THE EFFECT OF HYDROLOGIC ZONATION UPON THE ACID PRODUCTION POTENTIAL OF PYRITIC ROCK

by

Edward G. Leach III

Earth Management Systems
Columbia, South Carolina

and

Frank T. Caruccio

Department of Geological Sciences
University of South Carolina
Columbia, South Carolina 29208

ABSTRACT

Current coal mine reclamation strategies often attempt to limit acid mine drainage (AMD) by restricting the infiltration of water through the use of plastic liners and clay caps. Although these efforts may effectively reduce the infiltration of water, they cannot prevent the oxidation of pyrite and inundation of spoil has been suggested as an alternative means of significantly lowering acid loads from mines. This study was conducted to evaluate the effects of inundation upon acid loads.

Three broad hydrologic zones were evaluated in this study because of a corresponding zonation in oxygen concentrations within mine spoils: (1) the vadose zone or zone of high oxygen concentration (>0.5%) , (2) the zone of water-table fluctuation or zone of alternately high and low oxygen concentration , and (3) the saturated zone or zone of low oxygen concentration (< = 0.0015 %). Use of statistical design procedures allowed quantitative evaluation of three major factors affecting acid production: (1) lithology (rock type, neutralization potential, pyritic sulfur content and all other factors ascribed to a particular rock), (2) hydrologic zone, and (3) duration of leaching. Sulfate and acid load data collected from weekly leachings of columns simulating the exposure of a pyritic sandstone and shale to each of the hydrologic zones were used to determine weathering rates and rates of acid production. Statistical analysis using an analysis of variance (ANOVA) model found that there was a 99% or greater probability that hydrologic zone did affect sulfate and acid loads. Comparison of acid loads showed that the zone of water-table fluctuation yielded 24% less acid than the vadose zone and the saturated zone 95% less. Inundation appears to effectively limit acid loads from mine spoils even where a substantial zone of water-table fluctuation is

present. Maximum reductions in acid loads should result by saturating a maximum portion of the total spoil. Application of these findings to the design of active mines may substantially reduce AMD in the future.

BACKGROUND

Overview

Acid mine drainage (AMD), is frequently characterized by high total dissolved solids, low pH, high metal concentrations, free mineral acidity, and significant noncarbonate hardness (Biesecker and George 1965). AMD results from the exposure of metallic minerals, particularly pyrite, to atmospheric oxygen concentrations, followed by hydrolysis of the weathering products and transport of these materials from the mine site. Mitigation of the effects of AMD has become a vital concern of mining companies, regulatory agencies, and residents of coal mining regions. A review of prevailing AMD treatment technologies can be found in Caruccio et al. (1988).

Hydrology

-General-

Water is perhaps the most important single factor in AMD. Water acts as a reactant in pyrite weathering reactions, but may also function to restrict oxygen availability under submerged conditions (Watzlaf and Erickson 1986). Water solubilizes weathered salts to produce acidity and serves as a transport medium for the acidity and other dissolved constituents. Acidic water within the mine may accelerate hydrolysis reactions and acid production. Alkaline waters, on the other hand, may neutralize acidity and slow weathering reactions.

-Previous Studies-

One of the most comprehensive series of studies of the hydrology of a strip-mined basin was conducted by Musser(1964), Kreiger(1985) and Collier et al. (1964,1970) of the U.S.G.S. from 1955 - 1974. These studies evaluated water budgets, stream and lithologic characteristics, water geochemistry, and the impact of mining. The impact of mining upon water quality, sedimentation, and stream flow was established on the basis of contrasts afforded by a similar nearby basin which had not been mined.

Collier found that the spoil bank under study received almost all of its recharge, either directly or indirectly from local precipitation . A hydrologic profile of this spoil bank depicts distinct vadose and saturated zones. Pools, formed in lows of the mine floor north of the spoil bank, provided ground-water to the spoil bank during conditions of low water table. Direct infiltration, however, was found to be the dominate recharge mechanism. Rainfall events provided recharge within approximately 24 hours to the water-table both in the highwall and the spoil bank.

Hydrographs from the Beaver Creek site reveal that patterns of water-table fluctuation were typically composed of two days of rising water levels followed by three days of falling water levels. Also, water within the spoil bank and pools was found to be much more acidic than that in the highwall. Collier explained these elevated levels of acidity as a function of the high oxygen levels at these locations.

A study by Snyder (1987) found distinct saturated and vadose zones to exist within portions of the backfill of a reclaimed coal mine in Upshur County, West Virginia. The saturated zone was found to result from a combination of water seeping from the unmined areas into the more permeable fill, a rock barrier at the toe of the spoil, and the mine pavement dipping toward the highwall. This saturated zone persisted throughout the year and one-half duration of his study.

