

## 1. INTRODUCTION

The need for treatment of stream pollution caused by AMD (acid mine drainage) and, more recently, acid rain, has stimulated the development of methods for the neutralization of these acid discharges. While crushed limestone aggregate is usually the most economical neutralization reagent available, lime and powdered limestone are the most commonly used reagents due to their higher reactivities.

There are several reasons for the limited use of crushed limestone to date. The primary reason is a lack of practical process design procedures. Previous investigators found that slow reaction rates and coating of the limestone surfaces inhibited the neutralization process. However, once the limitations of limestone treatment are understood, rational design procedures can be developed which account for these factors.

There are several major advantages to be gained by using crushed limestone rather than lime for AMD neutralization. They include:

- Low reagent cost (about one sixth the cost of lime);
- Low sludge volume, and dense, easily dewatered sludge;
- The impossibility of overtreatment reduces process control costs;
- Safer reagent handling with minimal storage problems;
- Potentially simpler process design with reduced capital, and operation and maintenance costs.

**Study Scope:** The intent of the study described in this report is to evaluate the use of crushed limestone to neutralize the AMD from the Quakake Tunnel. The site was selected by the Department because of its low iron loadings, small flow fluctuations and moderate acidity; conditions which were considered conducive to the use of limestone for AMD neutralization. In order to accomplish the project objectives in a practical manner, the study was divided into, a series of logical steps. The first phase of the work consisted of gathering and analyzing all available data relative to limestone neutralization methods. In conjunction with the literature review, water quality and hydrologic data for the project site were gathered over a one year period (1973/74). Background data were also gathered on the streams receiving the tunnel discharges.

During the review of existing literature, it became apparent that the only proposed design procedures available were those developed by Pearson and McDonnell (1, 2, 3) at the Pennsylvania State University. These design procedures were based on theoretical derivations and empirical data obtained from laboratory experimentation. Small scale experiments were conducted using the Quakake AMD and were compared with Pearson and McDonnell's procedures. No conflicting data were produced by these experiments and the design of the chemical processes was determined in accordance with their proposed procedures.

After analysis of the data gathered in this initial stage, several promising limestone neutralization processes were identified. At this point, it was decided to construct several small scale prototypes of each of the viable processes, rather than commit

substantial funds to a larger scale project with an untried process. The prototypes were designed and constructed in 1978 and 1979 and operated for four separate trial periods during 1979, 1980, and 1981. Results of the individual trials were evaluated between operation periods and appropriate procedural adjustments were made for the subsequent trial runs. The data gathered during the prototype operations has been used to develop design procedures for full scale treatment of the Quakake discharge. These design procedures should be applicable to the abatement of AMD discharges from other sources.

**The Quakake Tunnel:** The Quakake Tunnel outfall is located in Packer Township, Carbon County, Pennsylvania. The tunnel discharges to Wetzel Creek, a tributary to Quakake Creek. Quakake Creek feeds into Black Creek and ultimately to the Lehigh and Delaware Rivers. The Quakake Tunnel AMD discharge is the largest single acid contributor to this drainage system. The project's general location is shown in Figure 1.1.

