SUMMARY AND RECOMMENDATIONS

This report covers the preliminary investigations, detail process design, site investigation, and preliminary design of a proposed acid mine drainage treatment plant to be located at Hawk Run near Philipsburg, Pennsylvania. The plant will utilize an ion exchange process developed by Rohm and Haas Company, Philadelphia, designated as the "Modified Desal Process" to remove mineral acidity. Subsequent treatment steps consisting of aeration, softening and filtration will remove iron, other metals and hardness and produce water meeting the U.S. Public Health Service standards for drinking water.

The proposed plant will have a minimum capacity of 500,000 gallons per day when supplied with water of the design composition and operated in accordance with standard ion exchange procedures. Under average raw water conditions and utilizing maximum feasible recirculation of water used for in-plant operations, the anticipated output is 620,000 gpd of treated water. Preliminary plans are presented for an expansion to 1,000,000 gpd of dependable output.

The total estimated construction cost of the proposed plant is $1,515,000. The estimated operating costs for chemicals and utilities are $103,400.

The studies presented in this report indicate that the treatment of acid mine drainage by the proposed process sequence is technologically feasible. Therefore, it is recommended that the Commonwealth of Pennsylvania proceed with the preparation of detailed construction plans, specifications, and other contract documents for the proposed treatment plant in accordance with the preliminary designs presented in this report.

Summary of Operating Data

Nominal plant capacity	500,000 gal per day
Normal operating conditions	
AMD water treated	684,000
In-plant use and waste	64,000
Treated water produced	620,000
Maximum output of Ion Exchange Resin when supplied with AMD water of design condition	820,000
Chemical and Fuel Requirements	
Ammonia (5% Makeup)	160 lb per day
Carbon dioxide	6,180
Lime	6,430
Fuel Oil	350 gal per day
Waste Products (Dry Basis)	19,160 lb per day

Design Water Quality

	AMD Feed	Product
Sulfate	1,000 mg/l	50
Hardness	550	70
Total iron	250	<0.3
pH	3-4	8.5
Total Solids	1,000	<300

AUTHORITY FOR WORK

In accordance with the service contract dated October 10, 1968 between the Commonwealth of Pennsylvania ("Commonwealth") and Burns and Roe, Inc. ("Engineers"), the Engineers have furnished services as set forth in Appendix B to the Contract with respect to the design, construction and operation of a plant to evaluate and demonstrate the treatment of acid mine drainage ("AMD") waters from abandoned coal mines in the Philipsburg, Pennsylvania area. This report covers the preliminary investigations, detail process design, site investigation and preliminary design of the proposed treatment plant.

SCOPE OF WORK

The services furnished by the Engineers have consisted of the following:

A.Preliminary Investigations

1. Study the requirements and means for regulating and controlling the temperature and flow rate of water up through the expanded resin beds. Advise Rohm and Haas concerning additional bench studies and field tests that may be required.
2. Compare the recovery of ammonia by means of lime treatment with concentration and sale of ammonium sulfate.
3. Compare aeration by bubbling air through a basin of water with aeration by downward flow of water through slat-filled towers.

B.Detail Process Design

1. Prepare material balances for the final process based on analyses of water samples from the three sources considered for use in the Plant.
2. Establish the detail process operating cycle.

3. Prepare criteria for tests to be performed in the completed Plant, and determine the features to be incorporated in the design to accommodate these requirements.

C. Site Investigations

1. Determine requirements and recommend to the COMMONWEALTH, the needs of any subcontracts for topographic surveys, utility surveys, soils investigations, laboratory tests and similar items. 2. Inspect work of subcontractors performing these services. 3. Review and evaluate survey and test reports.