In another study, Watzlaf and Hammack (1989) compared rates of acid production from leaching a pyritic shale under submerged nonflowing conditions and vadose conditions. They found that acid production was reduced by a factor of approximately 26 by submergence in nonflowing water. Watzlaf and Hammack attributed the contrast in rates of acid production to the 340 percent or greater reduction in oxygen concentration effected by submergence.

A study conducted by Lusardi and Erickson (1985) at an abandoned strip mine in Clarion County, Pennsylvania assessed site hydrology and pore gas composition and their relation to acid production. Among their findings were that: (1) the near surface strata contributed the largest portion of the total acid load, (2) that shallow interflow was highly acidic, (3) oxygen concentration generally decreased with increased depth, (4) pyrite oxidation had occurred for at least 20 years at the site, (5) acid salts accumulate within the spoil when infiltration is insufficient to provide transport and form a reservoir of acidity within the spoil, and (6) that acid load and concentration correlate in the vadose zone but not in the saturated zone.

OBJECTIVES

This study determined the impact of the hydrologic zonation of pyritic rock upon its acid production potential. The hydrologic zones (also referred to as hydrologic positions) used in this study were the vadose zone, zone of water-table fluctuation, and saturated zone. Vadose zone and saturated zone are widely used hydrologic terms. Zone of water-table fluctuation is a convention used for this study and shall be used to define that region which is alternately considered being in the vadose zone and the saturated zone; with the rise and fall of the water-table.

The viability of inundating backfill as a means of limiting AMD (Watzlaf and Hammack 1989) was addressed in this study by examination of the loads obtained from simulation of the three hydrologic zones expected to occur at sites in which inundation is implemented.

EXPERIMENTAL DESIGN AND METHODOLOGY

Overview

This experiment quantitatively evaluated the effect of hydrologic zone, lithology, and duration of leaching upon acid production by leaching two lithologies in columns simulating each of the three hydrologic conditions. Two repetitions of each of the six zone/lithology combinations were used to establish the natural variance of each combination. Leachings were conducted on a weekly basis to standardize duration of leaching effects. Sulfate load was used to evaluate weathering rates. Acid load was also evaluated because of the disparity between weathering rates and net acidity in many natural systems.

Simulation of Hydrologic Zones

Acrylic columns measuring 15.24 cm I.D. and approximately 60 cm. in length were modified according to three designs to model the three hydrologic zones. All columns were fitted with an porous acrylic plate which allowed the rock and water volumes in the columns to be calculated. The porous plate was overlain with approximately 0.6 cm of glass wool to retain fines in the column. The porous plates also allowed for an air-free saturated zone below the rock masses in the fluctuating water-table and saturated conditions. Each column contained approximately 0.01 m^3 of rock.

-Vadose Zone-

Vadose conditions were simulated by the apparatus shown schematically in figure 1. This design provided an oxygen gradient, such as exists in spoil banks, by use of a gas trap in the collection system. Leaching was accomplished by spraying the upper surface of the rock with 300 ml of deionized water to simulate rainfall. Three days of drainage time were allowed to provide ample time for gravity drainage.

-Zone of Water-Table Fluctuation-

The apparatus simulating the zone of water-table fluctuation is schematically depicted in figure 2. A gas trap was utilized in this design for the aforementioned reasons. Water is added through the funnel to provide conditions of a rising watertable. Water is withdrawn by loosening the tubing clamps below the column to simulate conditions of a falling water-table . An area of perennial saturation below the rock mass was maintained by draining water only to the bottom of the porous plate. In this manner, a more accurate representation of the relationship of this zone to the saturated zone was accomplished without requiring any of the rock mass to be perpetually submerged. Collection of drainage water progressed in a cumulative fashion with each days contribution flowing into the large collection bottle until the drainage cycle was completed. Over a period of one week the entire mass of rock was progressively submerged and then drained so that the entire mass was subjected to conditions similar to water-table fluctuation.

-Saturated Zone-

Simulation of the saturated zone was accomplished by the apparatus shown schematically in figure 3. Continuous circulation of water throughout the column was achieved by use of a peristaltic pump delivering 7 ml/ min.. This flow rate circulated two complete pore volumes per day through the column. A tracer test using a miscible tracer (2.5% FD&C yellow #5 & blue #1 dispersed in a propylene glycol and water base) provided a time of approximately 2 1/2 hours for full mixing and circulation of the tracer throughout the column suggesting that dispersion and diffusion may cause a faster rate of circulation of ions through the column. The discharge line was kept 1.3 cm or more below the surface to limit the input of oxygen to the system to that provided by diffusion from the atmosphere into the water. Furthermore, 2-5 cm layer of water covered the rock at all times. Samples were collected by drainage of 250 ml from the bottom of the column by loosening the tubing clamps.