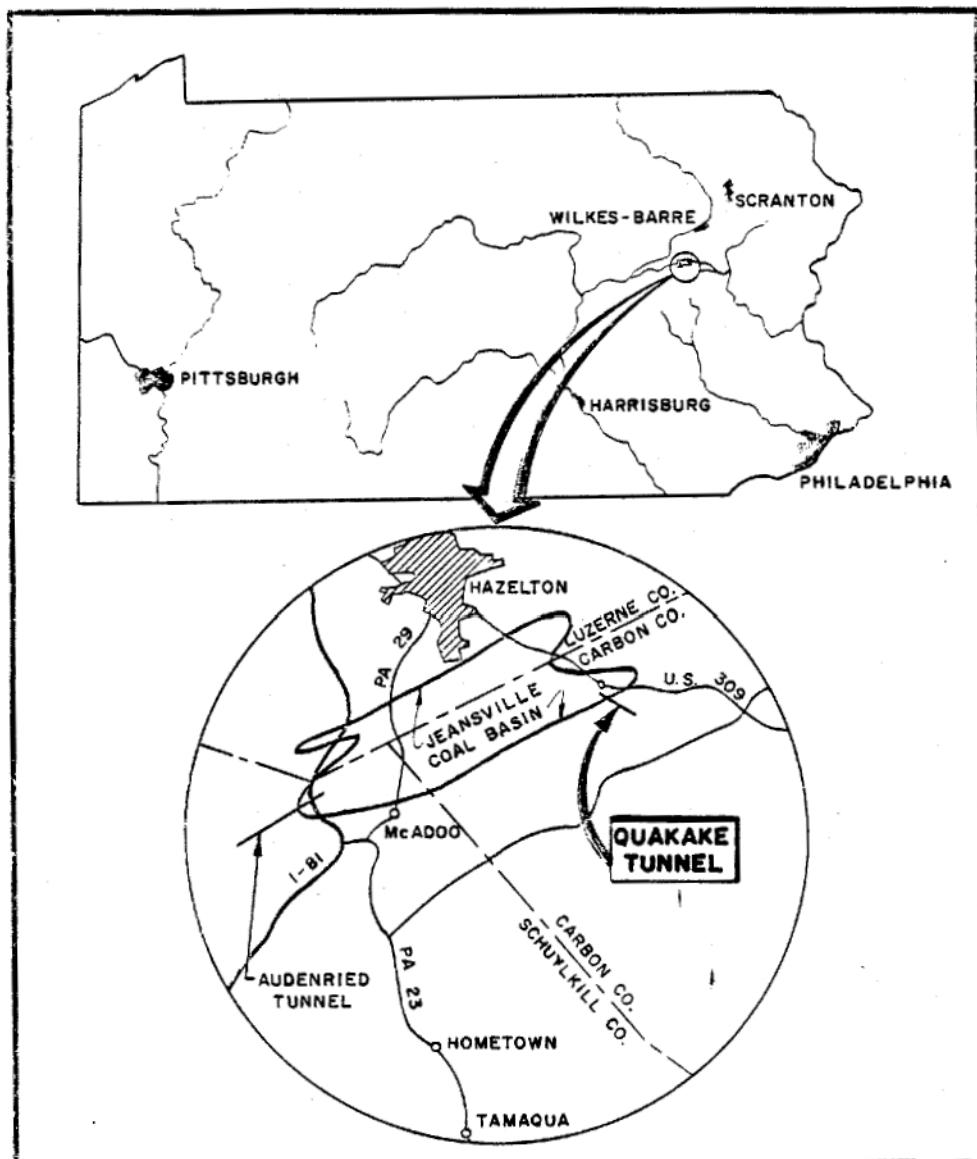
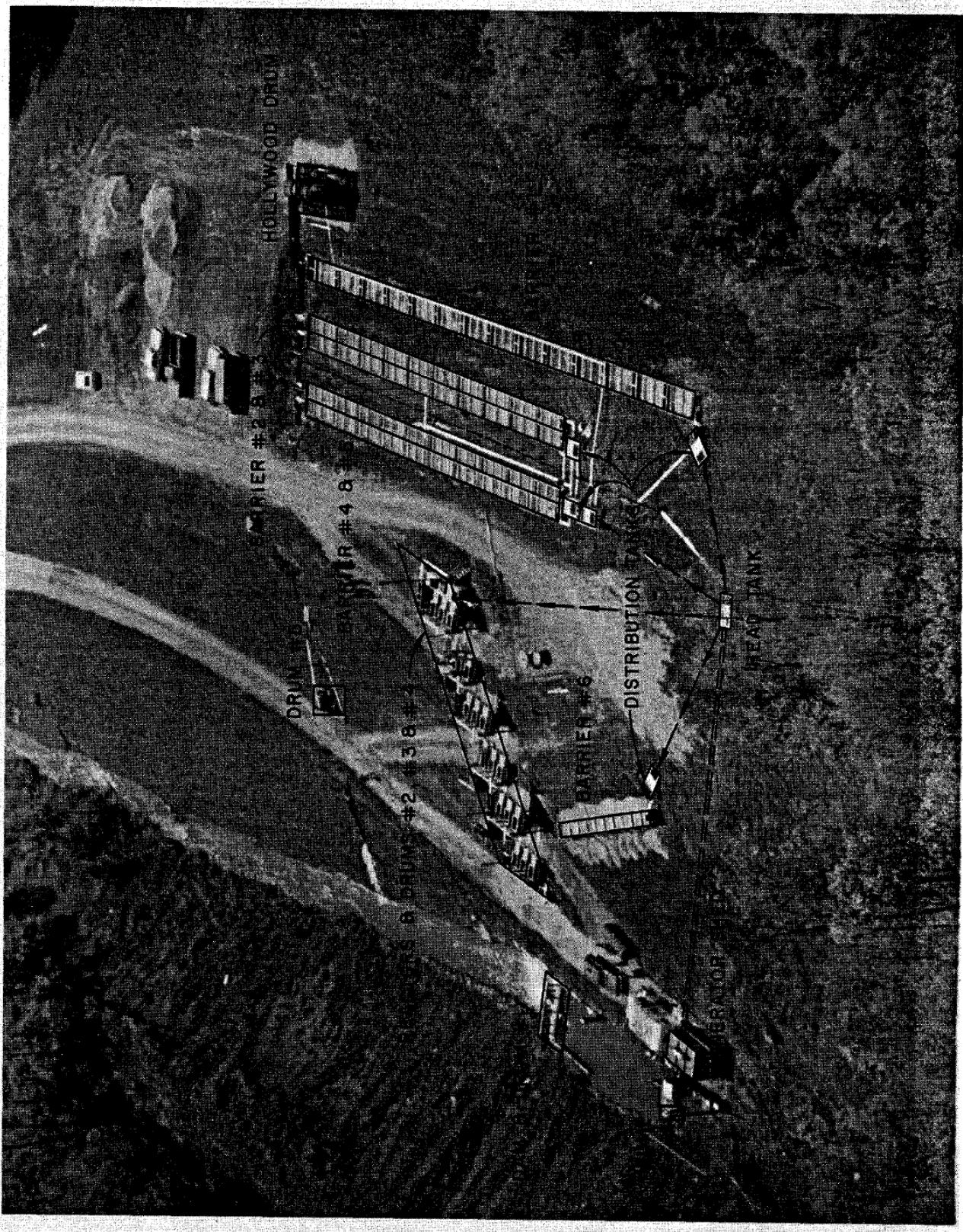
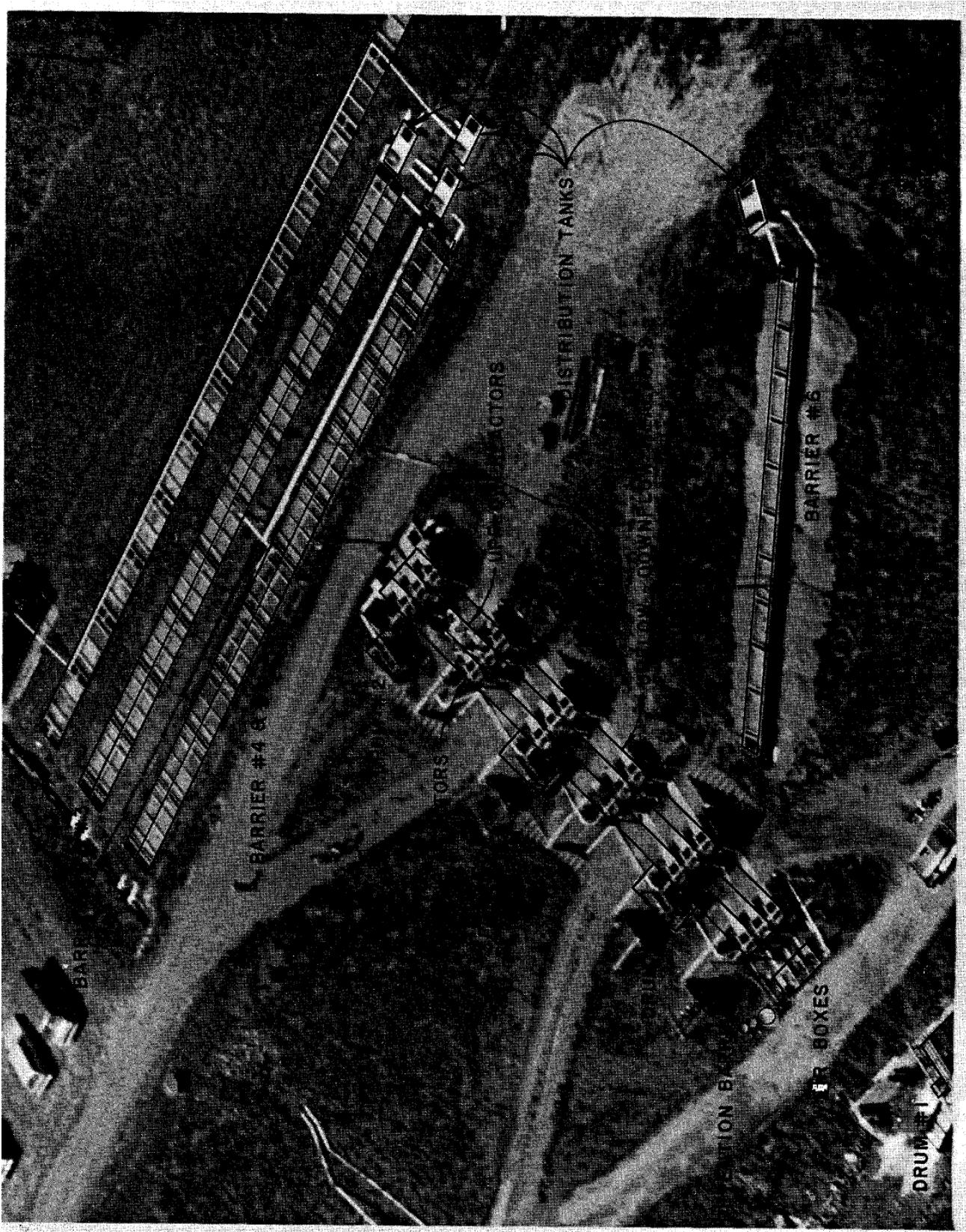