D. Preliminary Design

1. Prepare engineering flow diagrams and single line diagrams for the process and utilities, as applicable.
2. Prepare plot plan and Plant arrangement drawings.
3. Prepare outline specifications for major equipment and for Plant construction.
4. Prepare a preliminary cost estimate for construction of the Plant. The following services will be furnished upon acceptance and approval of this report by the COMMONWEALTH:

E.Final Design

1. Based on the preliminary design documents and any applicable COMMONWEALTH comments, prepare final drawings and specifications for use by COMMONWEALTH to solicit competitive bids for supply and construction of the Plant under a single contract.
2. Furnish technical information and data required for COMMONWEALTH to secure necessary approvals, permits and easements.
3. Prepare a final construction cost estimate.
4. Prepare bid invitations, bid forms and instructions to bidders for use by COMMONWEALTH.
5. Submit five copies of the final drawings, specifications, and cost estimate to COMMONWEALTH for approval.
6. Furnish one reproducible copy of the approved final drawings and specifications and five copies.
7. Furnish bid documents to prospective bidders at cost of reproduction.

F.Construction Assistance

1. Assist the COMMONWEALTH in evaluation of construction bids.
2. Provide general observation of construction, which includes review of shop drawings as required by the specifications prepared by ENGINEER, engineering advice on questions arising during the construction, and periodic one-man-day visits to the construction site (maximum of 20 man-days). During these visits review construction progress with the on-site representative of COMMONWEALTH.
3. Incorporate on the final tracings the "as-built" information furnished to COMMONWEALTH by the construction contractor.

G.Operation Assistance

1. Prepare procedures for startup and initial operation of the Plant.
2. Prepare a program covering a one-year period for test and evaluation of the Plant.
3. Furnish one engineer at the Plant for a continuous period of six calendar weeks to monitor the startup and initial operation.
4. Provide general observation of the one-year test and evaluation program, which includes engineering advice on questions arising during the program, monthly one-man-day visits to the Plant (maximum of 12 man-days) and a letter report following each visit.

GENERAL DESCRIPTION OF MINE DRAINAGE PROBLEM

The Federal Water Pollution Control Administration (FWPCA) estimates that in the Appalachia region alone, over 10,000 miles of streams are polluted by coal mining operations and that the total amount of acid discharged to streams is between 5 and 10 million tons annually. The problem is of particular importance in the Commonwealth of Pennsylvania, where 2,500 miles of streams are considered polluted by mine drainage containing an estimated 1,000 million gallons of mine drainage per day.

The type of drainage produced by a coal mine is a function of type of mine, deep or open pit, and the geological sulfur compounds associated with the coal. The presence of calcium also seems to have a significant effect. The drainage may have widely varying characteristics, not only from one location to another but also at any one particular site. The FWPCA recognizes four distinct classes of mine drainage, depending on the state of oxidation and the hydrogen ion concentration (pH). Within each of the classes, wide variations in composition and concentration are possible. The following Table 1 shows the principal characteristics of mine drainage waters of each of the four classes established by the FWPCA.

Table 1

Mine Drainage Classes

	Class 1 Acid Discharges	Class 2 Partially Oxidized and/or Neutralized	Class 3 Oxidized and Neutralized and/or Alkaline	Class 4 Neutralized and Not Oxidized
pH	2 - 4.5	3.5 - 6.6	6.5 - 8.5	6.5 - 8.5
Acidity, Mg/l($CaCO_3$)	1,000 - 15,000	0 - 1,000	0	0
Ferrous Iron, Mg/l	500 - 10,000	0 - 500	0	50 - 1,000
Aluminum, Mg/l	0 - 2,000	0 - 20	0	0
Sulfate, Mg/l	1,000 - 20,000	500 - 10,000	500 - 10,000	500 - 10,000

Source: In-house Studies, FWPCA

Of the four classes shown in the above table, Class 1, consisting of un-oxidized acid discharges, presents by far the most serious problem. This type of drainage results in the greatest impairment to quality of natural waters. At the same time, it causes significant damage to structures in contact with the waters. It is the predominating type of mine drainage encountered in the Commonwealth of Pennsylvania, particularly in older seams of the bituminous coal fields.