Rock Preparation

All rock utilized in the study was collected from mine spoil piles, broken to cobble size (20-30 cm), and transported to USC. Cobbles were reduced by hammer and jaw crusher until a fraction which would pass a 1.25 cm sieve was produced. Successive recombination of rock material at each crushing and sieving step produced at least 5 mixing events prior to final sizing of the rock to 0.63- 1.25 cm. At the completion of sizing approximately 90 kg of each lithology was divided randomly among 13 buckets, 2.7 kg at a time, to assure representative sampling of the rock.

Experimental Procedures

-Set-up-

A double layer of glass wool approximately 0.5 cm. thick was placed on top of the porous plate in all columns to retain fines. Rock was then collected in a ceramic cup, weighed on a triple beam balance to the nearest 0.1 gram, and hand placed so as to prevent compaction and provide uniform packing. Approximately 20 - 21 cups of rock (approximately 10 kg) were used to fill each column. Additionally, precautions were used to exclude excess air from those columns simulating fluctuating and saturated conditions. The glass wool was submerged immediately after filling and bubbles were eliminated by tilting and tapping the column and manipulating the tubing. Water was added incrementally with rock addition so as to maintain saturated bubble-free conditions. Fluctuating zone columns were filled with sufficient water so that only 0.5 cm of rock was exposed. Saturated zone columns were filled to approximately 3.8 cm above the rock level and circulation of water begun immediately after filling.

-Leaching Schedule-

Ideally, all columns should have been leached on exactly the same day throughout the experiment. This, however, was not possible because of time restraints imposed by the analysis schedule as well as periodic apparatus problems which required immediate attention. As the next best option, each group of four columns depicting a single hydrologic zone was leached on the same days and all groups were leached within the same week. Leachings were conducted on a 7 day interval. Vadose columns received 19 leachings and all others 18 leachings. 300 ml of deionized water was used to leach vadose columns, approximately 4.3 1 for zone of water-table fluctuation columns, and 250 ml for saturated columns.

-Analysis Performed-

Upon collection of effluent samples, volume was recorded to the nearest milliliter. A 100 ml aliquot was withdrawn and acidified for total iron and ferrous iron determination as proscribed by the phenanthroline method (Standard Methods 1980). Within 6 hours of collection pH, specific conductivity, hot pH, and acidity were determined. Sulfate was determined within 30 days from stored samples by colorimetric means using the automated methylthymol blue method as outlined in Standard Methods (1980) on a Technicon Auto-

Analyzer II (1977).

Determination of pH was made on a Fisher Accumet model 830 pH meter with combination electrode using a pH=3.00 standard buffer. Hot pH was determined after hot peroxide treatment (Standard Methods 1980) using a pH = 9.00 standard buffer. The same aliquot used for hot pH was then used in potentiometric titration of acidity with 0.002, 0.02, or 1.00 N NaOH to an endpoint of 8.3. Titrant normality was determined weekly by titrating with 0.05 N $KHC_8H_4O_4$.

Specific conductivity was determined by a Uniloc model 770 TDS/ Conductivity analyzer utilizing a cell constant of 2.0 with 0.001 N and 0.01 N KCl solutions. All measurements are reported as microsiemens/cm and corrected to 25oC.

Total iron was determined spectrophotometrically by measuring absorbance on a Perkin-Elmer model 306 Atomic Absorption unit at 248 ran UV with an air-acetylene flame (Perkin-Elmer 1982). Ferrous iron was determined on Bausch and Lomb Spectronic 20 after complex formation with phenanthroline. A blank solution containing all constituents other than the effluent was used to select the optimum wavelength prior to each run (generally 533 mn) [Bausch and Lomb] . Standards of 0.5, 1.0, 2.0, and 3.0 ppm Fe^{+2} were utilized to plot best fit lines for determining unknown concentrations (Fritz and Schenk 1979). Ferric iron was determined by subtraction of ferrous iron from total iron.

RESULTS AND DISCUSSION

Hydrologic Zonation Upon Acid Production

-Graphical Data-

A clear effect of hydrologic zonation upon sulfate and acid loads is indicated by plots of cumulative load. Plots of cumulative sulfate load vs. time for the Preston County sandstone (fig. 4), and for the Eagle Eye shale (fig. 5), shows a distinct division of the six columns into three distinct pairs of trends - each pair corresponding to a separate hydrologic zone. The abbreviations V-1 and V-2 were used throughout the report to represent the vadose columns, F-1 and F-2 to represent the fluctuating columns, and S-1 and S-2 to represent the saturated columns.

Plots of cumulative acid load vs. time follow (figs. 6 & 7) on successive pages. These plots utilize the same legends, but indicate a more pronounced separation of trends.