Figure 1.1 Project Location



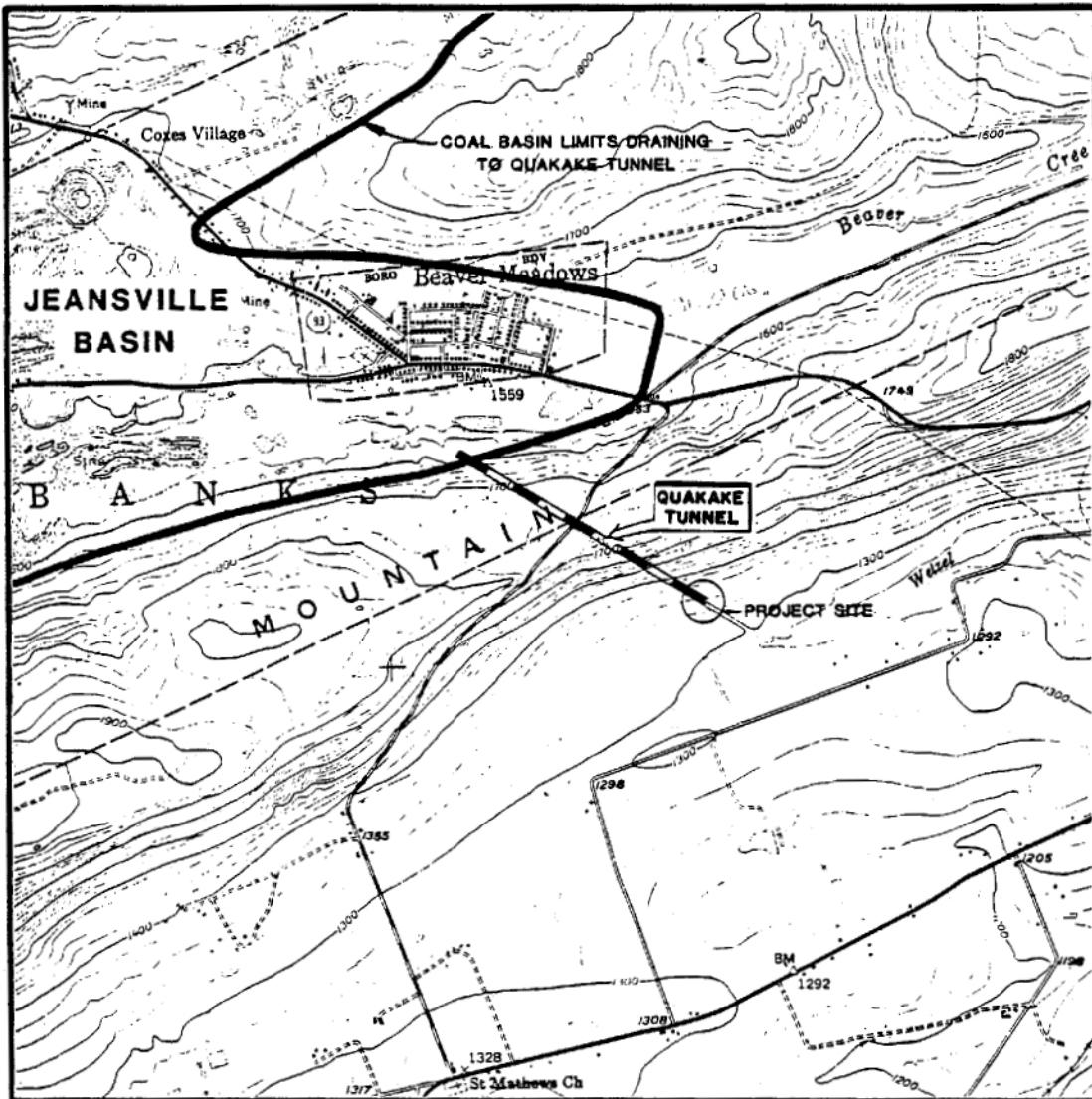


## **ACKNOWLEDGEMENTS**

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Gratitude is expressed to the Regents of the University of California for the assistance rendered by Dr. Frank Pearson, Assistant Director of the University's Sanitary Engineering Research Laboratory at Berkeley. Dr. Pearson's prior work provided the initial design criteria for the prototype facilities in the demonstration project. In addition, Dr. Pearson provided invaluable direction during the evaluation of the data obtained during the project and contributed to the preparation and review of this report.

Sincere appreciation must be given to the public spirited property owners Paul and Alex Chulock, the Tri-county Land and Coal Company, and Butler Enterprises, Inc. These companies and individuals demonstrated their concern for an improved environment by granting gratis easements for the construction and operation of the project.



*Figure 1.2 Topography in the Vicinity of the Project*

Quakake Tunnel AMD discharges originate in the abandoned deep mines of the Jeansville Coal Basin. The Jeansville Basin is located in Eastern Central Pennsylvania and extends into Luzerne, Schuylkill and Carbon Counties. The coal basin is split by the topographic drainage divide between the Susquehanna and Delaware River watersheds. The mine workings within the basin are drained by two tunnels; the Quakake Tunnel empties into the Delaware River Basin while the Audenried drains to the Susquehanna Basin.

General topographic features in the vicinity of the project site are illustrated in Figure 1.2. The basin is formed by a series of tightly folded anticlines and synclines. Resistant sandstone and conglomerate formations occur around the outer rim of the basin forming topographically elevated ridges. The Audenried Tunnel and the Quakake Tunnel were driven through these ridges during active mining to control the water level in the deep mines by gravity flow (4).

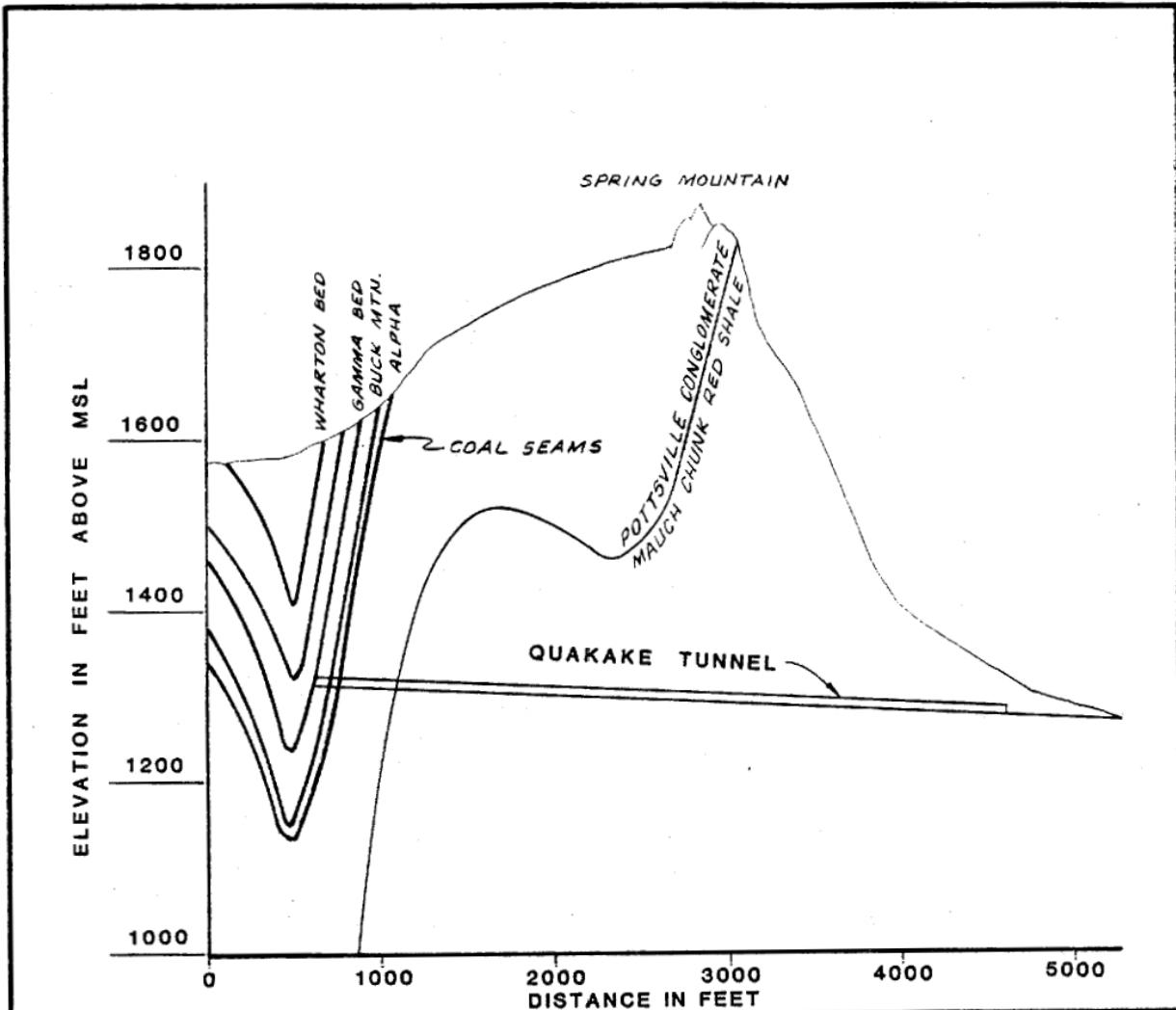


Figure 1.3 Quakake Tunnel Profile. The tunnel is approximately 4000 feet long and originates in the Gamma Bed workings of the Beaver Meadow Mine.