The problem is caused by the presence of sulfur and iron compounds in coal deposits. When these deposits are exposed to the atmosphere as the result of mining operations, the following oxidation occurs:

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$\text{(Pyrite)} + \text{(Water)} + \text{(Air)} \longrightarrow \text{(Ferrous Sulfate)} + \text{(Sulfuric Acid)}$$

The ferrous sulfate may or may not be subsequently oxidized to the ferric state. The factors influencing the kinetics of this process are not fully known, but the presence or absence of calcium seems to have a major effect on the rate of oxidation and therefore on the type of drainage produced. There is also some evidence that the process involves bacterial action.

<u>Prevention of Acid Formation</u>

There are two basic methods of eliminating or ameliorating the problems caused by mine drainage. One method is to prevent the formation of acid. The other is to treat the acid after it has been formed. Several techniques for reducing the rate of acid formation have been proposed and some of them have been tried out in demonstration projects. These techniques may be summarized as follows:

<u>Bactericides.</u> - Since bacterial action seems to have significant influence on the rate of oxidation, it has been suggested that sterilization by chemical treatment could be used to reduce the formation of mine acid. Practical application of this technique has been limited by the complex structure of the underground formations and because any local sterilization is rapidly re-contaminated from adjoining areas.

Mine Sealing - It has been suggested that the rate of oxidation of pyrites could be reduced if air could be excluded from the mine passages. Practical application of this technique, which must be limited to abandoned mines, has demonstrated that this method is not effective.

Hydrological Control. - Careful backfilling and compaction, detouring of surface drainage around stripping areas and other methods of minimizing the access of water to the mining areas have been attempted; however, because of the complex hydrological structure of the surface formations, this method also has met with only limited success.

In summary, none of the methods of preventing acid formation has thus far met with a significant degree of success. Under most circumstances, entry of water and air into the mine cannot be prevented. The only practical alternative, therefore, is to treat the actual discharge from the mines.

Treatment of Mine Drainage

The techniques for treatment of mine drainage fall into the following general categories:

Neutralization
Iron Removal
Biological Treatment
Desalting Techniques
Ion Exchange

These processes are discussed briefly in the following paragraphs.

Neutralization. - Neutralization of acid mine drainage has been used as a treatment method since the 1920's. The principle is to mix an alkali with the acid water to neutralize the acid and precipitate metallic salts. Because of economic factors, the neutralizing agent most commonly used is lime, either in the hydrated or calcined form. Limestone (calcium carbonate) has also been used. The major factors in selection of a neutralizing agent is local availability and cost. The cheapest agent capable of meeting the requirements is generally used. An important factor in neutralization is the type of sludge produced. Some neutralizing agents produce sludge that either settles too slowly or forms gelatinous compounds which cannot be successfully dewatered. Various studies have been undertaken to minimize the cost of neutralization and to develop a process which would produce precipitates of desirable settling characteristics. Existing demonstration projects utilizing neutralization techniques will be described later.

Iron Removal. - The treatment of mine drainage to remove iron is essential to prevent the formation of unsightly stream deposits and to make the water usable for human and industrial consumption. Since iron is more soluble in the ferrous form than in the ferric form, the removal of iron is best achieved by means of oxidation to the insoluble form. Methods available for the removal of iron include precipitation by alkali, aeration-settling-filtration, ozonation, radiation and chlorination. The major difference between the removal of iron from well waters and mine drainage waters is that the latter have, in some cases, iron concentrations as high as 10,000 milligrams per liter (mg/1). The most common method of iron removal is aeration, followed by hydrolysis, according to the following equation:

$$4\ Fe\ SO_4 + O_2 + 10\ H_2O \longrightarrow 4\ Fe\ (OH)_3 + 4\ H_2\ SO_4$$

The rate of this reaction is a function of pH, temperature, concentration of dissolved oxygen, and various trace catalysts. The rate increases rapidly with rising pH and with rising temperatures.