Two salient characteristics of these plots are: (1) the clear division of trends along hydrologic boundaries as seen before and (2) time related variations in the slope of those trends representing vadose and fluctuating conditions.

Lithology (i.e. shale or sandstone) is the most significant factor in this study in terms of impact upon sulfate and acid loads. Hydrologic zonation is also an important factor as indicated by the large contributions made by zone and zone/lithology effects. Duration of treatments played a lesser role in determining loads.

Role of Bacteria

During the first week of the experiment all columns were inoculated with 3 ml of 9K media containing active Thiobacillus which had been propagated from a standard culture. Confirmatory tests for Thiobacillus were then conducted weekly to biweekly for the duration of the experiment using observation of color change in the 9K media as prescribed in Standard Methods (1980). 'nose columns simulating the zone of water-table fluctuation showed rapid establishment of bacterial colonies.

Columns simulating the saturated zone developed a bacterial scum along the surface in the third week. This scum developed three days sooner in the columns filled with the Eagle Eye shale and showed a much greater development in these columns throughout the experiment. Saturated zone columns containing the Preston County sandstone developed a thin film of bacteria with locally visible accumulations of iron precipitates. Rapid development of a continuous sheet of precipitated iron across the entire surface of the columns containing the Eagle Eye was followed by the downward migration of a scum along the inner sides of the column beginning at the water-line.

Spheres of precipitated iron up to 1 cm in diameter also formed in the near surface zone of these same columns, probably as a manifestation of colonial bacterial development. Dr. Eleanora Robbins of the U.S. Geological Survey identified Leptothrix and Siderocapsa as well as euhedral hematite crystals from samples of the surface scum of these saturated zone columns during the fourth week of leaching. Vigorous precipitation of ferrihydrate followed by spontaneous dehydration to hematite is characteristic of the aforementioned genera (Robbins et al. 1988) and helps explain the thick floating layer of iron in the Eagle Eye columns.

Confirmatory tests of water from the bottom of saturated zone columns were negative until the eighth week. Positive confirmatory tests for the remainder of the experiment indicated that ' Thiobacillus or some other chemoautotroph was able to exist more than 50 cm below the surface in a flowing groundwater regime although no significant acid production was witnessed. Lack of significant acid production in the saturated columns may be accounted for by the oxygen dependency of the acidity reactions. Lau et al. (1970) noted the rate of reactions, and not the reactions themselves, to be affected by bacterial mediation. Both abiotic and biotic oxidation of pyrite proceeds by the reaction [1] and [2] (Singer and Stumm 1969) :

$$14Fe^{+2} + 3.5O_2 + 14H^+ = 14Fe^{+3} + 7H_2O \qquad [1]$$

$$FeS_2 + 14Fe^{+3} + 8H_2O = 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad [2]$$

Columns simulating the vadose zone were inoculated three times because of continued negative confirmatory tests. Evidence of elevated levels of ferric iron began at week ten for the shale and week eleven for the sandstone implying the action of Thiobacillus. Week twelve brought confirmation of chemoautotrophs using the 9K media.

The early response of the columns depicting the zone of water-table fluctuation appears to demonstrate that this zone is most conducive to growth of Thiobacillus. Sulfate load vs days plots for the zone of water-table fluctuation revealed that a large concentration of weathering products was solubilized in the first week of the experiment as a result of the initial drainage event. Large concentrations of dissolved iron and sulfate in a solution with a pH of 2.7 - 4.2 was brought into contact with the full rock volume over a 3.5 day period creating a highly favorable environment for bacterial growth.

CONCLUSIONS

A definitive impact of hydrologic zonation upon the rate of pyrite weathering and resultant acid load was established in this study. This impact is a direct consequence of the differences in oxygen concentration which characterize each zone as a result of differing conditions of saturation. The vadose or high oxygen zone produced the greatest weathering rates and acid loads. 'ne zone of water-table fluctuation or intermediate oxygen zone produced an intermediate level of weathering and acidity as indicated by sulfate loads 25-33% less than those of the vadose zone and acid loads 19-27% less. The saturated or low oxygen zone produced the lowest levels of weathering and acidity. Sulfate loads were 92-93% less than those of the vadose zone and acid loads 94-97% less.

The existence of lower sulfate and acid loads for fluctuating conditions than for vadose conditions is significant in that it indicates that conditions of rising and falling water-table may not result in the high acid loads predicted by many scientists and mine operators. This new knowledge of acid production in the zone of influence of the water-table should encourage those considering inundation as a means of limiting acid and sulfate loads. Water-table fluctuations which inevitably accompany the maintenance of a pool of water within the spoil, need not be considered as innately undesirable. This study demonstrated that a fluctuating condition is preferable to a vadose condition unless flushing of weathering products from the vadose zone can be prevented.