The general geology along the Quakake Tunnel profile is shown in Figure 1.3. Past deep mining activities developed eight large mine complexes in the Jeansville Basin. The Quakake Tunnel drains the Beaver Meadow, Coleraine, and a portion of the Spring Mountain deep mine workings. All complexes, however, were interconnected by the miners in an effort to increase gravity drainage from the mines. At present, surface water enters the mines by infiltration through fractured strata and abandoned strip pits. Natural drainage patterns of surface flows have been greatly disturbed by strip mining, which has created additional interconnections at higher elevations in the mine complexes. Water pumped from outside sources used in coal preparation facilities, and waste waters from municipalities within the basin also contribute to the tunnel flows.

## 2. QUAKE TUNNEL WATER QUALITY

**Initial Investigations - 1973/1974:** Prior to the design of the prototype installations, the tunnel discharge was sampled and flows were measured twice monthly from March 10, 1973 to May 29, 1974. Six monitoring stations were established at the locations shown in Appendix "A". The monitoring station at the tunnel portal was equipped with a Leupold Stevens Type F continuous water level recorder. Flow measurements were obtained using a propeller type "Ott" current meter. Water samples were collected in, plastic bottles and shipped to the commercial water quality laboratories then under contract with the Department of Environmental Resources.

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Monitoring stations downstream of the Tunnel were established to provide data on the impact of the Tunnel discharge on the receiving stream. Comparison of flows and water quality, taken on the same day, allowed an evaluation of the dilution effect from the unpolluted watersheds. Water quality monitoring results, tunnel discharge hydrographs and mass curves and precipitation data are presented in Appendix "A". A summary of the tunnel flow and quality data for the 1973/1974 samplings is presented in Table 2.1. This data formed the basis for the design of the demonstration prototypes.

**Prototype Operation 1979/1980:** Additional samples of the Quakake AMD discharge were collected and tested during the operation of the prototype facilities between July 10, 1979 and May 21, 1980. During this period, 238 untreated water samples were analyzed. A statistical summary of the various AMD parameters for this time period is presented in Table 2.1 for comparison with the initial test data.

Figure 2.1 presents the acidity, sulfate and metals concentration, grouped according to pH range showing that higher pollutant loadings are generally associated with decreasing pH.

TABLE 2.1 - FLOW AND QUALITY DATA FOR THE QUAKE DISCHARGE

Parameter and Unit	1973 - 74			1979 - 80			
	Ave.	Min.	Max.	Ave.	SD	Min.	Max.
Flow, cfs	21.2	10.1	33.6	-	-	-	-
Field pH	3.6	3.2	3.9	3.9	0.2	3.4	4.6
Lab pH	3.4	3.0	3.8	3.7	0.1	3.6	4.6
Free Acidity, mg/L	25	0	75	22	8	8	70
Total Acidity, mg/L	145	100	190	80	8	66	110
Iron (total, mg/L)	2.3	0.7	3.7	0.83	0.47	0.18	0.97
Aluminum, mg/L	16.6	6	24	9.8	1.5	5.5	17.0
Calcium, mg/L	12.6	1	24	14.1	3.9	6.0	39.8
Sulfate, mg/L	237	100	460	144	21	80	200
Temperature, °C	9	9	10	9	-	-	-