Radiation with alpha, beta and gamma rays accelerates the oxidation of ferrous iron. The effect appears due to the formation of either hydrogen peroxide or ozone as the result of radiation. Ozone can also be formed directly and used to oxidize the ferrous iron. Other oxidizing agents such as chlorine, iodine, and permanganate are used in water treatment for the removal of iron. Their applicability to the removal of the much greater quantities of iron from mine drainage depends largely on economics of chemical costs.

Biological Treatment. - The FWPCA notes that biological treatment has been suggested as a method of reducing the pollution resulting from mine drainage. Two types of biochemical reactions could be utilized. One of these involves the use of a sulfate reducing bacteria, which could feed on a source of organic nutrients, such as wood dust or sewage sludge, in an anaerobic environment and would in the process reduce sulfates to sulfides. The insoluble sulfides could then be separated. Another process uses an aerobic system in which bacterial growth converts ferrous ions to ferric ions in the presence of carbon dioxide. A sludge recycle system is employed to accelerate the reaction. The aeration step is followed by limestone neutralization.

Both of these processes are in early stages of development, with most of the work done on a laboratory batch scale. Because of the toxicity of hydrogen sulfide, anaerobic processes are generally difficult to control and to operate. The advantages of the aerobic biological process over straight aeration remains to be demonstrated.

The possibility of a combined treatment of mine drainage and municipal and industrial waste waters is appealing. However, any dual purpose system sacrifices efficiency of each component system in order to achieve compatability. If there is an optimum mixture of mine drainage and waste water, it is unlikely that nature will behave so as to maintain this ratio over any given period.

The FWPCA is currently supporting a number of projects in this area. There is need for much further research before the feasibility of this process can be established.

Desalting Techniques. - Desalting processes include reverse osmosis, electrodialysis, and distillation. Substantial research has been conducted on these processes under the auspices of the U.S. Office of Saline Water. Originally, this research covered primarily the production of fresh water from sea water. More recently, the emphasis has shifted to the treatment of so-called brackish waters. In view of the similarity between brackish ground waters and mine drainage, much of this research is applicable to mine drainage.

Reverse osmosis utilizes pressure as the driving force to squeeze water through a membrane which retains the salt ions. It produces water of low solids content but does not by itself raise the pH to an acceptable level. However, since the buffering salts have been removed, the adjustment of the pH is readily accomplished with small amounts of lime. Although the process is dependent on the solids concentration of the influent, the process pressure required to separate 2000-3000 mg/l solids from AMD water is not excessive compared to that required by 35,000 mg/l sea water. The main problems are (1) the development of membranes that can withstand the required pressures and (2) the precipitation or scaling of the various metallic salts encountered in mine drainage. The scale-forming concentration of calcium sulfate limits the degree of solids concentration in the waste. This separation technique produces a relatively ion-free water and a brine concentrate which contains all the solids. It requires considerable power to attain the necessary pressure of which a portion may be theoretically reclaimed.

Electrodialysis is a process in which an electric current is utilized to drive ions through selective membranes. Negative ions are driven towards a positively charged plate which is protected by a membrane that allows only negative ions to pass. Positive ions are driven towards a negatively charged plate protected by a membrane that passes only positive ions. Since both positive and negative ions are being removed, the solids concentration between the membranes is decreased.

Electrodialysis seems to offer some potential for the treatment of mine drainage. The electric current requirements and therefore the unit costs, vary directly with the dissolved solids concentration and inversely with the solids permissible in the product water. Thus, unlike other desalting processes, it is not necessary to produce ultra-pure water.

As in the case of reverse osmosis, the main problem lies in developing suitable membranes that neither foul nor lose their selectivity. Hardness, iron and manganese all tend to precipitate on the membranes. It is generally agreed that pretreatment for iron and manganese removal is necessary before electrodialysis can be used on mine drainage waters. Thus, electrodialysis produces a good quality water containing selected ions, discharges a concentrated brine and consumes a substantial amount of irretrievable power.