Based on the results of this study, reclamation schemes which will saturate a maximum amount of spoil should be encouraged. Acid loads in the zone of saturation are minimal and hence the greater the extent of the zone of saturation the greater the reduction in acid loads from the site.

Results of this study suggest that bactericides may be most effective if applied in that portion of the spoil which experiences water-table fluctuations. The development of a floating bactericide may be the most practical means of distributing such an inhibitory agent in this zone with the maximum success.

REFERENCES CITED

American Public Health Association. 1980. Standard Methods for the Examination of Water and Wastewater. 15" ed., Washington, D.C.:A.P.H.A. 1134p.

Bausch and Lomb. Spectronic 20 Spectrophotometer Operating Manual. 4th ed. Bausch and Lomb. Rochester, NY.

Biesecker, J.E. and J.R. George. 1965. Stream Quality in Appalachia as Related to Coal-Mine Drainage. U.S.Geol. Survey. Cir.526. U.S.Govt. Printing Office, Washington,D.C.

Caruccio, F.T., L.R. Hossner, and Gwendelyn Geidel. 1988. Pyritic Materials: Acid Drainage, Soil Acidity, and Liming. in Reclamation of Surface Mined Lands vol.l. ed. L.R. Hossner. CRC Press, Boca Raton, FL.

Collier, C.R. and others. 1964. Influences of Strip Mining on Parts of Beaver Creek Basin, Kentucky, 1955-59. U.S.G.S. Prof. Paper 427-B. U.S.Govt. Printing Office. Washington, D.C. 85p.

Collier, C.R., R.J. Pickering, and J.J. Musser. 1970. Influences of Strip Mining on Parts of Beaver Creek Basin, Kentucky, 1955-66. U.S.G.S. Prof. Paper 427-C. U.S.Govt. Printing Office. Washington, D.C. 80p.

Fritz, S.F. and G.H. Schenk. 1979. Quantitative Analytical Chemistry. 4th ed., Allyn and Bacon Inc., Boston, Mass. pp.69-109.

Kleinmann, R.L.P. and D.A. Crerar. 1979. Thiobacillusferrooxidans and the Formation of Acidity in Simulated Coal Mine Environments. J. Geomicrobiology 1:373-388.

Krieger, R.A. 1985. Influences of Strip Mining on Parts of Beaver Creek Basin, Kentucky, 1973-74. U.S.G.S. Prof. Paper 427-D. U.S. Govt. Printing Office. Washington, D.C. 63p.

Lau, C.M., K.S. Shumate, and E.E. Smith. 1970. The Role of Bacteria in Pyrite Oxidation Kinetics. in Proc., Third Symposium on Coal Mine Drainage Research, Mellon Inst. pp.114-122.

Lasardi, P.J. and P.M. Erickson. 1985. Assessment and Reclamation of an Abandoned Acid-Producing Strip Mine in Northern Clarion County, Pennsylvania. in Proc. 1985 Symp. on Surface Mining, Hydrology, Sedimentology, and Reclamation. University of Kentucky. Lexington, KY. pp.313-321.

Operations in Parts of Beaver Creek Basin Kentucky. U.S.G.S. Prof. Paper 427-A. U.S. Govt. Printing Office. Washington, D.C., 25p.

Perkin-Elmer. 1982. Analytical Methods for Atomic Absorption Spectrophotometry. Perkin-Elmer. Norwalk, Conn.

Robbins, E.I., G.L. LaBerge, and R.G. Schmidt. 1988. A Model for the Biological Precipitation of Precambrian Iron Formations-B: Morphological Evidence and Modern Analogs. in USGS Research on Energy Resources -1988 Program and Abstracts. USGS circular 1025. pp.97-139.

Singer, P.C. and W. Stumm. 1969. Oxidation of Ferrous Iron in Mine Drainage Waters. 157 th National Meeting, Am. Chem. Soc., Div. of Fuel Chem. Vol. 13, No. 2, pp. 80-87.

Snyder, D.T. 1987. The Partitioning of Flow Components of Acidic Seeps from Surface Coal Mines and the Identification of Acid Producing Horizons in the Backfill. M.S. thesis. Univ. of South Carolina. Columbia.

Stumm, W. and J. Morgan. 1981. Aquatic Chemistry: an Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley and Sons. pp.469-470.

Technicon. 1977. Technicon Auto-Analyzer 11, Sulfate in Water and Wastewater: Technicon

Industrial Systems. Tarrytown, NY

Watzlaf, G.F. and P.M. Erickson. 1986. Topical Amendments of Coal Refuse: Effect on Pore Gas Composition and Water Quality. in Proc. Nat'l Symp. on Mining, Hydrology, Sedimentology, and Reclamation. Lexington, KY, pp.313-321.