SD - Standard Deviation

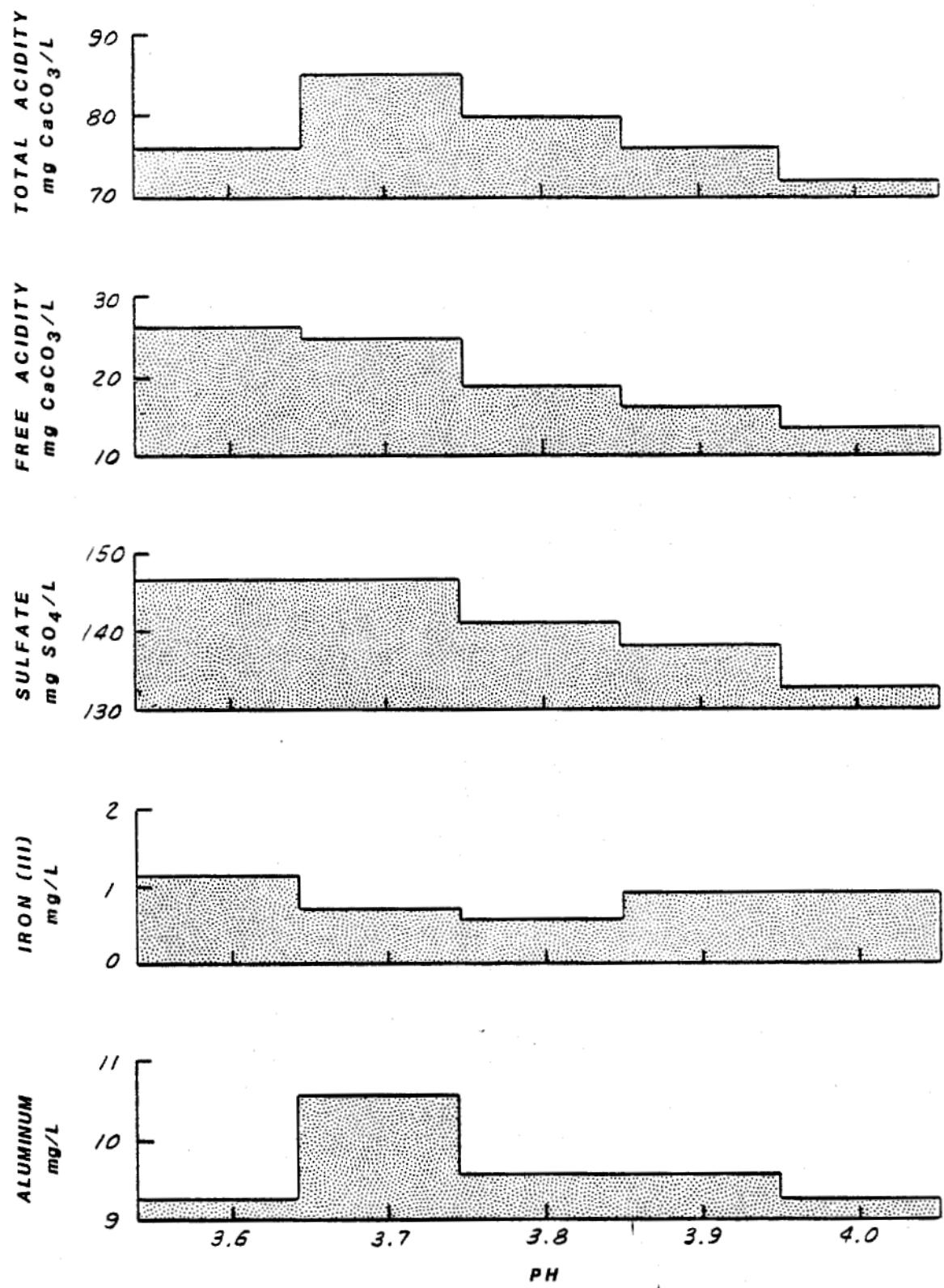


Figure 2.1 AMD Parameters Grouped by pH Values. The higher pollutant loadings