Distillation - Evaporative processes are currently the most successful method for desalting sea water. Numerous plants throughout the world are operating producing water of such high quality that it is often blended down with brackish water. The separation technique is simple. Sufficient heat is applied to the feed solution to vaporize the water and to concentrate the solids remaining in the brine. The gaseous water is collected by condensation on a cold surface and the pure liquid product, contaminated only by particulate carryover of brine, drops into a separate product tray whine the brine passes to successive stages in which the procedure is repeated. The brine concentration factor (usually on the order of 1:2 to 1:3) depends on the concentration of scale-forming materials in the feed. Thermal efficiencies of 90% have been reported for large desalting plants of over 1 mgd.

The main problems of applying distillation techniques to AMD waters are the same as with saline waters, scale and corrosion. The scale-forming materials, calcium carbonate and sulfate, are present, usually in higher concentrations and will come out on hot surfaces first. The scale problem is aggravated by the fact that calcium sulfate has an inverse solubility which means that its solubility decreases with increases in temperature, e.g., at 104° F, 1550 ppm; at 212° F, 1246 ppm. The scaling temperature, (the temperature at which scale forms in a given situation) limits the thermodynamic efficiency of a process, the scale causes losses in heat transfer efficiency and the coating of scale causes over-heating which can lead to failure of the materials of construction. Since highly acidic water is very corrosive, the contacting surfaces must be of relatively expensive materials. Thus, evaporative methods produce high quality water, discharge a brine about the concentration from reverse osmosis or electrodialysis, consume now cost heat (power) and require relatively expensive materials of construction.

Ion Exchange. - Ion exchange is the reversible exchange of ions between an insoluble solid material and a solution of these ions. Attached to the solid material, usually an organic resin of high molecular weight, are ions which can be exchanged for undesirable ions in the solution. These undesirable ions can later be released by changes in the chemical characteristics of the surrounding solution. Ion exchange resins are available for both anions and cations. The general reaction for an anion exchange is

$$RA_1 + A_2^- \longrightarrow RA_2 + A_1^-$$

with R = Resin site and A_1 and A_2 = Anions

The reaction is reversed by passing a concentrated solution of A_1 through the resin bed. This reversal is called regeneration.

In the treatment of acid mine drainage, the undesirable anions consist of mostly of sulfate ions (SO_4=) and a small amount of chloride (C1). The solids concentration of the water is reduced if the sulfate ions can be replaced by hydroxide ions (0H). In order to attach hydroxide ions to the resins, the resins must be regenerated with an alkali. Non-scale forming alkali such as ammonium or sodium hydroxides are usually selected for regeneration. The waste regenerant will then contain the cation of the alkali plus the sulfate released from the resin. Thus, ion exchange is essentially a concentration process, which removes undesirable ions from a dilute process stream and discharges them as a concentrate in the spent regenerant. Concentration factors of 1:5 and 1:6 can be expected. Under proper conditions, this concentration may produce insoluble end products, which can then be permanently separated from the process cycle.

Since ion exchange reactions are stoichiometric, each hydroxide ion added through the regeneration process results in an equivalent removal of undesirable ions from the process stream. Therefore, the cost of treatment by ion exchange is a direct function of the solids removed from the water processed. As a result of this relation, the ion exchange process has until recently been applied only to situations in which it was required to produce a relatively small volume of high quality water from a relatively low solids concentration raw water. Water containing dissolved solids concentrations in excess of 1000 mg/l generally could not be treated economically by ion exchange because of high regenerant costs. The following section describes recent process developments that will potentially reduce regenerant costs and make it feasible to treat mine drainage waters by ion exchange.

It should be pointed out that all of the desalting techniques reviewed for treating mine drainage produce high quality water and consume power in varying amounts and most require some special materials of construction. However, the volume of water discharged with the waste solids (waste concentration) for each system is different and the economy of waste volumes is a very important aspect of AMD control. It appears that ion exchange produces the smallest waste volume and is a technique that could be applied to the AMD problem.