Watzlaf, G.F. and R.W. Hammack. 1989. The Effect of Oxygen, Iron-Oxidizing Bacteria, and Leaching Frequency on Pyrite Oxidation. in Proc. 9th Annual W. Va. Surface Mine Drainage Task Force Symp., Morgantown, W. Va.

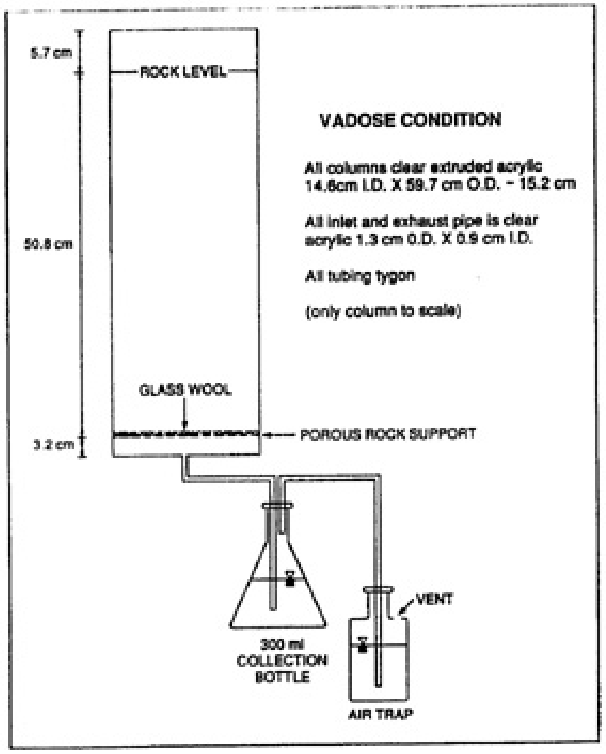

Figure 1- Schematic of Vadose Condition Column