are generally associated with decreasing pH and decreasing flow.

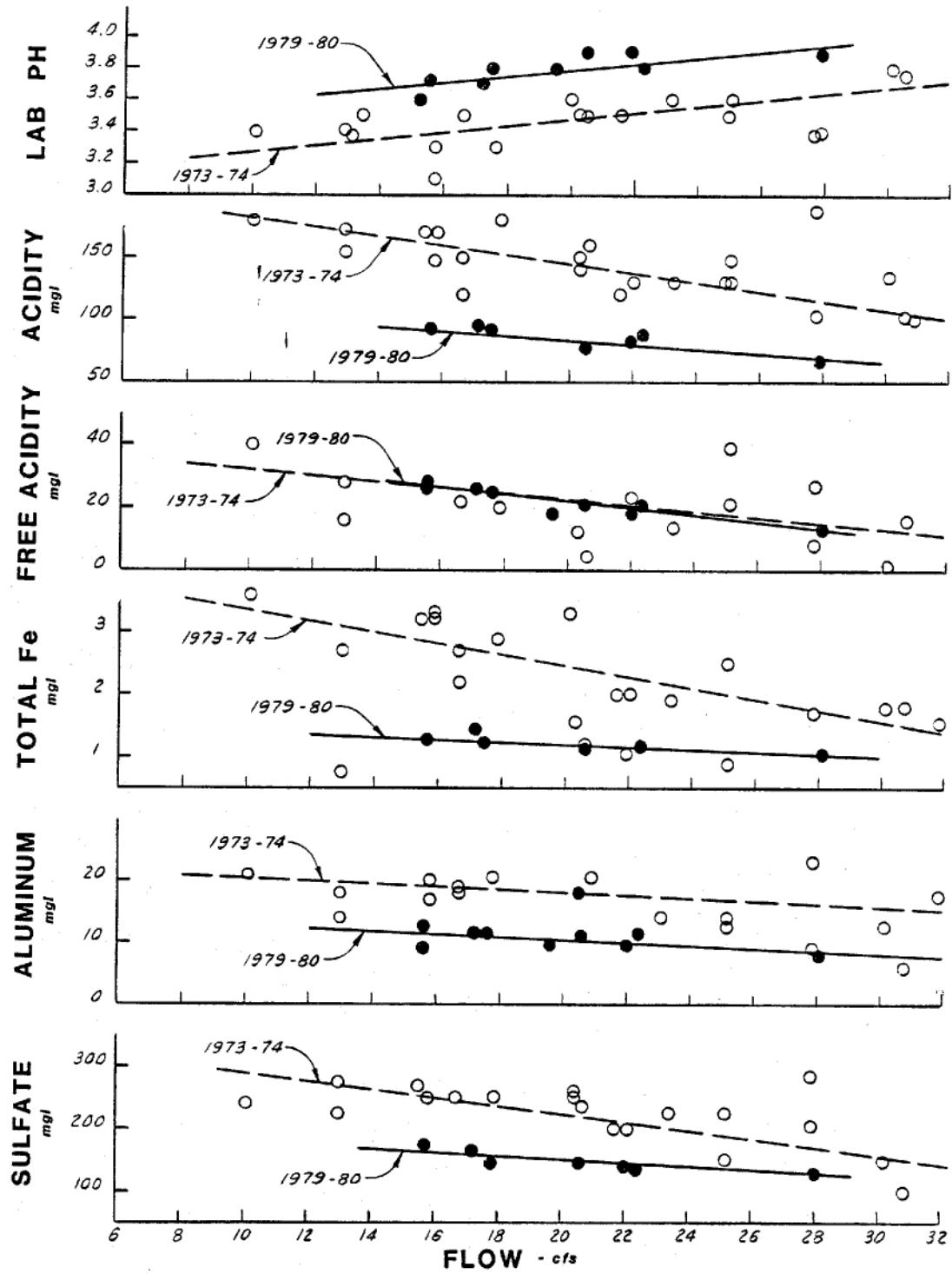
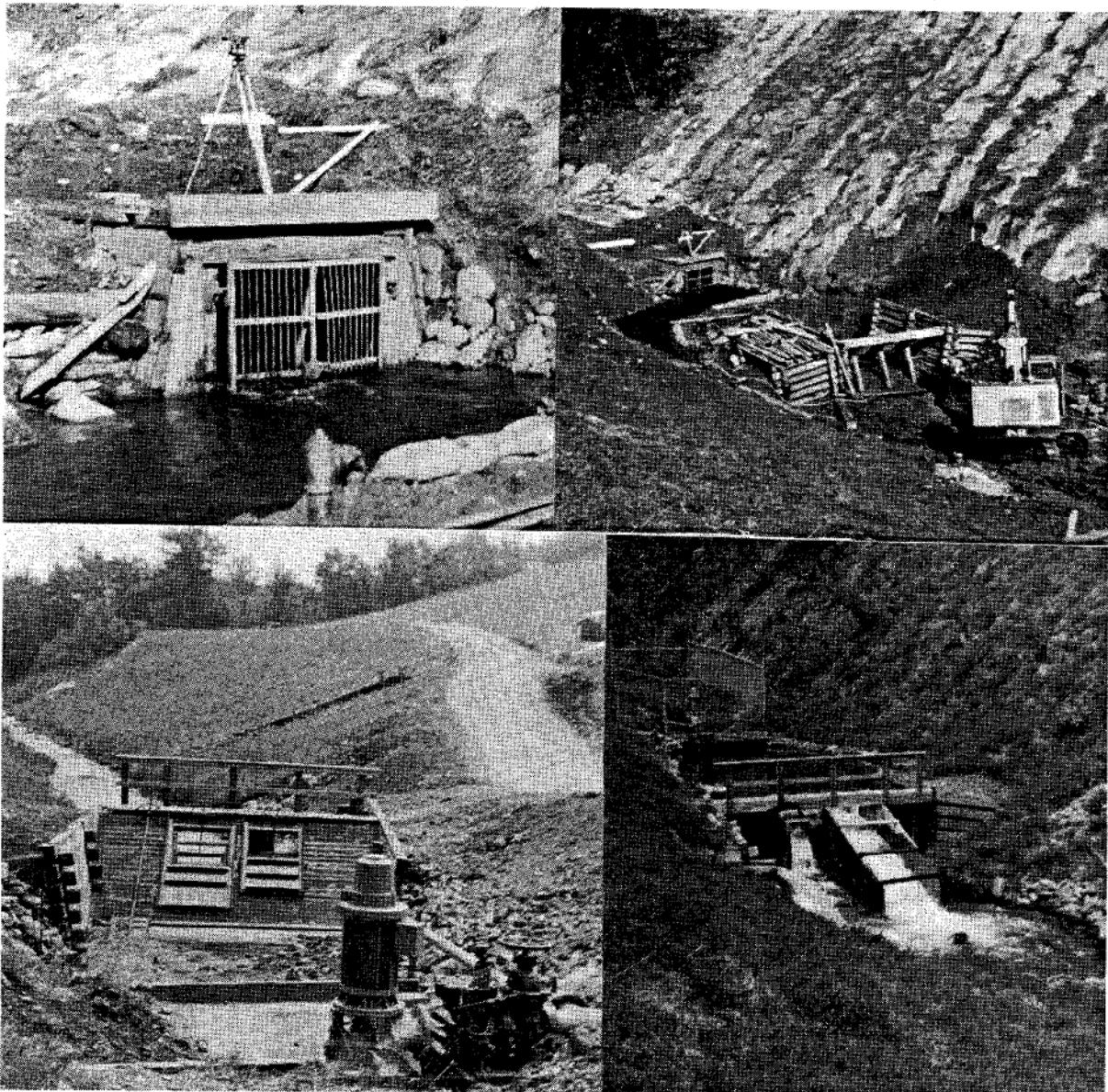


