2. Data describing system
3. Meteorological data

The user must furnish statements identifying the input and output channels of his computer installation. These statements have the form:

IN = Input channel number

IO = Printed output channel number

IP = Punched output channel number

The statements replace the IN, IO, and IP identities at the beginning of the program. These are channels 5, 6, and 7 respectively in the Ohio State University computer system. The other statements to be supplied in the main program are statements describing the fluctuations of the water table in relation to the coal seam. The new statements replace the section from statement 2306 through 2315. If inundation removal is unimportant, the water table section and also statements 1647 to 1653 may be deleted.

A description of the system is the first information to be read in as data. The variables and formats are shown in Table 8. The first data card contains the number of length (NFEET), layer (NLAYER), and depth (NDEPTH) increments which will be used to represent the coal seam. An output control (NPUNCH), described on the following page, is also read from the first card. The size, in feet, of the length (DI) and depth (DK) increments are read from the second card. Alkalinity of the ground water (ALKALI), the elevation of the top of the seam relative to a datum plane (TOP), and the slope of the seam relative to horizontal (SLOPE) are read from the third card. The fourth card contains an estimate of the water shed area of the mine (WSHED), the provisional water holding capacity (PWHC), and the initial root storage water level (PWATER). If no data are available, PWATER may be set equal to PWHC. Monthly values of the potential evapotranspiration are read from the fifth card. These values must be measured experimentally or estimated by an empirical technique (such as the Thornthwaite-Mather method (42)) for each site.

A set of NLAYER cards, one for each stratum or substratum, follows the initial data. In addition to the natural division between coal and shale layers, it is desirable to subdivide thick binder layers into thinner layers for computational purposes. In our test case, the coal layers were divided into sections of no greater than six inch thickness. The natural shale layers were one to four inches thick so no division was necessary. Each card contains a brief alphameric description of the stratum, the elevation of the bottom of the stratum relative to a datum plane, the oxygen consumption in the material in micrograms oxygen consumed per hour per cubic centimeter, and the void fraction of the binder.

The final batch of descriptive input data is the initial quantity of oxidation products stored in each incremental volume. If initial values are not known, they may be estimated by assuming they are zero (by inserting an appropriate number of blank data cards) and allowing the program to run for a simulated period of three to five years. Storage values will be built up in the STORE (I, J, K) array in this simulation. These values may be obtained as punched output by reading a positive value of NPUNCH on the first data card. The punched data may then be recycled as initial conditions.

Once the system has been described, day to day weather data are read into the program. Each daily data card contains the month and day, (AMONTH and IDAY), the inches of precipitation (RAIN), the hours of duration of the precipitation (RTIME), the mean temperature (TMEAN), and the oxygen mole fraction (OXY). Each of these data, except OXY, must be included on every card. OXY need only appear on the first card, and thereafter only when its value changes. The remaining data need only be read for positive changes, i.e., precipitation or temperature changes. Otherwise, the program will assume zero rainfall and constant temperature. During warmer weather, it is adequate to assume the monthly average temperature since the chief program use of the temperature data is the calculation of freeze-thaw information.

The month must be read in as standard three or four letter notation: Jan, Feb, Mar, Apr, May, June, July, Aug, Sept, Oct, Nov, Dec. No periods are to be used in these abbreviations.

In addition to the weather cards, output control cards may be included in the data deck. On these cards the word "Year" is punched instead of the month, and the year number of the preceding year may be punched. Placing a "Year" card at the end of a block of data will give a printout of the summary for total flow and acid load since the previous "Year" card. Monthly reviews are always printed, so the "Year" card permits quarterly or annual totals to be printed. The final data card must contain the word "End" in the month slot to terminate calculations.

The first output from the program is an echo of the descriptive data. The normal output from the program is the daily flow rate, acid load, and the quantity of precipitation. In addition, monthly totals of flow and acid load are printed. The monthly acid load is also divided into the amount removed by each of the three removal mechanisms. The total reflects the alkalinity of the ground water so it is less than the sum of the three subtotals. As was mentioned above, provision has been made for printing longer term summaries of flow and acid load data if such are desired.

TABLE 8

INPUT DATA FOR COMPUTER PROGRAM

Descriptive Data

		Variable	Format
Card 1			
	Columns 1-5	Number of layers	I5
	6-10	Number of depth increments	I5
	11-15	Number of length increments	I5
	16-20	Non-zero if final storage array desired as punched output	I5
Card 2			
	Columns 1-10	Length of perimeter increments, feet	F10.5
		Length of depth increments, feet	F10.5
Card 3			
	Columns 1-10	Ground water alkalinity, ppm $CaCO_3$	F10.5
	11-20	Maximum elevation of front of seam relative to datum plane	F10.5
	21-30	Slope of seam, per cent	F10.5
Card 4			
	Columns 1-10	Water shed area, square feet	F10.2
	11-20	Provisional water holding capacity, inches	F10.5
	21-30	Initial root storage water level, inches	F10.5
Card 5			
	Columns 1-5, 6-10 11-15, etc.	Monthly values of inches of potential evapotranspiration, in order, January through December	F5.2

TABLE 8
(continued)

		Variable	Format
		Descriptive Data	
Card 6 to NLAYER + 6			
Columns	1-8	Alphameric description of layer	2A4
	9-10	Blank	
	11-20	Elevation of front of layer relative to datum plane	F10. 5
	21-30	Oxygen consumption, micrograms per hour per cubic centimeter binder	F10. 5
	31-40	Void fraction, void volume per total volume	F10. 5
		Meteorological Data	
Normal data card			
Column	1	Blank	
	2-5	Month	A4
	6-8	Date	I3
	9-10	Blank	
	11-20	Precipitation, inches	F10. 5
	21-30	Duration of rainfall, hours	F10. 5
	31-40	Temperature, degrees Fahrenfeit	F10. 5
	41-50	Oxygen mole fraction	F10. 5
Summary card (as frequently as desired)			
Columns	2-5	The word "YEAR"	A4
	51-54	The year number, if desired	I4

TABLE 8
(continued)

Meteorological Data

	Variable	Format
Final card (place at end of data deck to terminate simulation)		
Columns 2-4	The word "END"	A3

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