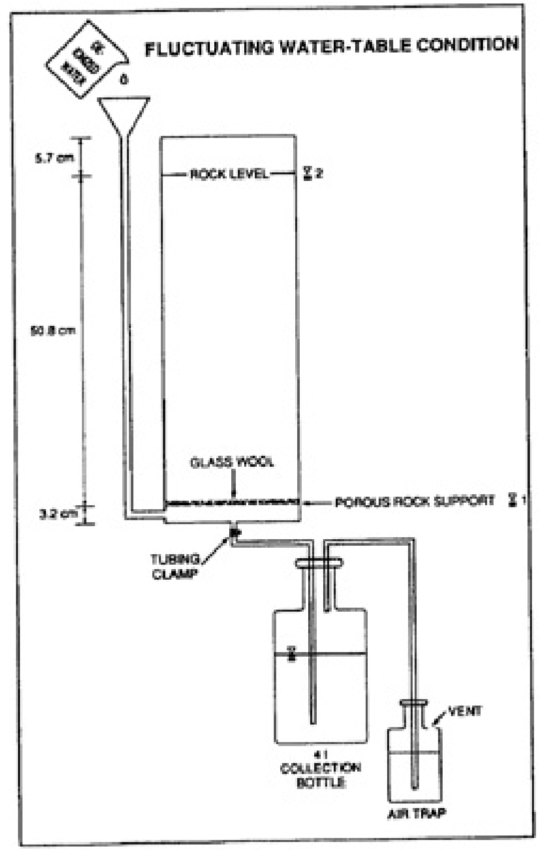

Figure 2 - Schematic of Fluctuating Condition Column

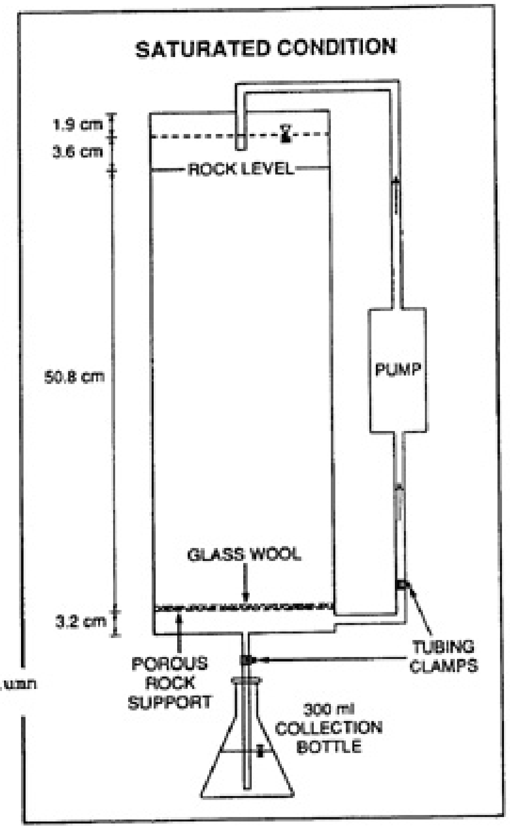

Figure 3- Schematic of Saturated Condition Column

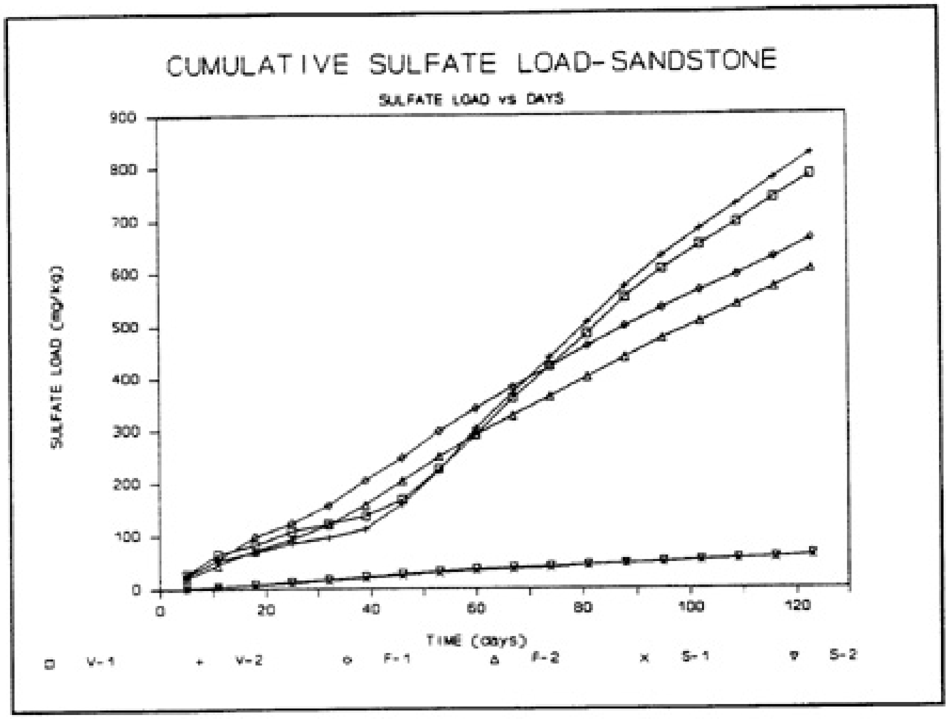

Figure 4 - Cumulative Sulfate Load vs Time:Sandstone