Figure 2.2 AMD Parameters Compared with Tunnel Flow

The concentrations of acidity, sulfate and metals declined with increasing flow. A marked improvement in water quality occurred between 1973-74 and 1979-80. The improvement is attributed to the restriction of air flow through the mine.

**Analysis of Water Quality Data:** During both sampling periods, the concentration of acidity, sulfate and metals declined with increasing flow, as shown in Figure 2.2. Figure 2.2 also indicates an improvement in water quality from 1973/74 to 1979/80, which can be partially attributed to reduced air circulation through the mine. An airlock was formed at the tunnel outlet when the small dam was constructed in 1977 to create a sump for the pump used in the prototype demonstration. Prior to construction of the dam, a strong air current circulated through the mine and discharged through the tunnel. The restriction of this air flow through the mine complex could have reduced oxidation of the acid-forming pyrite in the mine, resulting in an improvement of effluent quality. Similar results are reported by Moeks and Krikovic (5) where air sealing of a mine produced significant decreases in acidity and iron concentrations.



VIEWS OF THE TUNNEL PORTAL AND DAM DURING CONSTRUCTION

### **3. PRE-DESIGN INVESTIGATIONS**

**Literature Review:** A survey of recent literature pertinent to the treatment of acidic waters with crushed limestone was conducted prior to the formulation of the design process.

Early significant literature was concerned with the neutralization by crushed limestone of such acidic industrial wastes as nitrocellulose manufacturing wastes (6) and steel pickling liquors (7, 8). This work led to recommendations for the design of processes to treat these particular wastes. However, the applicability of the results of these methods to the treatment of acid wastes other than those studied is uncertain. Moreover, no reported use of these processes in the neutralization of acid mine drainage was found.

It is reported (9) that there had been a number of previous attempts to use crushed limestone as static beds placed in flumes to neutralize mine drainage. However, these processes were abandoned when coating of the limestone surface by metal hydroxides severely reduced the degree of AIM neutralization obtained within a short time after starting the process.

Autogeneous mills filled with crushed limestone have been successfully used in the neturalization of acidic water in pilot installations by Mihok (10) and others. The continuous abrasion caused by the tumbling movement of the pieces of crushed limestone over each other produced very fine particles (400 mesh grain size). The surface area to particle weight ratio is larger for fine particles than for coarsely crushed stone. Consequently, as AMD flows through the drum, the presence of fine particles increases the reaction rate and accelerates the neutralization process. Also, the continuous abrasion of the crushed limestone exposes fresh surfaces over the crushed limestone and reduces the effects of stone coating phenomenon.