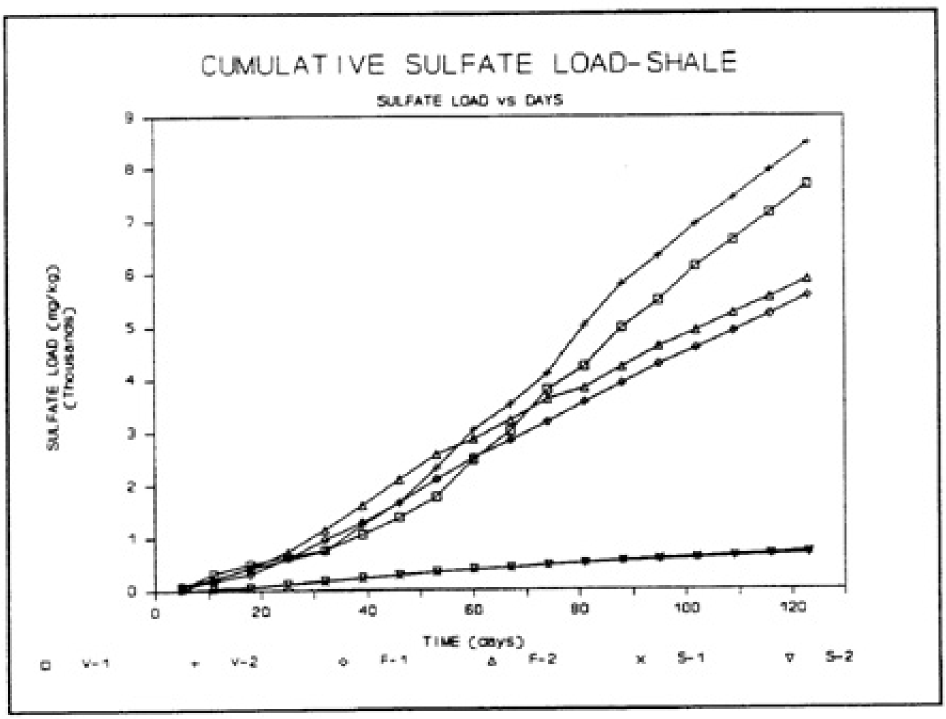

Figure 5 - Cumulative Sulfate Load vs Time:Shale

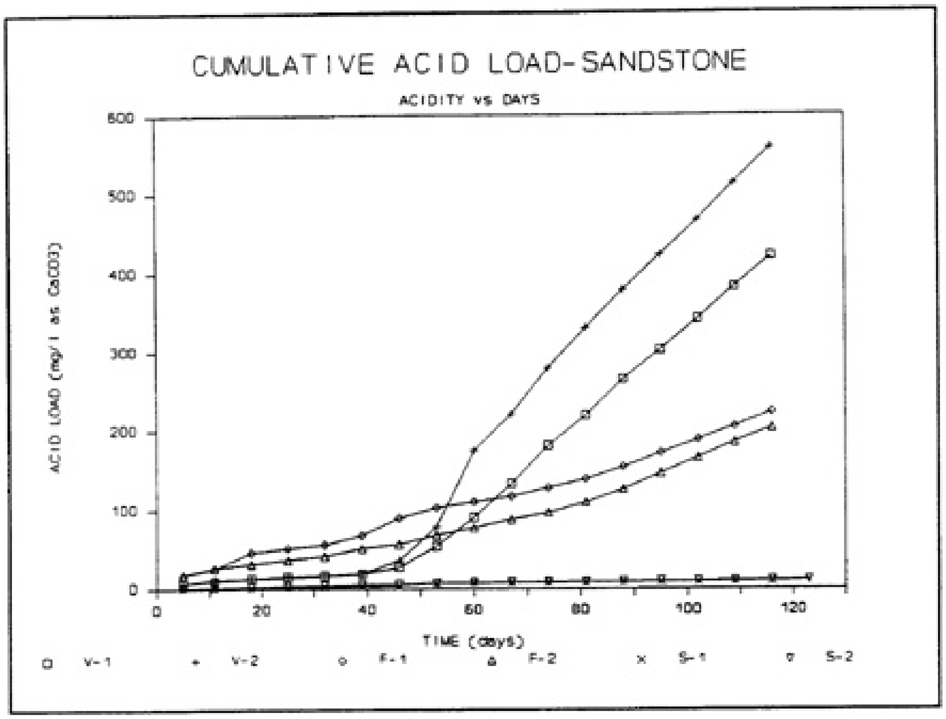

Figure 6 - Cumulative Acid Load vs Time:Sandstone

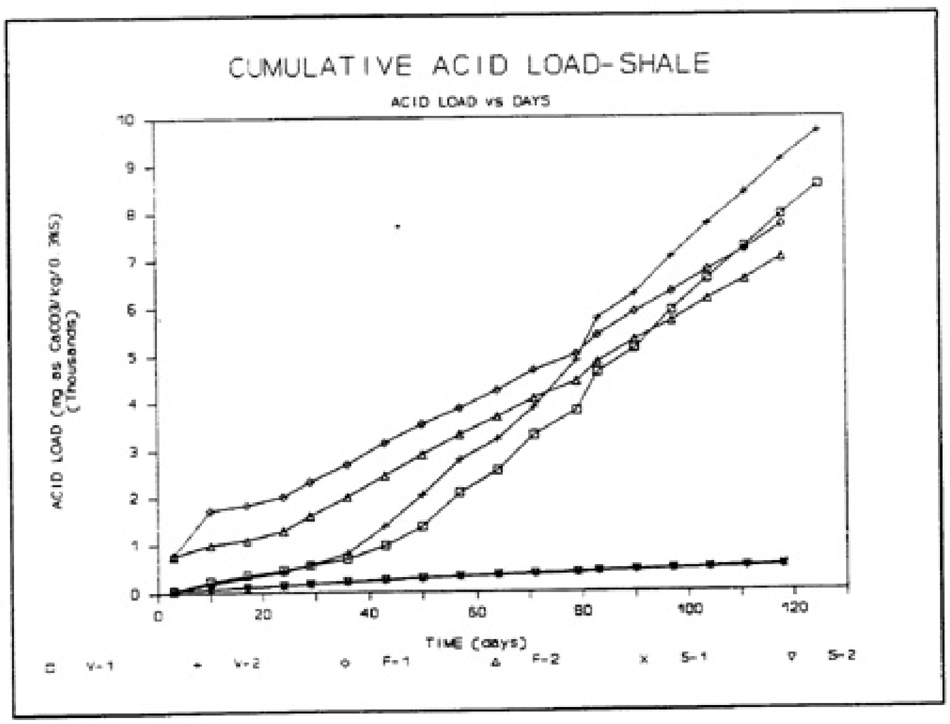

Figure 7 - Cumulative Acid Load vs Time:Shale