Lovells (21) work at the Hollywood experimental station of the Pennsylvania State University indicates that complete neutralization of AMD can be achieved by a revolving drum. In the Hollywood Plant, an autogeneous mill filled with crushed limestone and driven by a 25 horsepower motor was used to neutralize AMD flow at a rate of 0.5 cfs.

Frequently quoted is Hill and Wilmoth's (11) state of the art paper on the use of limestone to neutralize acid mine drainage, in which the observation is made that grinding of limestone to increase its reactivity, may raise its cost above that for lime.

Progress toward rationalization of the chemical and hydraulic processes occurring in the limestone neutralization processes has been made by a number of independent investigations at the Pennsylvania State University. In one such investigation (12), crushed limestone or discs cut from limestone were exposed to acidic water under a variety of conditions and the temperature coefficient and effect of flow velocity evaluated. Another investigation was conducted to evaluate the kinetics of exsolution of carbon dioxide as a function of temperature, ionic strength, and water turbulence (13). Jarret and Kountz (14) investigated the principle reaction between sulfuric acid and limestone and formulated a barrier design procedure.

Based on the results of laboratory studies, the Pennsylvania Department of Mines and Mineral Industries constructed six limestone barriers during 1970/71 in streams of the Trough Creek watershed (15). The barriers were installed to alleviate the acid-

pollution of the streams caused by coal mining in the watershed. In June 1972, high streamflows resulting from the Hurricane Agnes damaged or demolished five of the barriers. Three barriers were reconstructed and completed in November 1972. Stream water quality was monitored prior to and after construction of the barriers under a joint federal/state program. Another monitoring program was initiated by the Land and Water Research Institute of the Pennsylvania State University to evaluate the mechanisms that operate in limestone barriers and to provide for a more rational design (17).

These studies included a pilot-plant scale evaluation of the joint influence of the two rate-limiting chemical reactions on the overall performance of the process. These reactions are, first, the attack of limestone by acidic water and, second, the exsolution of carbon dioxide that is generated by the limestone dissolution.

Reaction rates are expressed per unit area of reacting surface (e.g. stone surface area) and are related to such environmental conditions as temperature, ionic strength, and flow turbulence. Differential equations expressing rates of the two limiting reactions are solved simultaneously to describe the overall neutralization process for comparison with data obtained from operation of the pilot plant (16).

The mathematical model developed for the limestone neutralization process from the pilot plant operating data was applied to predict the performance of the prototype limestone barriers operating in Trough Creek. Results showed that when the interstices within crushed limestone became clogged by silt or by iron or aluminum hydroxide, the limestone became inactivated as the acidic water had no access to the reactive surfaces. In free flowing streams, where no such clogging occurred, the reactivity of the limestone was 20 percent of the reactivity of clean stone as a result of the inhibitory effects of the coatings that formed on the stone. At lower concentrations of metallic ions no iron or aluminum hydroxide coatings accumulated, but a coating of clay-like material developed on the stone. As a result of this work, design procedures for limestone neutralization processes were developed (2).

The exsolution of carbon dioxide has an increased effect on the performance of the process as the final pH of the water rises above 5.0. Downstream of the limestone neutralization process the pH will continue to rise as carbon dioxide is lost from the water. Stumm and Morgan (18) deal with many of the chemical equilibria that pertain to the neutralization process. Their formulations provide a basis for estimating water quality after the carbon dioxide reaches equilibrium with the atmosphere.

Successful neutralization of a lightly buffered acidic stream by the use of crushed limestone filled drums was reported by Zurbuch (19, 20). The method was demonstrated at the Otter Creek installation in the Monongahela National Forest, West Virginia. The neutralization of Otter Creek raised the pH values from less than 5.1 to over 7 and sustained fish life in 12 miles of stream. This project was unique in that the power for grinding the limestone is obtained from the acid water itself. The drums were fitted with vanes and operated as overshot water wheels, utilizing the power of the stream for self-neutralization. Each drum was 44 inches wide and 50 inches in diameter. The inner drum containing the limestone was 34 inches in diameter. A minimum flow of 0.5 cfs was required to rotate a drum and agitate the crushed limestone. Flows exceeding 4 cfs were diverted to a second drum. The success of the Otter Creek installation encouraged Pearson and McDonnell to investigate the hydraulic, mechanical and chemical process design of the drums (3).

Of the literature reviewed, only Pearson and McDonnell (1, 2, 3) proposed rational and comprehensive design procedure based on both empirical and theoretical considerations. Accordingly, theoretical design of the chemical processes was determined in accordance with their proposed procedures.

**Pre-design Chemical Testing:** A limited number of laboratory and field tests using the Quakake AMD and limestone were conducted prior to the design. The tests were made to confirm that the behavior of the proposed prototype would be at least partially predictable by the theoretical methods used for design. The tests consisted of bench (laboratory) tests and field tests. In the bench tests, a known weight of limestone was placed in a known volume of AMD and the rate of change of pH with time was recorded. The experimental data generally confirmed the order of magnitude of the limestone loading required to produce a final pH of 6.

In order to evaluate the chemical coating which forms on the limestone particles field tests were made. These tests were made by submerging limestone chips in the tunnel discharge until the coatings developed. The limestone and coating were examined at the Pennsylvania State University by X-Ray diffraction techniques and scanning electron microscopy. These analyses indicated that the chips have three coatings:

- (a) An overall coating of re-crystallized calcite which is relatively porous;
- (b) A brown coating rich in iron, which is not as porous and flakes off when dry;
- (c) An off-white coating similar to (b), rich in aluminum and sulfur.

The exact chemical composition of the compounds in (b) and (c) could not be determined.

In general, the chemical tests indicated that the proposed design methods were reasonable and prototype design proceeded on that basis. A summary of the test methods and results is presented in Appendix "B".